Chapter:

# Atomic Spectroscopy

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## Atomic Emission Spectroscopy
## AES or AFES

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# Atomic Emission Spectroscopy

## Atomic Spectroscopy: AES/AFES

Study of electromagnetic radiations absorb or emitted by atoms.

~~#~~ It is used to determine the elemental composition b/c of characteristic of different Atomic spectroscu-

spectra of one atom does not match with the another element → this is the Beauty of spectroscopy.

① Flame photometry: → Also called Flame emission spectroscopy.

based upon behaviour of particles that exist in the ground state in the flame.

Flame photometry based upon those particles that are electronically excited in the medium.

# Bohar's Theory:

When an atom absorb energy Then it goes to the excited state but this is not stable for stability it Release energy and come back to the ground state.

Excited state has life ↓ 1-10 ns life

$$\Delta E = E_2 - E_1$$

- Cs → gives blue colour.
- Li → gives crimson Red color

★ **Ca →** gives Brick Red colour/orange

★ **K →** gives violet colour.

★ **Na →** Release energy in golden light Yellow — wavelength is 589 nm -

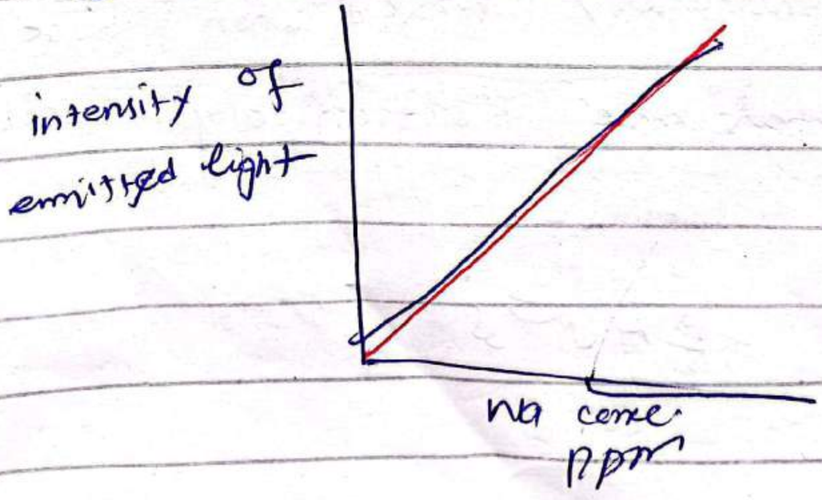
conc. of Na and intensity of emitted light. hence

