14.7 Application of Flame Photometry

1. The Qualitative Analysis. Flame photometry is only used to detect elements of groups I and II of the periodic table. These elements are sodium, potassium, lithium, magnesium, calcium, strontium, and barium. Some of these elements can be detected visually by the colour in the flame. An example is sodium which produces yellow flame. But this method is not very reliable. However, the best method is to use a flame photometer with a filter or monochromator to separate radiation with the wavelengths characteristic of the different metals from other radiations present. If the radiation of the characteristic wavelength is detected, this will indicate the presence of a metal in the sample.

The method to carry out detection of elements by flame photometry is fast, simple and if carried out with care, quite reliable. However, this method faces with some difficulties which are outlined as follows:

(*i*) This method is less reliable than atomic absorption spectroscopy.

(*ii*) This does not provide information about the molecular structure of compound present in the sample solution.

(*iii*) Non–radiating elements, such as carbon, hydrogen and halides cannot be detected by flame photometer. However, these can only be determined under special circumstances. For example, if chlorine is to be detected in a liquid sample, the best method is to precipitate it as silver chloride which is then aspirated into flame of a flame photometry to carry out the determination of silver. From the result, the chloride content can be calculated.

2. Quantitative Analysis. 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 elements besides that of I and II groups can also be determined. In the Table 14.4, there is a list of elements with their emission wavelengths and detection limits. All the elements present in this table have been determined successfully by flame photometry.

Table 14.4 : Detection Limits and Flame Spectra of the Elements

Element	λ Å	Detection limit ppm	Element	λ Å	Detection limit ppm
Aluminium	3962	0.5	Copper	3247	0.6
	4840	0.5			
Antimony	2528	1.0	Iron	3720	2.5
				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
Calcium	4227	0.07	Mercury	2536	2.5
	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 the radiation intensity, one can determine the concentration of metal present in the sample by employing one of the following methods :

(*a*) Standard addition method

(*b*) Internal standard method

Let us discuss these methods one by one.

(*a*) **Standard Addition Method.** In this method, the various solutions containing the unknown and known amounts of standard substance are used.

In this method, the first job is to know the signal intensity for the unknown X by aspirating its solution into the flame of a flame photometer. Then a series of solutions having the unknown X plus varying amounts of the standard A are prepared and their signals obtained by aspirating them into the flame. A plot is drawn between the signal intensity (Y–axis) against concentration of X plus concentration of standard A. From the plot, the concentration of the unknown can be determined from the intersection of the curve with the concentration axis. A typical curve illustrating this method is shown in Fig. 14.10.
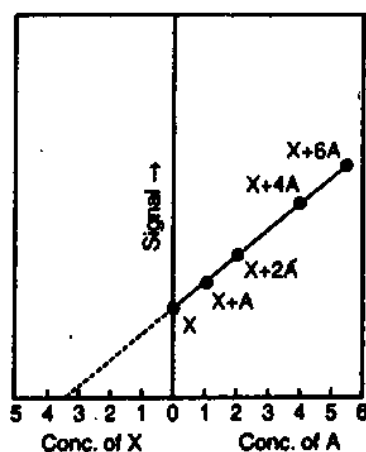

Fig. 14.10 : Illustration of standard addition method for the determination of the concentration of the unknown X, A is the known standard substance.

Advantages. (*i*) The method is useful for determining very low concentrations of the elements present in the sample.

(*ii*) This method compensates for any unexpected interfering material present in the sample solution.

(*iii*) 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.

(*b*) **Internal Standard Method.** When this method is applied to a simple flame photometer, following steps are involved:

(*i*) Prepare standard sample solutions containing known amounts of internal standard element (usually lithium). Then aspirate these standard samples into the flame and record the signal intensity for each of these samples.

(*ii*) Now aspirate the samples having unknown concentrations into the flame and record the signal intensity.

(*iii*) The ratio of the two intensities is calculated and is then plotted vs the concentration of the element to be determined. (The concentration of the internal standard element is kept constant). A calibration curve is obtained. From this, one can calculate concentration of the element present in the sample if its signal intensity is known by aspirating it into the flame.

When this 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 (Fig. 14.9) which gives a direct and simultaneous reading of the ratio of two intensities.

Every element cannot be chosen as the internal standard. However, it should fulfil the following characteristics :

(*i*) Its amount should be very small in the original sample.

(*ii*) It should give an emission line which reacts to interferences as the line of the element (to be determined) does.

One or both of these requirements are often violated, sometimes with disastrous results.

Simultaneous Multielement Analysis

This is relatively new application of flame emission spectroscopy. Various methods have been suggested for carrying out simultaneous multielement analysis. One of the methods was given by (Mitchell *et. al.*, 1973). They employed a vidicon detection system and an 0.25 m monochromator. A wavelength range of 1680 Å was displayed across the face of the vidicon system. By this detector, spectral lines as close as 20 Å were readily resolved. By Mitchell's method, the simultaneous determination of up to ten elements could be made in solution.

Another method to carry out simultaneous multielements analysis was suggested by Busch *et al.*, (1974). They employed a silicon diode vidicon detector with an 0.5 m monochromator. They reported spectral lines 1.4 Å apart to be resolvable and obtained data on eight elements (Mo, Fe, Ca, Al, Ti, Mn and K) simultaneously. Busch's method was used with a U.S. Geological Survey rock sample to determine Al, Fe, Ca and Ti contents in it.

4. Miscellaneous Applications. Flame photometry is very important in the analysis of biological fluids and tissues. In these elements like sodium, potassium, aluminium, calcium, cobalt and iron are detected by a flame photometer.

