



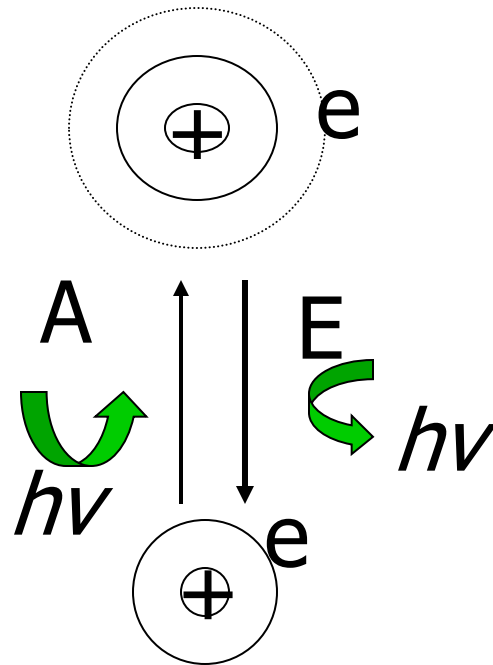
ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Instrumental Chemical Analysis I


Theory

- AAS : the commonest method for analysing of metals and metalloids
 - Metals : Na, K, Ca, Mg, Fe, Pb, etc
 - Metalloids : Al, Sb, As, Se, dan Te
- Is a quantitative analysis method based on absorption of UV radiation by atoms
- Absorption occurs when the energy of the photons matches the energy difference between two states of the material
