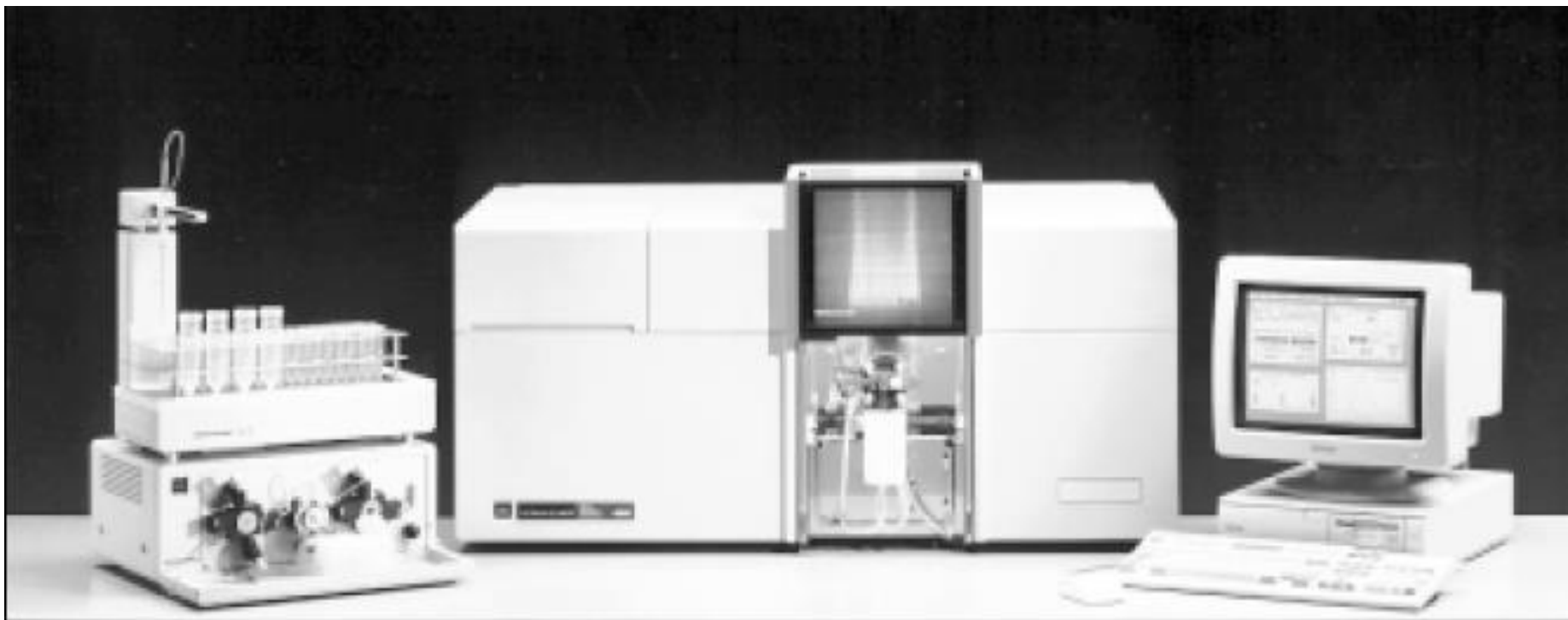


Emission Spectr. And Atomic Absorption Spectr



F E S and A A S



FLAME EMISSION SPECTROMETRY

ATOMIC ABSORPTION SPECTROMETRY

- What is it ?
- What for is it ?
- How is it work ?

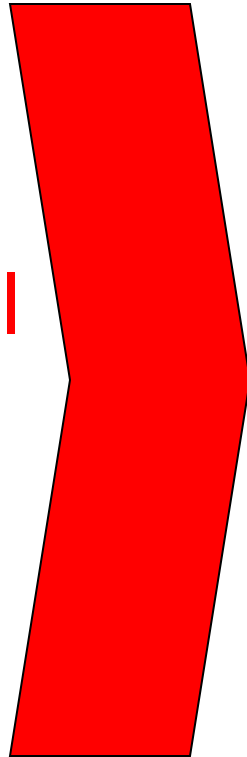
What is it ?

- Flame Emission Spectrometry (FES) and Atomic absorption spectrometry (AAS) are an analytical technique that measures the concentrations of total metals in sample.
- FES and AAS are so sensitive that it can measure down to parts per billion of a gram (μgL^{-1}) in a sample.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Application :

- Food analysis
- Clinical
- Environmental
- Pharmaceutic
- Industry
- Mining
- etc



Mg in drinking water
Ca in food
K in deadly fish

Pb in blood
Au in rock
Cr in liquid wastes
Hg in sediment
etc

How is it work ?

- The technique makes use of the wavelengths of light specifically emission or absorb by an element.
- They **correspond to the energies** needed to promote electrons from one energy level to another, higher, energy level.
- The energies emission or absorb are related to the concentration

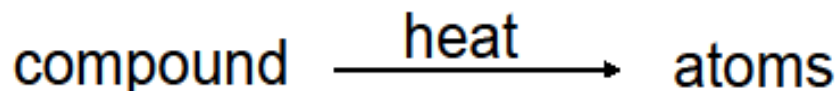
ATOMIC EMISSION SPECTROMETRY

is based on the same principle as the flame test used in qualitative analysis.

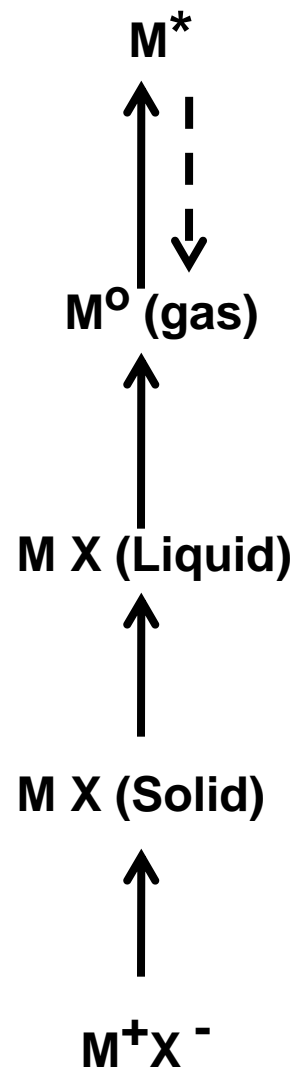
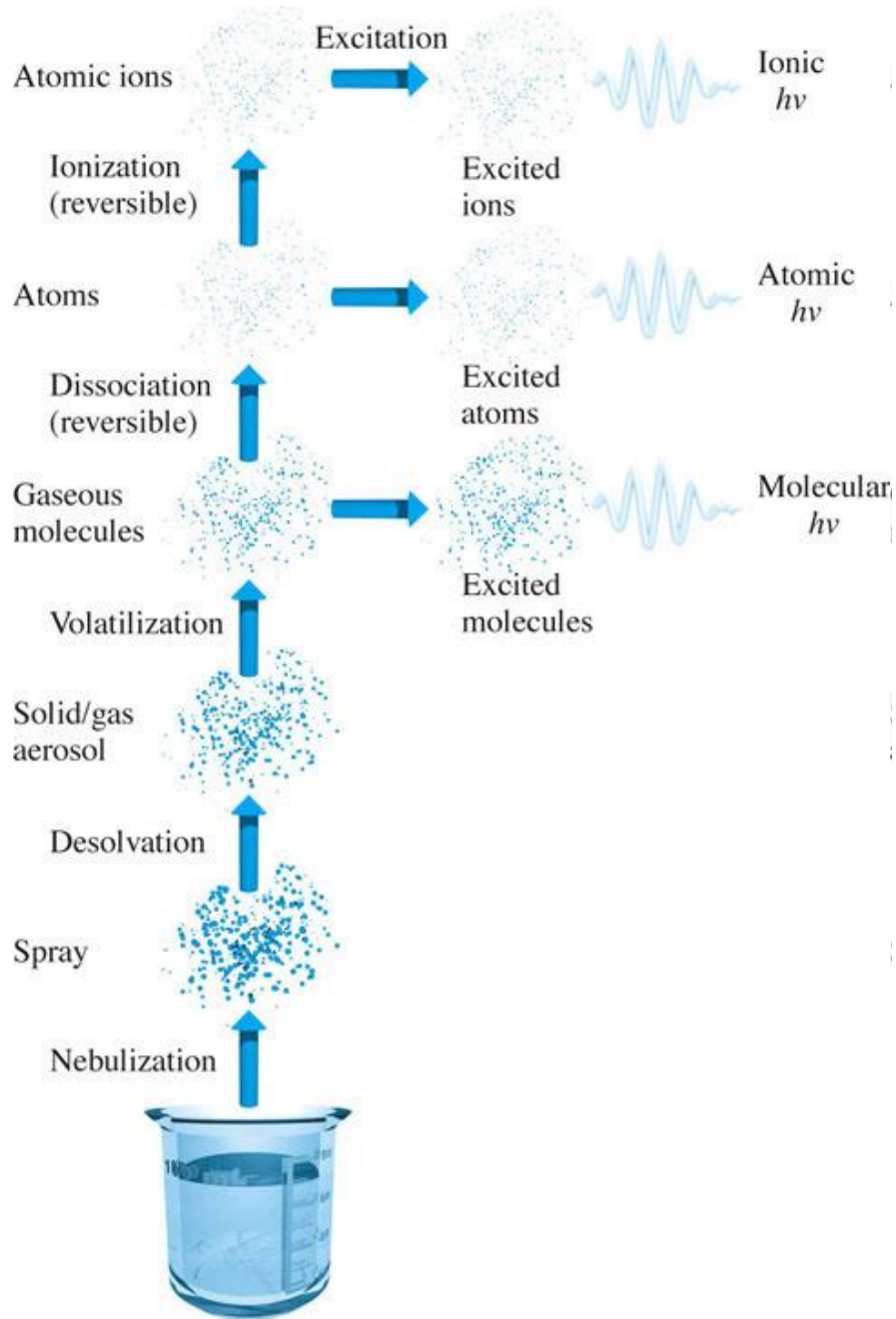
When an alkali metal salt or a calcium, strontium or barium salt is heated strongly in the Bunsen flame, a characteristic flame colour is observed:

