Flame Atomic Absorption & Emission Spectrometry

Introduction:

The first observation of atomic emission dates back to at least the first campfire where hominoids/humans observed a yellow color in the flame. This color was caused by the relaxation of the 3p electron to a 3s orbital in sodium (refer to the energy level diagram in Figure 2.3 given earlier), and in part by carbene ions. Slightly more advanced, but still unexplained observations were responsible for the first development of colorful fireworks in China over 2000 years ago. A few of the more relevant discoveries for atomic spectroscopy were the first observations by Newton of the separation of white light into different colors by a prism in 1740, the development of the first spectroscope (a device for studying small concentrations of elements) in 1859 by Kirchhoff and Bunsen, and the first quantitative analysis (of sodium) by flame emission by Champion, Pellet, and Grenier in 1873. The birth of atomic spectrometry began with the first patent of atomic absorption spectrometry by Walsh in 1955. In the same year, flames were employed to atomize and excite atoms of several elements. The first atomic absorption instrument was made commercially available in 1962. Since then, there have been a series of rapid developments that are ongoing in atomic and emission spectrometry including a variety of fuels and oxidants that can be used for the flame, the replacement of prisms with grating monochromators, a variety of novel sample introduction techniques (hydride, graphite furnace, cold vapor, and glow discharge), advances in electronics (especially microprocessors to control the instrument and for the collection and processing of data), and the development of atomic fluorescence spectrometry. Surprisingly, detection limits for the basic instruments used in flame atomic absorption and emission spectrometry have improved little since the 1960s but specialty sample introduction techniques such as hydride generation and graphite furnace have greatly improved detection limits for a few elements.

- **What is:**

Absorption?

Emission?

Methods of Flame Spectrometry:

FAAS/FES?

FAAS & FES Comparison:

The molecule's journey?

The relation between A & C,l?

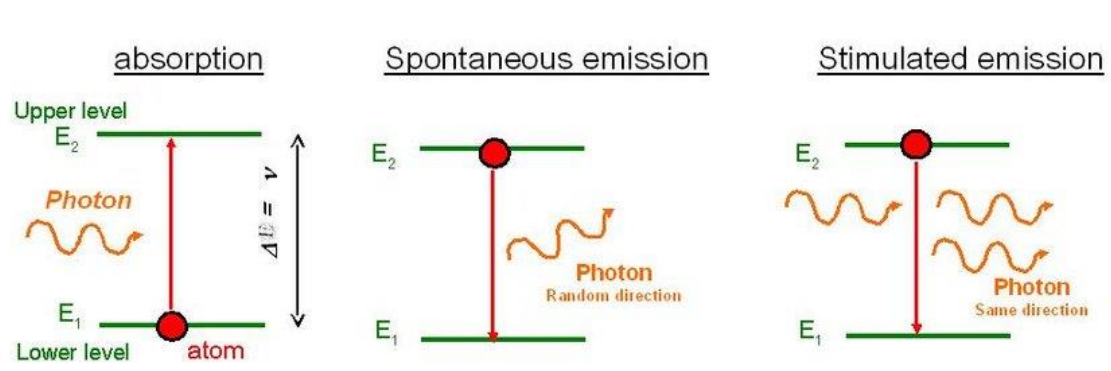
Beer–Lambert's Law?

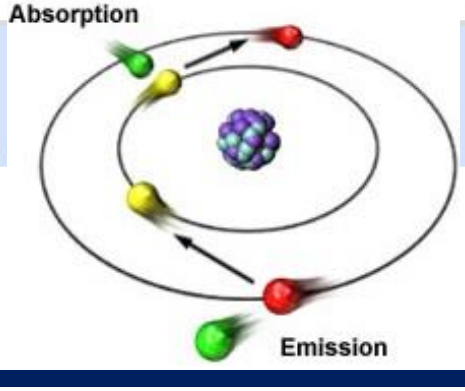
Absorption:

Absorption refers to how much light (or other waves) can be taken in by the material being measured.

Emission:

Emission refers to how much light (or other waves) can be released by the material being measured.





Methods of Flame Spectrometry:

a) **Flame emission spectroscopy (FES)**: We measure the intensity of molecular bands or atomic or ionic lines emitted by excited molecules, excited atoms or even by excited ions.

b) **Flame atomic absorption spectroscopy (FAAS)**: We let through the fire a light beam with such a wavelength that can be absorbed by ground state atoms and thus we measure the decrease of light intensity.

c) **Atomic fluorescent spectroscopy (AFS)**: We irradiate the ground state atoms with an external light source, however we measure the intensity of emitted light at the characteristic wavelength instead of the decrease of light intensity due to the absorption of light.

FAAS:

Flame Atomic Absorption is a very common technique for detecting metals present in samples. The technique is based on the principle that ground state metals absorb light at a specific wavelength. Metal ions in a solution are converted to atomic state by means of a flame. When light of the correct wavelength is supplied, the amount of light absorbed is measured and a reading for concentration can be obtained.

