

Flame Photometry and Flame Infrared Emission (FIRE)

14.1 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 the colour tells us what the element is, and the colour's intensity tells us how much of the element is present.

In early experiments, the visible colour of the flame was used to confirm the presence of certain elements in the sample, particularly alkali metals and alkaline-earth metals. Later the whole ultraviolet and visible range was utilized using a spectrophotometer. This instrument permitted us to select the wavelengths of the radiation and measure its intensity with considerable accuracy. The spectrophotometric technique has proven to be one of the most reliable and easily used techniques for the determination of concentrations of sodium, potassium, calcium, and magnesium.

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 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 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 of metals, it can be applied to non-metal analysis by utilizing the infrared region of the spectrum.

Flame photometry is a simple, rapid method for the routine determination of elements that can be easily excited.

14.2 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.

✓ 14.3 General Principles of Flame Photometry

When a liquid sample containing a metallic salt solution is introduced into a flame, the processes involved in flame photometry are complex, but the following is a simplified version of the events :

- (a) The solvent is vaporised, leaving particles of the solid salt.
- (b) The salt is vaporised or converted into the gaseous state.
- (c) 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 14.1.

$$E_2 - E_1 = h\nu \quad (14.1)$$

where h is the Plancks, constant, and ν the frequency of emitted light which is defined as follows

$$\nu = \frac{c}{\lambda} \quad (14.2)$$

On combining equations (14.1) and (14.2), we get

$$E_2 - E_1 = \frac{hc}{\lambda}$$

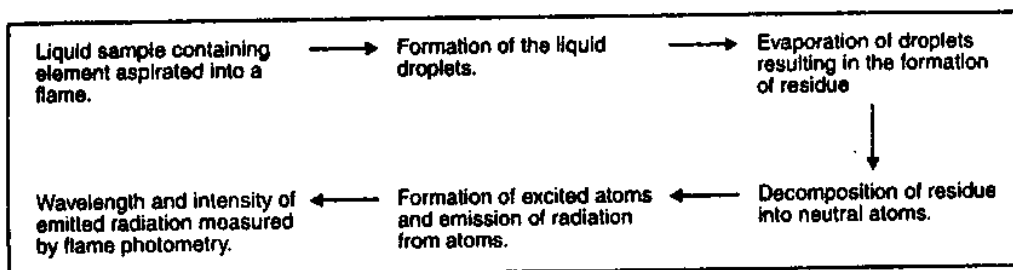
$$\text{or} \quad \lambda = \frac{hc}{E_2 - E_1} \quad (14.3)$$

From equation (14.3) one can calculate the wavelength of the emitted radiation which is characteristic of the atoms of the particular element from which it was emitted. When flame photometry is employed as an analytical tool, the wavelength of the radiation coming from a flame tells us about the elements which are present in that flame. Also, the intensity of the radiation enables us to know the amounts of those elements present. The following is a concise description of the sequence of events that normally occurs in flame photometry.

A portion of the neutral atoms or radicals formed in the flame may combine to form new gaseous compounds. As the formation of these compounds decreases the population of neutral atoms and hence the intensity is also decreased, this constitutes the chemical interference in flame photometry.

The fraction of free atoms that are thermally excited is governed by a Boltzmann distribution which is as follows:

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



$$\frac{N^*}{N_0} = A e^{-\Delta E/kT} \quad (14.4)$$

where N^* is the number of excited atoms, N_0 the numbers of atoms remaining in the ground state, A 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.

From equation (14.4) it follows that the fraction of atoms excited depends upon the temperature of the flame. Therefore, one expects higher number of excited atoms if the temperature of flame is increased. Thus, the fraction of atoms excited depending critically on the temperature of flame emphasizes the importance of controlling temperatures in flame photometry.

The temperature of fuel is controlled by the type of fuel and oxidant used. Some flame temperatures are given in Table 14.1.

Table 14.1 : Flame Temperatures of Typical Flames

Fuel	Oxidant	Flame Temp. (°C)
H ₂	O ₂	2800
H ₂	Air	2100
H ₂	Ar	1600
Acetylene	O ₂	3000
Acetylene	Air	2200
Acetylene	N ₂ O	3000
Propane	O ₂	2800
Propane	Air	1900

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 spectrography or plasma emission where much higher energy is available. However, it must also be stated that when we try to analyze 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.

The flame is a source of intense radiation especially for atoms inside the flame. It is probable that this is a source of excitation of the atoms (radiation excitation) which augments the thermal excitation expected from the Boltzmann distribution.

