Chapter:

Atomic Spectroscopy

Atomic Absorption Spectroscopy (AAS)

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Atomic Spectroscopy

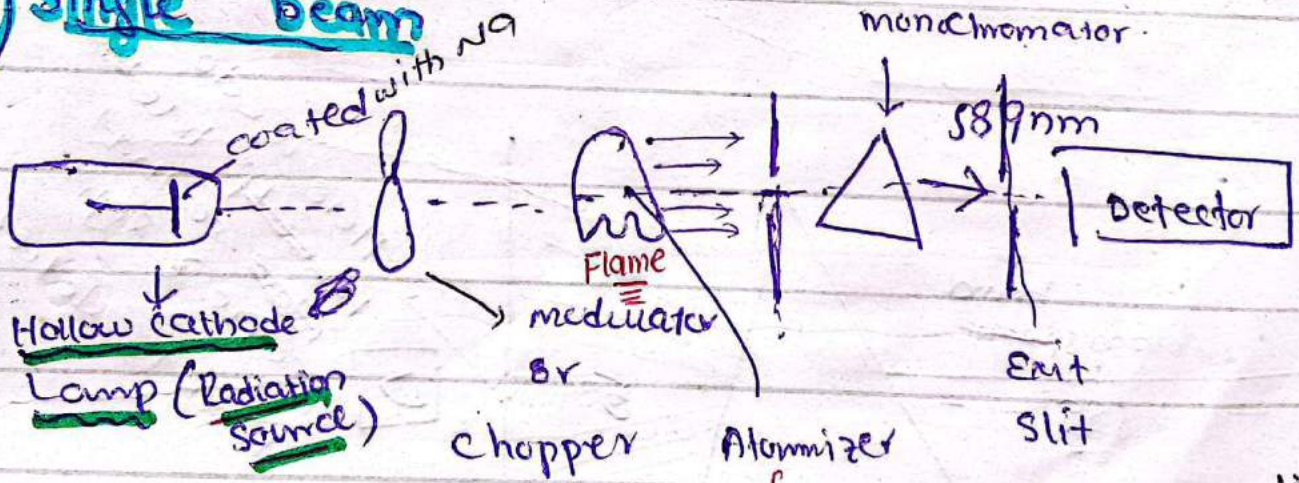
⇒ Atomic Absorption Spectroscopy :- (AAS)

Instrumentation

two types

1) Single beam A. Absorption S. photometer
2) Double beam A. Absorption S. photometer

A) Single beam



1) Hollow cathode Lamp (Radiation Source)

If you want to determine Na then cathode is coated with Na.

2) modulator

It Chopp the Radiation | modulate the Radiation from source | gives pulsing light.

but major Function for double beam spectrophotometer

metal converted into vapours → excite & deexcite and give specific Relevance wavelength that is equal $\frac{\Delta E}{c}$

3) Flame Atomizer:

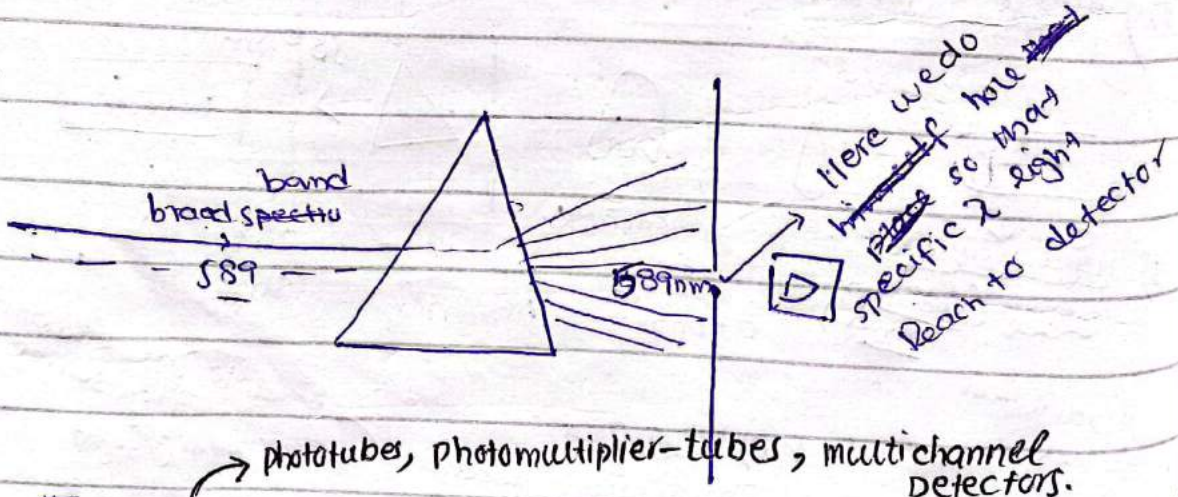
Radiation paves through Flam Atomizer → Free atoms absorb that wavelength - excite and deexcite -