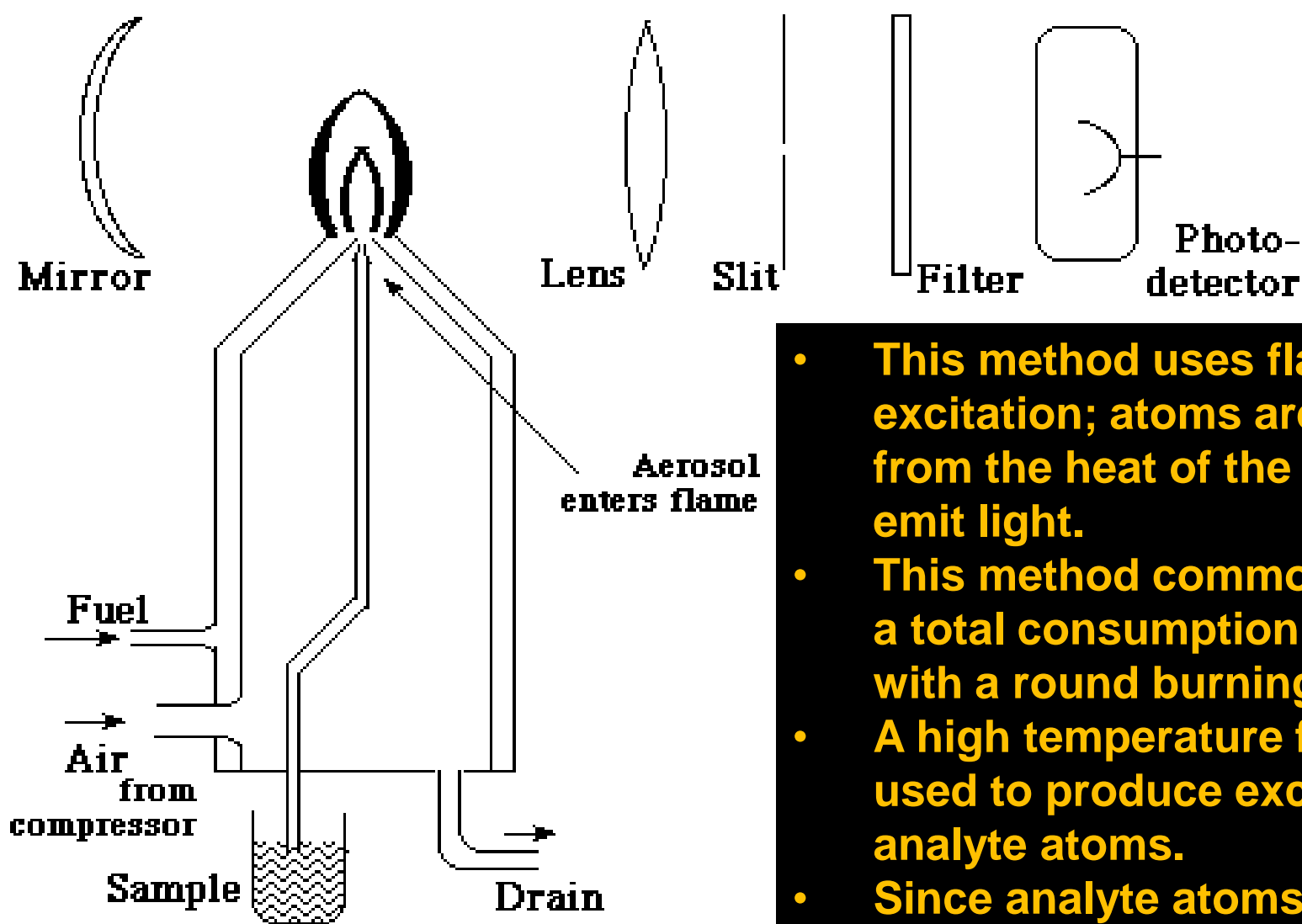
Na	⇒	yellow
Li	⇒	crimson
Ca	⇒	brick red
Sr	⇒	crimson
Ba	⇒	green

In the flame, the ions are reduced to gaseous metal **atoms**.



The high temperature of the flame excites a valence electron to a higher-energy orbital. The atom then emits energy in the form of (visible) light as the electron falls back into the lower energy orbital (ground state).



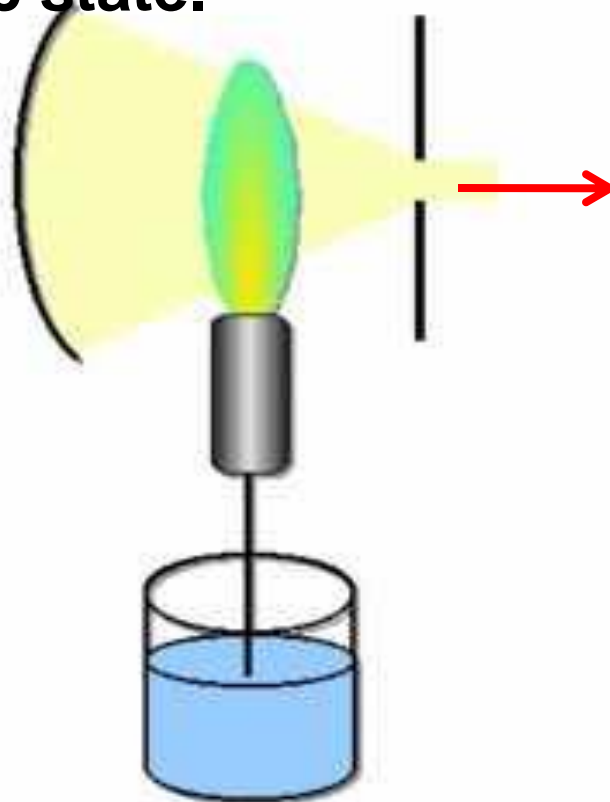


- This method uses flame excitation; atoms are excited from the heat of the flame to emit light.
- This method commonly uses a total consumption burner with a round burning outlet.
- A high temperature flame used to produce excitation of analyte atoms.
- Since analyte atoms are excited by the heat of the flame, no special elemental lamps to shine into the flame are needed.

Flame Emission Spectrometry

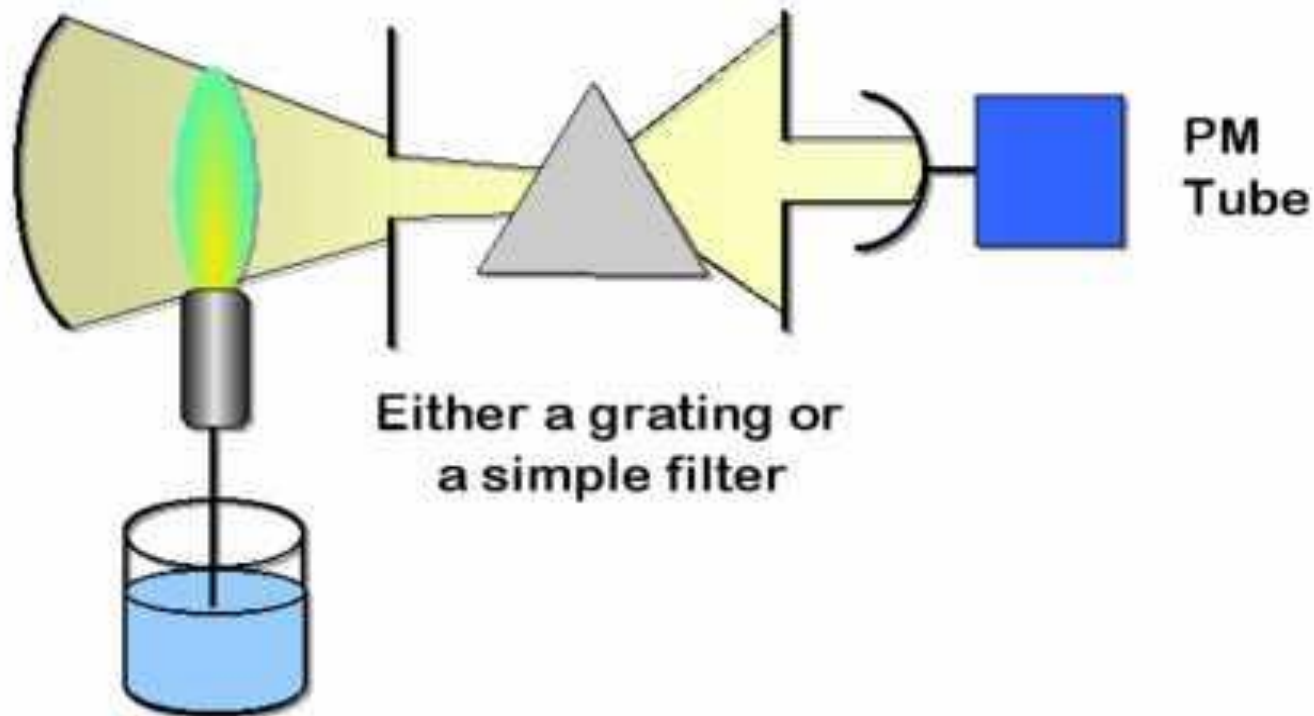
Liquid solution samples are aspirated into a burner or nebulizer/burner combination, desolvated, atomized, and excited to a higher energy electronic state.

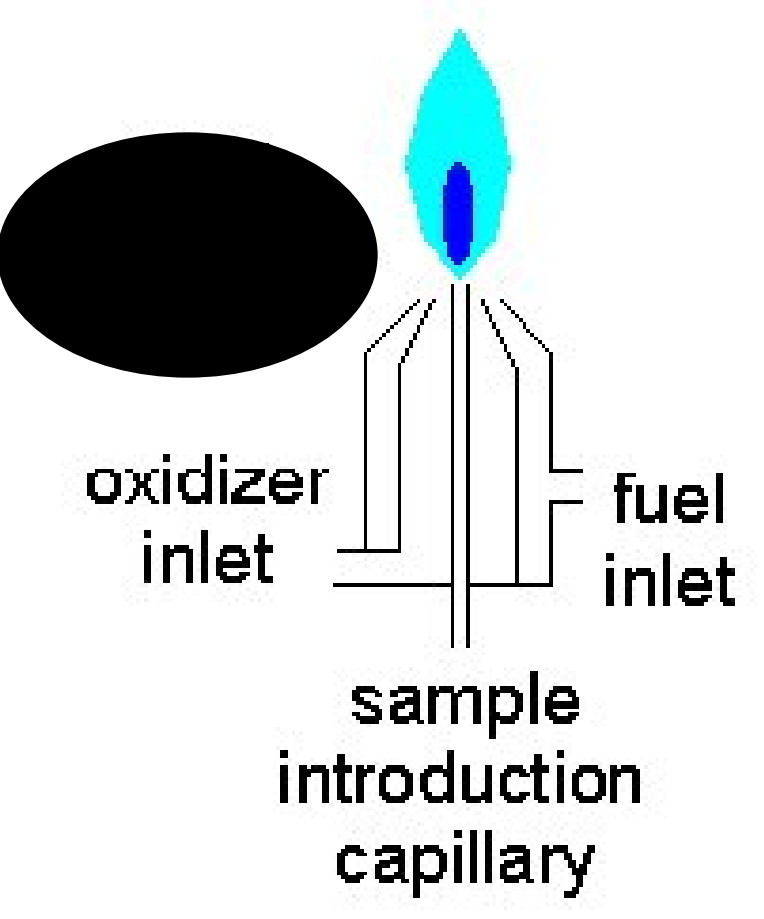
The use of a flame during analysis requires fuel and oxidant, typically in the form of gases. Common fuel gases used are acetylene or hydrogen. Common oxidant gases used are air, or nitrous oxide.