- The effect of absorption :
 - Transition of electron from ground state to excited state

Transition



The main processes in AAS

- 
- Atomization
 - Energy absorption
 - Detection of the absorbed energy

Atomization process : 2 ways

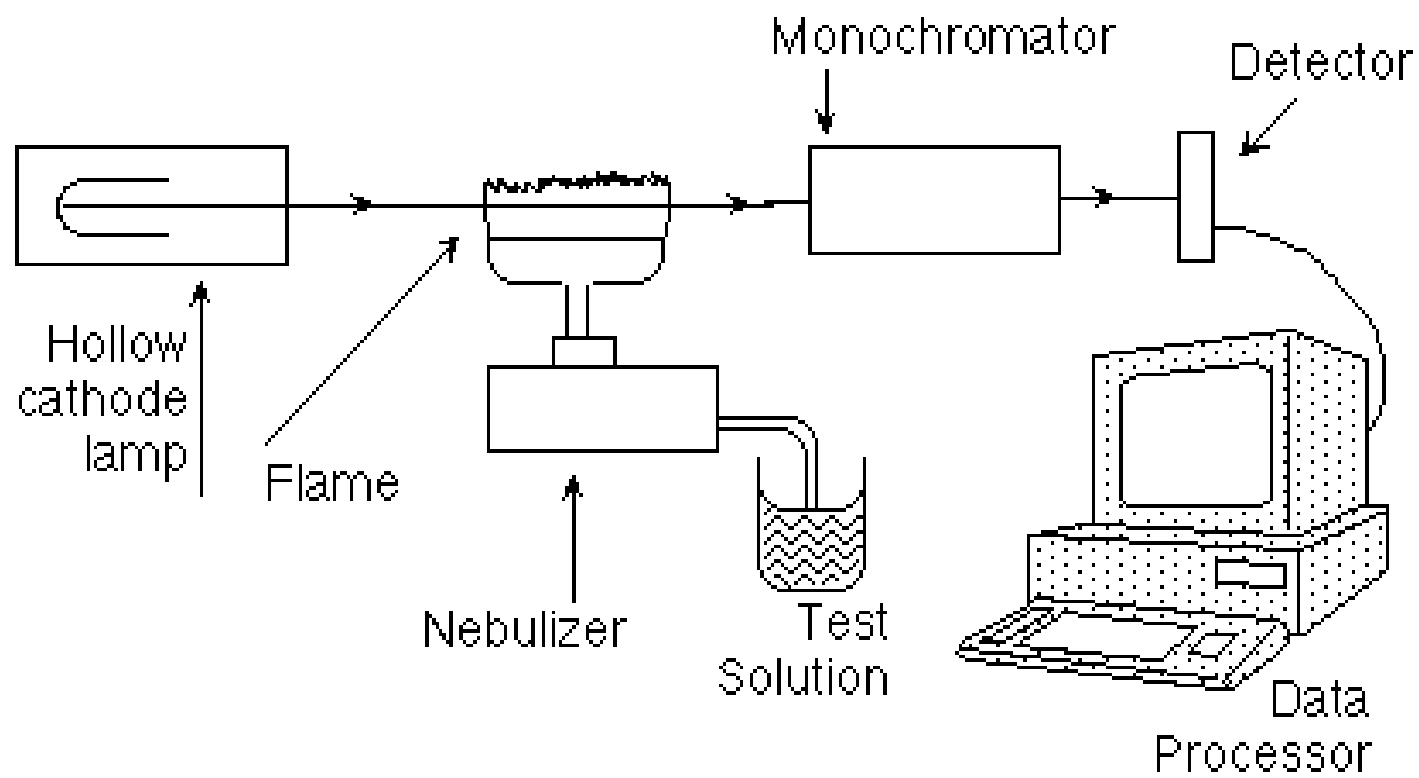
- Flame :
- Flameless :
 - Hydride
 - Cold Vapor-generation
 - Graphite furnace (electrothermal analysis /ETA)

