

AN INTRODUCTION TO ATOMIC SPECTROSCOPY

Atomic spectroscopy deals with the absorption, emission, or fluorescence by atom or elementary ions. Two regions of the spectrum yield atomic information- the UV-visible and the X-ray.

Atomic Spectroscopic methods are used for elemental qualitative and quantitative analysis .

The elements present in the sample are converted to gaseous free atoms by a process called **atomization** using either **flame** or electrical means . Then , these free atoms can be treated in several ways :

1 It can be excited by the flame itself and their ultraviolet/visible emission can be measured . The flame is both ,the atomization and the excitation mean . This technique is called **Flame Atomic Emission Spectrophotometry (FAES)** and it is the subject of this unit of this course .

2 It can be atomized and excited by an electrical mean and their ultraviolet/visible emission can be measured . These techniques are termed **Induced coupled plasma (ICP) and Arc Spark emission** and it will be the subject of units 8 and 11 of this course .

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۳- The free atoms in the flame can be irradiated using ultraviolet/visible source and their ultraviolet/visible emission (fluorescence) can be measured (atomization by flame or electrical mean while excitation by radiation) . This technique is named **Atomic Fluorescence Spectroscopy (AFS)** and it will be the subject of unit 8 of this course .

۴- The analyte is atomized by either the flame or electrical mean and the absorption of ultraviolet/visible radiation from a radiation source is measured (atomization by flame or electrical mean , then irradiation using radiation source)

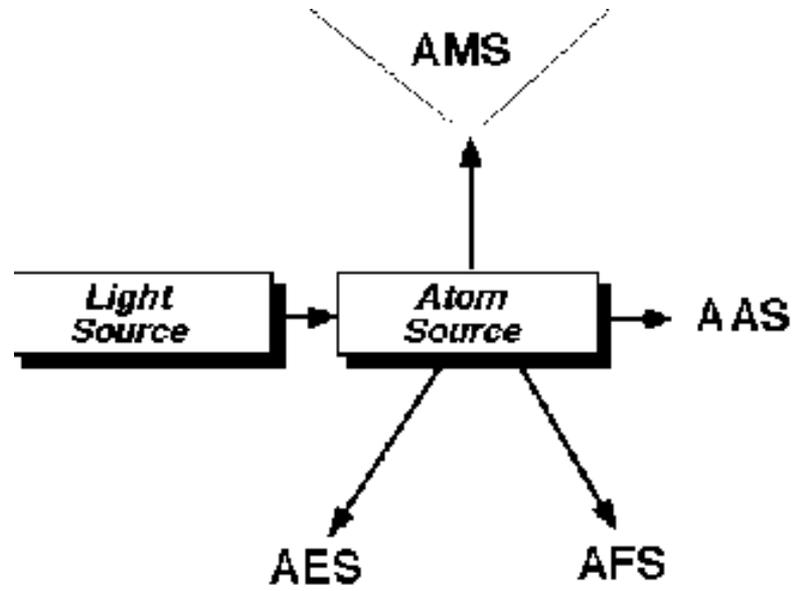
This method is called **Atomic Absorption Spectrophotometry (AAS)** and it will be the subject of unit 9 of this course .