These methods are often capable of analyzing metallic element analytes in the lower concentration ranges (ppm, ppb)
Light detectors are needed to detect light with the analysis information coming from the flame.

Flame photometer



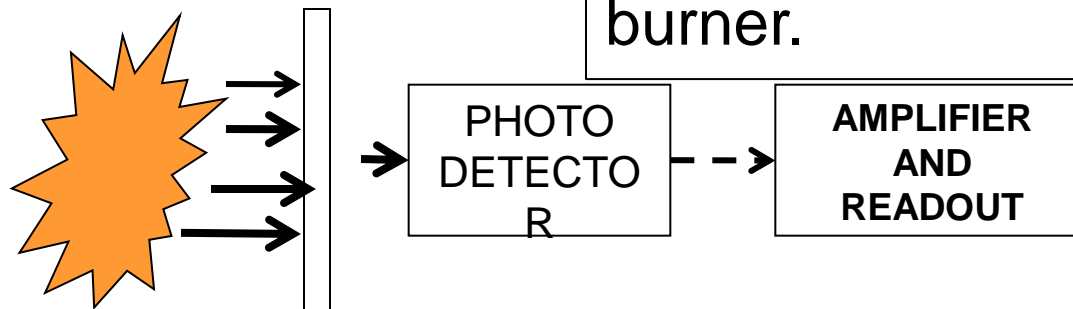


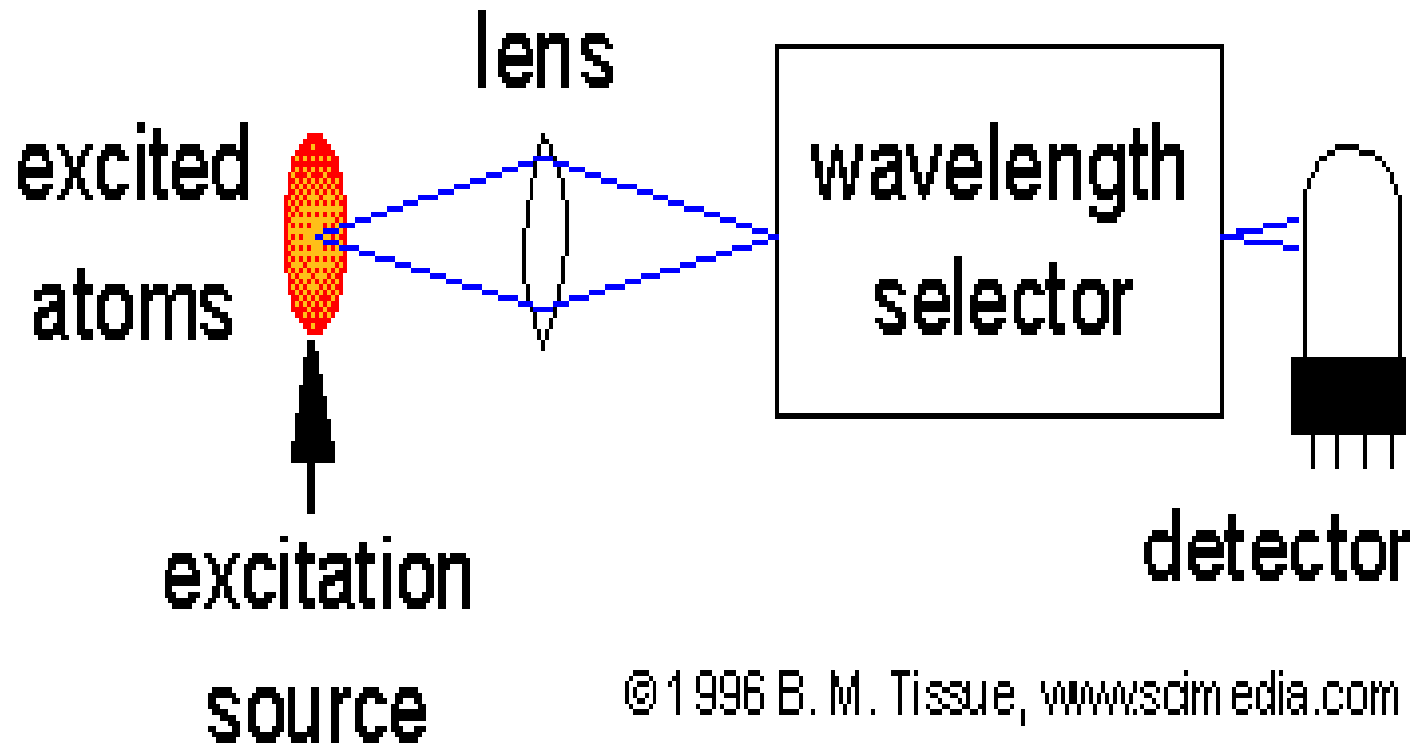
The figure shows a total consumption burner in which the sample solution is directly aspirated into the flame.

This flame design is common for atomic emission spectroscopy.

All desolvation, atomization, and excitation occurs in the flame.

Other flame designs nebulize the sample and premix it with the fuel and oxidant before it reaches the burner.

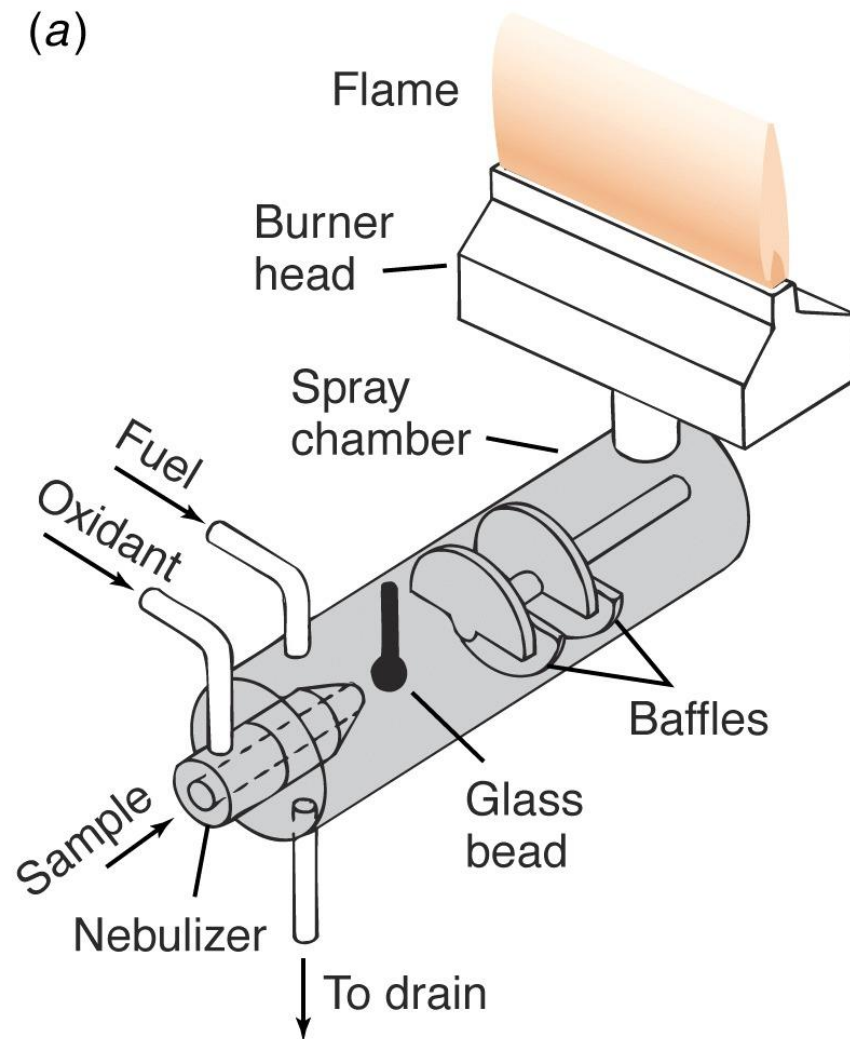




Application

Widely used in hospitals for the clinical and soil analysis of sodium, potassium and lithium in blood serum and soil
Used in the range $1 - 10 \text{ mgL}^{-1}$

(a)



OXYDANT -FUEL

	Max. flame speed (cm/s)	Max. temp. (°C)
Air-Coal gas	55	1840
Air-propane	82	1925
Air-hydrogen	320	2050
Air-50% oxygen-acetylene	160	2300
Oxygen-nitrogen-acetylene	640	2815
Oxygen-acetylene	1130	3060
Oxygen-cyanogen	140	4640
Nitrous oxide-acetylene	180	2955
Nitric oxide-acetylene	90	3095
Nitrogen dioxyde-hydrogen	150	2660
Nitrous oxide-hydrogen	390	2650

Flame Emission Photometry Resume:

1. Sample solution **sprayed or aspirated** as fine mist into flame.
Conversion of sample solution into an aerosol by atomiser (scent spray) principle.
No chemical change in the sample in this stage. [NB atomiser *does not* convert anything into atoms].
2. Heat of the flame **vaporizes** sample constituents. Still **no chemical change**.
3. By heat of the flame + action of the reducing gas (fuel), molecules & ions of the sample species are **decomposed and reduced to give ATOMS**.
eg $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
4. Heat of the flame causes **excitation** of some atoms into higher electronic states.
5. Excited atoms **revert to ground state** by **emission** of light energy, $h\nu$, of characteristic wavelength; measured by detector.

Sample preparation

Take about 5 mL of serum and dilute with deionised water, making up to the mark in a volumetric flask.

Advantages of FES

- Easy to use
- Cheap
- Selective for Na, K, Li

In this technique a natural gas/air flame is used to excite the atoms.

DISADVANTAGE of FES

- This has a low temperature and
- Only excite a limited number of elements
- Best only for one valence electron.

Atomic Absorption Spectrometry

Flame Emission Spectrometry,

is the method uses flame excitation; atoms are excited from the heat of the flame to emit light. This method commonly uses a total consumption burner.

Atomic Absorption Spectrometry,

Is the method which the sample is atomized and then light of a particular frequency is passed through the atom vapour.

