भारतीय संस्कृति, शिक्षा और दर्शन

विभिन्न संकल्पनाएं

सम्पादक : डॉ. दिनेश चन्द्र शर्मा

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रचना -
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आवरण -
श्रीनिवास प्रिन्टोग्राफिक्स, अजमेर

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Flame Photometry

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1. Introduction-

Atomic spectroscopy provides a powerful way to identify and estimate the elements present in a sample by studying the behavior of atoms in the presence of radiation or thermal energy. Among the different techniques of atomic spectroscopy, flame photometry occupies a special place due to its simplicity and effectiveness.

1.1 Historical Background -

The roots of flame-based analysis go back to the mid-nineteenth century when chemists like Robert Bunsen and Gustav Kirchhoff used the characteristic colors of flames to detect metallic elements. They demonstrated that each element emits radiation of specific wavelengths when introduced into a flame, leading to the discovery of new elements such as cesium and rubidium. Their pioneering work laid the foundation of emission spectroscopy. Over the decades, simple flame tests evolved into a quantitative analytical technique. By the mid-twentieth century, with improvements in optics, detectors, and fuel systems, the modern flame photometer was developed, transforming a simple laboratory test into a reliable instrument for chemical analysis.

In flame photometry, the sample solution is introduced into a flame where the dissolved salts are converted into free atoms by the process of atomisation. The high temperature of the flame excites a fraction of these atoms to higher electronic states. When the excited atoms return to their ground state, they emit light of characteristic wavelengths. The intensity of this emitted radiation is proportional to the concentration of the corresponding element in the sample. This forms the fundamental working principle of flame photometry.

The method is particularly useful for elements that are easily

excited at relatively low temperatures, such as alkali metals (sodium, potassium, lithium) and alkaline earth metals (calcium, barium). These elements play crucial roles in environmental studies, clinical investigations, and biological systems. For instance, the estimation of sodium and potassium levels in blood serum is routinely carried out using flame photometry because of its speed and accuracy.

Flame photometry is valued as a quick and economical analytical tool. It does not demand highly sophisticated instrumentation, yet it provides good sensitivity in the parts-per-million to parts-per-billion range.

2.1 Principle of flame photometry -

In flame photometry, the sample solution is first aspirated into the burner and converted into a fine spray, a process known as nebulisation. As the droplets enter the flame, the solvent evaporates, leaving behind tiny solid particles. These particles move to the hottest region of the flame where they undergo decomposition to form free atoms and ions. The thermal energy of the flame excites some of these atoms to higher energy levels. When the excited atoms return to their ground state, they emit radiation of characteristic wavelengths. The intensity of this emitted light is measured and directly related to the concentration of the element in the sample, which forms the basis of quantitative analysis.

These are very fine particles that are neither truly dissolved nor easily filtered out. They remain evenly distributed throughout the water and form a colloidal solution.

2.2 Five steps to understand the working of Flame Photometry -

(i) Desolvation: The sample containing metal particles is dehydrated by the heat of the flame and the solvent is evaporated.

(ii) Vapourisation: The heat of the flame vapourises the sample constituents. No chemical change takes place at this stage.

(iii) Atomisation: At this stage the metal ions that were in the solvent are reduced to metal atoms. For example, 2+ Mg (aq) + 2e ? Mg (g). By heat of the flame and action of the reducing gas (fuel), molecules and ions of the sample species are decomposed and reduced to give atoms.

(iv) Excitation: The atoms at this stage are able to absorb energy from the heat of the flame. The amount of energy absorbed

depends on the electrostatic forces of attraction between the negatively charged electrons and the positively charged nucleus. This in turn depends upon the number of protons in the nucleus. As electrons absorb energy they move to higher energy levels and are in the excited state.

(v) Emission of radiation: Electrons in the excited state are very unstable and move back down to the ground state or a lower energy state quite quickly. As they do so, they emit the energy in the form of radiation of characteristic wavelength, which is measured by a detector. For some metals this radiation corresponds to wavelengths of light in the visible region of the electromagnetic spectrum and is observed as a characteristic colour of the flame. As electrons from different energy levels are able to emit light as they relax, the flame colour observed will be a mixture of all the different wavelengths emitted by the different electrons in the metal atom under investigation. Fig. 2.1 gives a block diagram representing the processes.