This point has not been extensively studied but provided a catalyst for the evolution of atomic fluorescence. For example, a fuel-rich oxyacetylene flame generates intense radiation bands at short wavelengths (300-200 nm). Iron solutions injected into these flames strongly emit iron lines at many wavelengths down to 200 nm. On the other hand, oxygen-rich flames operating at the same temperature do not emit such broad-band radiation, and iron lines are not emitted from such flames. The emission intensity generated by thermally excited atoms should be the same according to the Boltzmann distribution but is clearly not the same. In the same paper, a demonstration of atomic fluorescence was described using a hollow cathode as a light source.

The advent of the nitrous oxide-acetylene flame has provided us with a flame with higher temperature than was hitherto available. This has increased the usefulness of flame photometry. Also, the use of the elongated burner as developed for atomic absorption spectroscopy has increased the sensitivity of the method. Because flames are a low-energy source they populate the first excited energy state E_1 reasonably well but the upper energy states E_2 , E_3 etc. only poorly. Flame photometry therefore utilizes the resonance transitions $E_1 \rightarrow E_0$ most commonly and other transitions only under special circumstances.

14.4 Instrumentation

A block diagram of the equipment used in flame photometry is shown in Fig. 14.4. The instrument possesses the same basic components as a spectroscopic apparatus has. However, the basic components are source, monochromator, slit system and detector system. The flame photometer also includes a burner which is utilised for burning the sample solution and exciting the atoms produced in the flame after burning.

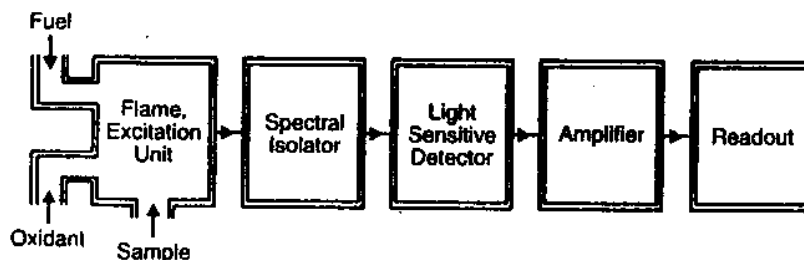


Fig. 14.2 : Block diagram of a flame photometer.

The various components of the instrument are described as follows :

1. **Burner.** The flame used in the flame photometer must possess the following functions :
 - (i) The flame should possess the ability to evaporate the liquid droplets from the sample solution, resulting in the formation of solid residue.
 - (ii) The flame should decompose the compounds in the solid residue formed in step (i), resulting in the formation of atoms.
 - (iii) The flame must have the capability to excite the atoms formed in step (ii) and cause them to emit radiant energy. For analytical purposes, it becomes essential that emission intensity should be steady over reasonable periods of time (1-2 min).

The temperature of the flame, which is primarily responsible for the occurrence of the above mentioned processes is controlled by several factors which are summarised as follows :

- (i) Type of fuel and oxidant and fuel-to-oxidant ratio;
- (ii) Type of solvent for preparing the sample solution;
- (iii) Amount of solvent which is entering into the flame;
- (iv) Type of burner employed in flame photometer; and

- (v) The particular region in flame which is to be focussed into the entrance slit of the spectral isolation unit.

In flame photometry, several burners and fuel-oxidant combinations have been used to produce the analytical flame. Some of these are discussed as below :

X Mecker burner. This burner was used earlier and employed natural gas and oxygen. As this burner produced relatively low temperatures and low excitation energies, this was generally used for the study of alkali metals only.

The flame produced by Mecker burner is not homogeneous chemically. It means that there are different regions in the flame, i.e., an "oxidising" region and a "reducing" region appear in the flame. As the processes leading to atomic excitation in the flame differ in the oxidising and reducing regions in flame, different concentrations of excited atoms are obtained in these regions.

These days Mecker burner is not used.

✓ (ii) Total consumption burner. A typical total consumption burner is shown in Fig. 14.3. In this burner, the fuel and oxidant are hydrogen and oxygen gases respectively. In this type of burner, the liquid sample is drawn into the flame. From the side tubings, hydrogen and oxygen are entering and both are burning at the top of the burner to produce a flame. As soon as the liquid sample is drawn into the base of flame, the oxygen aspirates sample solution leaving a solid residue. Atomisation and excitation of the sample then follow.

The name "total consumption burner" is used because all the sample that enters the capillary tube will enter the flame regardless of droplet size.

The flame produced by total consumption burner is noisy and turbulent but can be adjusted to produce high temperatures by proper control of fuel-to-oxidant ratio. This burner was used for a number of years but its use has been stopped and replaced by other types of burners.

