# FLAME EMISSION SPECTROMETERY

**Principle:**

Emission of electromagnetic radiation in the visible and UV region of spectrum by atoms after electronic excitation in flames.

Flame photometry (more accurately called flame atomic emission spectrometry) is a branch of atomic spectroscopy in which the species examined in the spectrometer are in the form of atoms. The other two branches of atomic spectroscopy are atomic absorption spectrophotometry and inductively coupled plasma-atomic emission spectrometry. In all cases the atoms under investigation are excited by light. Absorption techniques measure the absorbance of light due to the electrons going to a higher energy level. Emission techniques measure the intensity of light that is emitted as electrons return to the lower energy levels.

Combustion flames provide a remarkably simple means for converting inorganic analytes in solution in to free atoms. It is only necessary to introduce an aerosol of the sample solution in to an appropriate flame, and a fraction or all of the metallic ions in the aerosol droplets are eventually converted into free atoms. Once the free atoms are formed they may be detected and determined quantitatively at the trace level by atomic flame emission.

In flame emission relatively low temperature 2000 – 3000 °C is used and consequently lower energy available to induce electronic excitation. It follows that the flame induced emission spectrum of an element will be much lesser complex. Flame emission spectrometry is a particular useful technique for the determination of volatile elements with low excitation energies such as alkali and alkaline earth metals. Flame photometry is suitable for qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at a relatively low flame temperature (mainly Na, K, Rb, Cs, Ca, Ba, Cu).

This is in particularly due to a high sensitivity resulting from relatively low degree of ionization induced by cool flame and a longer residence time for analyte atoms in the flame.

**Instrumentation:**

Following are the main components of flame emission spectrophotometer.

Flame photometer or spectrophotometer incorporating nebulizer and burner, filters, prism or grating monochromator, photo cell or photomultiplier detection system.



The sample in the form of a solution is drawn into nebulizer where it is converted into a fine mist aerosol from there it passes into the flame along with air or oxygen and a fuel gas. Following their excitations the radiations emitted as excited atoms release is viewed by a photo cell or photo multiplier. The current generated in the detector circuit may be read directly or more conveniently, converted to a meter or a digital read out in an analyte emission resulting from flame excitation facilitates the almost instantaneous measurements of line intensities. Low temperature flames produce spectra that are sufficiently simple to allow the use of a narrow band pass filter to isolate the required emission line for quantitative measurement. Such an instrument being termed as flame photometer. If better resolution is needed to isolate lines in more complex spectra or to minimize interference from background emission, a flame atomic emission spectrometer incorporating prism or grating dispersion is necessary and the technique is known as flame atomic emission spectrometry.

**Flame characteristics:**

Flame used in analytical measurements is similar to those by Bunsen burners with the added provision of a mean of introducing the sample directly into the combustion zone. Support (oxidant and fuel gases) is fed to a nebulizer along with a sample solution. The mixed gases and the sample aerosol then passed through the jets of the burner where ignition occurs. For flame emission measurements burners of the meker type with the circular orifice covered by a grill are used where as in atomic absorption spectrometry, a slit burner is preferred. In both cases the flame consists of two principle zones or cones. The inner cone or primary reaction zone is confined to the region just above the burner orifice; it is here that combustion, atomization and thermal excitation occur. The combustion products consist largely of CO, H2, CO2, N2, H2O, and free radicals such as –OH. Above the primary zone is the outer cone or secondary reaction zone. In this region cooling occurs as result of mixing with surrounding atmosphere. This may lead in turn to the contamination of impurities such as sodium compounds which will increase back ground emission from the flame. A second problem concerns the buildup of water in the outer cone resulting in considerable emission by –OH radicals between 280 – 350 nm. One method of minimizing this has been to use divided flames. A cone of a gas, which may be existing support gas or a noble gas, is injected between the inner and outer cones, thus effectively, lifting off, the outer reaction zone, reducing the flame background and stabilizing the important inner cone. The maximum temperature of the non divided flame is reached at the junction of the inner and outer zone and the divided line is not always clear and an interconal zone may often be identified. The optical axis of the instrument is usually aligned on this zone but the optimum position for maximum sensitivity for each element varies, and should be chosen by experimental observation. The fuel gas will burn towards the burner orifice with a velocity of between 1 – 50 ms-1.  To prevent blow back it is necessary for the rate of fuel supply to exceed this burning velocity. It will be seen that high temperatures can be attained with hydrogen/ oxygen flames but at the expense of high burning velocity which leads to a low resonance time for the analyte. A good compromise is reached when acetylene in the fuel gas, as temperature of 2000 – 3000 °C may be achieved at moderate burning velocities.

**Flame process:**

Flame atomization and excitation can be divided into number of stages. Firstly the heat of the flame evaporates solvent from the droplets of sample aerosol leaving a cloud of small particles of the solid compounds originally present in the solution. These are then vaporized and molecular association broken down releasing free atoms (atomization) some of which undergo electronic excitation or ionization. The population of free atoms in the flame will be in an equilibrium value dependant on the rates of nebulization and atomization from the original sample solution and the rates at which the atoms are removed with exhaust gases, by chemical reactions within the flame gases or by ionization.

The various factors are summarized as follows:

1. **Rate of fuel flow:**

This affects the rate of nebulization and the residence time of the atoms inside the flame.