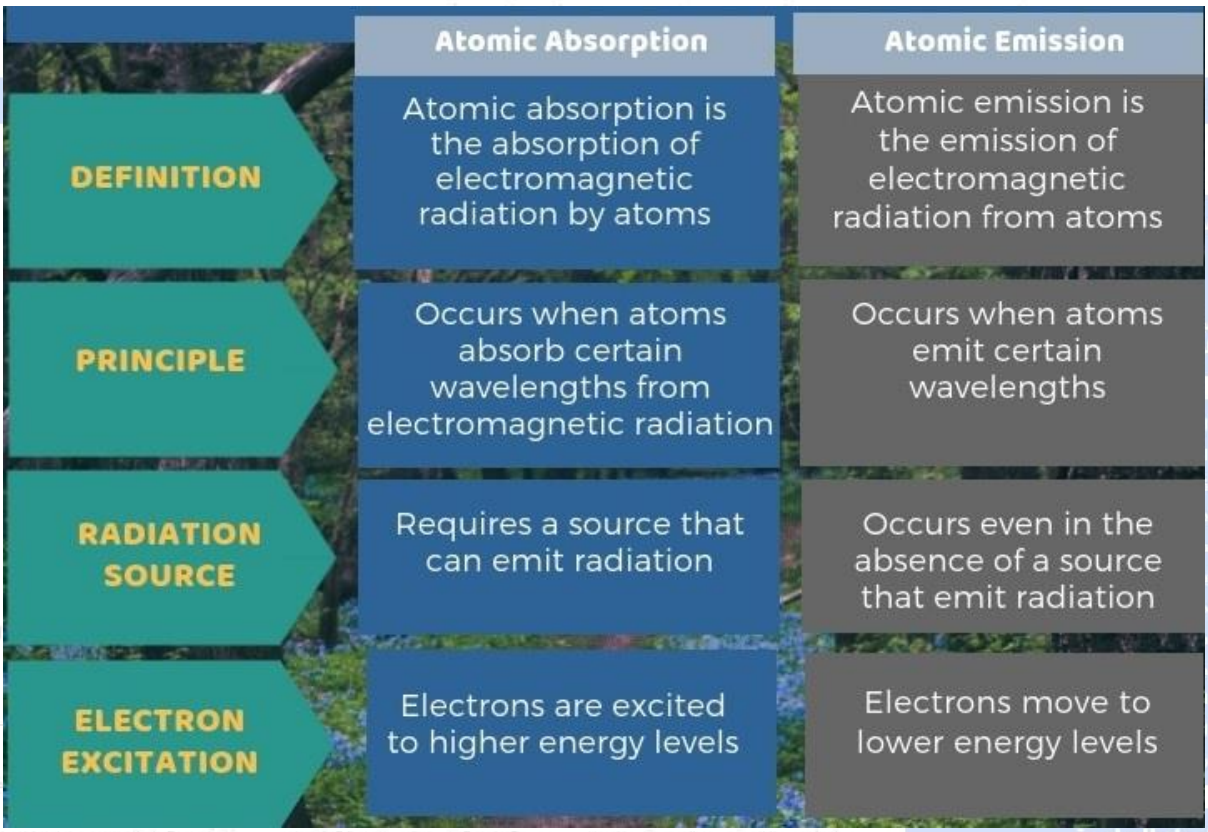
Flame atomic absorption is a very accurate quantitative technique and also a good qualitative technique. This is one of the main reasons it is the most widely used of the atomic absorption methods.

FES:

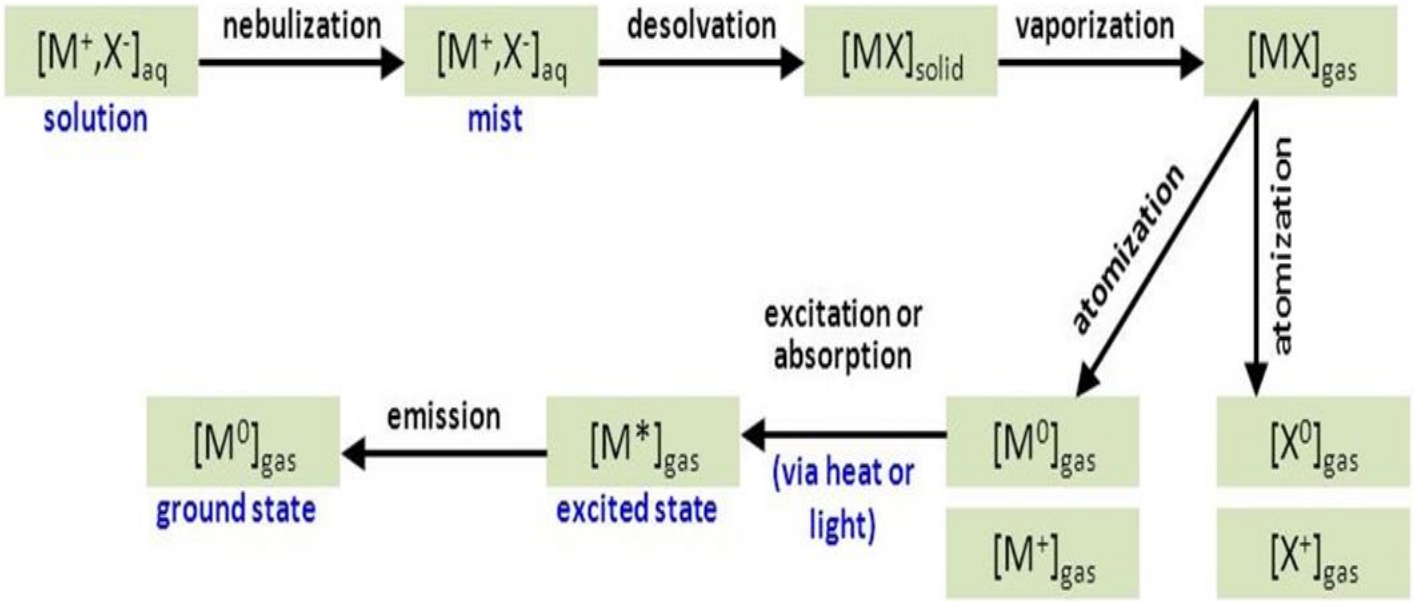
Atoms and molecules are raised to excited states via thermal collisions with the constituents of the partially burned flame gases. Upon their return to a lower or ground electronic state, the excited atoms and molecules emit radiation characteristic of the sample components. The emitted radiation passes through a monochromator that isolates the