4) Monochromator

Allow a specific wavelength to ~~path~~ Reach to detector

- If monochromator is not then All types of Radiation's wavelength then we can not calculate all cone of NA.

- Monochromator Allow Separates all light of Special wavelength.



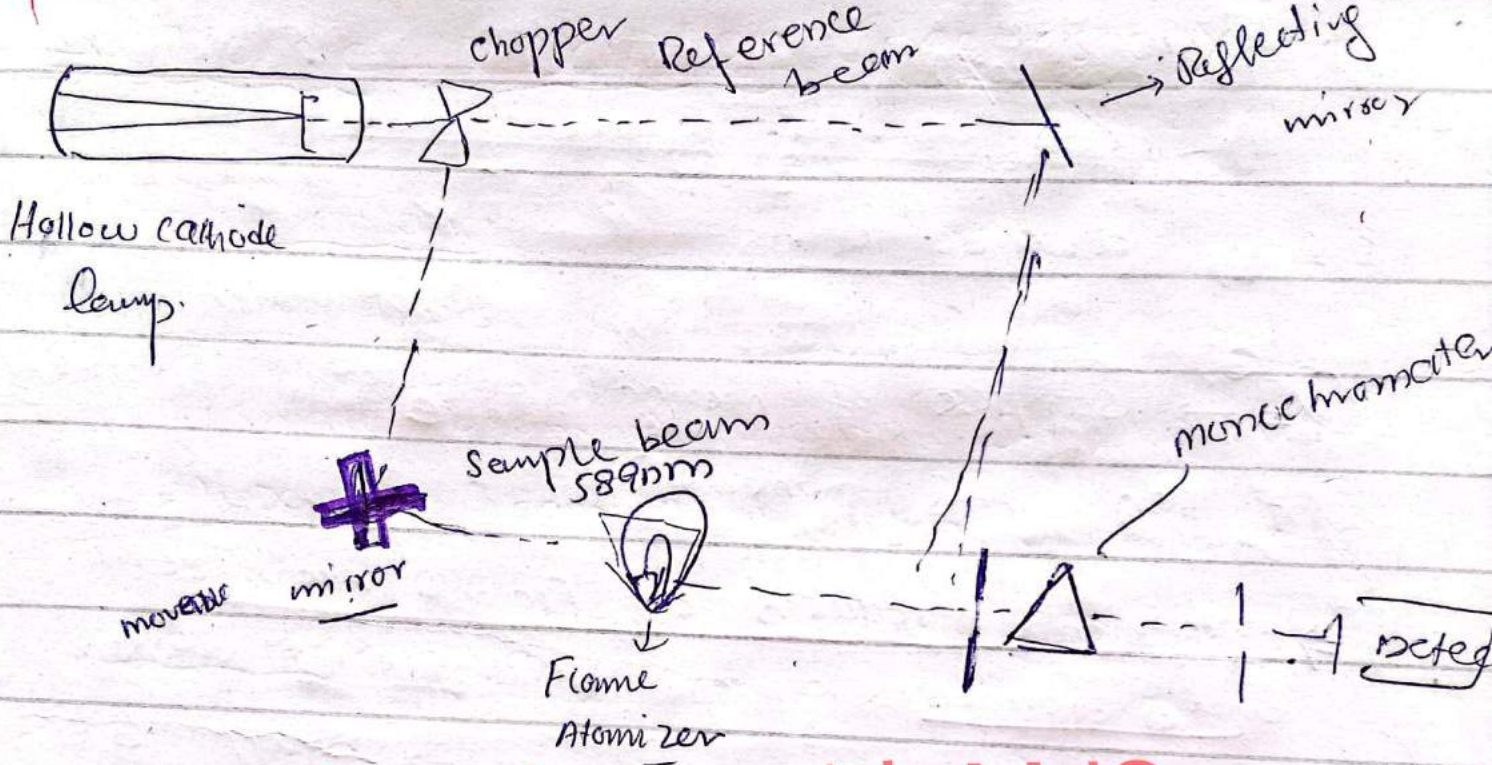
5. Detector → phototubes, photomultiplier-tubes, multichannel detectors. converted the light into electrical light-