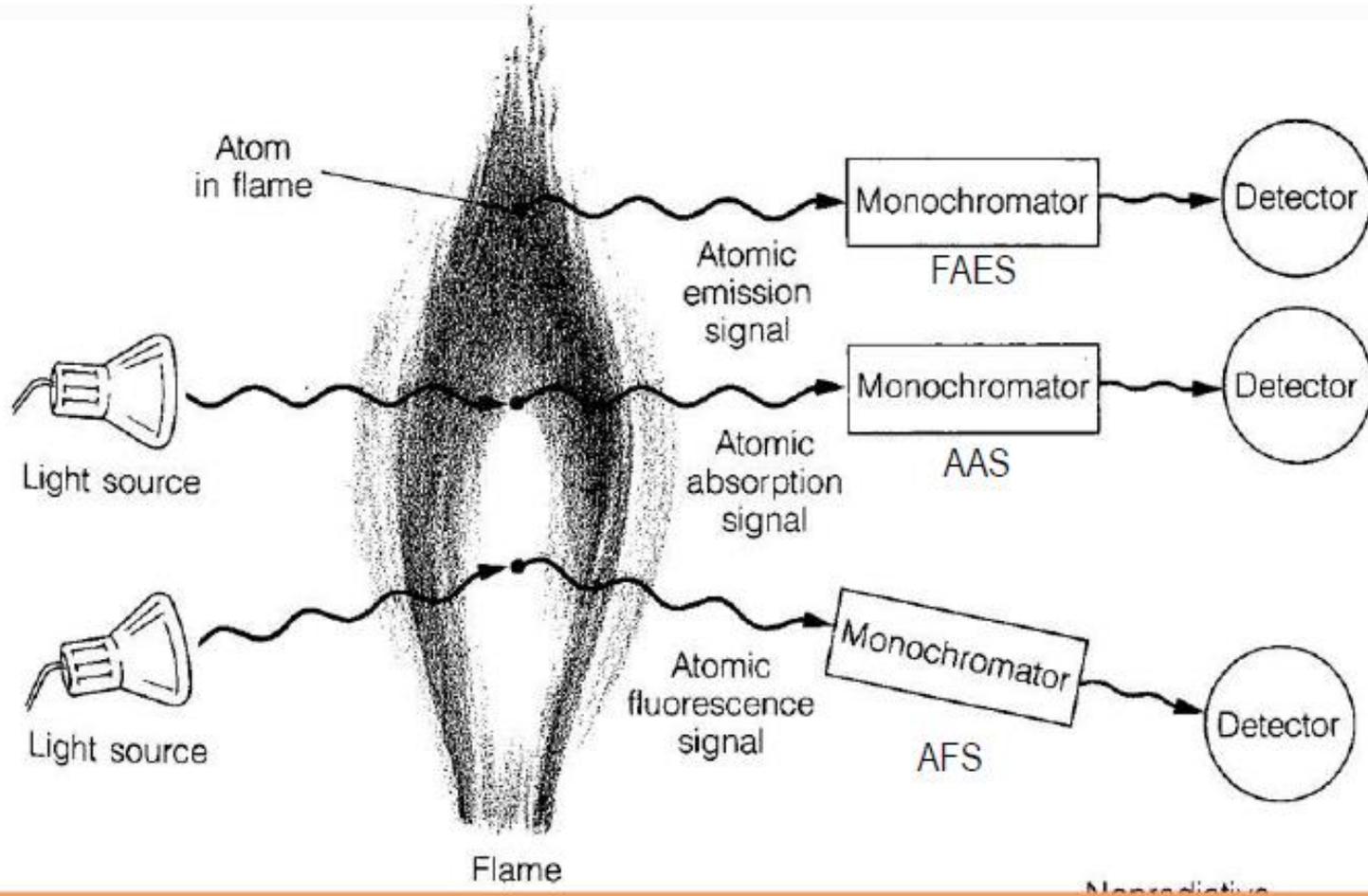
As atoms have no rotational or vibrational energy, transitions occur only between electronic levels and bandwidths in atomic spectra are very narrow (line spectrum) .

Atomic spectroscopic methods normally are classified according to the type of spectral process involved and the method of atomization used.

Atomic spectroscopy is used for the qualitative and quantitative determination of elements. Detection limits for many of these lie in the range of 10 to 1000 ppb.

To summarize : Once atoms are in the gas phase, they can be probed by any of several spectrometric techniques, including atomic emission spectrometry (AES), atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), atomic mass spectrometry (AMS), and several others.