Instrumentation of Flame-AAS


- The main parts of the AAS system are :
 - Light source : a hollow cathode lamp
 - Atomizer unit : nebulizer, flame
 - Optical system : detector, recorder

Instrumentation of AAS





3. Main components

- 
- 1. Light source
 - 2. Sample cell : atomisasi
 - 3. Specific light measurement

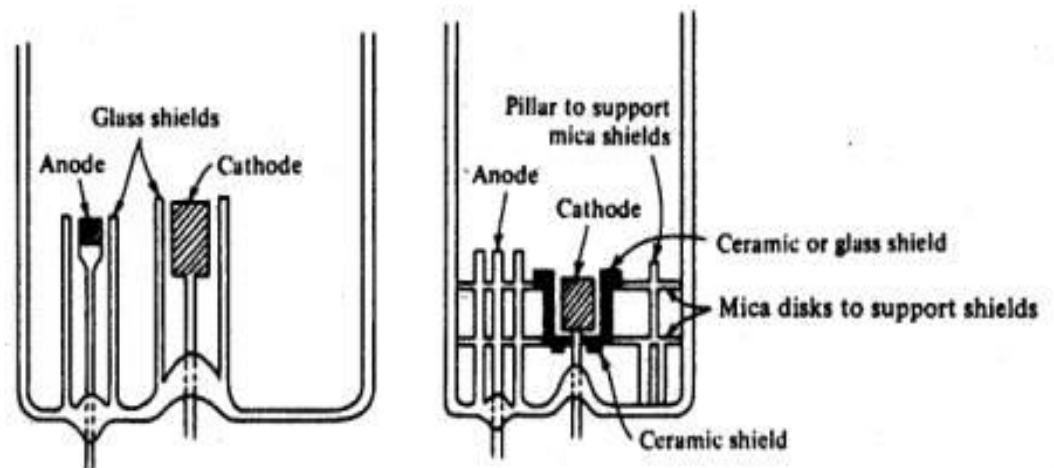
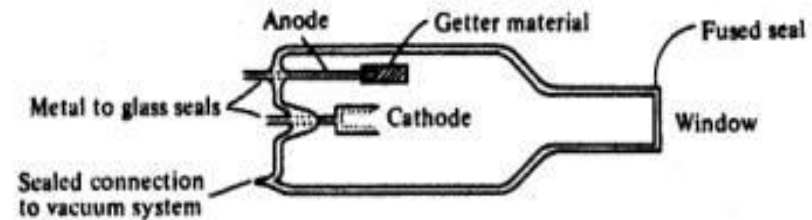
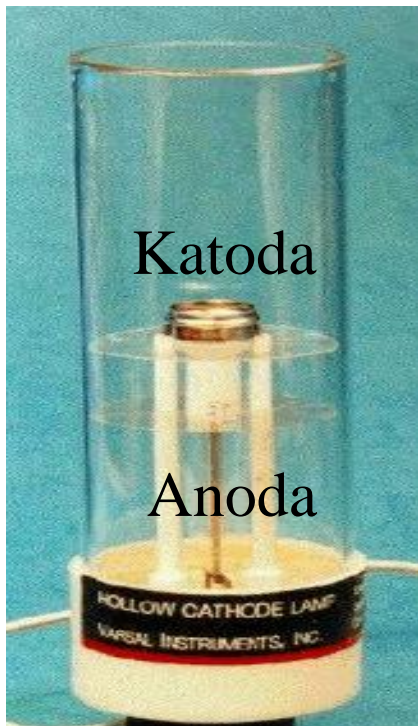
The function of the component