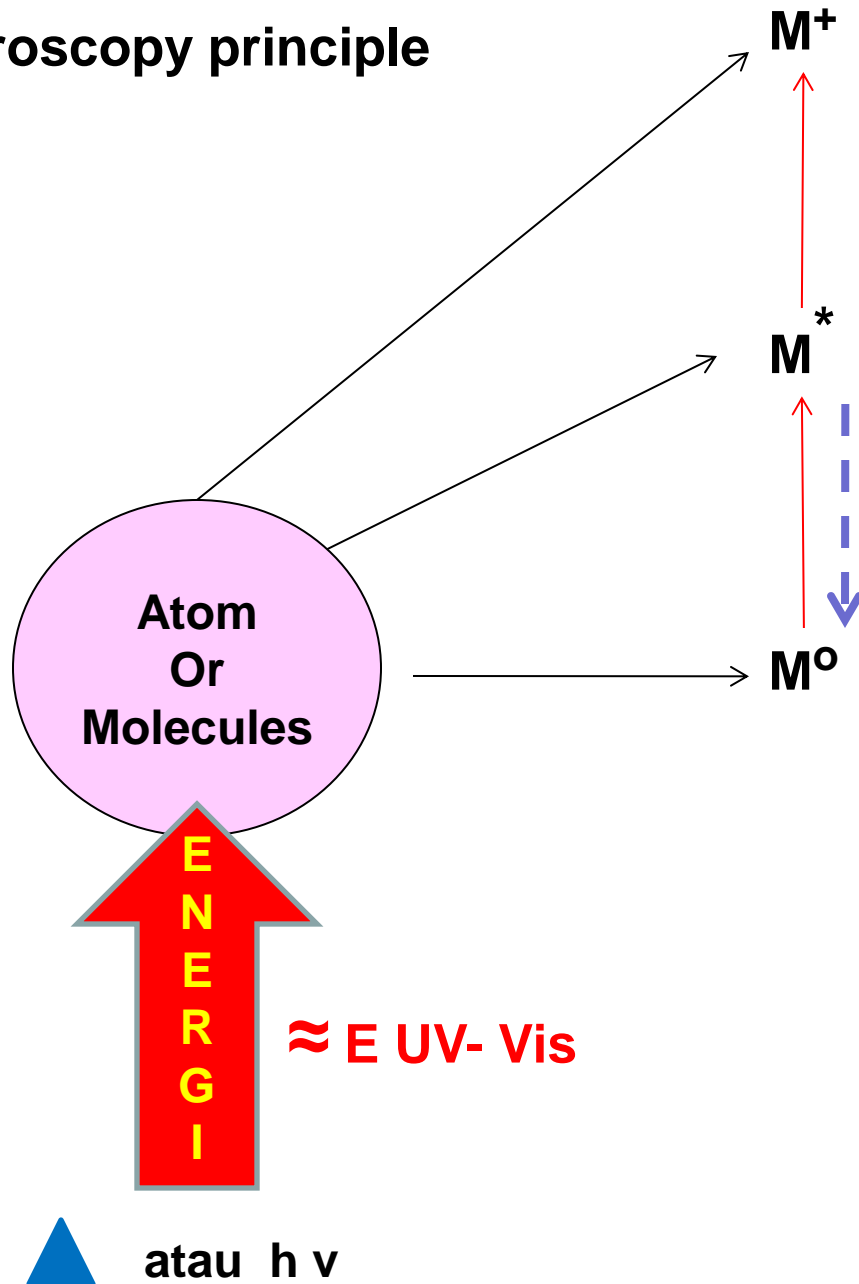
After calibration, the amount of emission or absorption can be related to the concentrations of various metal ions through the Boueger- Beer- Lambert law.

The method can be widely used to measure concentrations of total metal such as iron, calcium, magnesium, etc., in all kinds of samples.

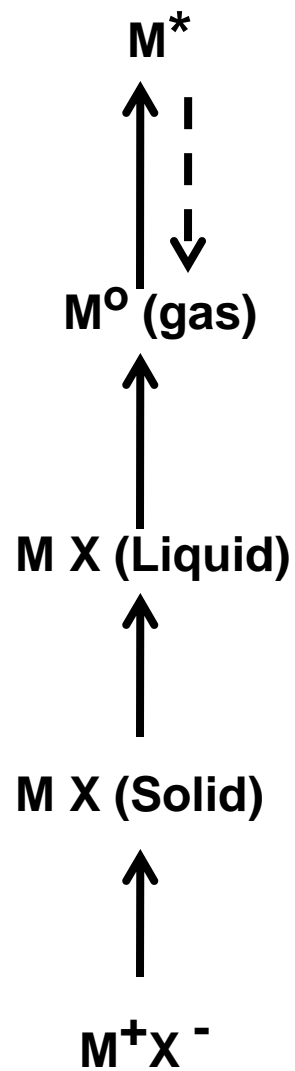
How is it work ?

- The technique makes use of the wavelengths of light specifically absorbed or emission by an element.
- They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level.
- The energies absorb or emission are related to the concentration

