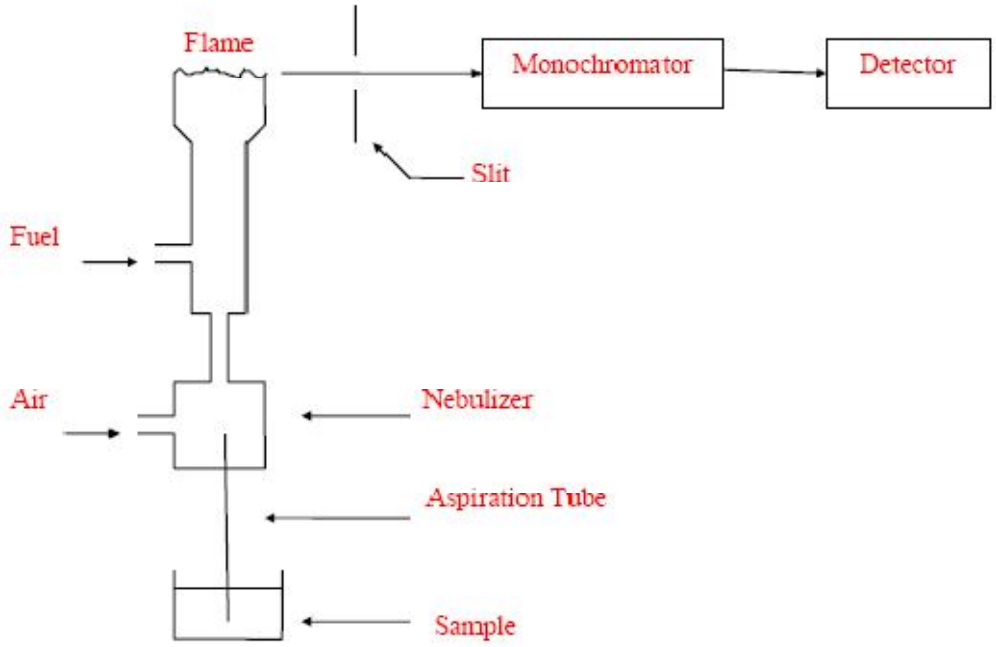
Flame Photometer

A simple flame photometer consists of a nebulizer, flame, lens, a screen with a slit, filter, detector and galvanometer.



Air is drawn in at a given pressure and passed into a nebulizer where it creates a partial vacuum resulting in suction which sucks in the sample solution as a fine spray into a small mixing of the chamber at the burner. Here it mixes with the fuel gas at a specific pressure into the flame. Emitted radiation from the flame passes through a lens which renders it parallel and through a slit to produce a narrow beam. It then passes through a filter which allows only the line of the test element to pass through to the detector (photocell) and a galvanometer which gives the reading. The flame is surrounded by a chimney to protect it from drought. It is primarily used for analysis of sodium, potassium, calcium and lithium.

Flame and Flame Temperature:

- It transforms sample from liquid or solid state to gaseous state.
- It decomposes molecular compounds into simpler molecules or atoms.
- It excites atoms to emit radiation.

Gases in flame are CO, H_2, CO_2 and H_2O (and N_2, if air is one of the gases), with smaller quantities of H, O and OH