1 ppm → NaCl solution → Less no. of Na atom goes to the Flame ⇒ Less int

1000 ppm → NaCl solution → more No. of Na+ when free atom deexci

↓

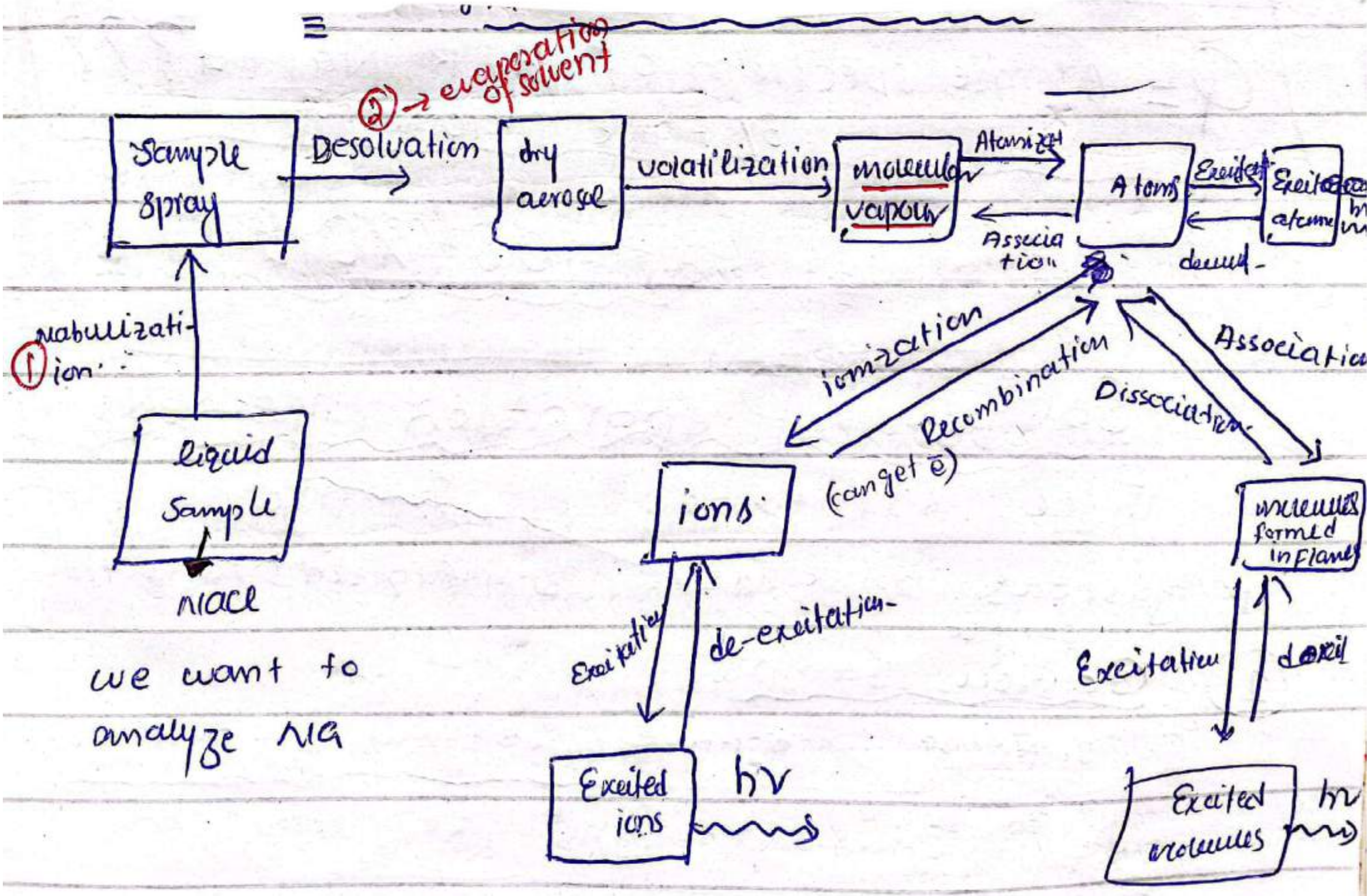
more intensity light emitted.