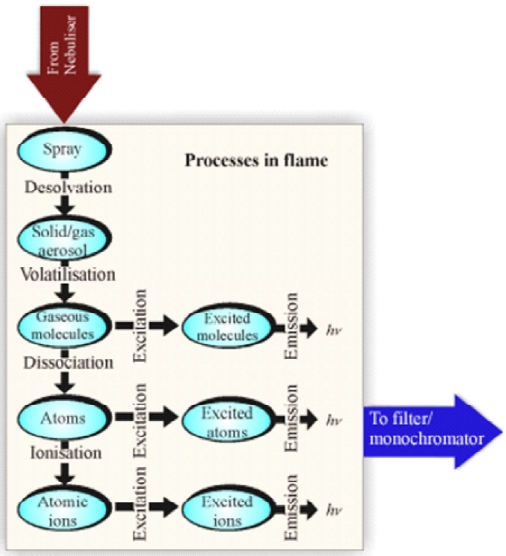

Fig. 2.1: Demonstration Of Flame Photometry In 5 Steps

The flame emission spectrum of the element sodium can be obtained by placing a solution of sodium chloride in a suitable flame. At the temperature of the flame (2000ºC to 3000 ºC) the outer elec-

tron of the sodium atom is promoted from the ground state 3s orbital to excited p orbitals (3p, 4p, 5p). The relaxation of the excited electron gives rise to the characteristic emission spectrum of the sodium atom. The emission spectrum of the sodium atom is relatively simple and consists of about 40 signals or lines; the most prominent emission signals being in the region of 285 nm, 330 nm and 590 nm. Fig.2.2 shows a portion of the flame emission spectrum for sodium atom; the excitation being done by an oxyhydrogen flame.

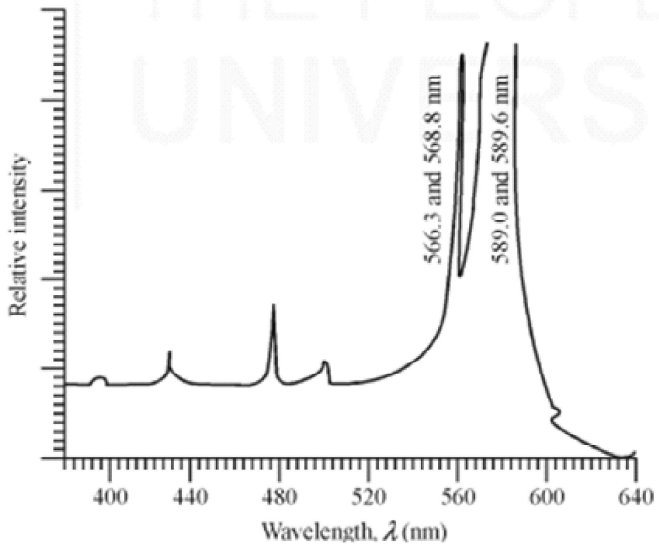

Fig. 2.2: Different Wavelength Of Sodium In Flame

You would observe an intense signal at 589 nm in the emission of the sodium atom. Flame Photometry This in fact consists of a pair of lines at 589 and 589.6 nm, which could not be resolved due to instrumental limitations. This pair of lines originates from the relaxation of the excited electron in 3p to the 3s level and is responsible for the characteristic yellow glow of the sodium light. The origin of the signals can be rationalised in terms of the energy level diagram, as given in Fig. 2.3.