specific wavelength for the desired analysis. 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.

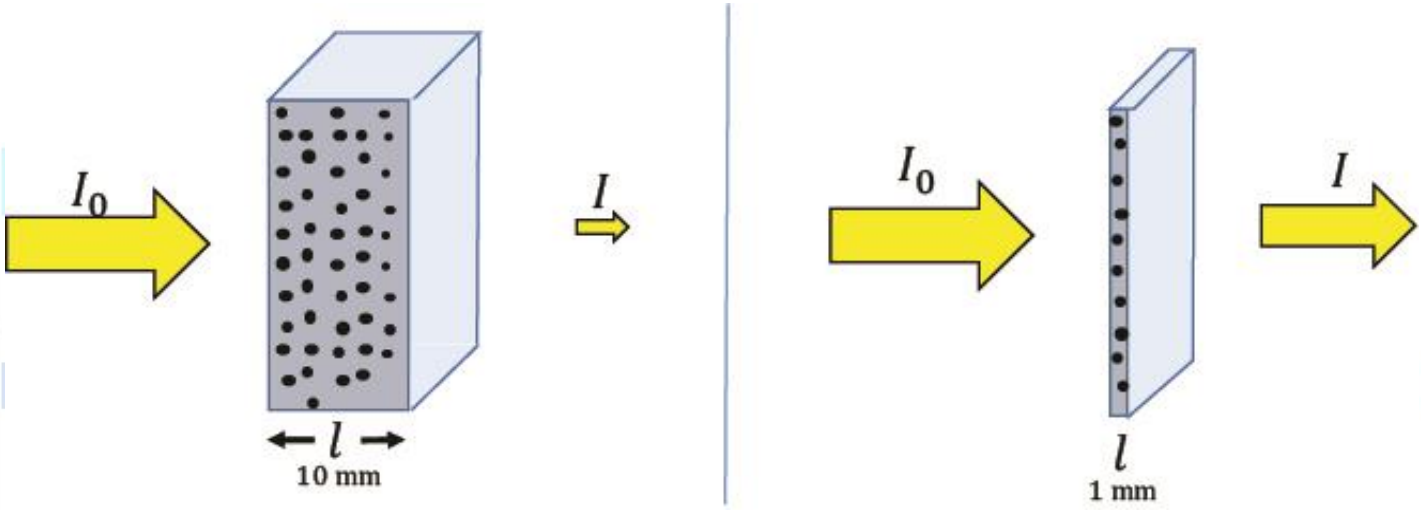
FAAS & FES Comparison:



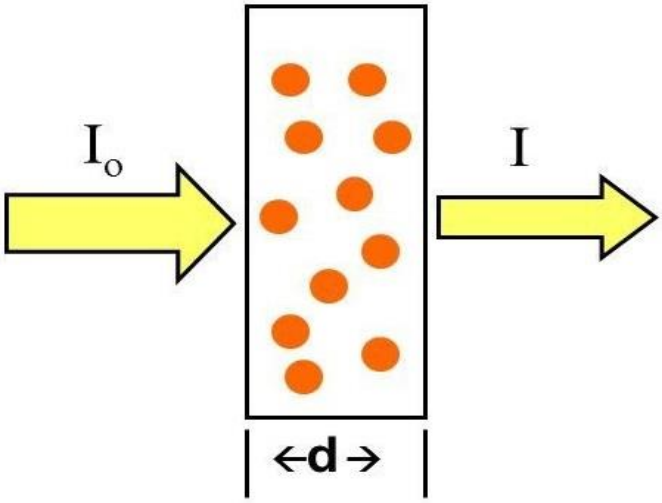
The molecule's journey:



The relation between A & C,l:



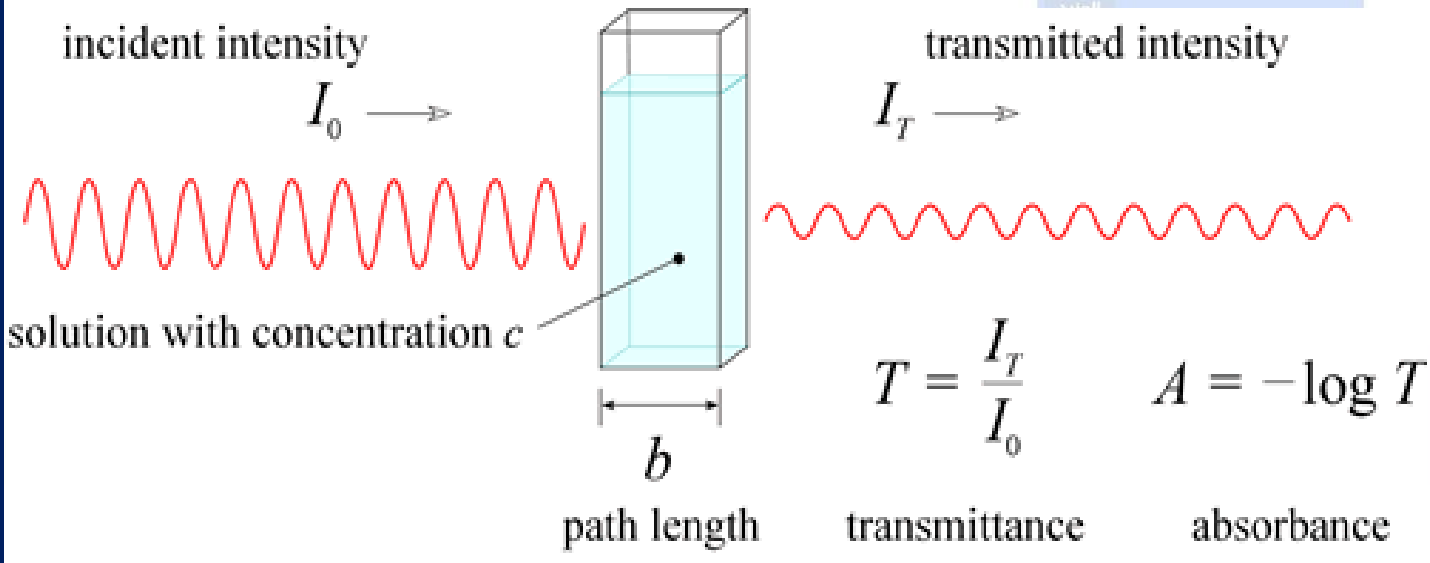
Beer–Lambert's Law:



$$I = I_0 10^{-\varepsilon \ell c}$$

I = light intensity
ε = extinction coefficient
ℓ = thickness
c = concentration

$$\text{Absorption (A)} = -\log(I/I_0) = \varepsilon \ell c$$



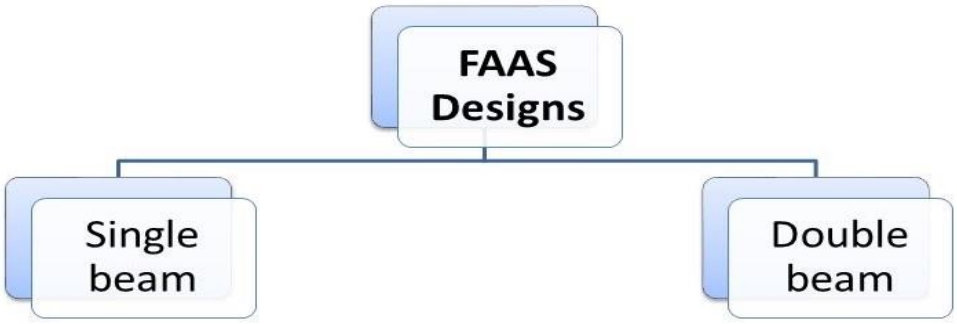
$$T = \frac{I_T}{I_0}$$

transmittance

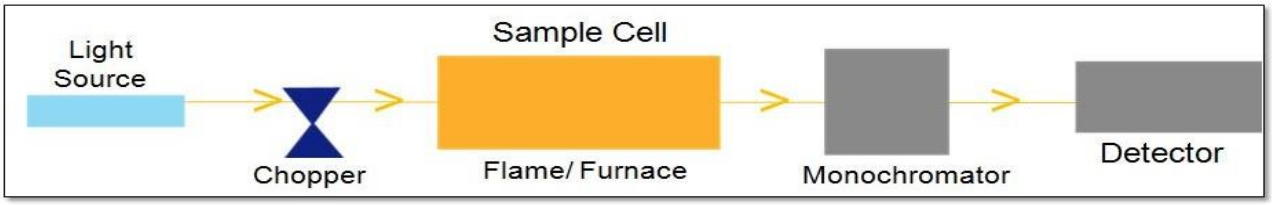
$$A = -\log T$$

absorbance

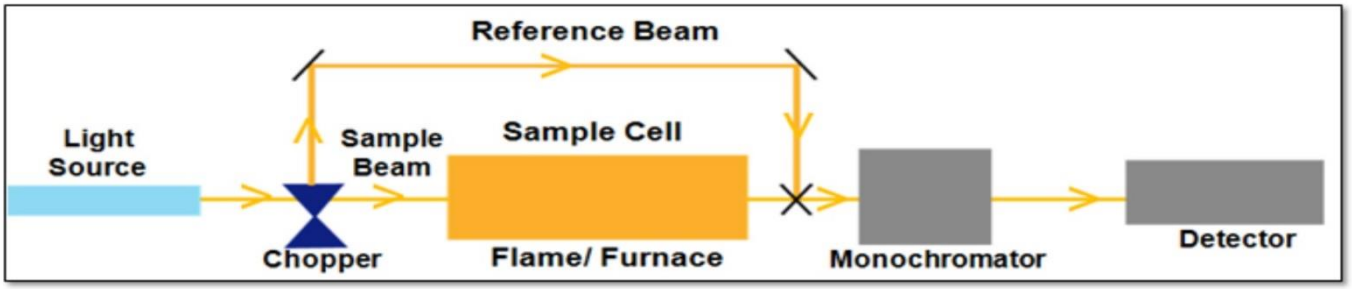
Instrument & Instrumentation:



Single-Beam AAS

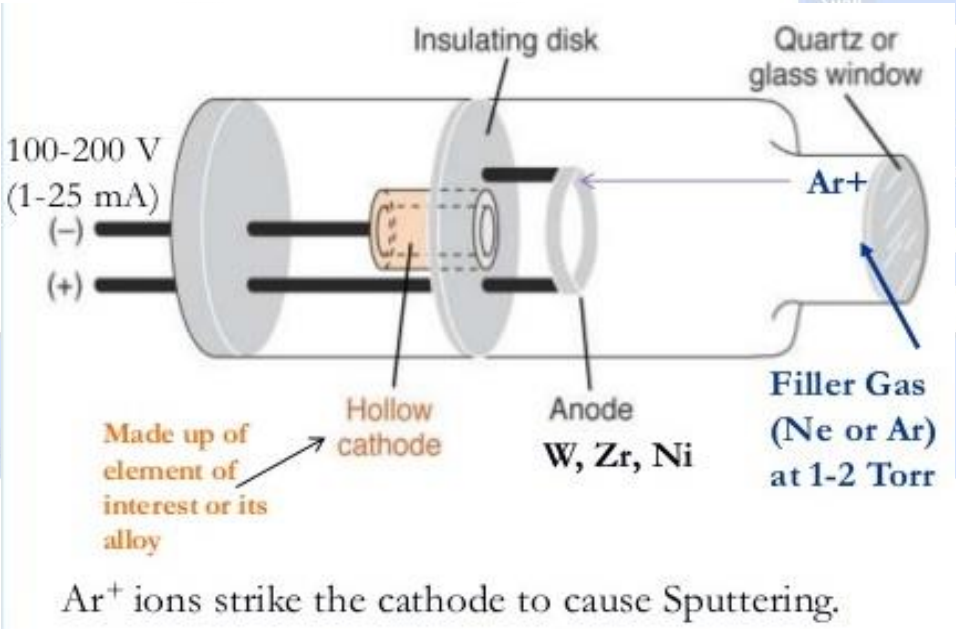


Double-Beam AAS



Radiation Source:

- HCL:



- Absorption:

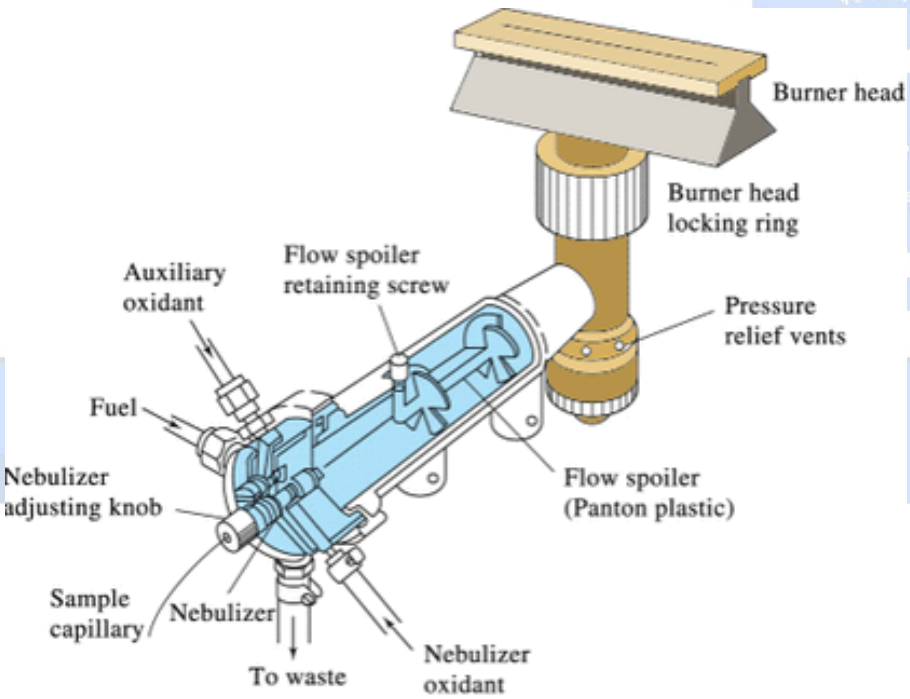
Type	Method of Atomization	Radiation Source
atomic (flame)	sample solution aspirated into a flame	Hollow cathode lamp (HCL)
atomic (nonflame)	sample solution evaporated & ignited	HCL
x-ray absorption	none required	x-ray tube

-Emission:

Type	Method of Atomization	Radiation Source
arc	sample heated in an electric arc	sample
spark	sample excited in a high voltage spark	sample
argon plasma	sample heated in an argon plasma	sample
flame	sample solution aspirated into a flame	sample
x-ray emission	none required; sample bombarded w/ e-	sample