# Flame Emission Process:

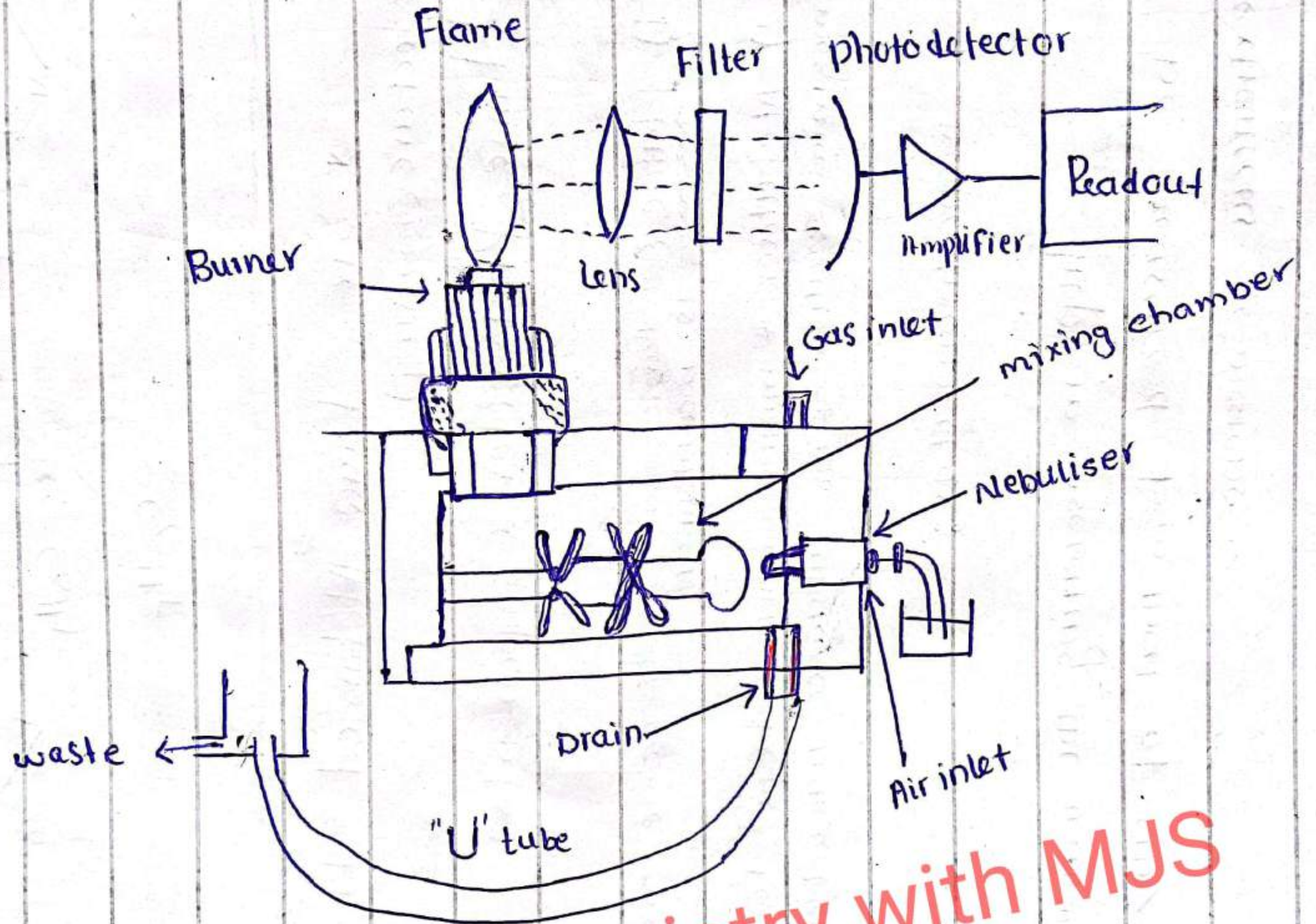
our Objective is to convert the Analyte into atom.

When we add sample into flam not only one process takes place there are some others process take place. They Effect The intensity of Atomization.