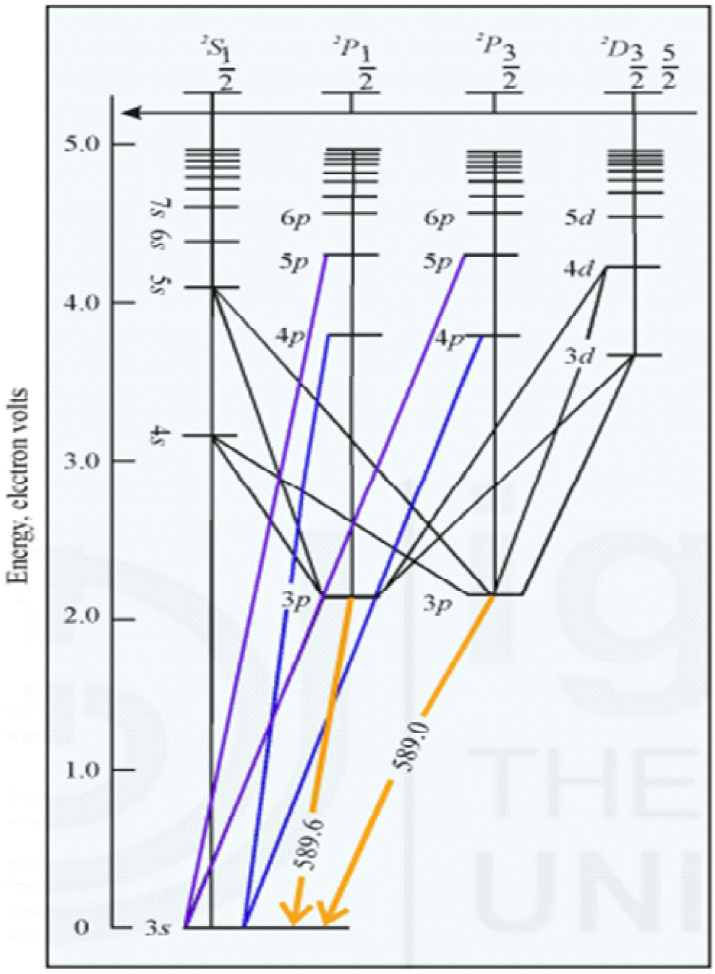

Fig. 2.3: Different Wavelength Of Sodium Orbital Form

As you have learnt above, in case of atomic emission spectroscopy, the intensity of emission signal depends upon the number of atoms in the excited state. In case of Na the ground state is 2S1/2 (3s) and the excited states are 2P3/2, 2P1/2 (3p), 2D5/2, 2D3/2 (3d), 2S1/2 (4s); 2P3/2, 2P1/2 (4p), etc. The intensity of the emission when the excited atoms return to the ground state will be maximum from the first excited state, if this transition is allowed (?s = 0, ?l = ±1). As in case of sodium, 2P3/2 and 2P1/2 states would be most popu-

lated and transition from this state to ground state is allowed (as it meets the selection rule given above, i.e., (?s = 0, ?l = ±1)); the intensity of emission from this state would be maximum. The fraction of atoms in the excited states (corresponding to the prominent spectral line) of different elements at various temperatures is presented in Table 2.1. The data shows that nearly all the atoms are present in the ground state.

Element	Emission Line λ in wave length	Temperature in °Kelvin		
Sodium	589	1×10^{5}	6×10^{4}	4 × 10−3
Potassium	767	1.7×10^{-4}	3.8×10^{-3}	1.8×10^{-2}
Lithium	670	4.4×10^{-5}	1.5×10^{-5}	9.4×10^{-3}
Calcium	422	1×10^{-7}	4×10^{-7}	6×10^{-4}
Magnesium	285	3.4×10^{-11}	1.5×10^{-7}	1×10^{-5}

Table 2.1: Different Wavelength Of Different Metals

The number of atoms in the excited state increases very rapidly with increase in temperature as shown in Table 2.1. Therefore, flames with higher temperatures will increase the number of excited atoms and make the method more sensitive. Higher temperatures are also required for decomposition of the compound having high lattice energies into atoms. However, higher temperatures may also cause ionisation of the atoms that may cause interference in the determination. We will take up this issue later in this unit (Sec. 7.7.5). Therefore, we need to optimise the temperature of the flame to be used.