Flame photometry has been used for determining sodium, potassium, aluminium, calcium, cobalt and iron in soil analysis. It has also been used for natural and industrial waters, glass, cement, petroleum products and metallurgical products. Boron has been determined in various types of organic compounds.

In summary, flame photometry is a simple, rapid method for the routine determination of elements that are easily detected.

14.8 Interferences in Flame Photometry

The radiation intensity may not accurately represent the sample concentration because of the 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 good analytical results. Following are the more commonly encountered interference processes in flame photometry:

(*a*) **Spectral Interference.** The first type of spectral interference arises when two elements or compounds may exhibit different spectra but their spectra may partly overlap and both are emitting at some particular wavelength. In this case, the detector cannot make distinction between the sources of radiation and will record the total signal. Thus an incorrect answer will be obtained. This type of interference is more common at high flame temperatures because numerous spectral lines are produced at high temperatures. An interesting example is that the iron line at 3247.28 Å overlaps the copper line at 3247.54 Å and the iron line at 2852.13 Å overlaps the magnesium line at 2852.12 Å. This type of error can be overcome by removing the effect of interfering element effect by using extraction method or using calibration curves which are prepared from a solution having similar quantities of the interfering element.

The second type of spectral interference can occur if spectral lines of two or more elements are close but their spectra do not overlap. This type of interference is especially troublesome when a filter is used as the spectral isolation device. With a filter, spectral lines separated by as much as 50–100 Å may be passed through the filter to the detecting limit thus resulting in an incorrect readout signal. The possibilities of such interference can be decreased to a considerable extent by increasing the resolution of the spectral isolation system. However, the interference cannot be eliminated entirely due to the use of finite width of the spectral isolation system and the finite slit widths in such systems.

A third type of spectral interference occurs between a spectral line and a continuous background. This type of interference arises due to high concentration of salts in the sample. This occurs especially in salts of the alkali and alkaline earth metals. A continuous background is also produced by some organic solvents. An example is methyl isobutyl ketone which is particularly troublesome in flame photometry. This type of interference can be corrected by the scanning technique.

The organic solvents in a sample may influence the emission intensity of spectral line by changing the viscosity and surface tension of the liquid, which in turn alters the rate at which the sample is delivered to the flame. In addition, organic compounds also affect the temperature of the flame itself through their contribution to the heat of combustion. An enhancement of the line intensities is the usual result.

(b) **Ionisation Interferences.** In some cases, some of the metal atoms may ionise in high–temperature flame, e.g.,

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

The sodium ion possesses an emission spectrum of its own, with different frequencies from those of the atomic spectrum of sodium. Thus, ionisation decreases the radiant power of atomic emission.

The interference due to ionisation can be overcome by adding a large quantity of a potassium salt to all of the solutions—unknown and standards. The addition of potassium prevents the ionisation of sodium but it itself undergoes ionisation. Thus, the sodium atom emission is enhanced.

This type of interference is restricted to the elements of the first group of the periodic table.

(c) **Cation–Anion Interference.** The presence of certain anions in a solution may affect the intensity of radiation emitted by an element and thus results in a serious analytical error. For example, anions such as oxalate, phosphate, sulphate, and aluminate may affect the intensity of radiation emitted by an element. For example, calcium in the presence of the phosphate ion apparently forms a stable substance, so the calcium signal is depressed because it will not decompose so easily, resulting in the production of lesser atoms. Another example is that a given concentration of barium sulphate produces low emission intensity than the same concentration of barium chloride, because barium chloride can be broken down more easily than barium sulphate.

This type of interference can be removed either by extraction of the anion or by using calibration curves which are prepared with the same predominant anion at the same concentration in the standard solution as that found in the sample.

(d) **Cation–Cation Interference.** Mutual interferences of cations have been observed in many cases. Cation–cation interferences invariably decrease the signal intensity of the element present in the sample. These interferences are neither spectral nor ionic in nature and mechanisms of their interactions are unknown.

An example of cation–cation interferences is that aluminium interferes with calcium and magnesium. Also, sodium and potassium have cation–cation interference on one another.

(e) **Oxide Formation Interference.** This type of interference arises due to the formation of stable oxides with free metal atoms if oxygen is present in the flame. Thus, the emission intensity is lowered because a large percentage of free metal atoms have been removed from the flame. All of the alkaline earth elements form oxides and are subject to this type of interference.

This type of interference can be overcome by either using very high temperature flames to dissociate that oxides producing free atoms for excitation or using oxygen–deficient environment to produce excited atoms.

14.9 Factors that Influence the Intensity of Emitted Radiation in a Flame Photometer

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

(*a*) **Viscosity.** The addition of a substance which increases the viscosity of the solution (*e.g.,* surcose) decreases the intensity of light emission. This decrease results in due to a reduction in the efficiency of atomization.

(*b*) **Presence of Acids.** When an acid is present in the sample solution, this decreases the light intensity. This decrease arises due to the disturbance of the initial dissociation equilibrium.

(*c*) **Presence of Other Metals.** If other metals are present, these also alter the intensity of emitted radiation. In order to remove this defect, special filters are used which will absorb radiation due to the element which is to be estimated in the sample solution.

14.10 Limitations of Flame Photometry

(*i*) 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.

(*ii*) Flame photometry cannot be used for the direct detection as well as for the determination of the inert gases.

(*iii*) Only liquid samples may be used. In some cases, lengthy steps are necessary to prepare liquid samples.

(*iv*) 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.

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