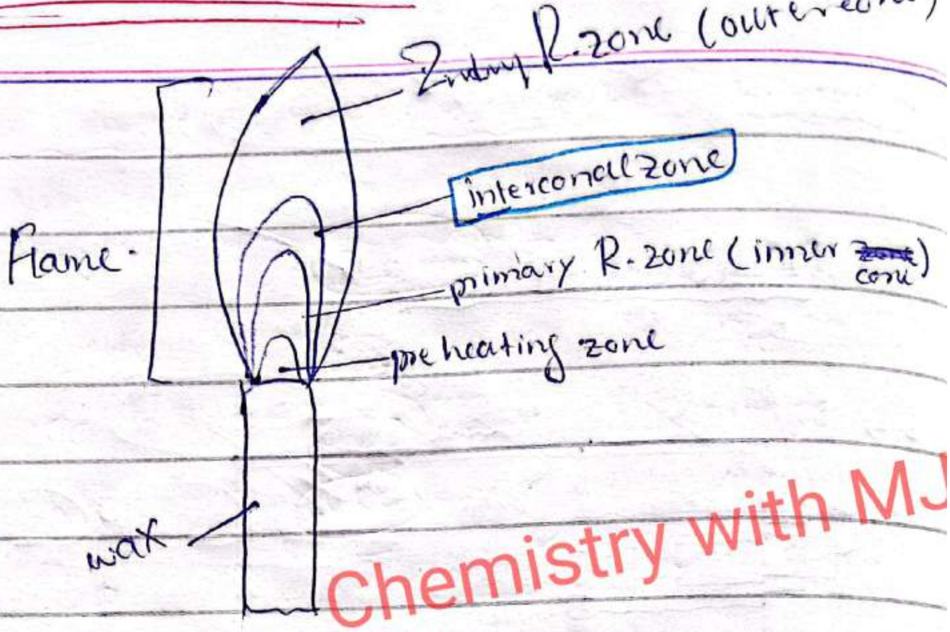
we want to analyze Na

As a Result we get number of emitted light.



"schematic diagram OF Flame photometer"

# * Structure Of Flame



→ 1mm thick

1. preheating zone: in this mixed gases are heated to the ignition temp. by conduction and radiation from the p. reaction zone.

2. primary Reaction Zone (inner cone)

↳ surround the preheating zone.

- species present in this zone are not in Thermodynamic equilibrium.
- Complex Reactions occurring in this Region are incompletely understood.
- in this zone - conc. of free Radicals is more.
- The phenomena of chemiexcitation occu in this zone.

3. Interconal ~~Zone~~ Layer:-

- is very narrow but can acquire the height of several centimeters in Fuel rich acetylene Flame.
- outside the P. Reaction Zone.

- hottest part* of the Flame → most intense emission
- species attain thermal equilibrium.

## 4. Secondary Reaction Zone: /outer cone/ plume of Flame

- Area where combustion is completed and Reaction products become transformed into stable molecular species by interaction with entrained Air.
- This secondary R. zone appears as blue sheath over the Flame which is especially appearant in hydrocarbon Flame.

## ✳ Fuel-oxidant Temperature

### * Hydrocarbon Flames:

✳ $\underbrace{C_2H_2 + O_2}$ ⟶ 3373—3410 K ≈ 3400K

✳ $C_2H_2 + N_2O$ ⟶ 2950 K ≈ 2950 K.

✳ $C_2H_2$ + Air ⟶ 2450—2480 K ≈ 2450 K

✳ $CH_4$ + Air ⟶ 2148 K ≈ 2150 K

### * Hydrogen Flames:

$H_2$ + air ⟶ $\boxed{2300K}$

→ We have different txpes of Fuels

| Fuels | oxident |
|---|---|
| $CH_4$ | |
| | air |
| propane | |
| | $O_2$ |
| butane | |
| Astylene $C_2H_2$ | $N_2O$ |

For burning purpose mostley we Fuel-

in some cases more heat is produced

* Astylene and oxygen has high temperature than Air and methane. that depend upon the availabilitx and nature and use of specific flame. which type of Flame we will use ???

Air + Astelene Flame temp measured 2400 K 2600K calculated

a) Q = If Analyte is excited at lower temperature Lets 900°c then we will use the ($CH_4$ — Air) Flame-
↳ 2148 K

b) For higher temp. Flame should be ($C_2H_2$ — $O_2$) (3373-3410K), ($C_2H_2$ — $N_2O$) (2950K)

* If our analyte is easily Atomized then we not need to utilize high temp. Analyte Cr, *Be excite at 3000 K so we will utilize → $C_2H_2 + O_2$ or $C_2H_2 + N_2O$ Flame.

Suppose $C_2H_2$ + Air → excite more than 45 elements.

$C_2H_2$ : Air (Flame)

Q = Can we use that Flame for variety of elements???

⇒ Above discussed flames are Stochiometric Flames

Stochiometric Flam → where Fuel and oxidant are present in mole ratio and that Flame gives highest temp.

$$2C_2H_2 + 5O_2 \overset{2552^{K}}{\rightleftharpoons} 4CO_2 + 2H_2O$$

five moles of oxygen React with two moles of Astelene. to form 4 moles of $CO_2$ and 2 moles of water.