(Spectroscopy)

B) Double beam spectrophotometer:-

$A = \log(\frac{1}{T})$

Instrumentation: double beam sp— photometer.



* If Na hallow cathode lamps. Then it is coated with Na. When we applied voltage- Na is vaporized - Atomic vap. absorb energy excite & when deexite emit Radiation of spacific wavelength -

Spacific wavelength of Na = 589nm.

* chopper | Rotating mirror - when it is present horizontaly beam of light goes to ⟶ before mirror. (when there is no free atoms in the path. Tranmittance will be 100% Abs. will be zero.

* when chopper is  in this position. beam Reflect towards below mirror when we heat in Atomizer here free atoms are present in this path Transmittance (less than 100%) less ⟶ Abs- more.

Detector gives ⇒ net value of absorbance.

Q= ⟶ Suppose of monochromator is not present then whats problem?

⇒ combustion products of flame Atomizer are formed. absorb heat excite when deexcite ⟶ emit Radiation ⟶ may be this Radiation very close to 589nm of Na - then % transmittance will increase / Absorbance decrease our Result will underestimation (one of analyte less in our Sample) -

* ~~of another element~~ monochromater does not allow an unwanted Radiations-

Hollow Cathode Lamp:

Instrumentation — Radiation source

↓

hollow cathode lamp.

- Radiation source in UV-visible spectroscopy:

↓ tungsten lamp

↓ give very good Range of wavelength

1) single element hollow cathode lamp

2) two elements // // //

3) Multi elements // // //

usualy these are expensive.

But for multi-elements Hollow Cathode lamp price is Reduced.

- but H-C. single lamp are stable and long life than multi H-C-L lamp.

WORKING Principle:

How it Gives Specific wavelength?

* cathode is coating with desired elements

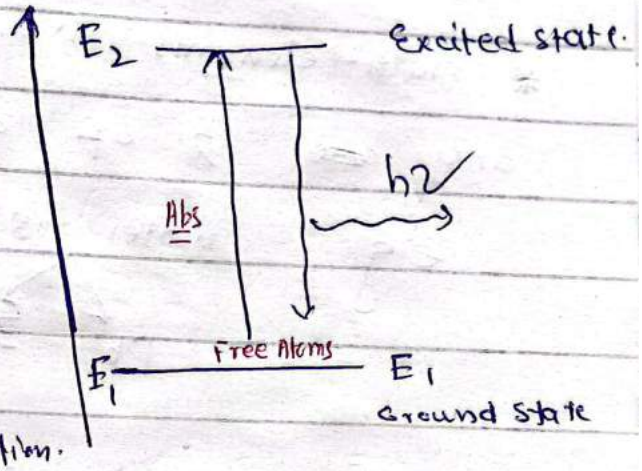
e.g Pb in our sample.