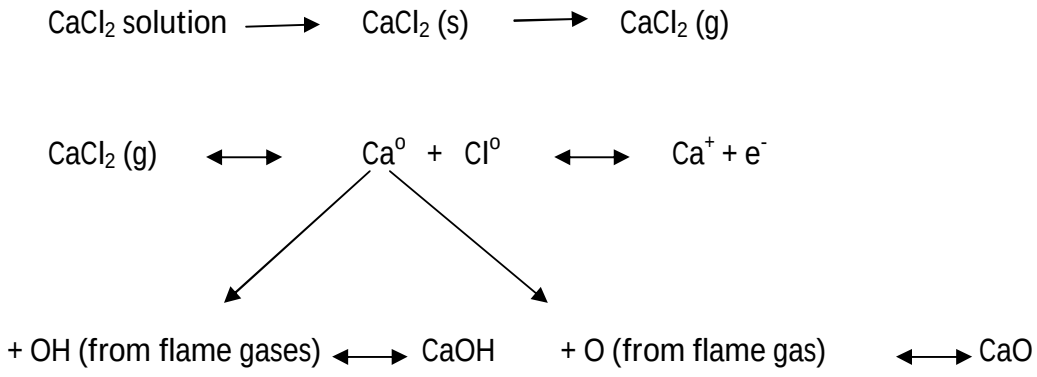
Temperature of flame depends on fuel gas and supporter.

Fuel gas	Air	Oxygen
Illuminating gas	1700	2700
Propane	1925	2800
Butane	1900	2900
Hydrogen	2100	2780
Acetylene	2200	3050
Cyanogens	2330	4550

Emission Spectra

On aspiration into flame following in rapid succession;

- Water or solvent vaporized, leaving minute particles of dry salt.
- Salt vaporized; part or all gaseous molecules dissociated into ground state atoms.
- Some atoms combine with radicals or atoms in flame gases.
- Vapours of ground state metal atoms or molecules containing the atoms absorb energy from flame – excited. Some ionization may occur.
- Species return to ground state – emit excess energy. E1 – E2 = hv. Return may be in one step or in several steps. Most prominent line is equivalent to the lowest excited level and ground state.



Applications

Simple flame photometers using butane air flame with element filters are used to routinely determine easily excitable elements, K, Na, and Ca – elements with low ionization energies.

However, with hotter flames like oxyacetylene flame and use of spectrophotometers and very narrow slit widths, more elements (up to 70) can be determined.

Spectral Interference

In relatively cool flames, refractory molecular oxides and hydroxides form. Molecules have energies and energy levels of rotational, vibrational and electronic excitation. Each electronic transition is accompanied by a whole lot of vibrational and rotational ones - a broad emission spectrum rather than a narrow band. The bands interfere with and make measurement of analytical line difficult and inaccurate if adjacent to or overlapping analytical line. Examples of such molecules are CaOH, SrOH, BaOH, MnOH, CaO etc. Also, background emission from flame due to –OH, CO, O_2, CH, C_2, and H_2O.

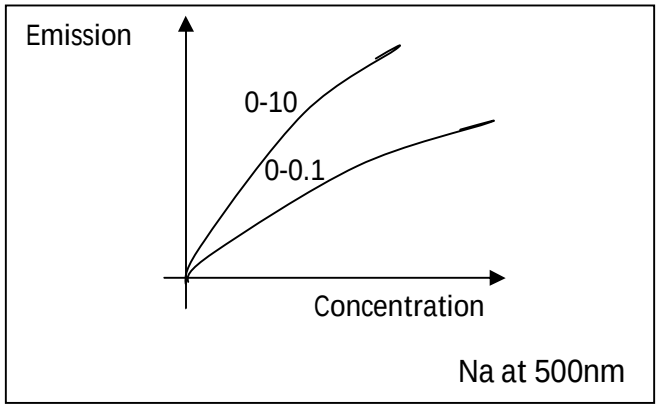
Usually prevalent with filters and reduced by monochromators. If improved, resolution cannot correct it, another line must be found.

Background Emission

This is emission both from flame and sample matrix. This must be corrected to avoid serious errors. If only from flame gases, aspirate pure solvent to zero. If monochromator, used, background measured in presence of test element and subtract background signal.

Self – Absorption

Excited atoms release excess energy in discrete amounts. The radiant energy travels some distance in flame before getting out. Collides with other ground state atoms and get absorbed which leads to decrease in signal. Self – absorption increases as the number of ground state atoms in flame increases. Work at low concentration.