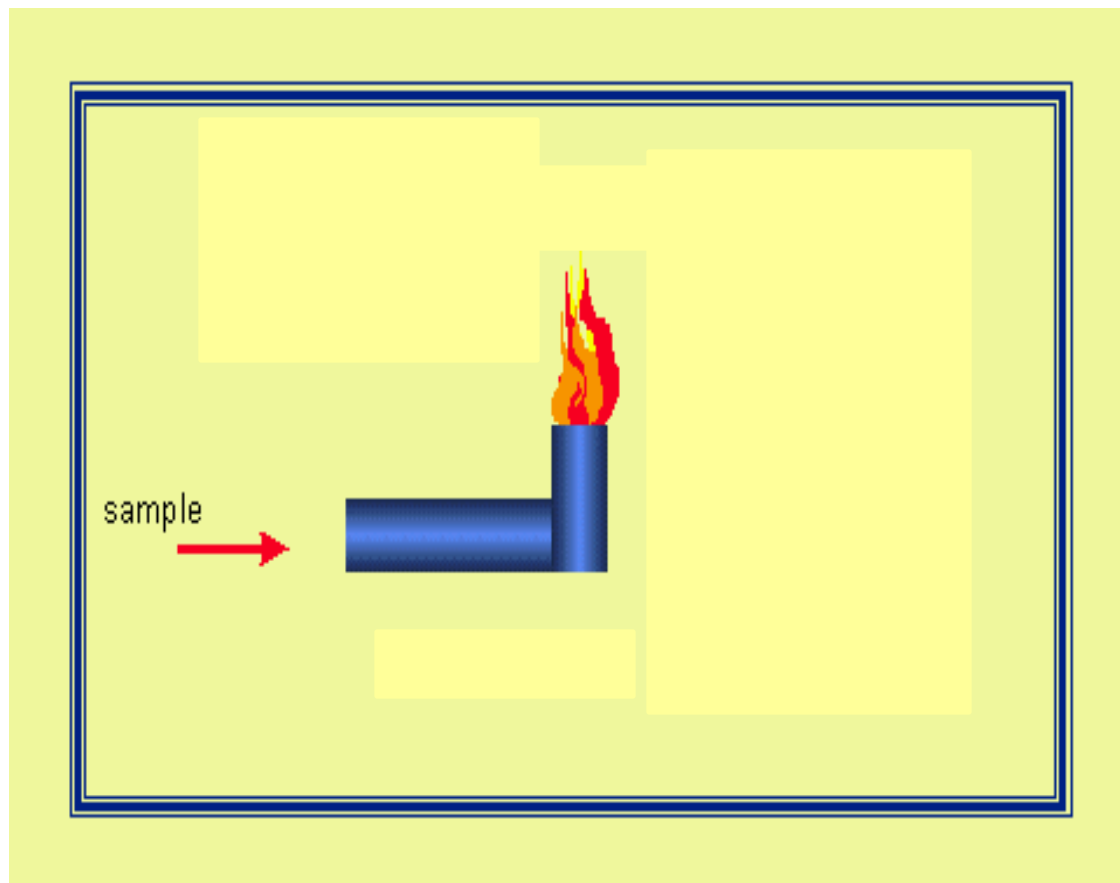
Spectroscopy principle



Herschel (1823):
COLOUR IN FLAME
Sodium ?
Potassium ?
etc

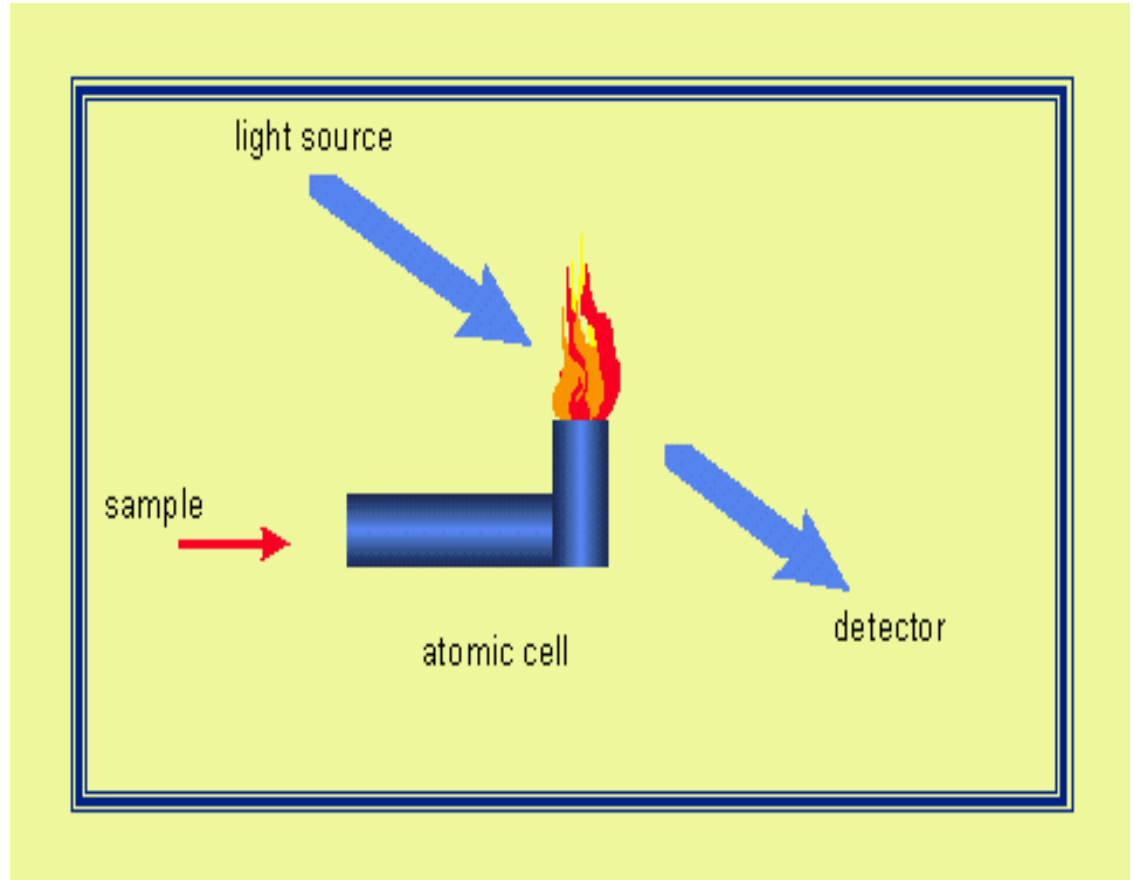


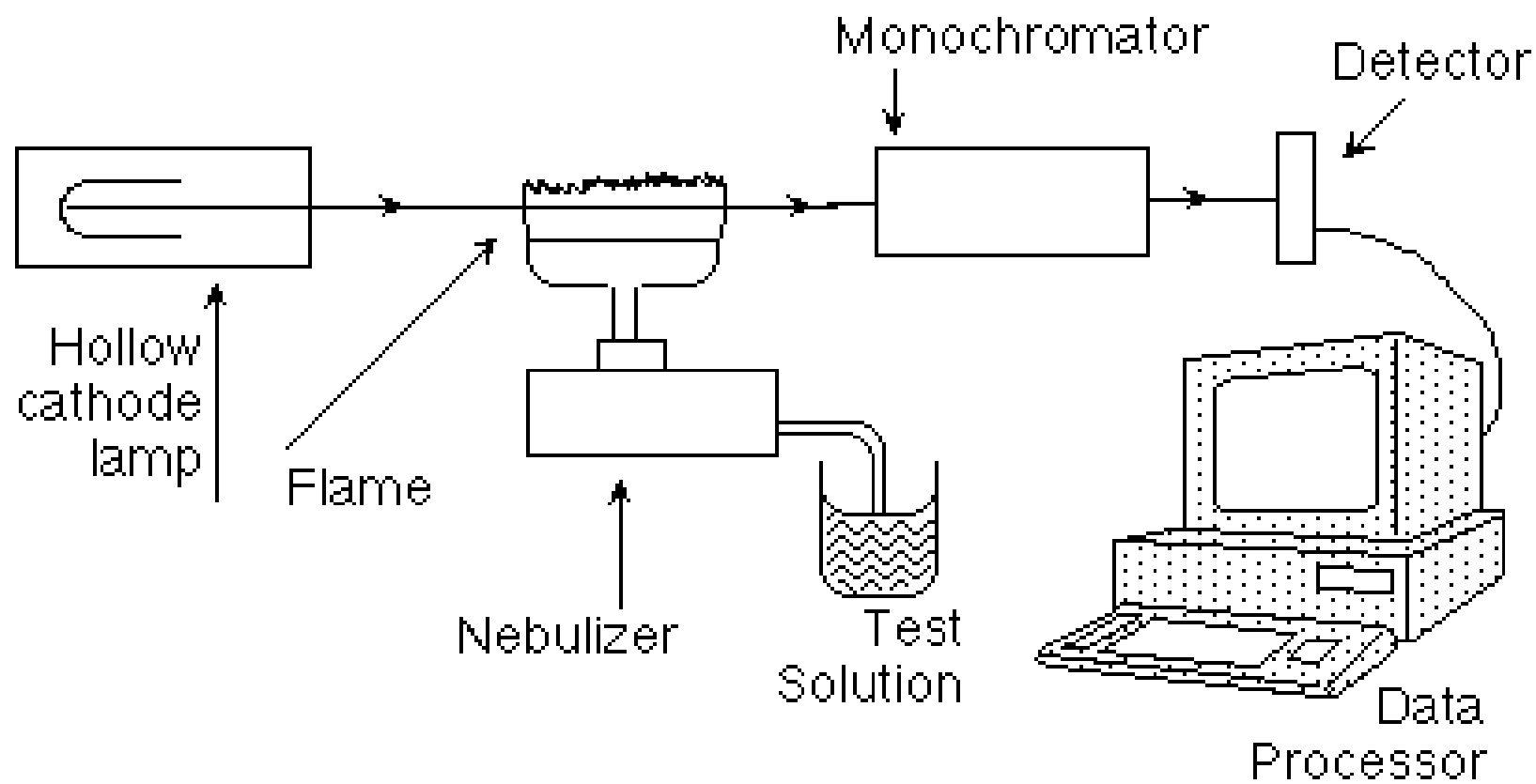
WHAT HAPPENED ?



Consequently an atomic absorption spectrometer needs the following three components:

1. a light source;
2. a sample cell to produce gaseous atoms;
3. a means of measuring the specific light absorbed.





PRINSIP:

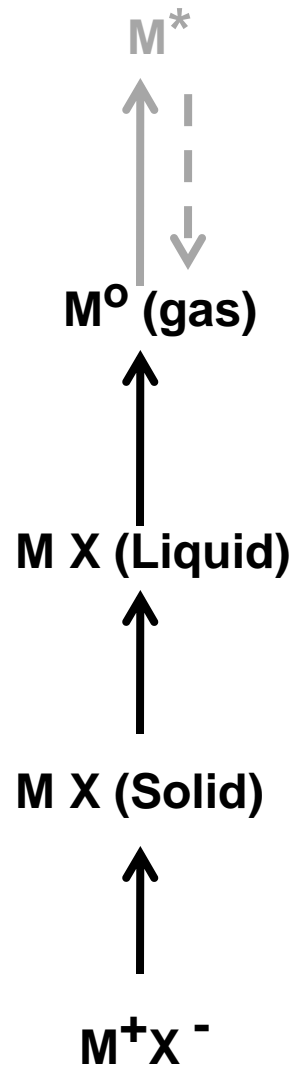
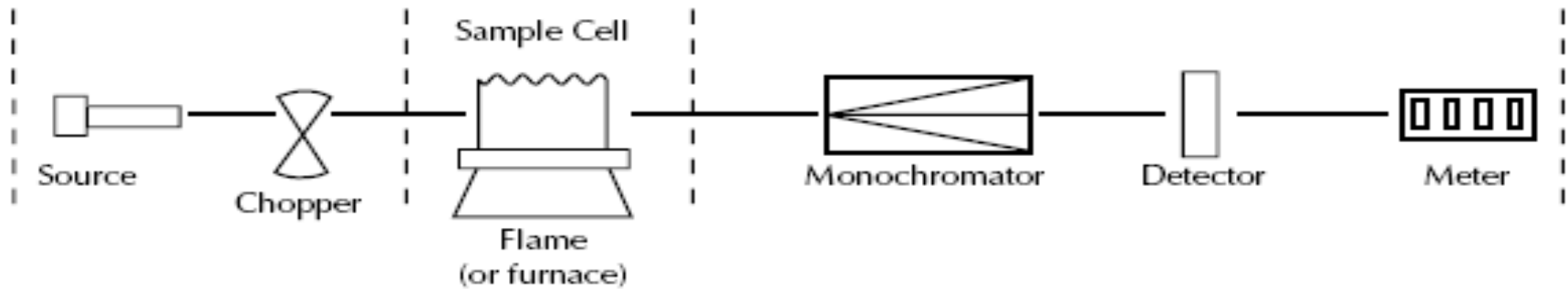