1. **Viscosity of the solvent:**

This affects the rate of nebulization.

1. **Chemical nature of the solvent:**

This may lead to the formation of stable solvated species and a modification of flame conditions depending on the degree of inflammability.

1. **Other chemical species in the solution or flame:**

This may form stable non volatile compounds with the analyte.

1. **Flame temperature:**

This will control the rate of solvent evaporation, the breakup of molecular associations containing the analyte and the extent of ionization of analyte atoms.

Careful control and optimization of the above factors is necessary in all techniques involving flames i.e., flame photometry and flame emission spectrometry. These two require a maximization of the number of excited atoms in the flame and the number which relax by the emissions of the electromagnetic radiation. An additional factor affecting the emission process is the possibility if relaxation of the excited atoms by non-radioactive transition. These are caused by collision with other particles within the flame there by dissipating their excess energy and resulting in a decrease in emission intensity.

**Emission spectra:**

The comparatively low thermal energy of the flames results in the production of simple atomic and molecular spectra. Atomic lines from transitions to the ground state from the first two or three excited levels will predominate, the most intense one originated from the lowest excited level. The degree of ionization is very small in low temperature flames (<2500 °C) except for some of the alkali metals, although it may approach 100% at flame temperatures exceeding 3000 °C. The number of the spectral lines observed from the ionized species is therefore highly dependent upon the analyte and the operating conditions.

**Quantitative measurements and interferences:**

The intensity of a spectral line and concentration of analyte is directly proportional. However, the intensity of the spectral line is very sensitive to changes in flame temperature because such changes can have a pronounced effect on the small proportion of atoms occupying excited levels compared to those in the ground state. Quantitative measurements are made by reference to a previously prepared calibration curve or by the method of standard addition. In either case, the conditions for measurement must be carefully optimized with reference to the choice of emission line, flame temperature, concentration range of samples and linearity of response.   
Relative precision is of the order of 1 to 4 %. Flame emission measurements are susceptible to interferences from numerous sources which may enhance or depress line intensities.  
**Spectral Interferences:**

Spectral interferences may arise from the close proximity of other emission lines or bands to the analyte line or by overlap with it. They can often be eliminated or maximized by increasing the resolution of the instrumentation, e.g. changing from a filter photometer to a grating spectrophotometer. Alternatively another analyte line can be selected for measurements. Correction for background emission is also important and is made by monitoring the emission from a blank solution at the wavelength of the analyte line or by averaging measurements made close to the line and either side of it.

**Self absorption:**

**Self absorption** is a phenomenon where emitted radiation is reabsorbed as it passes outwards from the central region of the flame. It occurs because of interaction with the ground state atoms of the analyte in the cooler outer fringes of the flame and results in alteration of the intensity of the emission. It is particularly noticeable for lines originating from the lowest excited level and increases with the concentration of the analyte solution. The presence of species in the flame other than those of the analyte may alter the emitted intensities of analyte lines through chemical interactions. Thus, easily ionized elements in the hot flames will suppress the ionization of the analyte atoms thereby increasing the intensity of the atom lines. The effect can be used to advantage in eliminating variations due to sample composition, the matrix effect, and improving sensitivity. This is achieved by adding large amounts of an easily ionizable element to samples and standards. Inorganic ions generally lower the emitted intensity of metallic analyte lines by compound formation is the sample aerosol which reduces the population of atoms in the flame. Sulphate, nitrate, phosphate and aluminate are notable examples whose effects have been well studies in the determination of the alkaline earth metals. The addition of the releasing or the chelating agents, e.g. EDTA, which protect the metal from the interfering ion is the recognized way of eliminating the effect. Organic solvents enhance emitted intensities mainly because of a higher resultant flame temperature and a more rapid rate of feed into the flame because of the generally lower viscosity, and the formation of the smaller droplets in the aerosol because of reduced surface tension. The resultant enhancement of spectral line intensity may be 3 to over 100 folds. Conversely, the presence of salt, acids and other dissolved species will depress the intensity of emission from the analyte and underlines the need for careful matching of samples and standards.

Flame photometry has many advantages. It is a simple, relatively inexpensive, high sample throughput method used for clinical, biological, and environmental analysis. On the other hand, the low temperature makes this method susceptible to, particularly, interference and the stability (or lack thereof) of the flame and aspiration conditions. Many different experimental variables affect the intensity of light emitted from the flame. Fuel and oxidant flow rates and purity, aspiration rates, solution viscosity, concomitants in the samples, etc. affect these. Therefore, careful and frequent calibration is necessary for good results and it is very important to measure the emission from the standard and unknown solutions under conditions that are as nearly identical as possible.

**Applications of Flame photometry and Flame emission spectrometry:**

Flame emission spectrometry is used extensively for the determination of trace metals in solution and in particular the alkali and alkaline earth metals. The most notable applications are the determination of Na, K, Ca and Mg in body fluids and other biological samples for clinical diagnosis. Simple filter instruments generally provide adequate resolutions for this type of analysis. The same elements, together with B, Fe, Cu and Mn, are important constituents of soils and fertilizers and the technique is therefore also useful for the analysis of agricultural materials.   
Detection limits for flame emission spectrometry is 0.01 to 10 ppm. Flame emission spectrometry is used for elements which are easily ionizable.