■ 1. Light source –

- It is designed to emit the atomic spectrum of a particular element.
- Specific lamps are selected according to the element to be determined.
- The hollow cathode lamp (HCL) or electrodeless lamps (EDL) are widely used.

Light source : hollow cathode lamp

■ anoda



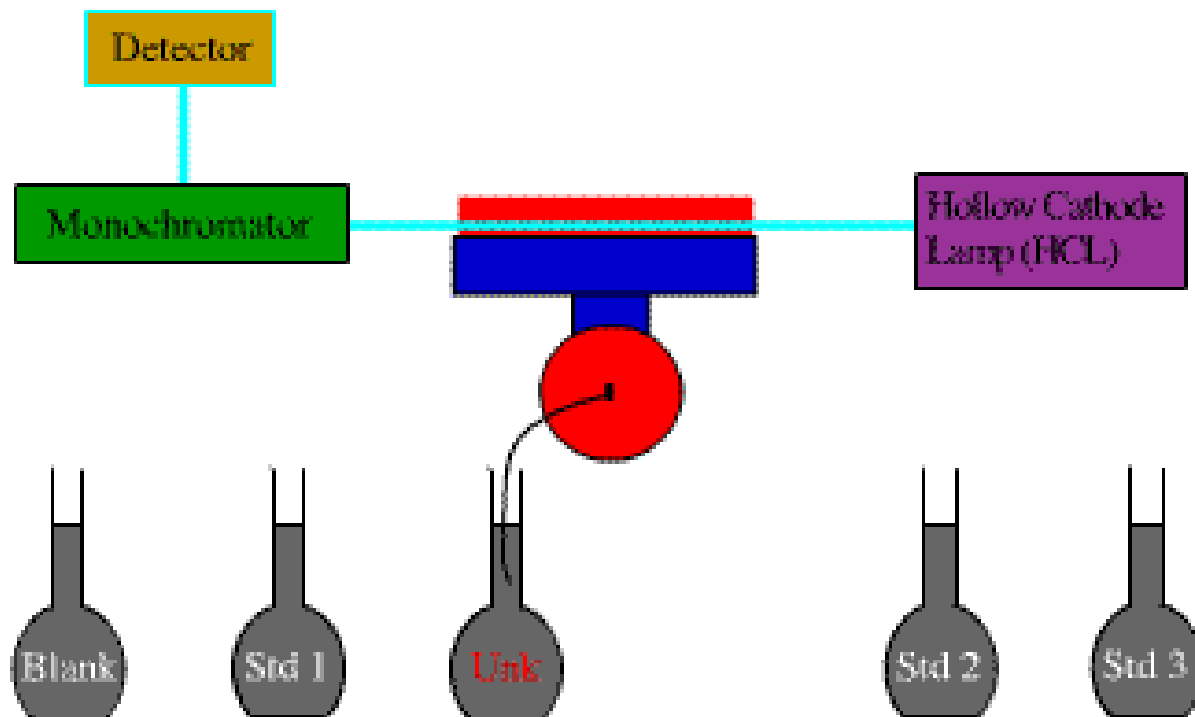
Optimization of the current in HCL



■ Current

- Too Low : Less sensitive
- Too high : self absorption

Atomization Process



Sample cell- Nebulizer

■ 2. Sample cell –

- Where an **atomic sample vapor** is generated in the light beam from the source.
- Nebulizer :
 - Suck up liquid sample at a controlled rate
 - Create a fine aerosol for introduction into the flame
 - Mix the aerosol and fuel and oxidant thoroughly for introduction into the flame

Flame



- Create atoms (the elemental form) of the element of interest
 Fe^0 , Cu^0 , Zn^0 , etc.

Temperature of the flame

- Depends on the combination of oxidant and fuel :
- Fuesl : acetilene, nature gas, hydrogen
- Oxidants : air, N_2O
- Destroy any analyte ions and breakdown complexes

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

3. Specific light measurement - Includes several components:

- a) a **monochromator** to disperse several wavelength of lights that are emitted from the light source to isolate a particular line of interest,
- b) a **detector** to produce an electrical current that is dependent on the light intensity. This electrical current is **amplified** and processed by the instrument electronics to produce a signal, which is a measure of the light attenuation occurring in the sample cell and,
- c) this signal is further processed to generate an instrument **readout** in concentration units.

Quantitative Analysis

- Beer' law :

- When a light with intensity I_0 is passed through a solution with concentration C , the intensity decreases into I_t that is proportional with C
- Giving $I_0/I_t = k \cdot C$

- Lambert-Beer's law

- When a light with intensity I_0 is passed through a solution having b thickness the intensity decreases into I_t that is proportional with b
- Giving $I_0/I_t = k \cdot b$

Lambert –Beer's Law

- $I_0/I_t = e^{k b C}$
- $\ln I_0/I_t = k.b.C$
- $\log I_0/I_t = k/2,303 .b C = abC$
- $I_t/I_0 \times 100 \% = T \%$
- $\log I_0/I_t = \log I/T = A$
- Therefore
- **$A = abC = \epsilon b. C$**

Validity of Beer's Law

$$A = a b C$$

- For absorption spectroscopy

- For low concentration

High concentration : interaction among the atoms is stronger than that of between the atoms and the light →

- Minimal mistakes :