2.3. STRUCTURE OF THE FLAME –

Flames are not uniform in composition, length or cross section. The structure of a premixed flame, supported as a laminar flow is shown in Fig. 2,4

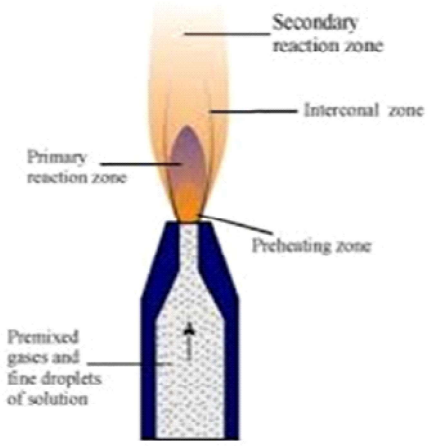

Fig. 2.4: Schematic structure of a laminar flow flame showing various zones

As seen in the figure, the flame may be divided into the following regions or zones.

(i) Preheating zones

(ii) Primary reaction zone or inner zone

(iii) Internal zone

(iv) Secondary reaction zone

The first or the innermost region of the flame is the preheating zone where the combustion mixture is heated to the ignition temperature by thermal conduction from the primary reaction zone. The second zone is the primary reaction zone or inner zone. This zone is about 0.1 mm thick at atmospheric pressure and is visible by virtue of its blue green light ascribed to radicals . C2 and . CH. There is no thermodynamic equilibrium in this zone and the concentration of ions and free radicals is very high. This region is not used for flame photometry.

Immediately above the primary reaction zone lies the third or interconal zone or the reaction free zone which can extend up to considerable height. The maximum temperature is achieved just above the tip of the inner zone. The higher temperature favours both production of free atoms and maximum excitation for atomic emission spectroscopy. Therefore, this zone is used for flame photometry.

The outermost fourth zone is the secondary reaction zone. Within this zone, the products of the combustion processes are burnt to stable molecular species by the surrounding air.

The shape of an unmixed flame is generally different. The inner zone can still be recognised, but it is very vague and is thickened. A laminar flame makes a strong hissing noise which gets louder when a liquid is atomised into it. We shall now look into the reactions which are taking place when the element is placed in flame\

2.4.Reactions in Flames - The most important reactions occurring in the flame are given below.

(i) Dissociation of moleculesM

X $\rightarrow$ M + X, Kmx = Pm Px/Pmx

(ii) Formation of compounds with flame components

M + Y $\rightarrow$ MY, Kmy = Pm Py /Pmy

(iii) Ionisation of atoms

M $\rightarrow$ M+ + e ... , KP = Pm P / Pm - e - + +

In these equations, p is the partial pressure of the species indicated in the subscript. The partial pressure of the flame gas components is much larger than the partial pressure of the given element. It is, therefore, considered constant and included into the equilibrium constant. The most important of the flame gas components forming compounds with the elements are oxygen, the hydroxyl radical and hydrogen. The most common compounds formed in flames burning with air or oxygen and metal monoxides. For example, a major fraction of alkaline earth elements is present as monoxides unless very fuel rich flames are used. However, alkali metals practically do not form any oxides. Hydroxide species are present for some alkali and alkaline earth elements in hydrocarbon flames. Sodium forms practically no hydroxide, while the concentration of LiOH molecules often exceeds the atomic lithium concentration by a factor of 10. None of the alkali metal hydroxides emit spectral bands in the visible or UV region; whereas the spectral bands of alkaline earth monohydroxide can be used for the determination of these elements.

3.1 INSTRUMENTATION FOR FLAME PHOTOMETRY

A flam photometer is consist the following equipments –

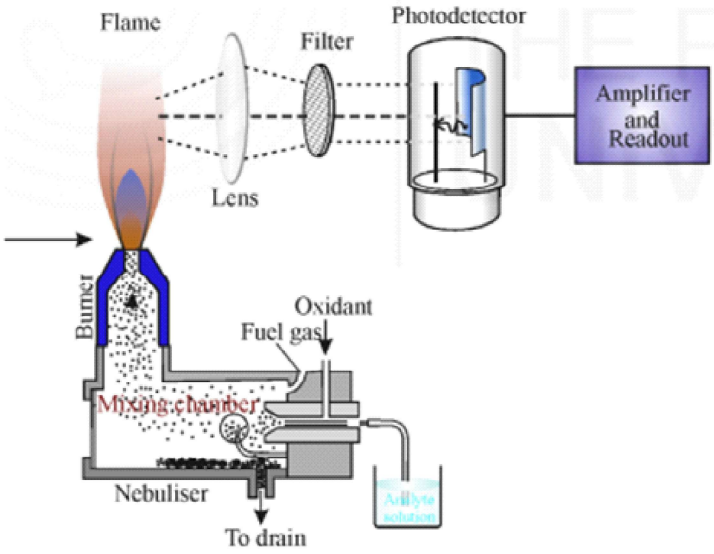

Fig. 3.1: Schematic diagram showing the layout of various components of a flame photometer