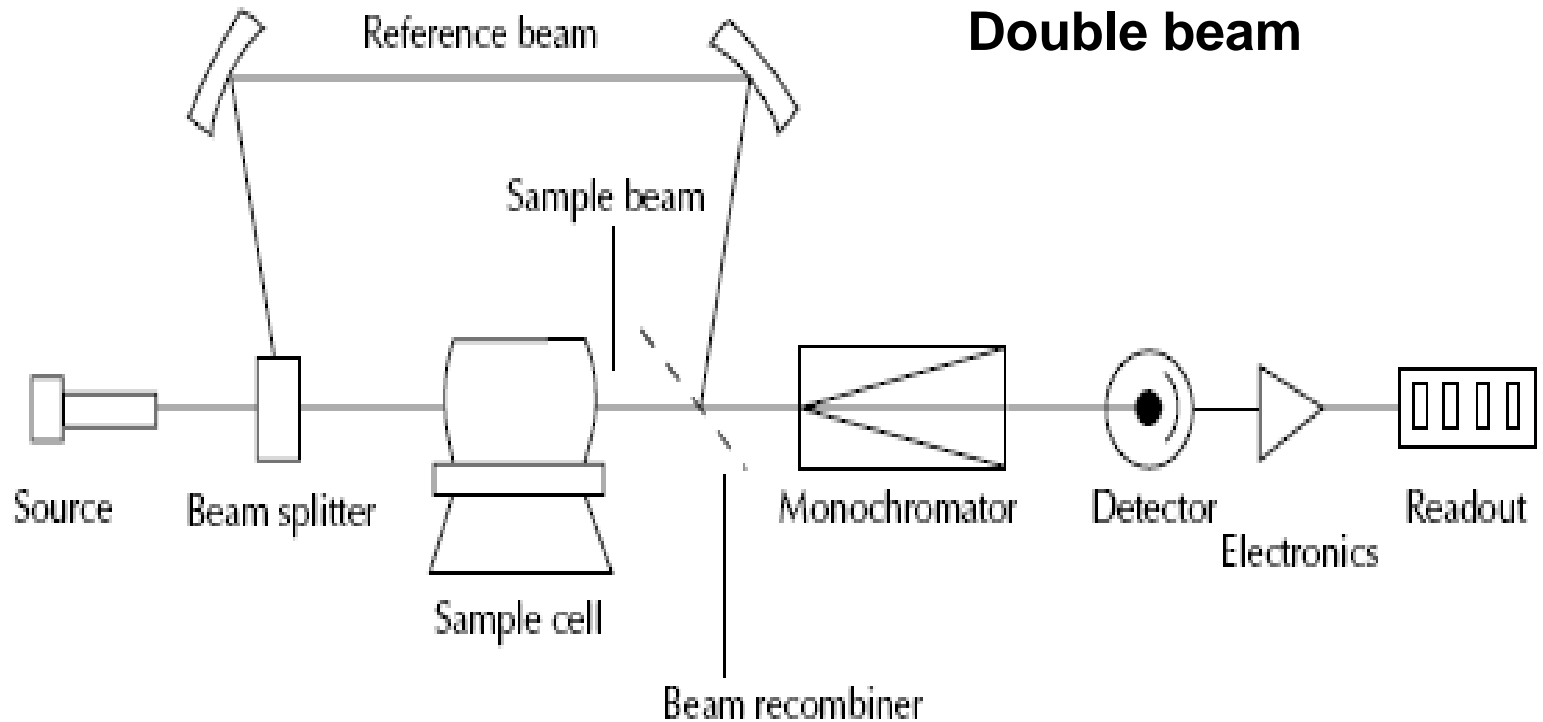
TABLE 9-1 Properties of Flames

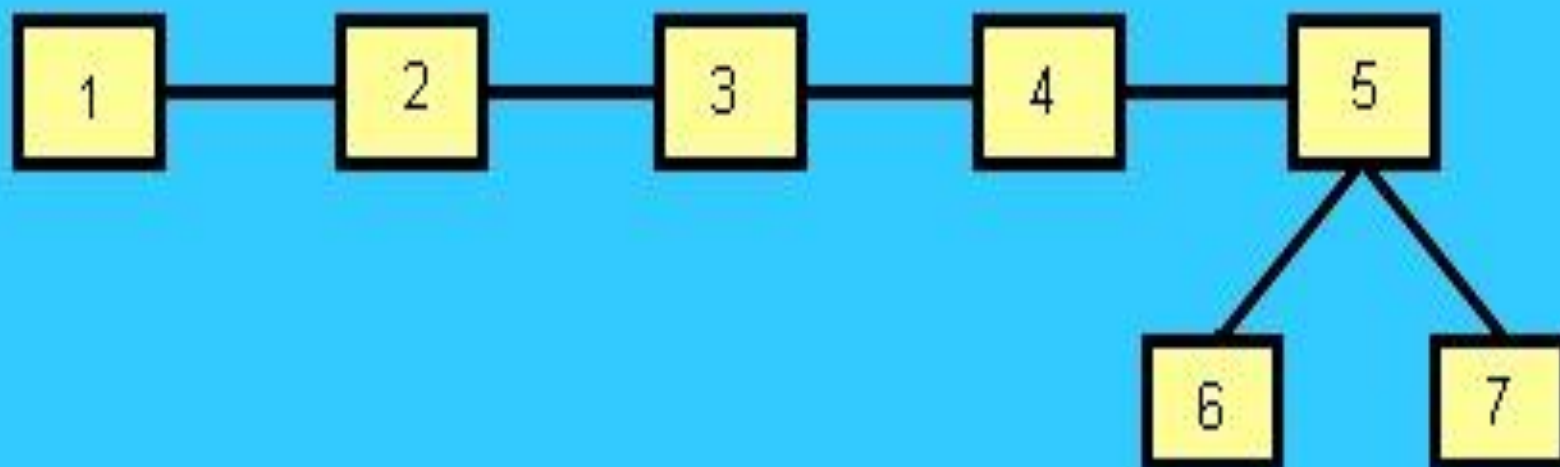
Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, cm s⁻¹
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

Single Beam



Double beam



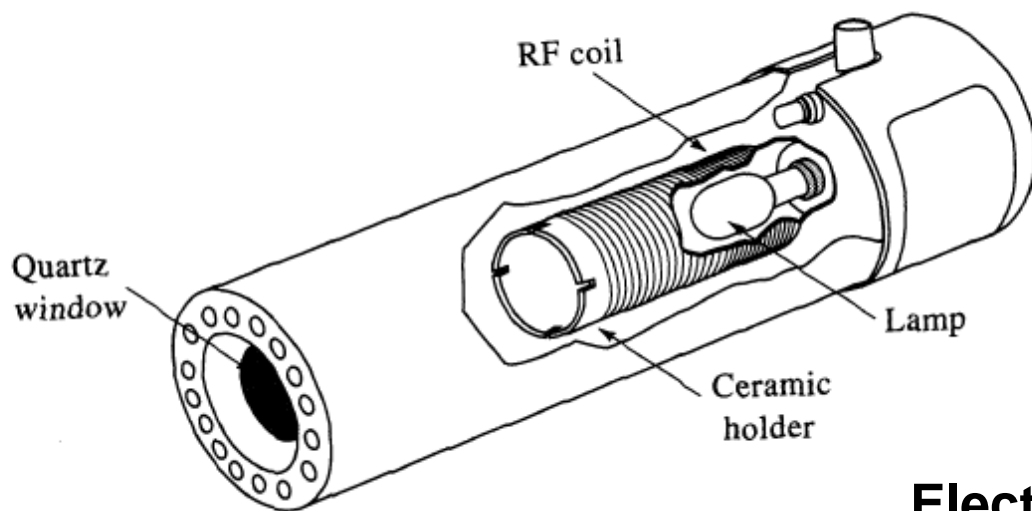
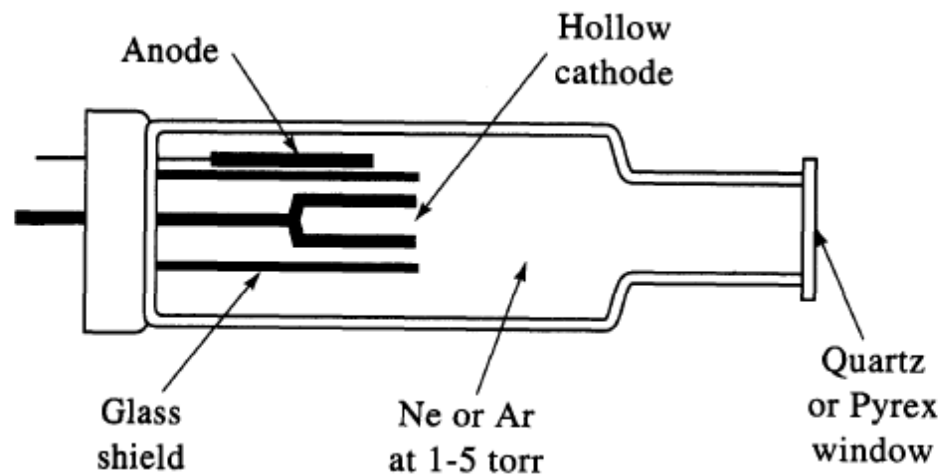


1. light source 2. atom cell 3. monochromator 4. detector
5. amplifier 6. signal display 7. data station

Schematic of basic instrumental parts of atomic absorption spectrometer

Light Sources

Hollow Cathode Lamp



Electrodeless Discharge Lamp

Electrodeless discharge lamp

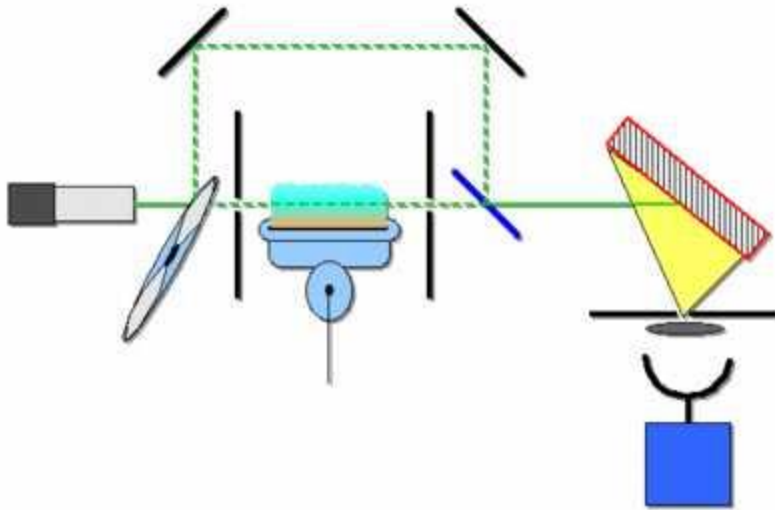
An alternative to the hollow cathode lamp.

A salt containing the metal of interest is sealed in a quartz tube along with an inert gas.

An RF field is used to excite the gas which in turn causes the metal to be ionized.

Light intensity is about 10-100 times greater but are not as stable as HC lamps.

Signal modulation



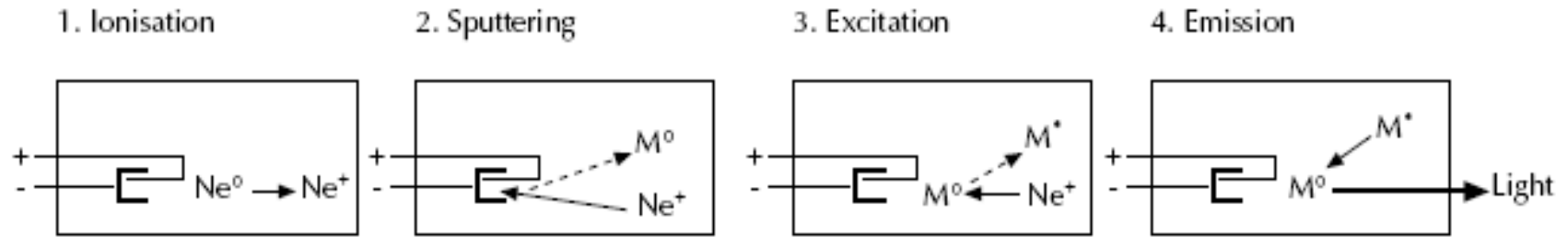
Chopper

A chopper is used to provide signal modulation - in conjunction with a lock-in amplifier.

Its not practical to have two separate cells, so the light is simply split, with half being sent around the atomization source.

This reduces some noise from the atomization source and accounts for instrumental variations.

How is Hollow Cathode Lamp work ?