coat with Pb element. when we electrically heat. Pb → volatilize → free atom

→ Free atoms → go to excited state

Principle

excited state is unstable state come back atoms and E decicite. Energy Release. there is in the form of electromagnetic Radiation.



$$\Delta E = E_2 - E_1$$

$$\Delta E = h\nu$$

Pb = λ = 217 nm (specific λ)

Atomize Pb

- when we ~~heat~~ absorb hν light
- If element not absemb hν → specific Resonance wavelength

Al

Q = What whould happened if we use multi hallow cathode lamp ???

e.g Zn Pb Cd - - - -

when we Apply energy and cathode is coated with these Five elements. monocathode lamp will get multiwavelengths are emitted.

specific wavelengths

Those elements coated with close wavelength valu-

* multi-elements. We want to measure only ~~one~~ λ of one element.

e.g water Sample

Pb Zn

we want to measure only Zn

There will be no effect on Zn - Result due to Pb

b/c Zinc has specific wavelength and Pb has its own specific λ.

⇒ Drawbacks of multi-elements Cathode lamp:

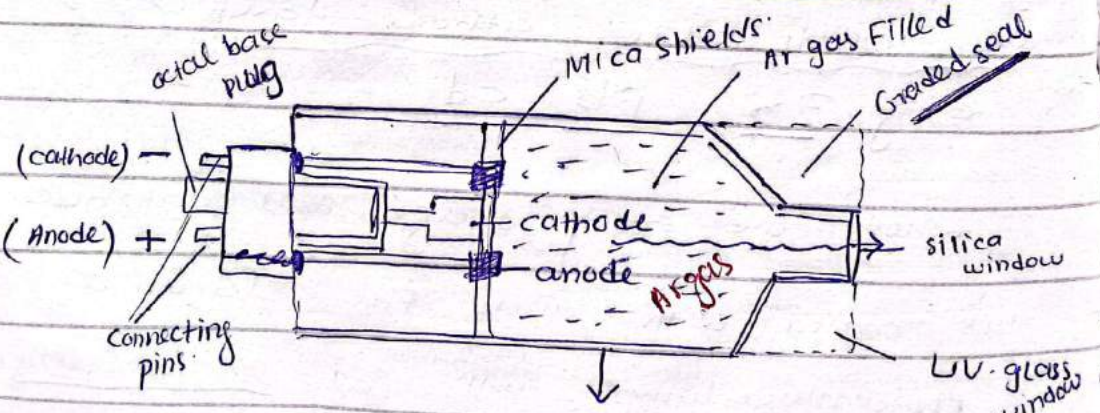
a) Sample is wasting.

b) Life is Reducing - short life

* At one time we measure only one element

Modified A.A. spectrophotometer available.

⇒ Construction of Hollow Cathode lamp:-



Q= why we use ~~the~~ silica window?

window

• Glass will not allow to pass UV. Radiations.

Silica window allows UV. Radiations.

- pressure of gas (Ar) = 0.5 to 1.3 kPa

1st glass tube is evacuated and then Filled gas and then seal it. (Ar or Ne)

- ⇒ diameter of cathode → 3–5mm
- Anode coated with (W) tungsten, Ni, Zr, tantalum
- cathode made up of metal of interest.

when we Apply voltage

1st of all inert Ar gas ionized.

↓

Gas Molecules strike to each other and also strike with the wall of cathode here ions produce – phenomena called sputtering

Due to sputtering some of the atoms of coated surface → excited → desired Give diff. of energy in the Form of Radiation → Give specific Resonance

MODES OF AAS:

1. Flame Atomization AAS
2. Graphite Furnace AAS → Electrothermal AAS

(i) tube wall Atomization ET AAS.
(ii) plate form Atomization ET AAS.
(iii) probe Atomization ET AAS.