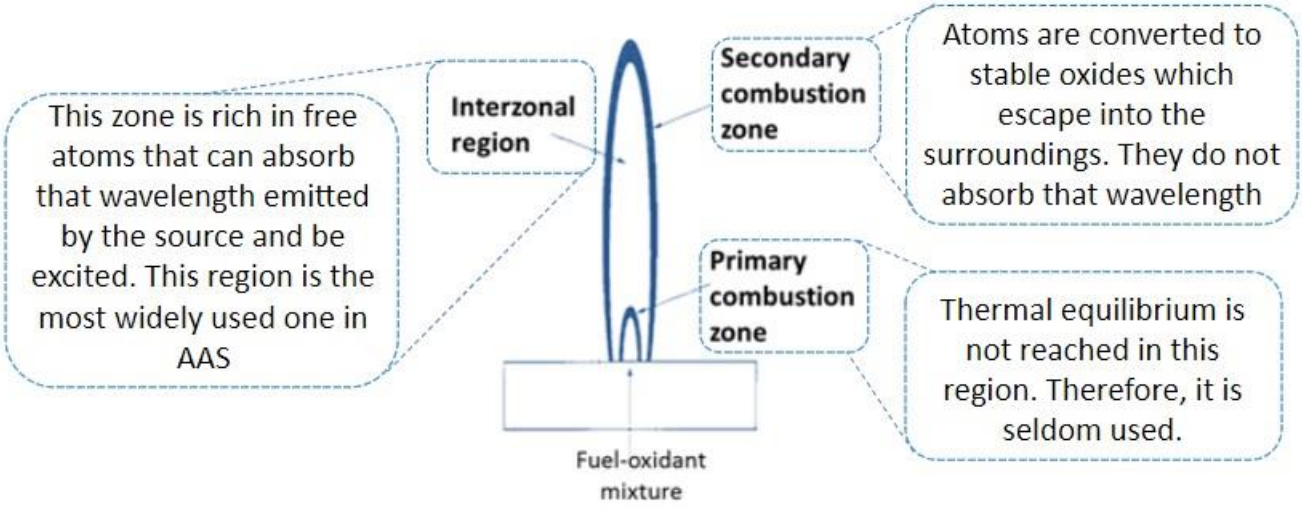
Nebulizer:

The nebulizer converts the sample solution into a mist or aerosol. The nebulized sample is then carried into the flame.

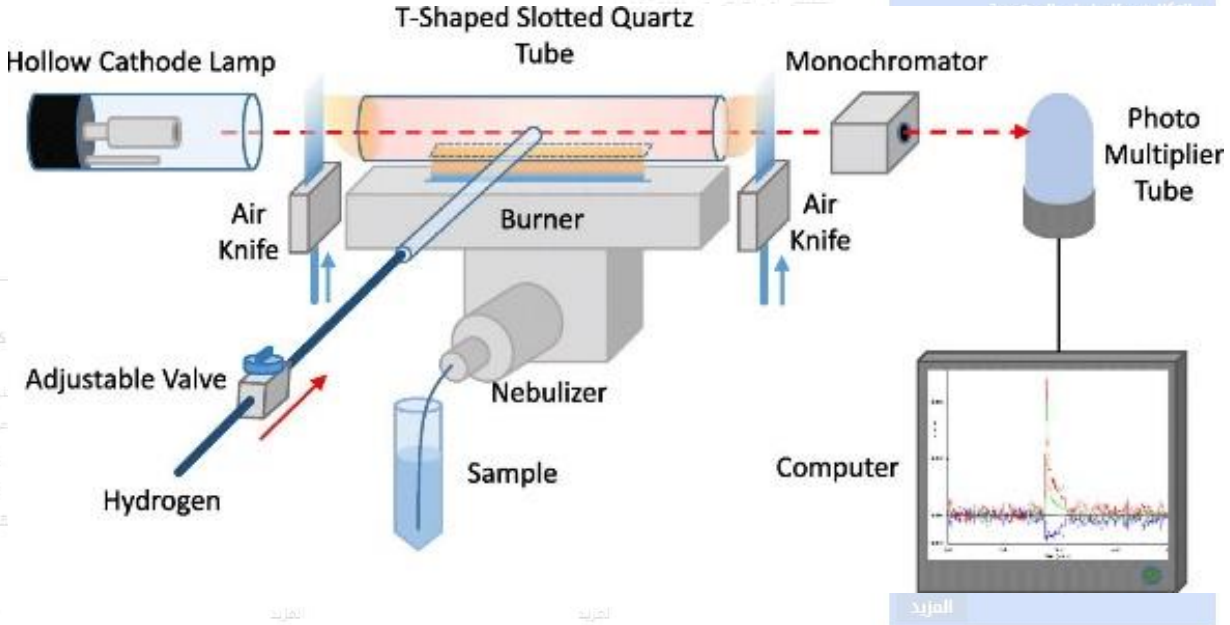


Burner:

-Flame zones:



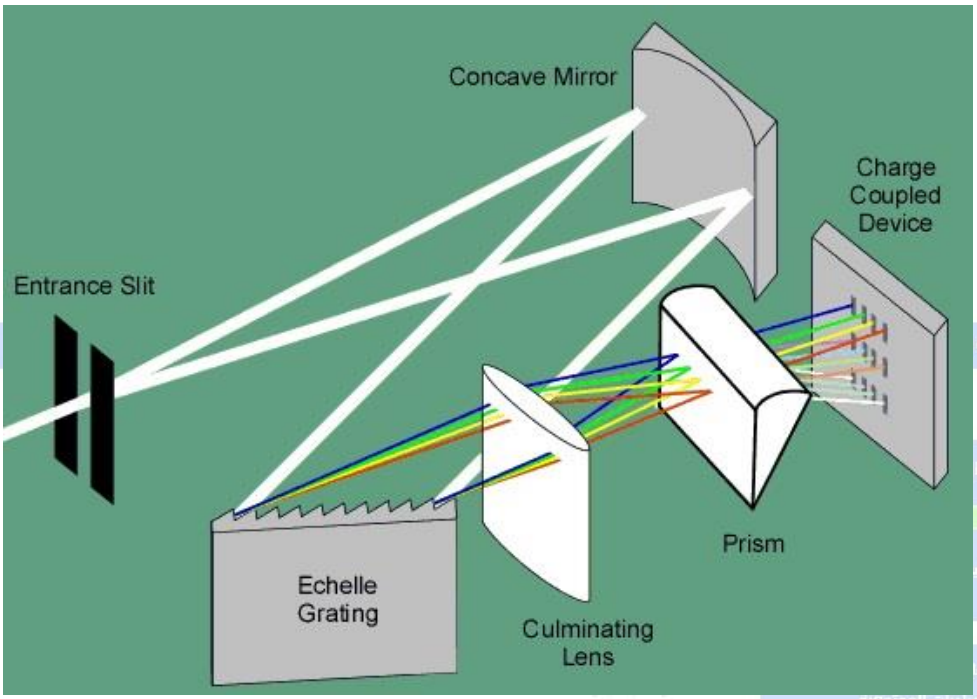
-Structure:



-Flame Main Types:

OXIDANT	FUEL	TEMPERATURE, C
Oxygen	Natural Gas	2700-2800
Oxygen	Hydrogen	2550-2700
Oxygen	Acetylene	3050-3150
Air	Natural Gas	1700-1900
Air	Hydrogen	2000-2100
Air	Acetylene	2100-2400
Nitrous Oxide	Acetylene	2600-2800

Monochromator:



Detectors:

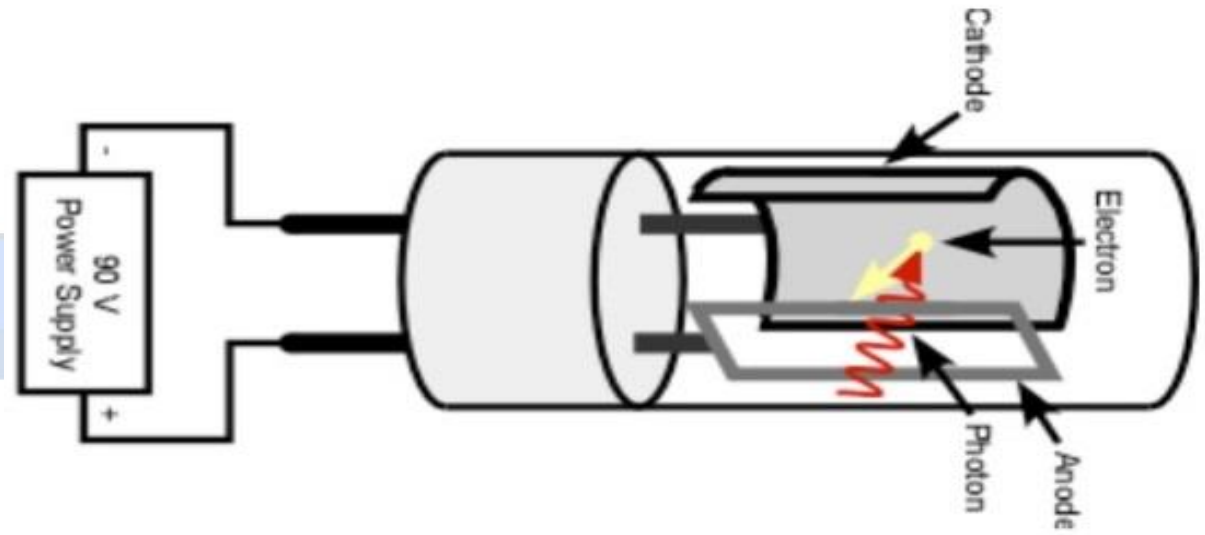
-Photomultiplier Tubes (PMT):

(pros.)

Standard device
Large signals
Large active areas possible
Fast rise times possible

(cons.)

Large physical dimension
High Voltage (typical 700 V) required
Gain instability as function of temperature
Sensitive to magnetic fields
Background radiation



-Photodiodes (SPD):

(pros.)

Small dimension (thin)
Low Voltage operation
Very stable signal height
Rugged
Insensitive to magnetic fields

(cons.)

Limited surface area
Low energy noise threshold
Noise at elevated temperatures

-Silicon Photomultiplier (SiPm):

(pros.)

Small dimension (thin)
Low Voltage operation
high QE (PDE) also > 500 nm
Insensitive to magnetic fields

(cons.)