- Flame Atomizer
- Nebuliser
- Atomizer Burners
  a. Pre-mix or lundegarh burner
  b. Total consumption burner
- Monochromator
- Detector
- Amplifier and Readout Device

1. Flame Atomizer - The role of atomiser is to generate the vapours of analyte which get excited by the thermal energy of the flame and then emit characteristic radiation that is measured. The flame atomiser assembly consists of two components. The prior is a nebuliser where the sample in the form of a solution is drawn in and converted into a fine mist or an aerosol. It is then passed onto the second component i.e. the burner along with air or oxygen and a fuel gas. In the flame a number of processes occur that convert the analyte into excited species. Let us learn about the nebulisers used in flame photometers. You would learn about the burners in the next subsection.

2. Nebuliser - is a device used for sample introduction into the flame. The process is called nebulisation and consists of thermal vapourisation and dissociation of aerosol particles at high temperatures producing small particle size with high residence time. A number of nebulisation methods are available. A few are listed below.

- Pneumatic nebulisation
- Ultrasonic nebulisation
- Electrothermal vapourisation
- Hydride generation (used for certain elements only)

(However, we would discuss about the pneumatic nebulisation only. It is the most commonly employed nebulisation method in flame photometers)

(i) Pneumatic Nebuliser is the most commonly used nebuliser for introducing aqueous/ liquid samples. In this the sample solution is fed or aspirated into the nebuliser which converts liquid into a fine mist, or aerosol which is then fed into the flame. A common type of pneumatic nebuliser is called concentric pneumatic nebuliser, as shown in Fig. 3.2. The concentric pneumatic nebuliser consists of a fine capillary surrounded by concentric tube with a small orifice near one end of the capillary. The capillary is dipped into a solution of the analyte while the outer tube is connected to a high pressure gas supply. The analyte is sucked into the capillary by the high pressure gas stream flowing around the tip of the capillary using the Bernoulli effect. The process is called aspiration. The high velocity gas breaks up the liquid into various sized fine droplets. The other types of the pneumatic nebulisers also work on the same principle.

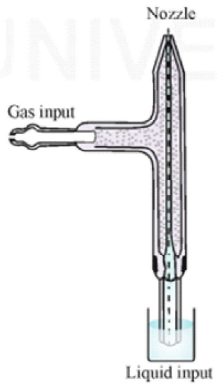

Fig. 3.2: Concentric type pneumatic nebuliser

3. Atomizer Burner - The sample is introduced in the form of a fine spray at a controlled rate into the flame of a burner with the help of nebuliser. In the burner, the analyte undergoes a number of processes as mentioned earlier. Two types of atomisation burners have been used in flame photometry which are given below and explained in the following paragraphs..