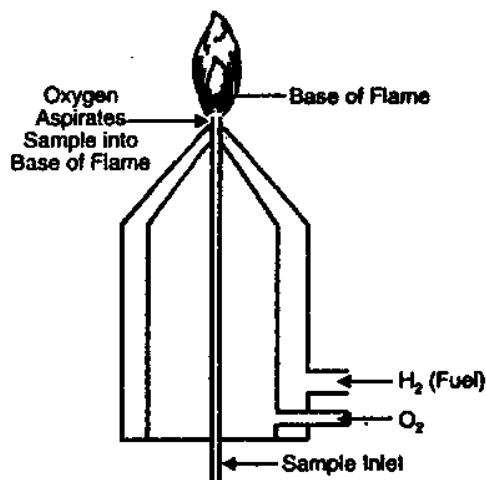


Fig. 14.3 : Total consumption burner.

✓ (iii) Premix of laminar-flow burner. A typical premix or laminar-flow burner is shown in Fig. 14.4. In this energy type of burner, aspirated sample, fuel and oxidant are thoroughly mixed before reaching the burner opening and then entering the flame. In this burner the gases move in non-turbulent fashion, i.e., in laminar flow.

An important feature of laminar-flow burner is that only a small portion (about 5%) of the sample in the form of small droplets reaches the flame and is easily decomposed. By the easy decomposition it means that an efficient atomization of the sample in the flame will take place. Larger droplets from the aspirator impinge on the side of the spray chamber and are drained off. Thus, in this burner 95%

of the sample may be wasted, thereby, resulting in a loss of sensitivity. However, this loss must be balanced against the loss of larger droplets.

The flame produced by premix burner is non-turbulent, noiseless and stable. Another advantage is that in this burner easy decomposition of the sample takes place which results in an efficient atomization of the sample in the flame. Premix burners can handle solutions up to several percent without clogging.

The main disadvantage of premix burner arises when the sample contains two solvents. When this is aspirated into the flame, the more volatile sample will evaporate in the spray chamber, leaving the sample in the form of undissociated atoms in the less volatile component. Thus, a smaller, number of atoms would reach the flame. This will reduce the emission intensity, giving incorrect results.

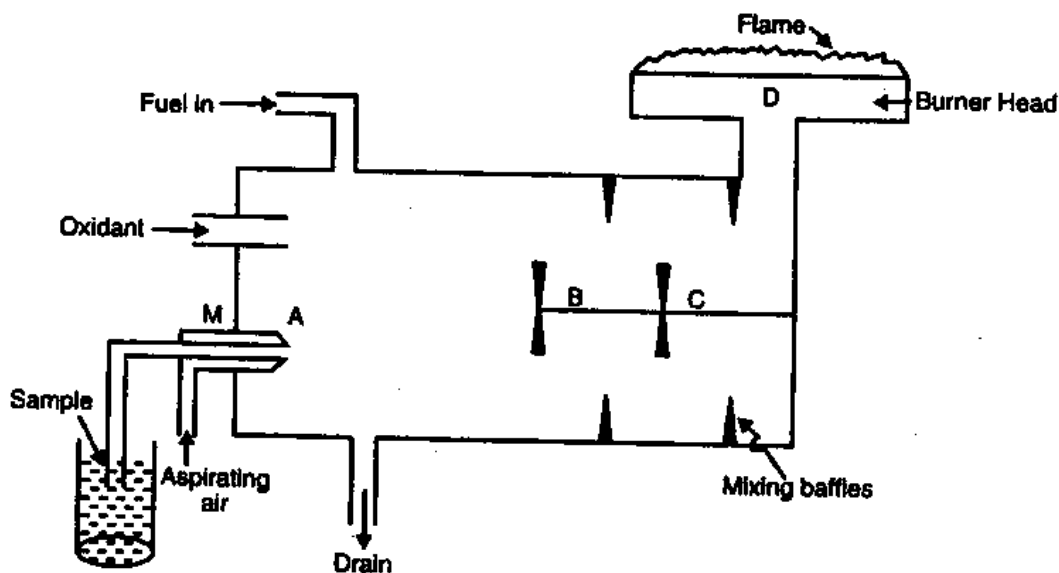


Fig. 14.4 : Premix of laminar-flow burner.

Sequence of Events in a Flame

The sequence of events occurring in rapid succession in the flame are given below:

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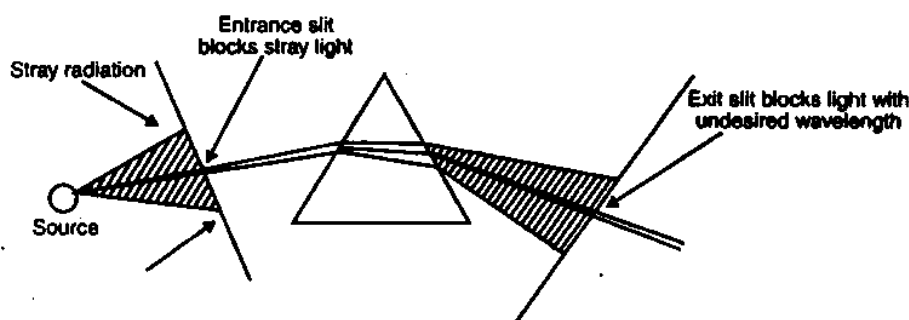
2.375