Absorbance = 0,44 or 0.2-0.8

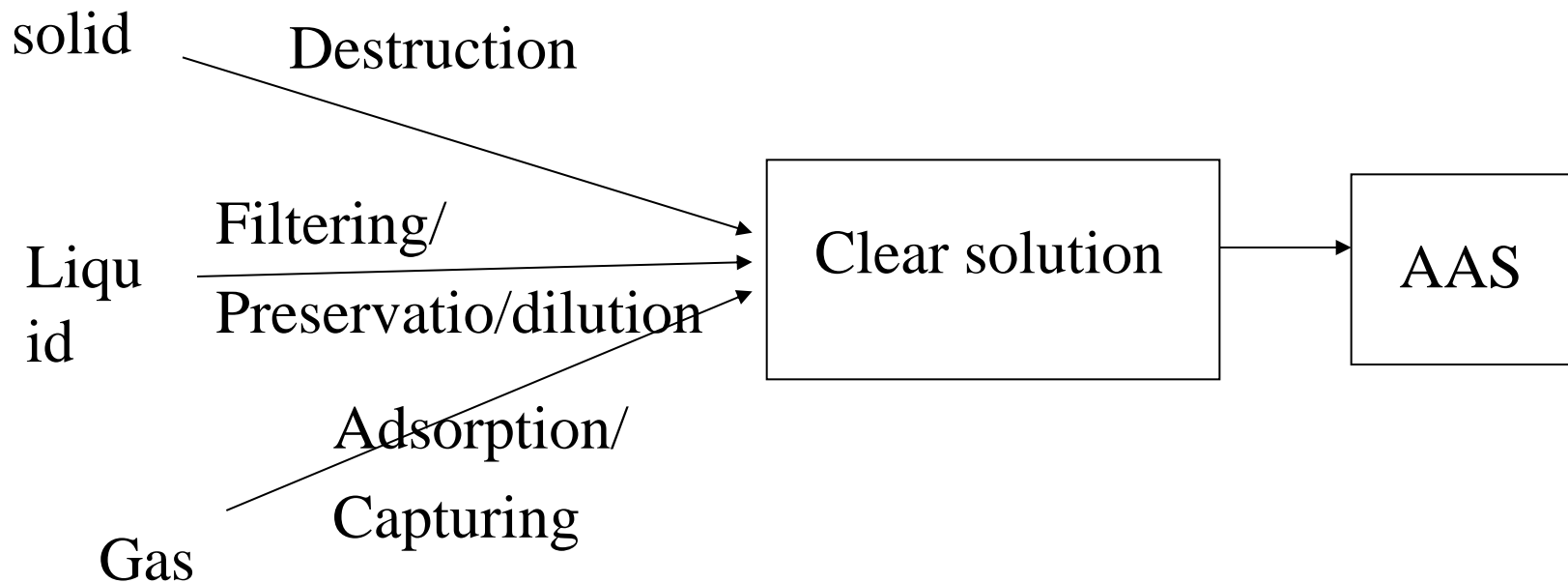
- For very low concentration → low A → It nearly same as I_0 → big mistake

The use of Lambert-Beer's Law

- **By comparing Absorbance of sample solution towards Absorbance of standard solution**
 - **Single Standard**
 - **Standard curve calibration**
 - **Standard addition**