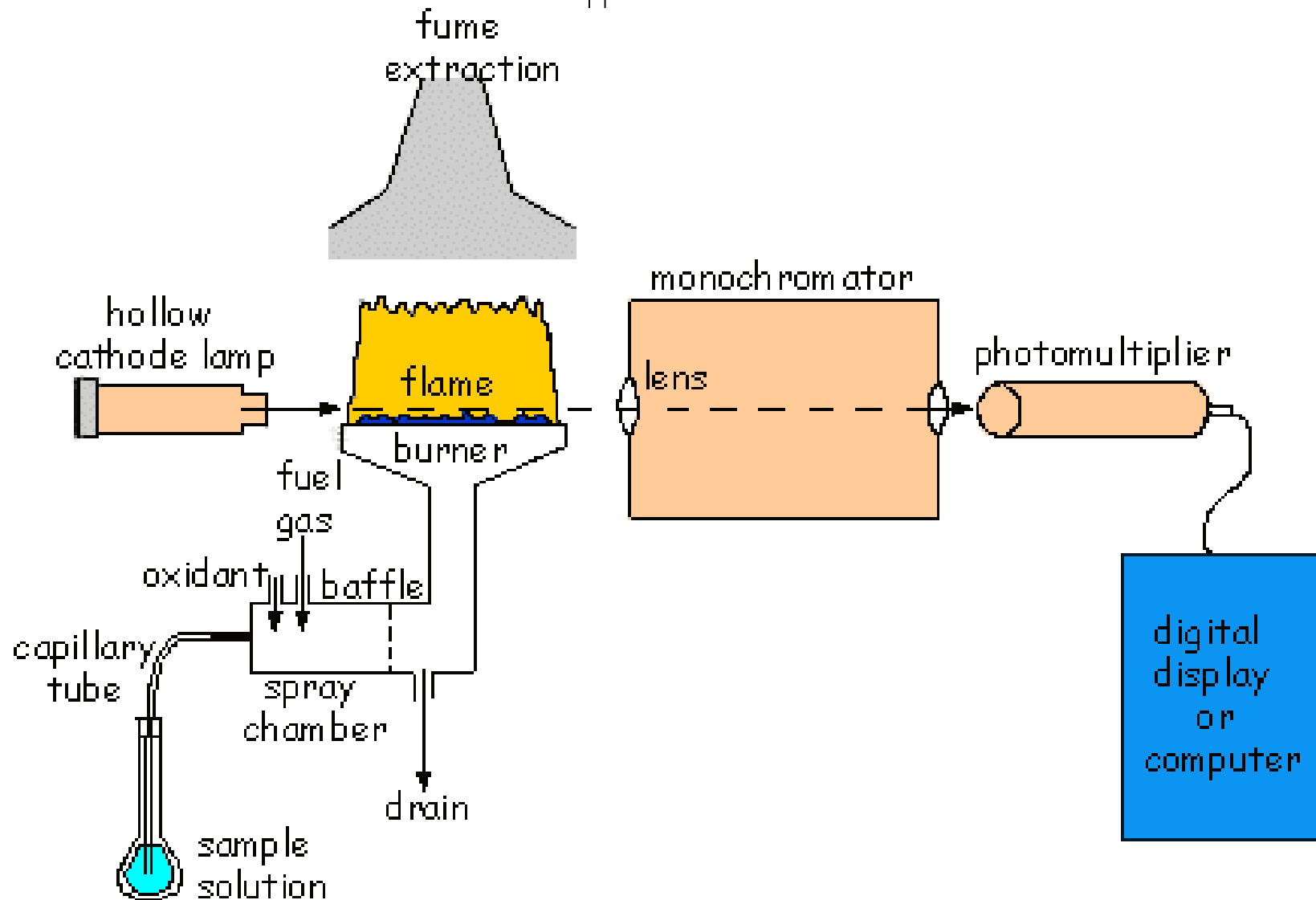
- The ionisation of some gas atoms occurs by applying a potential difference of about 300–400 V between the anode and the cathode.
- These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called sputtering.
- Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state – eg $\text{Pb}^* \rightarrow \text{Pb} + h\nu$.
- The shape of the cathode concentrates the radiation into a beam which passes through a quartz window, and the shape of the lamp is such that most of the sputtered atoms are redeposited on the cathode.

Sample cell

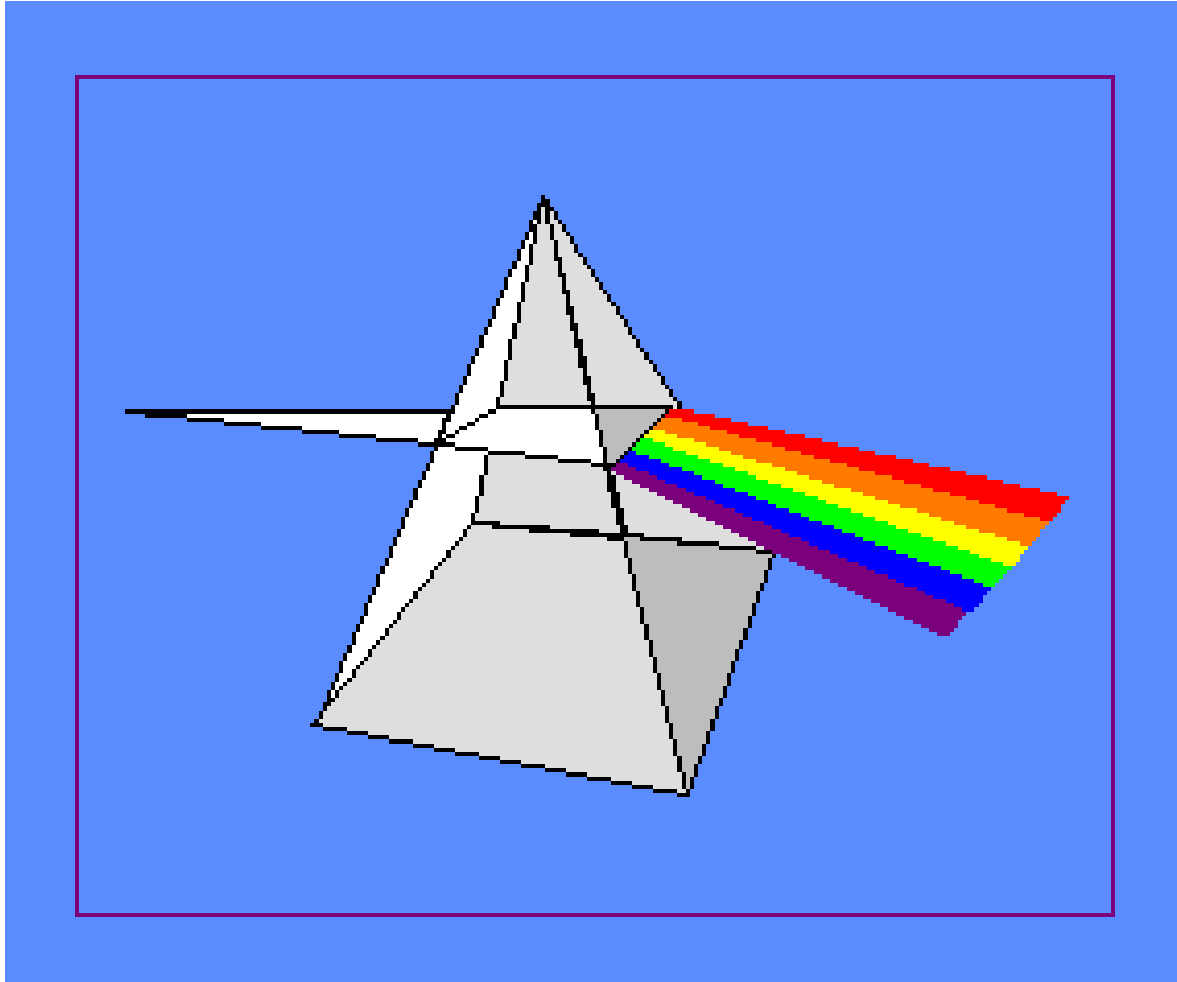
sample cell cell function are to produce gaseous atoms