- (i) The water or other solvent is evaporated, leaving minute particles of the dry salt.
- (ii) The dry salt is vaporized or converted into the gaseous state.
- (iii) A part or all of the gaseous molecules are progressively dissociated to give free neutral atoms or radicals.
- (iv) A part of the neutral atoms may be thermally excited or even ionized.
- (v) A portion of the neutral atoms or radicals in the flame may combine to form new gaseous compounds.

2. **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 get 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 of 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 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, e.g., from acid vapors in a hood. Great care should be taken to protect them by keeping the instrument away from corrosive atmospheres.

3. **Slits.** 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 very narrow, that is, of the order of a few nanometers. This is necessary if emission lines from other components in the flame have a wavelength similar to those of the emission lines of the elements being determined. The slit must prevent such interfering lines from reaching the detector. The function of the slits is illustrated in Fig. 14.7.



✓ Fig. 14.7 : Monochromator system shown without collimator lenses for simplification.

4. **Monochromators.** In simple flame photometers, the monochromator is the prism. But in expensive models, the grating monochromators are used.

Quartz is the material most commonly used for making prisms even though its dispersive power is less than that of glass. The reason for this is that quartz is transparent over the entire region.

The grating monochromator employs a grating which is essentially a series of parallel straight lines cut into a plane surface.

5. **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 such a material which is transparent over a narrow spectral range. When a filter is kept between the flame and detector, the radiation of the desired wavelength from the flame will be entering the detector and be 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 this is that a large number of filters are employed.

✓ 6. **Detectors.** The radiation coming from the optical system is allowed to fall on the detector which measures the intensity of radiation falling on it. The detector should be sensitive to radiation of 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.

✓ 14.5 Effect of Solvent in Flame Photometry

The solvent used in the sample affects the signal in two ways. First, viscosity controls the rate at which the sample is aspirated into the flame. There is an optimum sample flow rate, which has to be experimentally determined. If the flow rate is too great, the flame is swamped and the signal drops off; if the flow rate is too low, then the signal is decreased because insufficient sample finds its way into the flame.

The second effect of the solvent is caused by the difference between aqueous or organic materials. If it is aqueous, then the sample requires energy to evaporate it. Generally an inorganic salt is left, which requires more energy from the flame to decompose it. These are two endothermic steps, which slows down the atomization process. On the other hand, if the solvent is organic, it burns on introduction to the flame and usually leaves an organic residue, which in turn burns inside the flame. Each of these steps is exothermic, the atomization efficiency is increased, and there is an enhancement of signal. This is the reason for signal enhancement when organic solvents are used rather than aqueous solvents.

It can be seen from these comments that in order to get good quantitative data it is necessary that the sample introduction note, the solvent used, and flame conditions, including the fuel and oxidant, be the same for both the samples to be analyzed and the preparation of calibration curves. Any variations in these conditions cause a major variation in flame intensity and therefore in the analytical data obtained.

✓ 14.6 Instruments

There are a large varieties of flame photometers in widespread use, ranging all the way from very single-beam filters photometers to multichannel spectrometers with automatic background correction.

(i) **First Type.** The simplified diagram of a flame photometer is depicted in Fig. 14.8.

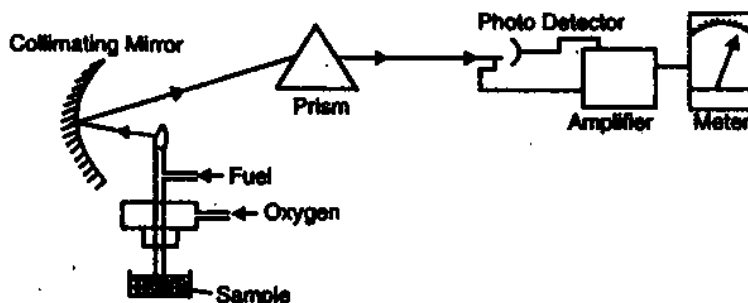


Fig. 14.8 : Schematic diagram of a modified flame spectrophotometer.

The burner used in flame photometer shown in Fig. 14.8 is a total consumption type, but a premix burner can also be used. In Fig. 14.8, a collimating mirror is used behind the flame to increase the emission

intensity. But this mirror is often omitted when premix burners 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 fine spray. Spectral emission comes from the excited atoms 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 appropriately selected wavelength strikes a photo detector and the magnitude of the electrical signal developed is read 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 meters in the gas lines (not shown in figure).