Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-3

Flame Photometers

4. PRINCIPLE OF FLAME PHOTOMETRY

Flame photometry is a method used for the determination of elements which can be easily excited for example, alkali and alkaline earth metals. This method is based upon the measurement of intensity of radiation emitted, in the visible region, when a metalatom is introduced into a flame. The wavelength of the radiation (or the colour), emitted tells us what the element is, and the intensity of the radiation tells us how much of the element is present. The International Union of Pure and Applied Chemistry (IUPAC) Committee on Spectroscopic Nomenclature has recommended abbreviation **FAES** (flame atomic emission spectrometry) for this technique. Let us learn about the processes occurring when a solution of the analyte is put into the flame.

4.1 Fate of the Sample in the Flame

In a typical flame photometric experiment, a solution containing the relevant substance to be analysed is aspirated into the burner and dispersed into the flame as a fine spray. This process is called **nebulisation**. In the flame, the solvent evaporates first, leaving finely divided solid particles which move to hottest region of the flame where gaseous atoms and ions are produced. The atoms are excited by absorbing energy available from the flame. As the excited atoms return to a ground state of lower energy, radiation of wavelength, characteristic of the element, is emitted. The intensity of the emitted radiation is then measured, which can be related to the concentration of the element present, which forms the basis of quantitative analysis. The following processes occur in the flame.

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) + 2*e* _ 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. 4 gives a block diagram representing the processes.

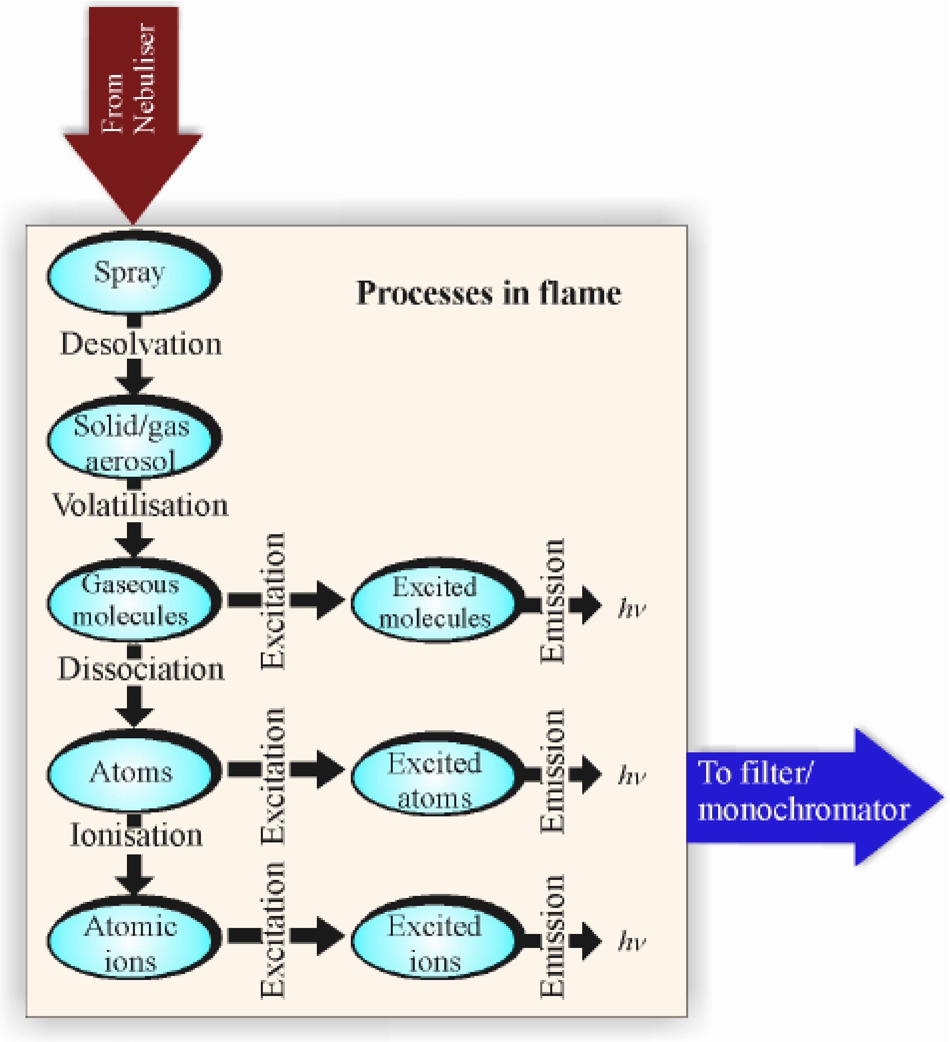


Fig. 4: Diagrammatic representation of the processes occurring in flame obtained from any hydrogen flame

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 (2000°C to 3000 °C) the outer electron of the sodium atom is promoted from the ground state 3*s* orbital to excited *p* orbitals (3*p*, 4*p*, 5*p*). 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 5 shows a portion of the flame emission spectrum for sodium atom; the excitation being done by an oxyhydrogen flame.