Sample preparation

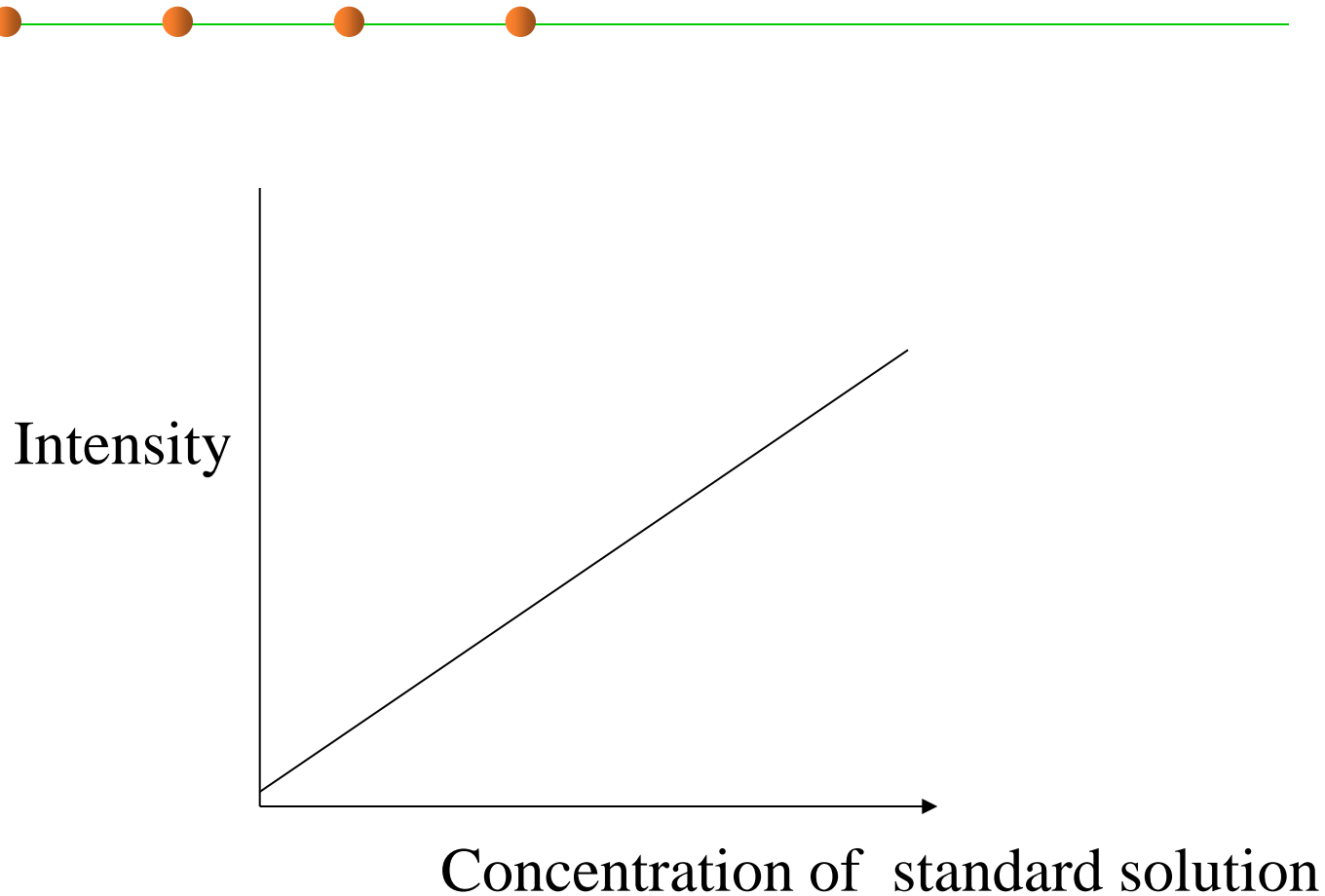
■ Clear solution from samples



Problem examples

1. Standard solution Pt 5 mg/L \rightarrow $T = 65\%$. Waste water sample 10 ml is diluted into 50 ml \rightarrow $T = 45\%$
What is Pt concentration in the liquid waste(mg/L)
2. A soil containing gold with 2 gram of weight was dissolved into 100 ml by using strong acid, and gives Absorbance = 0.54. The standard solution 10 mg/L shows $A = 0.24$. Determine the concent of Au in the soil