Various flame atomization techniques

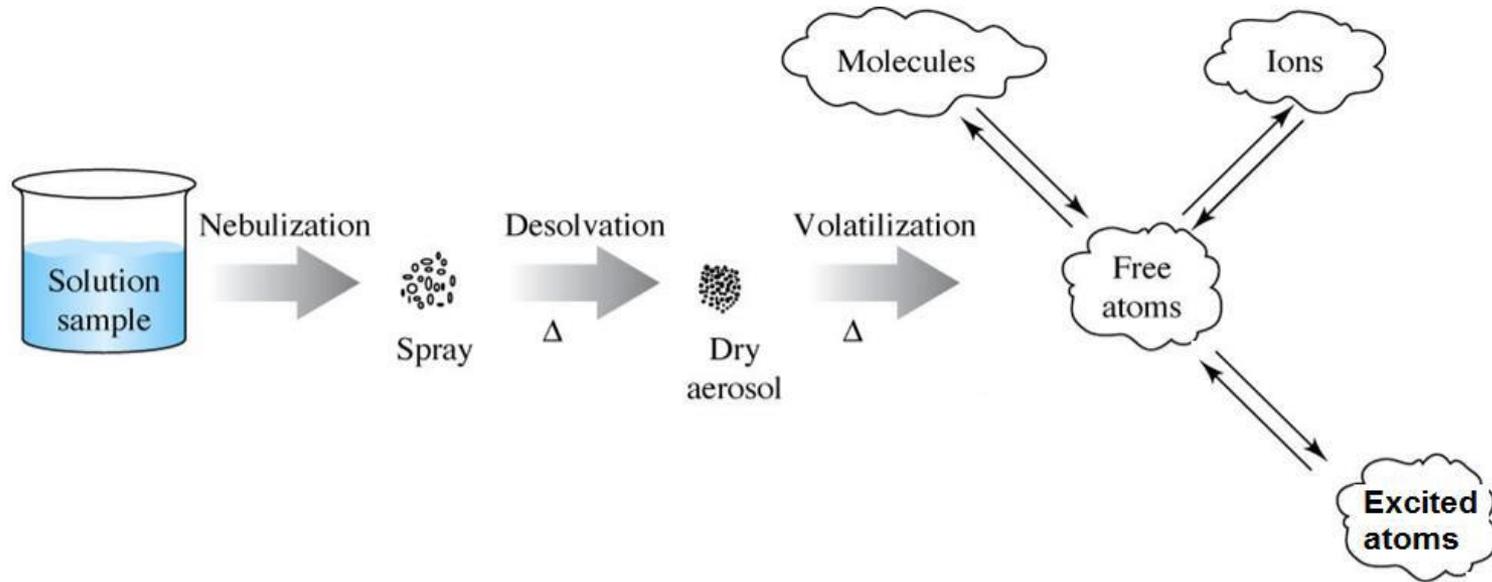
PRINCIPLES OF FAES

In flame emission spectrometry, the sample solution is nebulized (converted into a fine aerosol) and introduced into the flame where it is desolvated, vaporized and atomized, all in rapid succession. Subsequently, atoms and molecules are raised to excited states via thermal collisions with the constituents of the partially burned flame gases. Upon their return to a lower or ground electronic state, the excited atoms and molecules emit radiation characteristic of the sample components. This means that the flame plays the role of atomization and excitation processes. If the temperature of the flame is high enough, the atoms may be converted into ions as we will explain later.