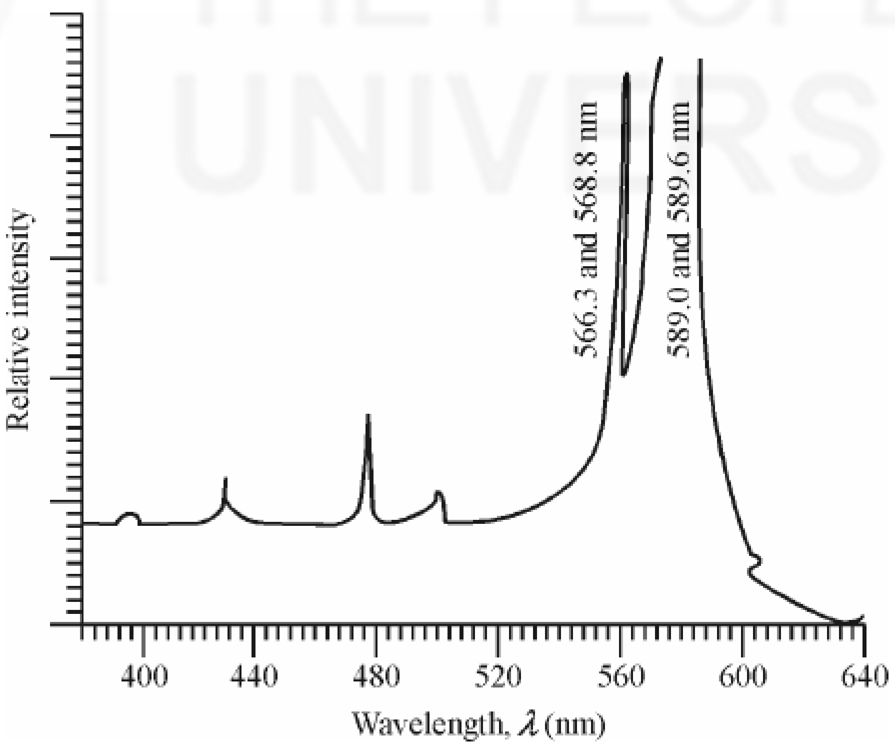


Fig. 5: Truncated flame emission spectrum for sodium atom obtained from oxyhydrogen flame

You would observe an intense signal at 589 nm in the emission of the sodium atom. 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 3*p* to the 3*s* 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. 6.