Ionization

Some atoms ionized rather than being excited if flame is hot enough. Increase in the number of atoms and decrease in signal.

$$M \longleftrightarrow Mn^{+} + ne$$

Add a second easily ionizable element e.g. Na or K. Excess electrons drive equilibrium to left hand side. More metal atoms, higher signal. This is more easily observed in acetylene-air or oxy-acetylene flames.

Acetylene air

Effect of Na on K emission

	+20 ppm Na	+100 ppm Na	+1000 ppm Na	+2000 ppm Na	+5000 ppm Na
K 5 ppm	+17	+56	+92	+96	+97

Add large amount of easily ionizable element to standardize the sample.

Effect of Anions (Refractory Compound Formation)

Some anions from acids or salts depress signals of metallic emission. Significant above 0.1M H_2SO_4, HNO_3 and in particular H_3PO_4 are very prominent. For example, Ca and other alkaline earth metals depressed by $PO4^{3-}$ and Al_2O4. The compound formed is refractory and does not volatilize or decompose.

Use releasing agent e.g. La^{3+} or protective chelation – polyhydroxy alcohols (glycerol) or EDTA.

Procedure for Analysis

Calibration curve and standard addition.

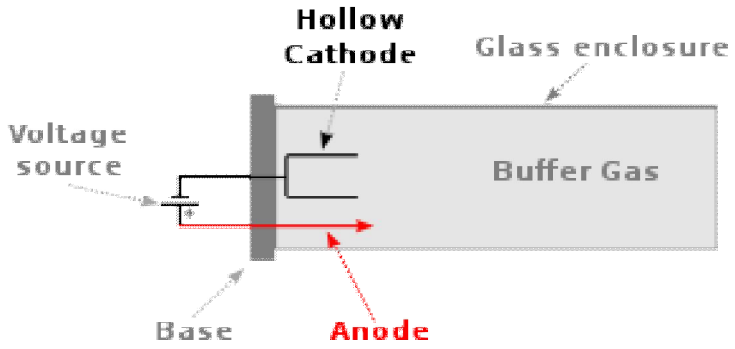
ATOMIC ABSORPTION SPECTROPHOTOMETRY

Principle

Measurement of light absorbed at wavelength of a resonance line by unexcited atoms of element. It is useful for elements which cannot be excited by flame. It can also be used for

some excitable ones since about 99% of all atoms remain unexcited in normal air – acetylene flame. The flame is like a trough or sample cell of the absorbing gas and the absorption follows Beer's law i.e. proportional to path length of flame and concentration of atomic vapour in flame.

Instrumentation



Source

This provides the resonance line of element. It is usually a hollow cathode lamp which emits the specific monochromatic wavelength.

Cylindrical hollow cathode made of the element to be measured or an alloy of it. Anode is tungsten. It is enclosed in glass tube with quartz window (most wavelengths in UV region) reduced pressure and filled with inert gas, Ar or Ne. high voltage across tube, electrons released by anode, ionize gas , positive gas ions accelerated to cathode. They bombard the cathode, cause metal to sputter and vapourise. Metal atoms excited by collision with more ions. They return to ground state and emit characteristic wavelength. Filler gas also emits line but not close enough to interfere. It is passed through flame and get absorbed. Most absorbed is usually but not always the resonance line. This is equivalent to transition from ground state to lowest excited state.

Multi element Lamp

These are alloys of several elements. They emit lines of all the elements. They are used for two or three elements but have shorter life span. Radiation lines from hollow cathode lamp narrower width than absorption line of atom in flame.

Burner and Nebulizer

Nebulizer breaks the solution into a fine spray and introduces the spray into the flame at a steady and reproducible rate.

There are two types of nebulizer:

1. The one with total internal combustion or direct aspiration; aspirates all the solution into the flame.
2. The one with premix chamber in which the solution goes through a chamber where the large drops are removed and only the fine droplets mix with the flame gases and go into the flame.

The advantages and the disadvantages are as follows.