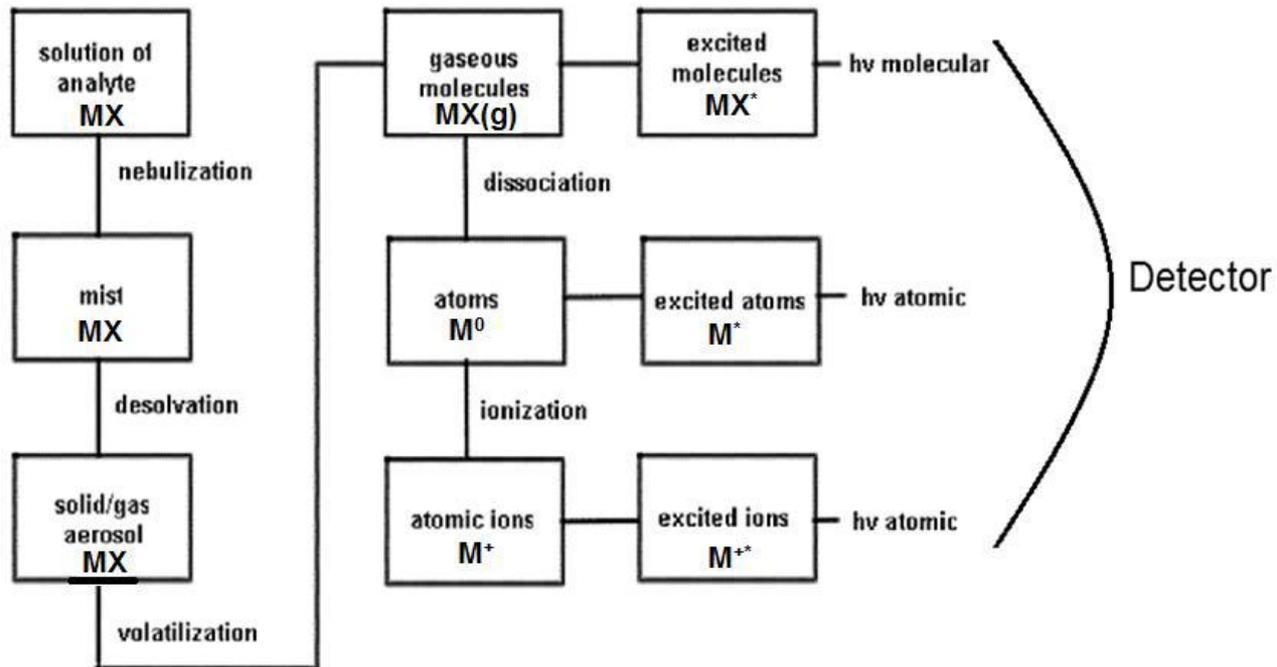
The emitted radiation passes through a monochromator that isolates the specific wavelength for the desired analyte . A photodetector measures the radiant power of the selected radiation, which is then amplified and sent to a readout device, meter, recorder, or microcomputer system .

Pretreatment of Sample :

AFES requires that the analyte be dissolved in a solution in order to undergo nebulization . The analyst must be aware of substances that interfere with the emission measurement. When these substances are in the sample, they must be removed or masked (complexed). Reagents used to dissolve samples must not contain substances that lead to interference problems.



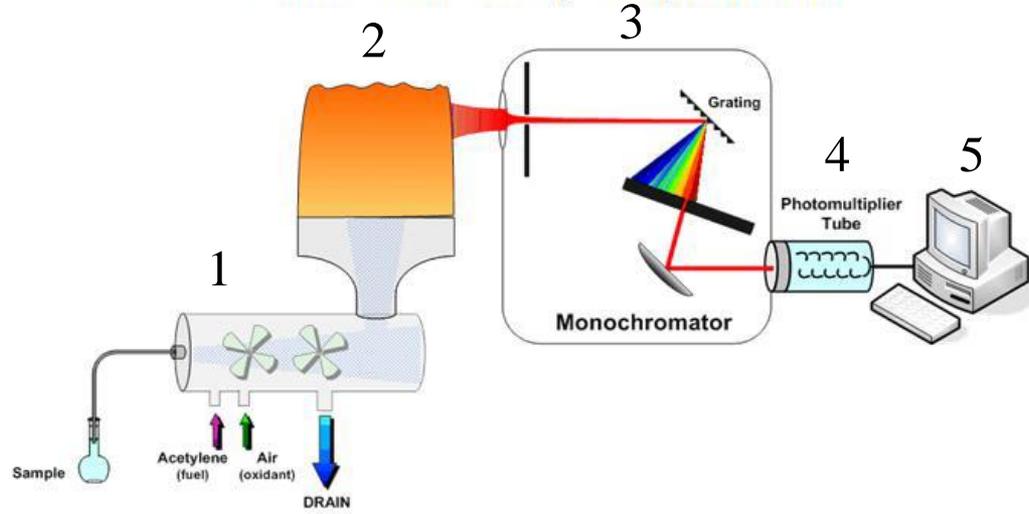
What happens to the sample in the flame ?