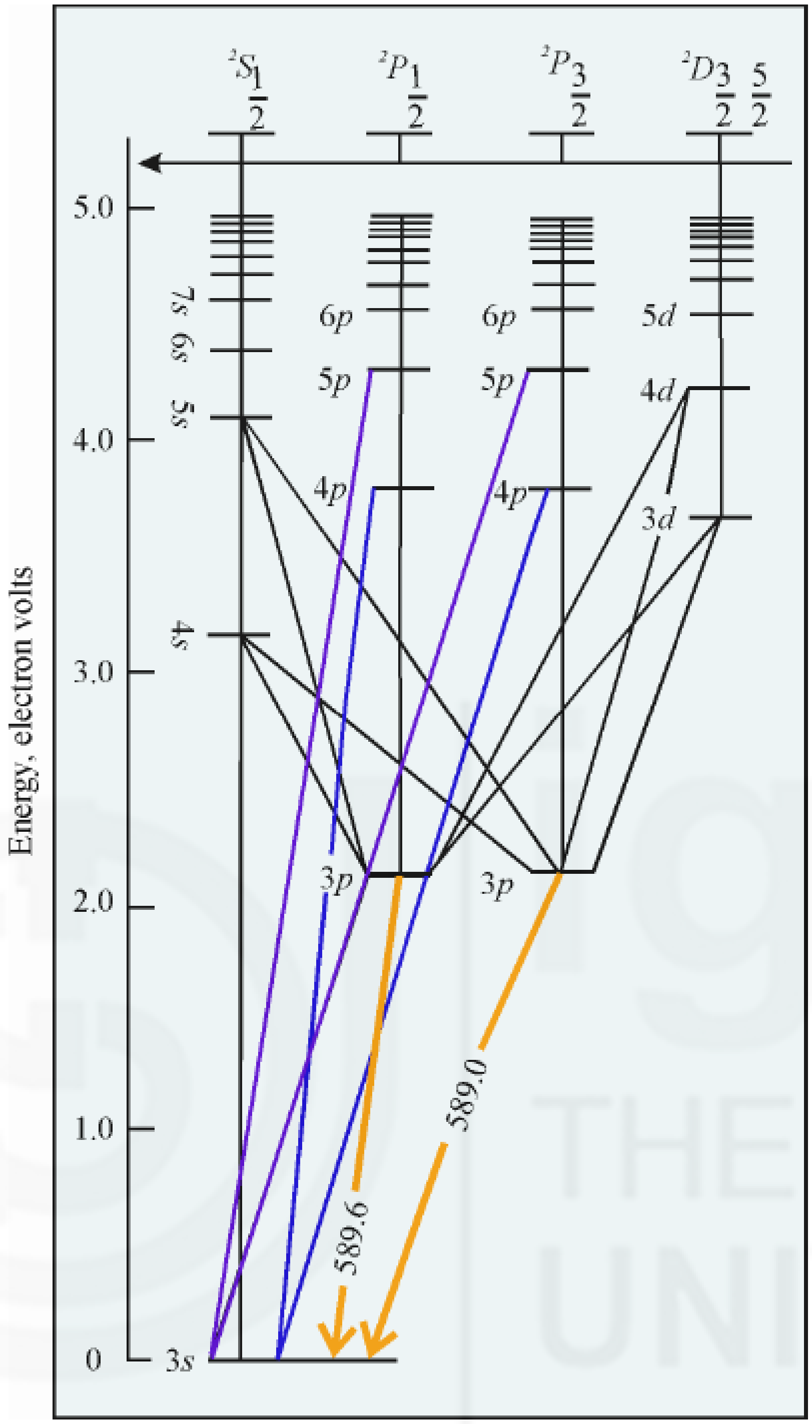


Fig. 6: The energy level diagram for sodium atom

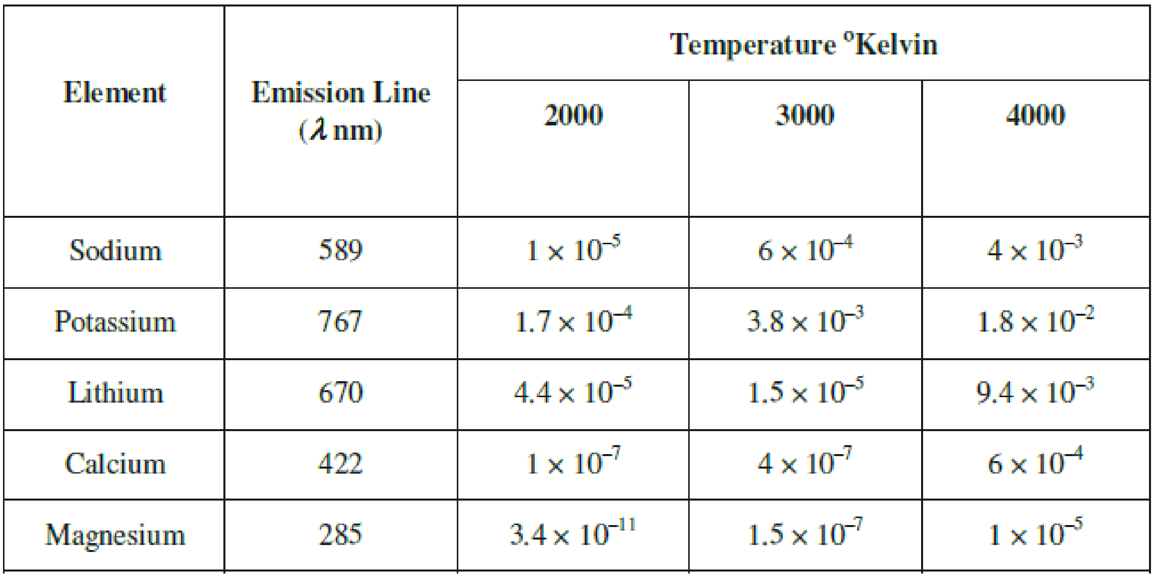
As you have learnt above, in case of atomic emission spectroscopy, the intensity of emission signal depends upon the number of atoms in the excited state. In case of Na the ground state is $2S_{1/2}$ (3s) and the excited states are $2P_{3/2}$, $2P_{1/2}$ (3p), $2D_{5/2}$, $2D_{3/2}$

(3*d*), $2S_{1/2}$ (4*s*); $2P_{3/2}$, $2P_{1/2}$ (4*p*), 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

$(\Delta s = 0, \Delta l = \pm 1)$

As in case of sodium, $2P_{3/2}$ and $2P_{1/2}$ states would be most populated and transition from this state to ground state is allowed (as it meets the selection rule given above, 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 1. The data shows that nearly all the atoms are present in the ground state.

Table 1: Fraction of atoms in the excited states of different elements at various Temperatures



Element	Emission Line (λ nm)	Temperature °Kelvin		
		2000	3000	4000
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}

The number of atoms in the excited state increases very rapidly with increase in temperature as shown in Table 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 . Therefore, we need to optimise the temperature of the flame to be used. We have so far learnt about the origin and classification of atomic spectroscopic methods, the characteristics of atomic spectrum and the principle of flame photometry. As flame has a crucial role to play in flame photometry, let us now learn about the flame and its characteristics before taking up the instrumentation required for the measurement of atomic spectra.