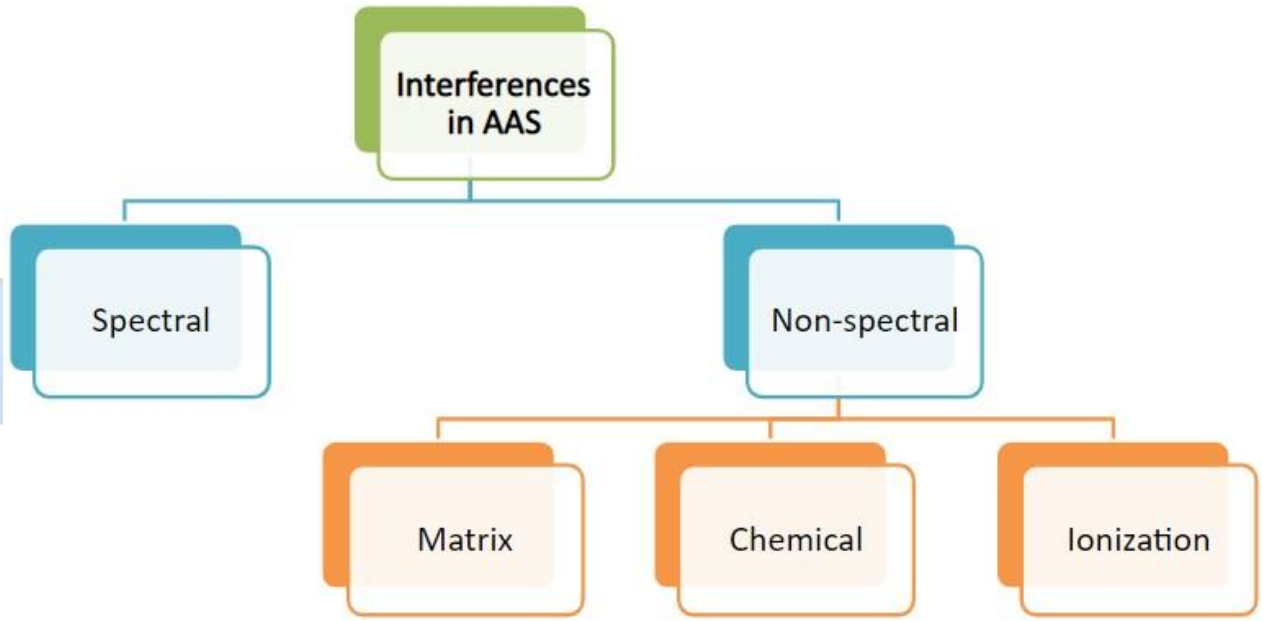
Linearity of pulse height spectrum strongly depending on bias voltage and scintillator speed

Temperature dependent gain typically -1.3 % per degree C

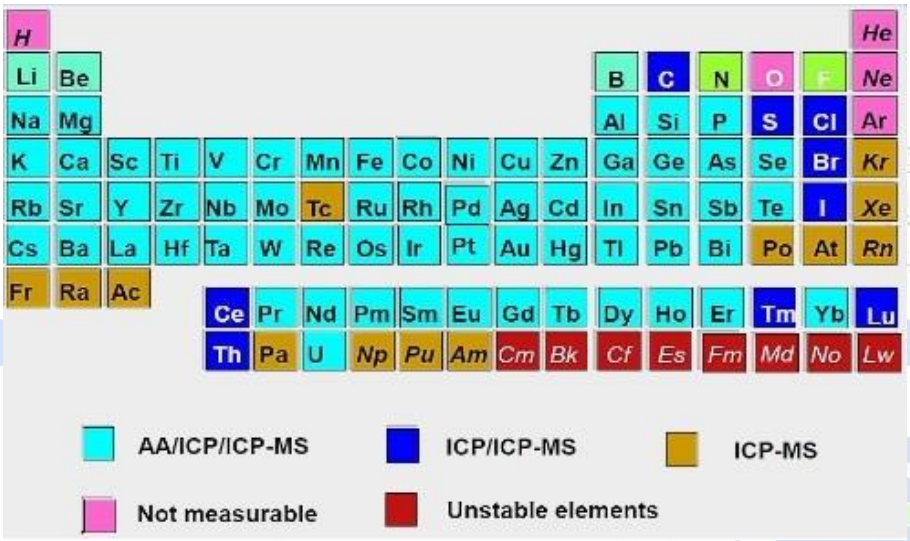
Strong noise increase at elevated temperature. Maximum temperature approx. 50 degrees C

Large cost per cm^2

Interferences:



Applications:



Atomic Spectroscopy Applications by Market

Market	Typical Applications	Commonly Used Techniques		
		AA	ICP-OES	ICP-MS
Environmental	Water Soil Air	□ □ ■	■ ■ □	■ ■ ■
Food	Food Safety Nutritional Labeling	■ ■	■ ■	■ □
Pharmaceutical	Drug Development Quality Control	□ □	□ ■	■ □
Petrochemical	Petroleum Refining Lubricants and Oils	■ □	■ ■	■ □
Chemical/Industrial	Quality Control/Product Testing	■	■	■
Geochemical/Mining	Exploration Research	■ □	■ ■	■ ■
Biomonitoring	Biological Fluids	■	□	■
Agriculture	Soils	■	■	□
Semiconductor	Wafers High-Purity Chemicals	□ ■	□ □	■ ■
Nuclear Energy	Low-Level Waste Process Water	□ □	■ ■	■ ■
Renewable Energy	Biofuels Solar Panels	□ □	■ ■	■ ■
Nanomaterials	Research	■	□	■

Frequency of Technique Used: □ ■ ■ ■