INSTRUMENTATION FOR FAES

The basic components of FAES instruments provide the following functions : (1) deliver the analyte to the flame, (2) atomization and excitation of the analyte by the flame, (3) isolate the spectral line required for the analysis using a prism , a grating or a filter , (4) measure the intensity of the emission at the isolated line using a phototube or a photomultiplier tube , and (5) record these intensity data. Number 3 (prism or grating) and 4(phototube or photomultiplier tube) have been discussed in unit 3 so here we will investigate only 1 and 2 .

Atomic Emission Spectrophotometer



1- Sample Delivery :

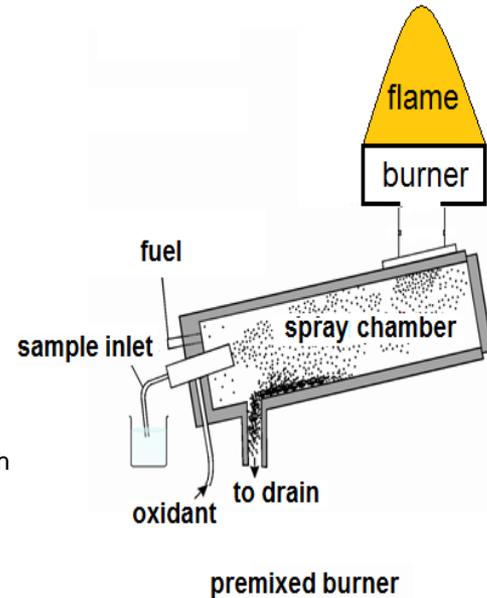
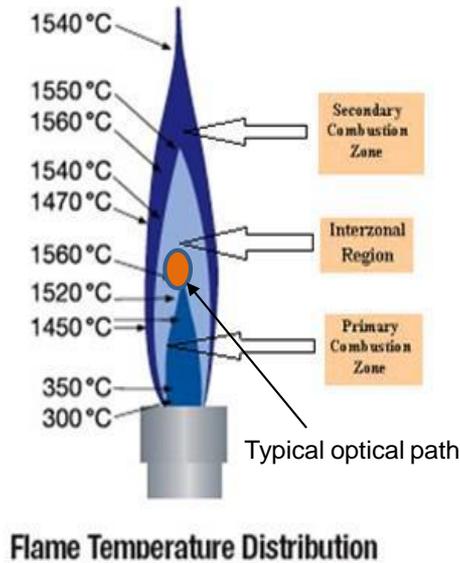
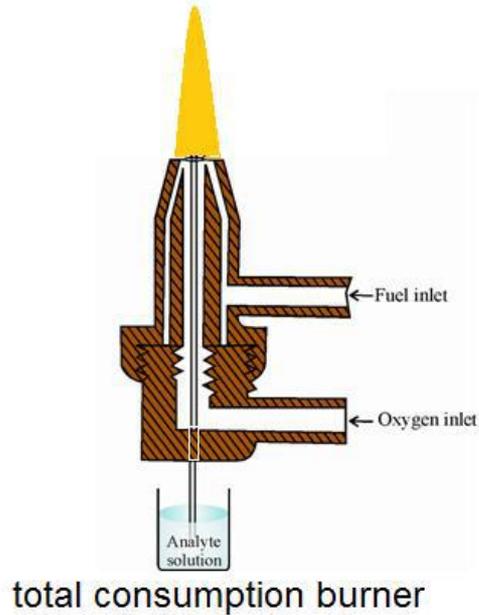
The device that introduces the sample into the flame plays a major role in determining the accuracy of the analysis. The most popular sampling method is nebulization of a liquid sample to provide a steady flow of aerosol into a flame. An introduction system for liquid samples consists of three components: (a) a nebulizer that breaks up the liquid into small droplets, (b) a spray chamber that removes large droplets from the stream, allowing only droplets smaller than a certain size to pass into the flame and atomizer that converts the analyte into free atoms.