(a) Pre-mix or Lundegarh burner

(b) Total consumption burner

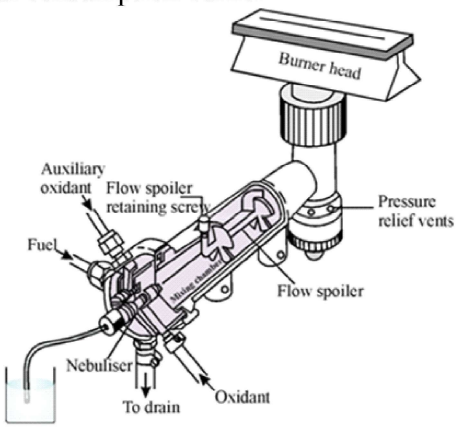

Fig. 3.3: Schematic diagram of a premix burner

(a) Premix or Lundegarh Burner - In the premix burner, fuel and oxidant are thoroughly mixed inside the burner housing before they leave the burner ports and enter the primary-combustion or inner zone of the flame. In this type of burner, the solution of the analyte is aspirated with the help of a nebuliser from the sample container into the mixing chamber in which the fuel gas is also introduced. The larger drops are stopped by baffles in the mixing chamber and are drained off. Pressure and density fluctuation of the aerosol due to atomisation are smoothened in the mixing chamber and mixture of aerosol, fuel gas and oxidant burns to yield stable noiseless flame. A Schematic diagram of a premix burner is mention in fig 3.3.

The advantage with the premix burner is that it is quiet to operate and the analytical signal is significantly less noisy than that of total consumption burner (described below). However, it also has certain disadvantages like; most of the sample solution goes down the drain which leads to loss of sensitivity in the determination of a given analyte. Further, special precautions are necessary to avoid a

flash back as the fuel and oxidant both are present and well mixed in the mixing chamber before combustion.

(**b) Total Consumption Burner -** A total consumption burner combines the functions of nebuliser and burner. In this type of burner, the suction created by the compressed oxidant streaming past the inner capillary, introduces the sample directly into the flame even if it included suspended particles or large solvent droplets; hence the name "total consumption burner. Fig 3.4 Total Combustion burner

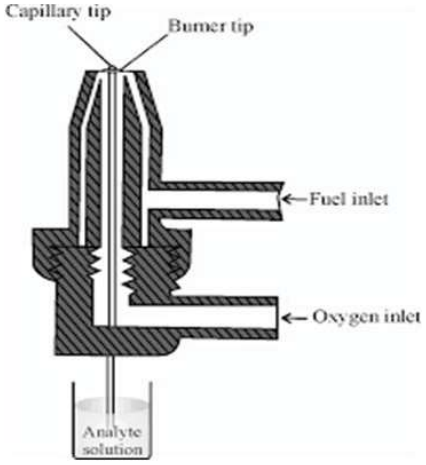

Fig. 3.4: Schematic diagram of a Total Consumption Burner

4. **Monochromator -** You have learnt about monochromators in Unit 2 on UV-VIS spectrophotometry. Generally a grating or a prism monochromator is employed. The role of the monochromator is to disperse the radiation coming from the flame and falling on it. The dispersed radiation from the exit slit of the monochromator goes to the detector. In case a low temperatures flame is used, the spectral lines from only a few elements are emitted. In such a case, for most routine analyses, a filter can be used as a monochromator to isolate a particular spectral line. Filters are generally made from materials which are transparent in a small selective wavelength region. The filter chosen is one which has a wavelength range in which it is transparent to emission from the element of interest. In such a case, a condenser lens system is employed to collect the emitted light and send the rays through the filter as an approximately collimated (parallel) beam to reach the detector. Filters have been designed for use in the determination of lithium, sodium, potassium, calcium and

other elements.

5. Detector - The function of a detector is to measure the intensity of radiation falling on it. Photoemissive cells or photomultiplier tubes are commonly employed for the purpose. These detectors are also used in UV-VIS spectrophotometers. You have learnt about these in Unit 2. You are advised to have a relook at subsection 2.4.3 to recall the functioning of different types of detectors.

6. Amplifier and Readout Device - The output from the detector is suitably amplified and displayed on a readout device like a meter or a digital display. The sensitivity of the amplifier can be changed so as to be able to analyse samples of varying concentrations. Nowadays the instruments have microprocessor controlled electronics that provides outputs compatible with the printers and computers thereby minimising the possibility of operator error in transferring data.

4.1. APPLICATIONS OF FLAME PHOTOMETRY –

Qualitative Applications - Flame photometric methods are widely used for the determination of alkali and the alkaline earth metals in samples that are easily prepared as aqueous solutions. Some of these elements can be detected visually by the colour in the flame, e.g. sodium produces yellow flame. However, this method is not very reliable. The best method is to use 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, it will indicate the presence of the metal in the sample.