1. Flame (F-AAS)
2. Graphite Furnace (GF-AAS)
3. Hydride generation (HG-AAS)
4. Cold Vapour (CV-AAS)
5. etc

Sample cell

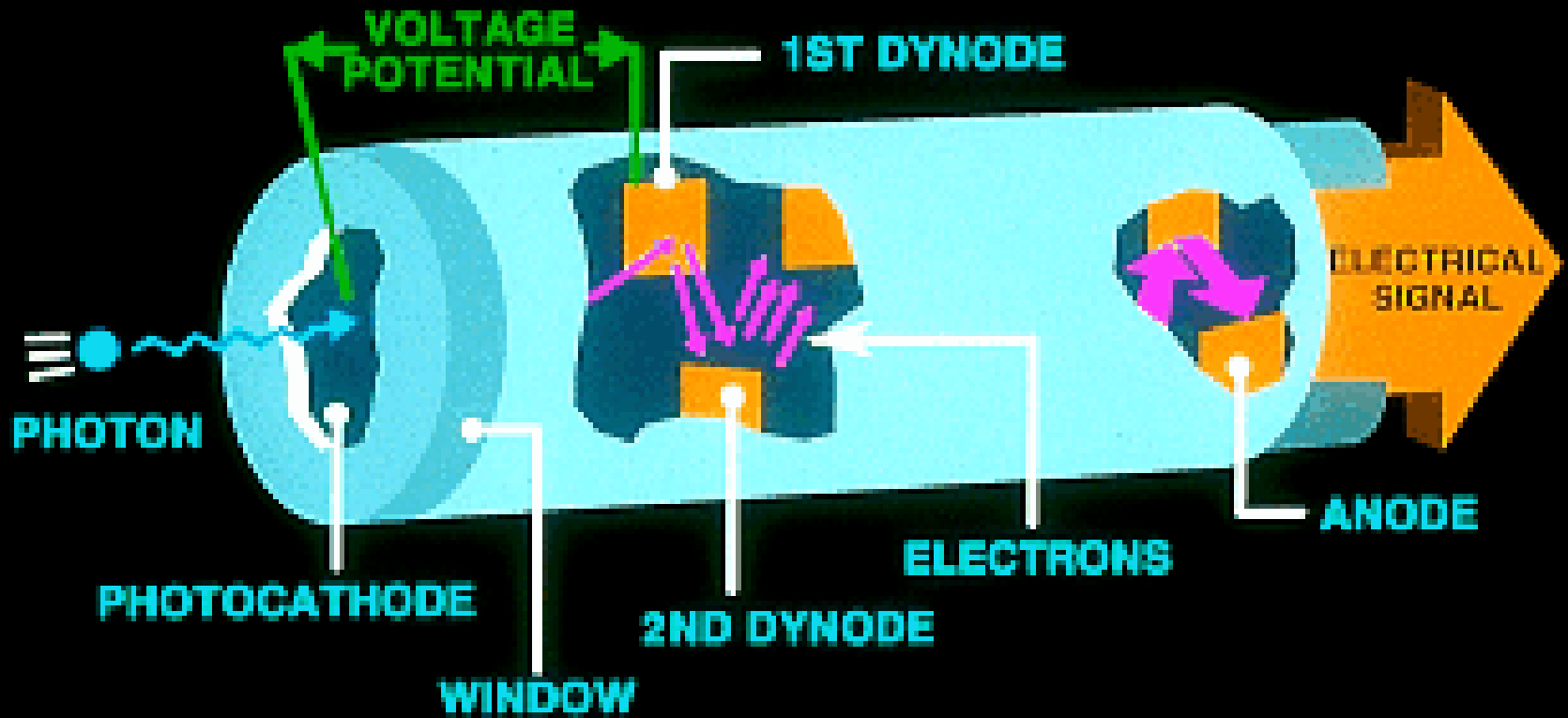


Monochromator



Detector

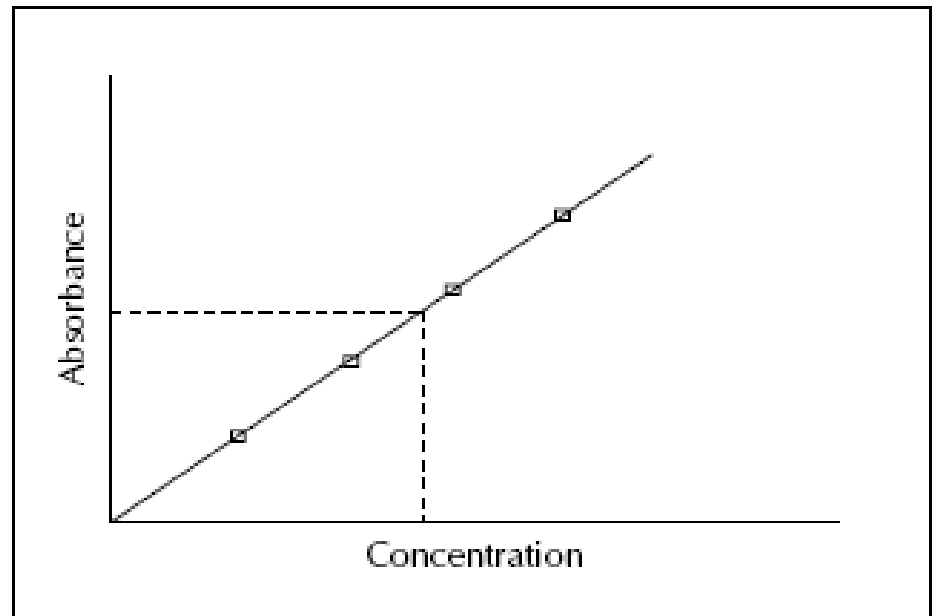
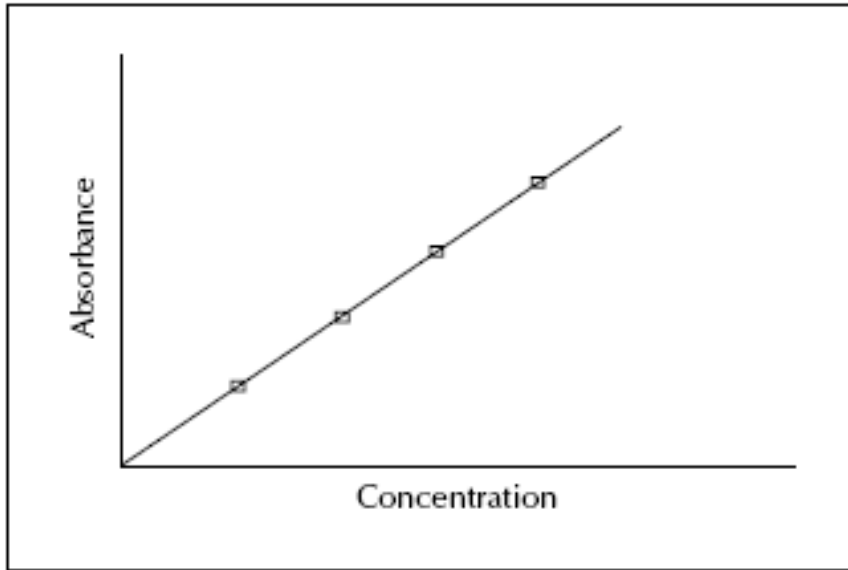
PHOTOMULTIPLIER TUBE DETECTOR



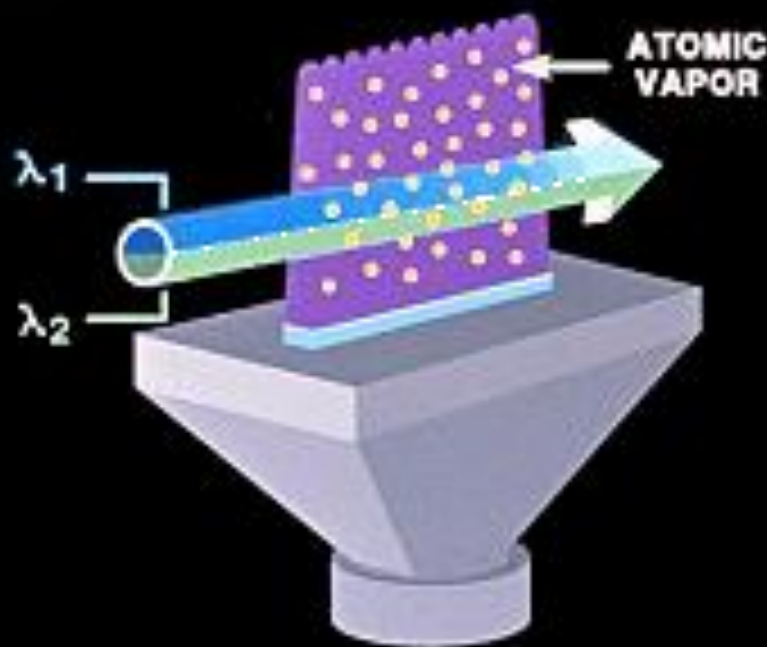
How it is works

1. Atoms of different elements absorb characteristic wavelengths of light.
2. Analysing a sample to see if it contains a particular element means using light from that element.
3. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample.
4. In AAS, the sample is atomised – ie converted into ground state free atoms in the vapour state – and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporised sample. Some of the radiation is absorbed by the lead atoms in the sample. The greater the number of atoms there is in the vapour, the more radiation is absorbed. The amount of light absorbed is proportional to the number of lead atoms.
5. A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown.
6. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample.

How to Analysis?



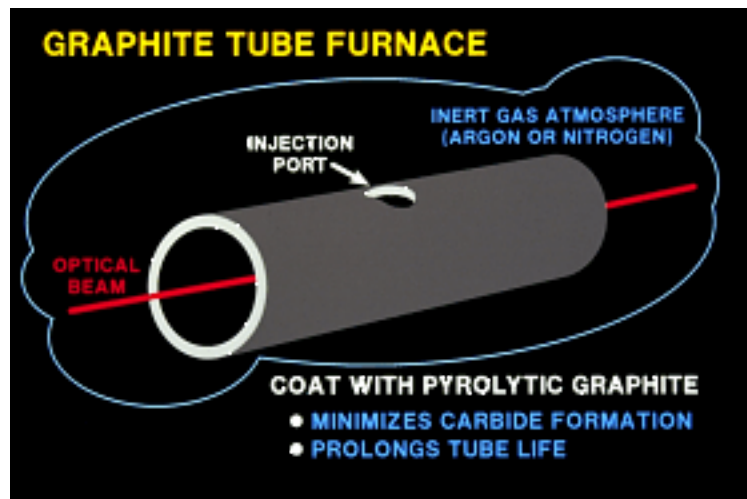
SELECTIVE ABSORPTION



- NARROW WAVELENGTH RANGE...ABSORPTION "LINE"
- WAVELENGTH CHARACTERISTIC OF ELEMENT
- ABSORPTION INDICATES CONCENTRATION

Three step sample preparation for graphite furnace:

- (1) Dry - evaporation of solvents (10->100 s)
- (2) Ash - removal of volatile hydroxides, sulfates, carbonates (10-100 s)
- (3) Fire/Atomize - atomization of remaining analyte (1 s)



Burner nebulizer Step

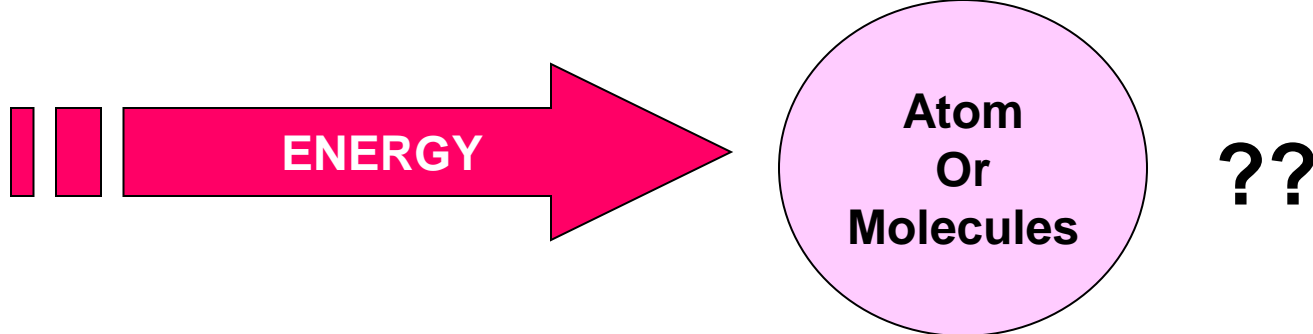
Three steps are involved in turning a liquid sample into an atomic gas:

1. Desolvation – the liquid solvent is evaporated, and the dry sample remains
2. Vaporisation – the solid sample vaporises to a gas
3. Volatilisation – the compounds making up the sample are broken into free atoms.

Atomic Emission Spectroscopy - This method uses flame excitation; atoms are excited from the heat of the flame to emit light. This method commonly uses a total consumption burner with a round burning outlet. A higher temperature flame than atomic absorption spectroscopy (AA) is typically used to produce excitation of analyte atoms. Since analyte atoms are excited by the heat of the flame, no special elemental lamps to shine into the flame are needed. A high resolution [polychromator](#) can be used to produce an emission intensity vs. [wavelength](#) spectrum over a range of wavelengths showing multiple element excitation lines, meaning multiple elements can be detected in one run. Alternatively, a [monochromator](#) can be set at one wavelength to concentrate on analysis of a single element at a certain emission line. Plasma emission spectroscopy is a more modern version of this method. See [Flame emission spectroscopy](#) for more details.

[Atomic absorption spectroscopy](#) (often called AA) - This method commonly uses a pre-burner nebulizer (or nebulizing chamber) to create a sample mist and a slot-shaped burner which gives a longer pathlength flame. The temperature of the flame is low enough that the flame itself does not excite sample atoms from their ground state. The nebulizer and flame are used to desolvate and atomize the sample, but the excitation of the analyte atoms is done by the use of lamps shining through the flame at various wavelengths for each type of analyte. In AA, the amount of light absorbed after going through the flame determines the amount of analyte in the sample. A graphite furnace for heating the sample to desolvate and atomize is commonly used for greater sensitivity. The graphite furnace method can also analyze some solid or slurry samples. Because of its good sensitivity and selectivity, it is still a commonly used method of analysis for certain trace elements in aqueous (and other liquid) samples.

Atomic Fluorescence Spectroscopy - This method commonly uses a burner with a round burning outlet. The flame is used to solvate and atomize the sample, but a lamp shines light at a specific wavelength into the flame to excite the analyte atoms in the flame. The atoms of certain elements can then [fluoresce](#) emitting light in a different direction. The intensity of this fluorescing light is used for quantifying the amount of analyte element in the sample. A graphite furnace can also be used for atomic fluorescence spectroscopy. This method is not as commonly used as atomic absorption or plasma emission spectroscopy.



If a substance is irradiated with electromagnetic radiation:

- The energy of the incident photons may be transferred to the atom or molecules.
- It will raising them from the ground state to an excited state
- WHAT IS: ABSORPTION,EMISSION, FLUORESCENCE, PHOPHORESENCE !