Standard Curve



Examples

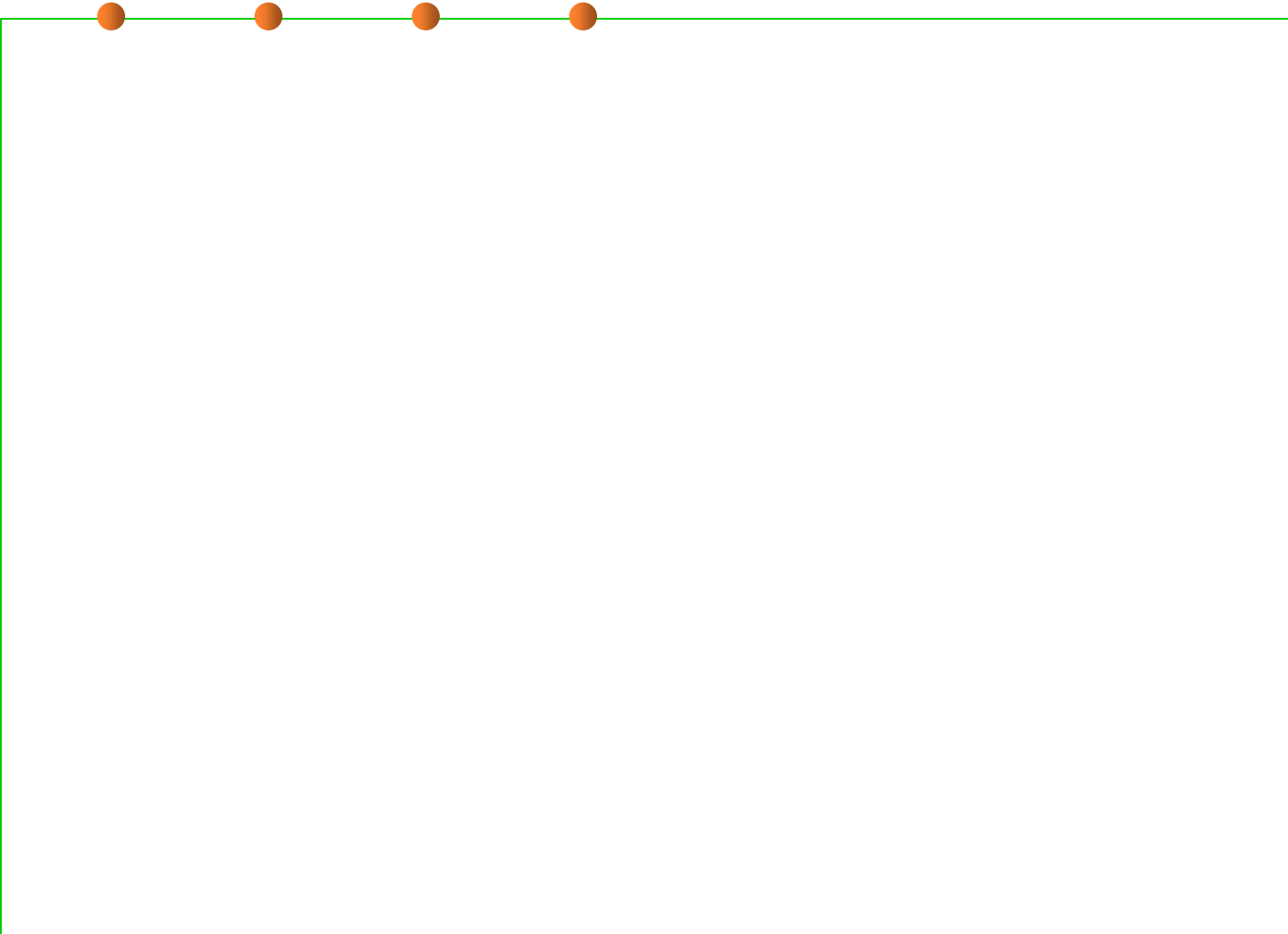
■ Standard sol of Ag	A
■ 2	0.12
■ 4	0.21
■ 6	0.33
■ 8	0.42
■ 10	0.51

When 1g is dissolved into 100ml, and taken out 5ml to be diluted into 50ml, gives $A = 0.35$. What is the percentage of Ag in the sample ?

Standard addition

- For solving matrix interferences → to make the standard and sample solutions are in same condition
- Method :by mixing the standard and sample solutions

Volume sampel (mL)	Volume larutan standar Cu 10 ppm (mL)	Absorbance
10	0	0.201
10	10	0.291
10	20	0.378
10	30	0.467
10	40	0.554



Sensitivity and limit detection

- **Sensitivity** : analyte with a concentration that can absorb a light giving Absorbance = 0.0044
- **Detection limit** : the lowest concentration that gives a signal as high twice as a baseline

Interferences :Spectrum and chemical

- **Spectrum Interference:**

- Analyte spectra is overlap with that of the interference due to the close absorption wavelengths ($\Delta\lambda < 0.1 \text{ A}$)
 - λ for V = 3082.11 A for Al = 3082,15 A and **3092,7 A** (the latter is used)
- A firing giving a wide spectra → disperse radiation → decreasing intensity → should be corrected by using blank