3. Cold vapour AAS: (CV-AAS)
4. Hydride generation AAS - (HG-AAS)

~~2) Graphite Furnace AAS:~~

1) Flame Atomization AAS:

★ We convert sample into free atoms by using Fl and oxidents. Atoms formed are capable of absorbing the specific resonance wavelength.

i) Tube Wall GF-AAS: → Graphite rod made up of pure Graphite. Then a hollow Graphite tube with one hole was made up of graphite → electricity applied glow red hot (3000°c). They put electrothermal contact at both ends & applied voltage. current flows & tube becomes hot due to Flow.

We inject sample through the wall of the tube

At high voltage, it glows red hot and Temp is 3000°c & it is atomized.

Electricity heated the tube,

Q: If we apply low voltage what should be temp??

Ans: Temperature will be Low

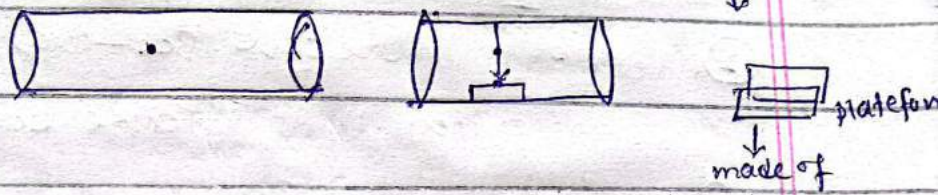
bcz T ∝ voltage

By controlling voltage we can control temperature of the Graphit tube.

GF AAS → tube wall Atomization - GF-AAS.
Disadvantage: loss of analyte occur so we use

⇒ (ii) plate form Atomization GF-AAS:

↓ Here we not inject sample through the wall of the tube. inject sample by plateform.



when you introduce sample through a micropipette.

Advantage

Basically Related to dissipation of heat away tube.

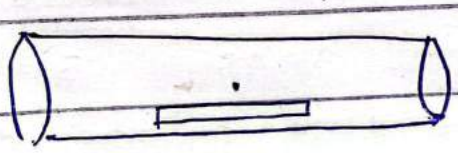
* when tube wall of GF-AAS were → and appy voltage. Then creat problem

Advantage

⇒ but in case of plate form. 1st tube is heated after this Plateform is heated. Temperature Same so analyte loss is minimized

(iii) Probe Atomization GF-AAS:

here scientis like ~~professor~~ Jan. used a ~~plate~~ probe → develop a probe made up of Graphite



~~they made~~

probe made of Graphite.

③ Cold Vapour AAS:

→ Hg is analysed by CV-AAS bic Hg is volatile in temp. when Temp ⇒ increase Then it will evaporate. so we have to use cold vapour AAS method

you can easily measure Hg of Mercury by using this technique

here we, dont use any Graphite furnace or any flame bic mercury is volatile

Hg → is a neurotoxic

Hg²⁺ is dangerous.

* Hg → is a neurotoxic

imp in order to measure Hg → CV-AAS.

Basically if you look any sample Hg present in the form of Hg^{2+}

* $SnCl_2$ solution used → Reducing agent.

and Hg is Reduced to metallic form

$$Hg^{2+} + Sn^{2+} \rightleftharpoons Hg^{0} + Sn^{4+}$$

↓

free Atoms

when we get Atomic mercury it absorb its specific wavelength Radiation.

you have a flask → introduce Sample

→ Here no → need of heating.

4) Hydride Generation - AAS:

Pb, Ge, Bi, Se, As, etc

They are capable of forming hydrides.

we also use hypophosphoric acid.

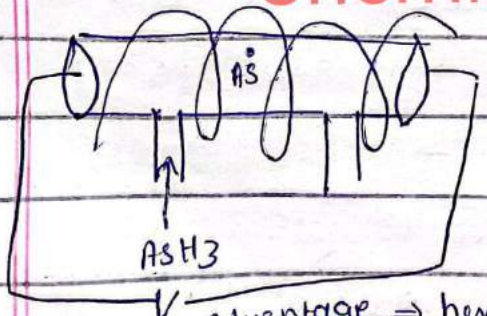
Sodium Borohydrate, hydrazine & $SnCl_2$

These are Reducing agents.