* Reducing Flames: / Fuel Rich Flame

Go to excited stat

↓ It is used for less temperature. than stochiometric Flame.

$$2C_2H_2 + 4O_2 \longrightarrow 4CO_2 + 2H_2O$$

Imp Q1 Good man

* Oxidizing Flame: / Fuel lean Flame

▼ Temperature again will be lower than Stochiometric Flame.

$$C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

Imp!

* For Barium (Imp) → $\boxed{C_2H_2 + N_2O}$ ✓ Flame is used.

↓ 554nm ↓ gives green colour in Flame

when half element excite and dexicite then sensitivity of our technique decrease

# Sample preparation Methods:

## ① Gaseous Sample:

Na, K, ca Also present in Air in the form of particulate matter, or dust.

⇒ Na in Air ↓ It is difficult to introduce in the Flame so we have to sample prepared -

1- volume of gases can be measured in different units - e.g L or $m^3$

① ⇒ collect air ($m^3$) → we have to determine Na in Air sample

② ⇒ Solubilize the Na

How solublize Na?

You prepare 0.1M dil. $HNO_3$ solution.

Then you pass all your sample through this medium (Air) thus $Na^+$ produce - dissociate and

— diss

## ② Liquid Sample:

water may be of Any type.
If there is no suspended particle
Then introduce direct sample
to Flame photometer.

a) : If suspended particles in the sample:

* If suspended particles →
Then we have to Remove these
particle otherwise errors can
occurs.

It may collague | block the
opening of the tube of Flame photometer
Flow rate will decrease.
efficiency of evaporation will
decrease. by suspended particles.

⇒ Analyte may be Adsorb on
the suspended particles. It will
~~not~~ the part of

- usually we have to use 0.45 μm fiber
Glass Filters. This size is very
Small It stops the suspended particles
size and dissolve the Analyte Then we
can measure Na, K, Ca in sample.

→ over estimated Results ↓ For this Dilution done

liquid Form
**b)** * ⇒ of Sample is highly conc:---
Some times concentrations are high-
Range of your Standard 1— 10 ppm-
but your Actual sample 1000 ppm:
↳ Result in over estimation
This is the out of Range - we
have to dilute the sample
and form the measuring Range.
This is by Hit and trial-
You make different dilutions-
of Sample is highly concentrated.

~~then~~ **c)** * of Real sample concentration is
very low
↓ Results underestimation
↓ Thus preconcentration is done
→ Give Result of underestimation.

## 3)* Solid Sample:

sample these solids can not introduced directly -

pretreat that sample.

different ways to hand the solid sample:

Acid digestion* ~~Acetylation~~ method: ✓

Dry Ashing* method. ✓

## ~~I)~~ (i) Acid DIGESTION METHOD: — ✓

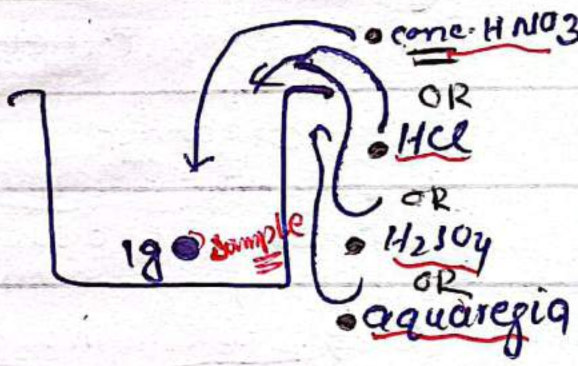
Your sample may be blood, urine, Ash, ~~from~~ Any metal.