Chemical interference

- **Due to a chemical reaction :**
 - Formation of compounds having low volatility
 - Ionization in the flame
 - Association and dissociation
- **Matrixes**
 - The viscosity of the standard solution is not same as that of the analyte

Solving the chemical interference

- **Matrix :** By using standard addition
- **Chemical reaction :**
 - **Formation of non-volatile compounds**
 - Using high flame temperature
 - Adding a Masking agent
 - Applying a Releasing agent
 - **Ionization**
 - Addition of an other ion having lower ionization energy (K of Na)

Flameless Atomization

■ **Grafit furnace or electro thermal atomizer (ETA) :**

- Penghantar panas listrik : batang grafit C atau Ta, yang dialiri gas inert untuk mengusir udara yang menyebabkan oksidasi/ pembakaran
- Sampel dalam μl diuapkan di atas permukaan furnace
- Pemanasan furnace dimulai 100°C dengan cara mengalirkan arus listrik : penguapan pelarut atau pengeringan sampel padat
- Suhu dinaikkan sampai $700\text{-}1000^{\circ}\text{C}$ sehingga sampel terbentuk abu. kemudian suhu dinaikkan menjadi $2000\text{-}3000$ dengan menaikkan arus sampai 100mA → terjadi atomisasi. Sisa pembakaran dihembus dengan gas Ar

ETA

- all of the sample used is atomized in furnace (electrothermal) atomizer.
- detection limit is ≈ 100 - $1000\times$ lower than with aspiration techniques.
- only a few mL of solution is used.
- **Basic Principle:**
 - sample container resistively heated to vaporize the metal atoms.
 - sample dried (evaporate solvent) at $\approx 110^\circ\text{C}$;
 - ash sample called "burn off" (200 - 300°C);
 - atomization. (2000 - 3000°C)
 - comparison with flame atomization:
- interaction with sample matrix and electrode
- poorer reproducibility
- detection limits of 10^{-10} - 10^{-12}g (or 1ppb) are possible.

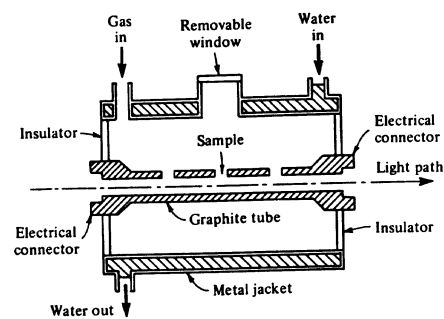


FIGURE 5-11 Cross section of a heated graphite atomizer. (Courtesy of Perkin-Elmer Corp.)

Advantages of ETA

- Advantages :

- Small volume is needed
- Solid sample can be directly analyzed
- High sensitivity

- **Kelemahan :**

- Carbide compounds are possibly formed between reactive elements in the samples with the carbon of the furnace → can not be analyzed well

Hidryde compound formation

- For elements having both very low and high atomization temperature : As, Bi, Sb, Se, Te, Ge, and Pb
- The elements are converted into volatile hydride compounds :
 - Reduction of the element by NaBH₄ in the acid or base media → AsH₃, BiH₃
 - The metal hydride vapor is brought by inert gas into atomization unit → AsH₃ atomization → As⁰
 - As⁰ + $h\nu$ → absorption

Cold Vapor generation (CV-AAS): only for Hg

- Reduction of Hg(II) by using SnCl_2 :
 - $\text{Hg}^{2+} + \text{Sn}^{2+} \rightarrow \text{Hg}^0 \text{ atom (vapor)} + \text{Sn}^{4+}$
 - $\text{Hg}^0 + h\nu \rightarrow \text{absorption}$
- High sensitivity ($< 1\text{ppb-ppt}$)
- Hg vapor is dangerous