Nebulization :

Pneumatic nebulization is the technique used in most atomic spectroscopy determinations. The sample solution is introduced through an orifice into a high-velocity gas jet, usually the oxidant. The sample stream may intersect the gas stream. Liquid is drawn through the sample capillary by the pressure differential generated by the high-velocity gas stream passing over the sample orifice. The liquid stream begins to oscillate, producing filaments. Finally, these filaments collapse to form a cloud of droplets in the spray chamber. The final aerosol, now a fine mist, is combined with the oxidant / fuel mixture and carried into the burner .

2 - Flame Atomizer :

The efficiency with which the flame produces free and excited analyte atoms is of very importance. Some factors interfere with the production of free and excited analyte atoms. These factors include: (1) excitation and emission of radiation by $\text{MX}(\text{g})$ molecules, (2) reaction of M^0 atoms with flame components at high temperatures to produce molecules and ions that also absorb and emit radiation, and (3) formation of M^+ ions, which, in addition to reducing the efficiency of free and excited atom production, . complicate the analysis by adding ionic lines to the spectrum.



The flame gases (e.g. hydrogen – oxygen or acetylene – oxygen) that their combustion velocity is more than their flow rate can not be used with the premixed burner otherwise an explosion may occur . Open oxidant first and close fuel first .

A satisfactory flame source must provide the temperature (which depends on the identities of the fuel and oxidant and their ratio and also the point in the flame where the emission is measured i.e. burner's height) that required for a given analyte . In addition, the spectrum of the flame itself (flame background emission e.g. from OH^* , C_2^* , CH^*) should not interfere with the emission line of the analyte..

Parts of the flame :

- 1- Primary combustion zone : high background emission .
- 2- Interzonal region : low background emission and hottest part of flame , suitable for measuring emission .
- 3- Secondary combustion zone : high background emission not suitable for measuring emission .

Properties of flames.

Fuel	Oxidant	Temperature °C	Maximum burning velocity (cm s ⁻¹)
Natural gas	Air	1800	40
Natural gas	Oxygen	2750	400
Hydrogen	Air	2000	400
Hydrogen	Oxygen	2600	1200
Acetylene	Air	2250	200
Acetylene	Oxygen	3100	2000
Acetylene	Nitrous oxide	2700	300

Only very small portion of the free atoms (less than 5 %) in the flame will be converted into excited atoms because the energy of the flame is very low . See the following table .

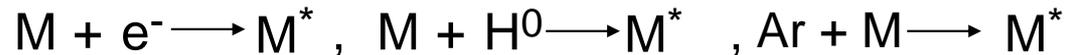
Table shows the percentage of the excited atoms for some elements at the resonance line and at various flame temperature .

Analyte (λ_{\max} nm)	Excitation energy (eV)	percentage of the excited atoms (%)		
		2000 K	3000 K	4000 K
Cs (852.1)	1.46	0.04	0.72	2,98
Na (589.0)	2.11	1×10^{-3}	0.06	0.44
Ca (422.7)	2.93	4×10^{-5}	1×10^{-3}	0.06
Zn (213.9)	5.80	1×10^{-13}	6×10^{-8}	1×10^{-5}

Only the elements with low excitation energy can be determined by AFES .

Mechanism of the atomic excitation in the flame

- physical excitation : caused by collision of e^- , Ar atoms or H^0 radicals ...etc. with analyte free atoms M in the flame where the mechanical energy of e^- ..etc. is converted into excitation energy in M thus :



Note that during collision some of the internal energy of excited atoms or molecules Z^* (e.g. CH_2^* , N_2^* , H_2^* ...etc.) in the flame may transferred into M :



The physical excitation is more likely to happen in hot flames .