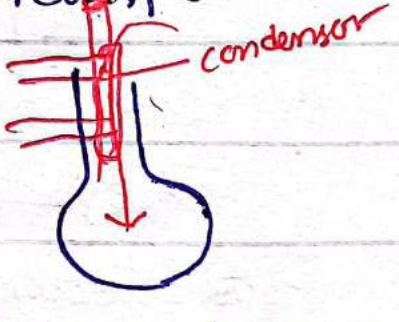
Example:

e.g 10g Fresh — To extract metal From plant leave:

plant leave → dry → constant wt → put leaves in oven heat slowly 50°C for longer time → time will come weight will constant $H_2O$ evaporate → Ground to make fine powder → took only 1g from Sample. Then mix with single Acid. Leave it for some time. digestion Start. mater start to decompose. desire metal coming in the Acid solution → transfer in Round bottom Flask Reflex condenser. Heat boil it. All material solubilize. Analyte which is bonded — Bond break down thus sodium in the ionic form in solution → cool down → if Solution is clear no need to filter → if solution is not clear then Filter it.

fix





## (ii) DRY ASHING Method:-

1g dry ~~powder~~ leave in Furnace.
sintered glass ~~crucible~~. burning

organic matter burn → $CO_2$ and water produce. inorganic Residues only left. we have to soulblize it

which only that analyte will move out is volatile at high temp.

If ~~analyte is not~~

cool down the crucible

* We will add conc HNO3 - Aqua regia - in and it inorganic Residue will dissolve and filter it if need- Filterate is Ready For Analysis.

Imp ✓

# Evaluation Methods:

four types of methods to evaluate analyte Sample.

✓ Calibration Method ✓

✓ Standard Addition Method. ✓

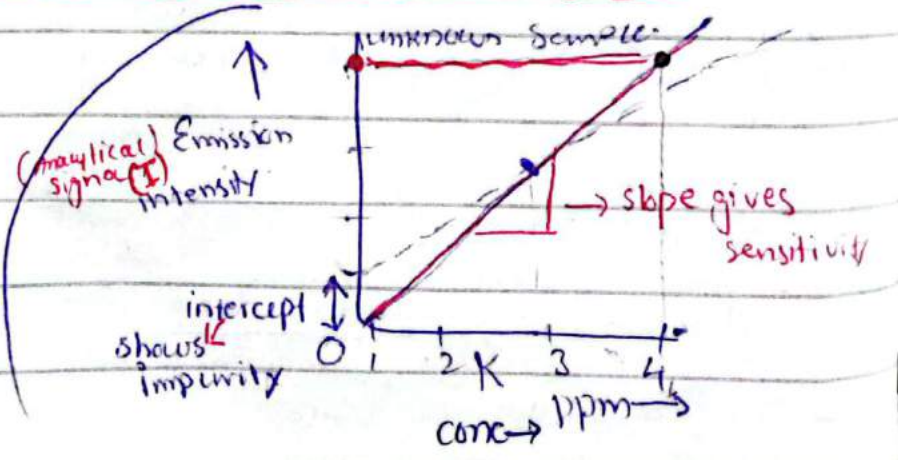
internal standardard method. ✓

1)- Calibration Method: Method for determing the conc. of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.

⇒ drinking water sample. Determine the K conc. in that Sample. What will be the Method used???

✓ in this we prepared diff. standard solution and Run. After this we run our unknown sample