Name of the element	Emitted wavelength range (nm)	Observed colour of the flame
Potassium (K)	766	Violet
Lithium (Li)	670	Red
Calcium (Ca)	622	Orange
Sodium (Na)	589	Yellow
Barium (Ba)	554	Lime green

Fig. 3.4: Table to understand the flam color by present of metal

Quantitative Applications – (i)Flame photometry was developed by Lundegarh to determine the concentration of various soil components. The concentration of various alkali and alkaline earth metals is important in determining the suitability of the soil for cultivation. Very often an analysis of shed leaves of the plant for K+ and Ca2+ is carried out. This gives an idea of the concentration of these ions in the soil which can be taken up by the plant. For agricultural purposes, an analysis of a proper mixture of surface soil and subsoil is carried out to determine the fertilizer requirement of the soil. In all these analysis, the soil or the ash is evaporated to dryness with conc. hydrochloric acid and the residue is treated with water or dilute hydrochloric acid to get these ions.

(ii) In clinical chemistry, it is very important to determine the concentration of sodium and potassium ions in body fluids since their ratio controls the action of muscles including the heart. Since these ions form few insoluble compounds and exhibit essentially no acidic or basic properties, they cannot be determined readily by conventional wet chemical techniques and are usually measured instrumentally. Flame photometry is the usual technique employed in determining these ions. This is achieved by diluting the blood serum and aspiration into the flame.

(iv)Very often internal standard lithium is added to take care of matrix effects. For example, in calcium analysis, La(III) or EDTA must be added to the solution to avoid interference due to phosphate. Food and drinks are usually analysed by ashing and leaching out the ash with mineral acid to leach out these elements. Soft drinks, fruit juices and alcoholic beverages can sometimes be analysed by using flame photometry.

(v) Analysis of water from various sources is carried out to determine its suitability for drinking, washing, agricultural and industrial purposes. Analysis of effluent water from different industries is carried out to suggest the possible methods of treatment of this waste water.

Other Applications - A relatively new application of flame emission spectroscopy is called simultaneous multi-element analysis. A number of methods have been suggested for carrying out simultaneous multi-element analysis. By using a suitable detection system and monochromator, the resolution of 2.0 nm can be achieved

and simultaneous determination of upto ten elements have been carried out by this method. In addition to the determination of metals, flame photometry can also be applied to nonmetal analysis by utilising the infrared region of the spectrum using flame infrared emission technique.

5.1MERITS AND LIMITATIONS OF FLAME PHOTOMETRY

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. The metals mainly are Na, K, Rb, Cs, Ca, Ba and Cu. The salient features of analysis by flame photometry can be summarised as follows.

- Propane-air or natural gas-air mixtures that give good flame with strong heat and minimal background light emission are used for the atomisation.
- A solvent blank is run for setting zero emission.
- As the concentration intensity relationship is not valid for all concentrations, the solutions are suitably diluted to fall within linear part of the calibration curve.
- The use of solutions of very low concentration of Na + and K+ solutions are avoided as these may encounter problems of contamination; especially in case of Na+ , which leaches slowly from glass and on contact with skin.
- The interference effects of anions and cations can cause errors and need to be suitably accounted for.
- The random flame instability and random dilution errors can be minimised by using an internal standard (lithium). Let us learn about the merits and limitations of the flame photometry method.

5.2 Merits –

- The sensitivities of the flame photometry for most alkali and alkaline earth metals lie in the ppm and sub-ppm range.
- Flame photometry is also successful in determining certain transition elements such as copper, iron and manganese.

5.3 Limitations –

- As natural gas and air flame is employed for excitation the temperature is not high enough to excite transition metals, therefore the method is selective towards detection of alkali

and alkaline earth metals.

- The low temperature renders this method susceptible to certain disadvantages, most of them related to interference and the stability of the flame and aspiration conditions. Fuel and oxidant flow rates and purity, aspiration rates, solution viscosity, affect these. It is therefore very important to measure the emission of the standard and unknown solutions under identical conditions.
- The relatively low energy available from the flame leads to relatively low intensity of the radiation from the metal atoms, particularly those that require large amount of energy to become excited. The status of the flame photometer is similar to that of the colorimeter (which uses filters) compared to the spectrophotometer (which uses a monochromator).

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