If we treat them with $NaBH_4$ Thermally Metal hydrides are form.

AsH_3 → Arsene gas is produce → entered in electrically heated we get As

these hydrides are thermally unstable. If we provide energy and we get As oxidation state zero which is capable of Absorbing specific Resonance wavelength.



Adventage ⇒ here no loss of analyte.

simply take Flask and take As. Add Reagent thermally heat and this As in ~~Atomic~~ Zero oxidation state. get.

Applications of AAS:

we need to discuss each and every application.

(1) Q = characteristics Features of AAS merits & demerits??

↳ high sensitivity-

→ low detection limit.

beauty of this method: → Element specific- e.g Zn, Na, Any other specie will not absorb-

→ cost is moderate-

→ 80 element ca be measured by this technique including lanthanides & Actenoids-

→ easy to handly use-

→ High Sample through put

→ Applicable to wide variety of Samples-

- its sensitivity is very high-
- cost is not very high not. Low but moderate. 25- lack to 70 lak price.
- easy to handle.
- High sample through put.

many Samples e.g one thousand Sample per day can be analyzes.

one sample take around 5- minutes.

AAS

- ★ Alkali metals.
- ★ Alkaline – earth metals. } Flame

- ★ Transition metals.
- ★ Actinides
- ★ Lanthanides
- ★ non-metals.

⇒ Advantage

⇒ Hg, As, Cd, Pb, ... can be Analyzed

Different industries → people analyze these elements frequently.

- in Nuclear Chemistry → U → can be ana
- Food industry e.g Zn can be analyzed
- Clinical Na, K, Ca etc can be analy
- cold vapour determination of Hg in Fish Sample.

★ water analysis:

- Rain water
- drinking water
- sea water
- waste water
- lake water
- river water.

Composition of All these water is diff

Food Sample:-

Food industry → variety of Food is available e.g rice, meat, sugar cane etc. seeds, barley.

sometimes new products are formed.

we can Analyze busicut, milk, meat, egg, honey etc.

of childs & adults are dificient in Zinc →

* If you eat 1g of pure Fe metal → death occur.

* Reasearch → in multan → about children 1–10 age → they were deficient of Fe & Zn.

Reason

some children belong to Rich, poor & middle.

poor & middle class has ~~an~~ higher Zn as compared to rich class.

Reason poor people eat everything → which contains ~~an~~ Zinc → Fe

but Rich class → not every thing they eat Fast Food → trace element depicient.

⇒ Fertilizers ⇒ cements

⇒ clinical ⇒ glass

⇒ Biological material

* Fertilizzers :-

⇒ variety of Fertilizers contain Ca, P, Fe, Na necessary for the Fertility of soil- we can analyse.

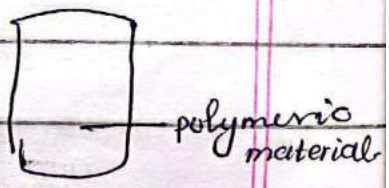
* cement & glass also analyz :-

current glasses are due to some metals e.g Mg etc.

↓ to determine any metal.

Only one Acid HF → Hydrofluoric acid dissolve the glassy material but taking cares of using HF. It is highly corrosive. not touch the body part with HF otherwise it holes

purpose of HF → solubilize the All materia.



* clinical samples :-

→ blood Sample → serum
→ plasma

→ urine Sample ↔ complex one → large no. of other species but it can be analy by AAS FE

→ CSF (cerebrospinal Fluid) → From spinal cord.

Suppose → whole blood → containg Fe → more quantity

you have to analyze with Flame Spectro

→ of CSF → many analytes-

* Biological Samples → plants, meat,

Fish, where can be analyzed by AAS for metal determinatio

Good Luck