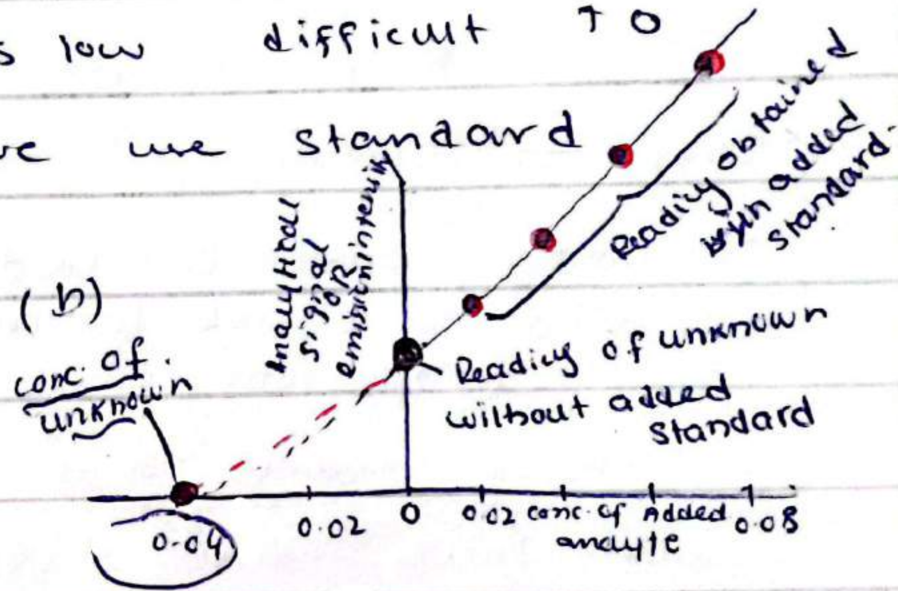
* prepared standard solutions of K



2) **Standard Addition Method:** A method to determine the Amount of Analyte in an unknown where known quantities of ~~sample~~ same analyte (standard) are added to an unknown (Sample)

→ known Amount of Same Analyte (standard) - is added

Imp If Analyte conc. is low difficult to measure. thus we use standard addition method. in



emission entensity increase.

Note v.v. imp

- when our Analyte is very low and not detectable by instrument then we use the standard Addition method in this we add known amount of standard of same Analyte in this way now our Analyte can be detecty by subtracting from

Analyte (conc). = Standard (conc) known — unknown Analyte

- This method invowe Addition of Same Analyte ⇒ Emission Intensity will not increase by adding the Same Analyte ~~suppose of NA~~

emission entensity will not increase.

---

in this method we add another analyte (not same) to increase the Atomization or efficiency. for Suppress the ionization

emission Intensity will increase by adding another Analyte

## 3) * internal standard method:

↓ we add diff analyte to get good emission intensity.

we Add the known amount of another element in sample blank

* some times we obs- our analyte easiey ionized when this easily ionize at low potential — Lesser will be Atomized.

* If we get more ions Rather than atoms → intensity will decrease — basically sensitivity of our method will decrease. we would not be able to measure low conc.

* If ions are more → they absorb energ and then deexicite but their line is different in Flame

# INTERFERENCES:

## 1) Physical interferences:

Viscosity ] physical ~~inte~~ interferences.
S. Tention. ]

1) viscosity:

⇒ If solvent is viscous than water
↓ to form our solution — ↓ Standard

- flow Rate will decrease
- drop size ↑, drop will condense go to drain
- intensity decrease thus sensitivity decrease.

Remedy
- solvent should be less viscous.

2) Temperature.

⇒ If Flame T is less:
- lesser no. of atoms excite & deexcite.
- E. intensity decrease.
- sensitivity decrease.

Remedy:
- we have to use such Flame which Atomize with proper way.

3) ⇒ Surface-Tension: (strongly bonding)

If S.T value high
- Flow rate decrease
- large drop form
- drop will condense and go to drain (wastage)
- intensity decrease
- sensitivity decrea

Remedy
- Surface tension should be less.

4) less soubility (more viscous)

Q = If our anaiyte is less souble in our anaiyte ?
↳ intensity will denease
↳ sensitivity will denease

Answer: sometime we may Add another solvent then its viscosity will decrease - and our Flame temp. will increase -

— overlap of Analytical line with another line.

## ② spectrometric interferences:

three types

### (i) Flame back ground emission → underestimation Results.

any of the F. product → absorb energy Excite and dexceite → Radiation emit these Radiatiation overlap with the line of anaiyte.

* Bands shown due to Flame product speeiecies e.g C–C, OH, CN, C–H

* ✓ If conc. of sample → emission intensity greater.