- Chemical excitation (chemiluminescence) : The chemical reaction of hydrogen radical for example produce energy which can be used to excite M thus :(more likely in cool flame)



INTERFERENCES

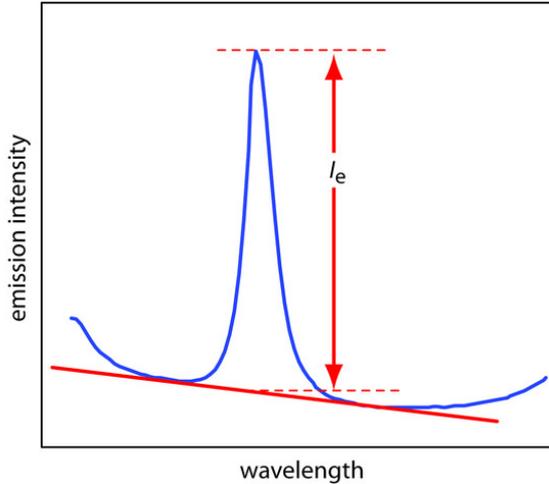
Ionization Interference :

At elevated flame temperatures, atoms with low ionization potentials become ionized. Any ionization reduces the population of both the ground state and the excited state of neutral free analyte atoms, thus lowering the intensity of the emission. This problem is readily overcome either by using cooler flame or by adding an excess of a more easily ionized element such as K, Cs, or Sr to suppress ionization in both sample and calibration solutions. The more easily ionized atoms produce a large concentration of electrons in the flame. These electrons, by mass action, suppress the ionization of analyte atoms. The addition of suppressants is even more important in analysis that require the hotter acetylene/nitrous oxide flames.

Spectral interferences :

The most important spectral interference is broad, background emission

from the flame gases (e.g. CH_2^* , N_2^* , H_2^* ...etc.) .
Background corrections for this flame emission are made by scanning over the emission line and drawing a baseline (see below Figure) .



Chemical interferences :

Flame emission is subject to chemical interferences where free analyte atoms form thermally stable compounds e.g. oxides in the flame due to low flame temperature . This will reduce the number of excited atoms and hence the intensity of emission . These interferences are minimized by adjusting the flame's composition , using hot flame or adding protecting agents, or releasing agents,. An additional chemical interference results from **self-absorption**.. If an excited state atom in the flame's hottest center emits a photon, then a ground state atom in the cooler, outer regions of the flame may absorb this photon, decreasing the emission intensity. For more details see unit 9 .

Physical interferences

The physical properties e.g. viscosity , density , surface tension affect the flow rate and the size of the droplets of the sample solution which affect the intensity of the analyte emission .

Therefore the physical properties of analyte solution and standard solutions must be the same .

APPLICATIONS :

To find the concentration of the analyte we use either the standard calibration curve method , the standard addition method (see unit 4) or the **internal standard** method (see unit 11) .

Most applications of FAES have been the determination of trace metals, especially in liquid samples. It should be remembered that FAES offers a simple, inexpensive, and sensitive (down to 0.001 ppm can be determined) method for detecting common metals, particularly the alkali and alkaline earths, as well as several transition metals such as Fe, Mn, Cu, and Zn. FAES has been extended to include a number of nonmetals: N, P, and S. FAES detectors for P and S are commercially available for use in gas chromatography.

FAES has found wide applications in agricultural , environmental, industrial, and clinical analysis of body fluids (e.g. blood and urine analysis) .

Experiment

Flame Photometric Determination of sodium, Potassium, and Lithium

Background

FAES is widely used for routine analysis of samples containing species like Na, K, Li, and Ca. Emission signal at a specific wavelength is proportional to the concentration of analyte which emits at that wavelength.

Chemicals and Reagents

1. Standard Na, K, and Li solutions (1000 ppm each).
2. Sample of unknown concentrations of Na, K, and Li.
3. Prepare standard Na, K, and Li solutions that are 1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 ppm of each metal ion.

Procedure

1. Follow instructions for the correct operation of the flame photometer available.
2. Adjust the signal, using the Na filter, to zero using distilled deionized water.
3. Read the signal for the Na set of standards and then that of the unknown sample.
4. If the signal obtained for the sample is out of range, dilute a portion of the sample properly till a signal within the range is obtained.
5. Construct a calibration curve for Na in the sample and report your results in ppm.

6. Repeat steps 2-5 for K and finally for Li and find the concentration of each species in the sample. Results should also be reported in ppm analyte.

Note: The sample unknown can be a sample of any drinking supply. Therefore, each student is asked to bring his own sample and the class is asked to report an overview of water quality in the different areas of the city as compared to accepted values