Total Internal Combustion

Disadvantages

a) It has a shorter path length.
b) Large droplets are not completely vapourized; leaves solid particles in light path which scatter light which is recorded as absorption (error).
c) Nebulization efficiency is greatly affected by viscosity of sample.

Advantages

a) Absorption is proportional to gas flow than in pre-mix.
b) Viscous liquid and high solids can be aspirated.

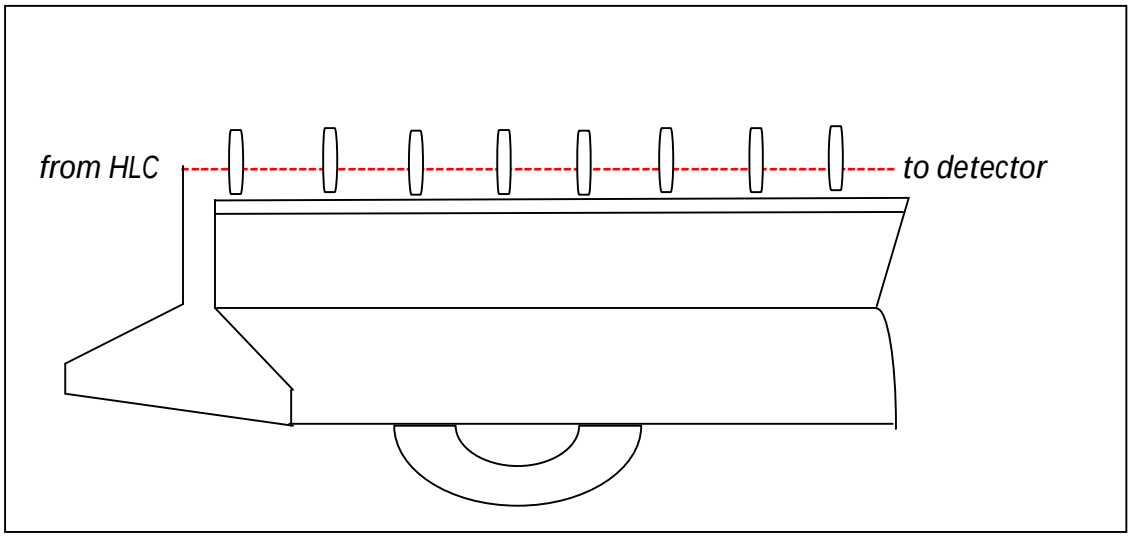
Pre-mix

Advantages

a) Fine droplets which are easily vapourized.
b) Nebulization efficiency is greater.
c) Path length is longer.
d) Combustion is very quiet while total internal combustion is noisy.

Therefore, pre-mix is better.

Burner head, mostly longer than optical path length.



The flame is like a cell of ground state atoms which absorb resonance line from the hollow cathode lamp while the rest of the signal goes on to the detector which measures the absorbance.

Flames are the same as emission.

Oxy – acetylene 3060^{o}C

Nitrous oxide-acetylene 2955^{o}C. They are the highest used.

Interferences

1. **Spectral Interference**
   Similar to emission. Refractory molecular band emission with d.c. source but is eliminated with a.c. If molecule absorbs source radiation, positive interference in AAS is minimized by using line source.
   Light scatter by solid particles result to positive interference especially less than 300 nm with high salt solution. Measure absorbance at a line close to line of element to get background absorption – subtract, since interference over broad area.

2. **Ionization Interference**
   Similar to emission.

3. **Refractory Compound Formation**
   Similar to emission.
   Compounds formed with flame gases e.g. MO, MOH etc. use hotter flames to decompose e.g. nitrous oxide-acetylene or air-acetylene.

Application

Get solution of sample. If interferences absent, chemical form does not matter. Hence, it is used in biological samples blood, urine, csf etc. Aspirate directly or after suitable dilution into flame to prevent clogging of burner.