CO = 3881.9 A° ⇏ match with the CN band (3883.4 A°)

–OH species in the ↓ It gives to broad band b/w 2800 to 4000 A°

✓ * Ba = 5535.6 A° ⇒ match with C–C (554

* Bi, analytical lines come at 3067.7

Anaiyte

Bi = 3067.7
Sn = 3175.0
V = 3185.4
Cd = 3261.1
Cu = 3247.4
Ag = 3280.7

} signal ⇒ match with the –OH band

~~37.15~~

OH = 2800 – 4000 A°
CH = 3872 A°
✓ CN = 3883.4 A°
✓ C–C = 5541 A°

* Co = 3873.1
Mn = 4030.8
Pb = 4057.8
} ⇒ signal match to CH band (3872 A°)

when each line overlap our Analytic line makes our Result wrong.

**Remedy:** use optical multi-channel Analysers to Remove back ground emission which naturally follow something.

## (ii) Emission of Concomitants:

→ an phenomena

→ other species present in the Sample solution of Sample

e.g { Ag = 3382.9 A° Af measuring silver
Ni = 3380.6 A° ~~and~~ Nickle is present interfere our analyte.

Ag + Ni
↓ wanted, ↓ unwanted.

e.g { Zn = 4810.5 A°
Sr ~~Stortium~~ = 4811.9 A°

Strontium

e.g { Co = 3453.5
Ni = 3452.9.

**Remedy:** to extract test element by solvent Extraction or another method.

## iii) Spectro interference (Self Absorption):

when analyte atom excite when deexcit emit specific Radiation. more Radiation absorb by free* atom in cooler ~~colder~~ Region of the flame called Self Absorption.

↳ underestimation: Results

✓ Self Absorption increases when conc. of Analyte increases.

**Remedy** solution to this problem
↓
**We** should dilute our Sample.

solvent Extraction or complexing agent.

or make one Reagent.

Flame back ground emission solution

we use doterium* Lamp

↓ it gives the Result of

only ~~for~~ back ground

## ③ Chemical interferences:

→ occurs when another substance is present in the sample that supress the Atomization of the Analyte.

any chemical species which interfere our analyte

⇒ underestimation Results

e.g 1) *Ionization:

Atoms → ionized → emission intensity decrease - this

Remedy: Add suppressant or radiation buffer - this increase the conc. of $\bar{e}$'s in the Flame → shift the ionization equilibrium toward unionized form.

2) stable oxide:

Lets say you get atoms:

e.g befor excite & deexcite they React with another element to form Stable oxide in the Flame it is also Example of chemical interference.

this is underestimation. $M + O \rightarrow MO$

Remedies: i) increase T of Flame (↑ atom production) $M + 2(OH) \rightarrow M(OH)_2$

(ii) use less oxidant.

e.g 3) Effects of *anions:

anion & and others metels present, if phosphates or sulphates present. (no need) →

Anions like $SO_4^{2-}$ & $PO_4^{2-}$ can bind to metal ions like calcium to lower the Amount of calcium atoms that actually Atomize - intensity will decrease.

under estimation Results

Lete say Analyte is Ca

AS Ca Atomize at React with $SO_4$

at form stable $Ca_3(PO_4)_2$ species -

Remedy:

solve ⇒ we Add $La_3(NO_3)_2$ (Releasing Reagent)

La Reacts with phosphate Release Ca and we get good Results.

4) **metals:**

* ~~There is one~~ e.g Ca depresses The signals of Ba, Ga & in

of Analyte

called depressive effects-

Remedy: to Remove the depressive metal -

[redacted]

5) Formation of non-volatile / Less volatile compound

↓ Additives to Remove such Compounds e-g EDTA

~~less~~ +

Remedy:

solution:- Seperate these metals from your analyte Then there will be no depression.

# Applications:

before 1955

① A large & no. of element from their prericdictable conc were measured - but not in low conc. at that time ( before 1955 )

10ppm 0.01ppm
↓
not measured by Flame emission spectroscopy -

After 1955 → Atomic Absorbtion spectroscopy was measured then low conc - can be measured either 0.01ppm.

some → element were frequently used.

* Alkali or Alkaline earth metals - easily detected.

* diff- dxne of Fruit material -

Na in
→ soil sample - (long process)

→ drinking water sample -

→ Urine sample -

→ blood sample

→ pharmaceuticals -

→ plant materials -