ATOMIC SPECTROSCOPY

CEB 4032: ANALYTICAL CHEMISTRY
CFB3032: ANALYTICAL INSTRUMENTATION

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Chemical Engineering

Inspiring Potential·Generating Futures

Recap: Topics under Spectroscopy

Atomic Spectroscopy

- Atomic Absorption
- Atomic Emission
- Atomic Fluorescence
- Use of X-rays

Molecular Spectroscopy

- Fourier Transform Infra-red (FT-IR)
- Organic UV-Vis Absorption
- Effect of Solvent
- Inorganic UV-Vis Absorption
- Qualitative Analysis
- Quantitative Analysis
- Spectrophotometric Titrations
- Molecular Fluorescence
- Equipment for Molecular Spectroscopy

At the end of the topic:

1) Instrumentation of atomic spectroscopy.

2) Principle operation, differences, advantages and disadvantages between AAS, AES and AFS.

3) Quantitative analysis of an element in an unknown sample.

Introduction

- In atomic spectroscopy, samples vaporized at 2000-6000 K and the atomic concentration are determined by measuring adsorption, emission or fluorescence at characteristic wavelength.

- High sensitivity → ability to distinguish one element from another in a complex sample.

- Ability to perform simultaneous multi-element analyses.

- Measuring analyte concentration at the parts-per-million level, parts per trillion.

- Precision → 1-2%, expensive, widely available.

Types of atomic spectroscopy:
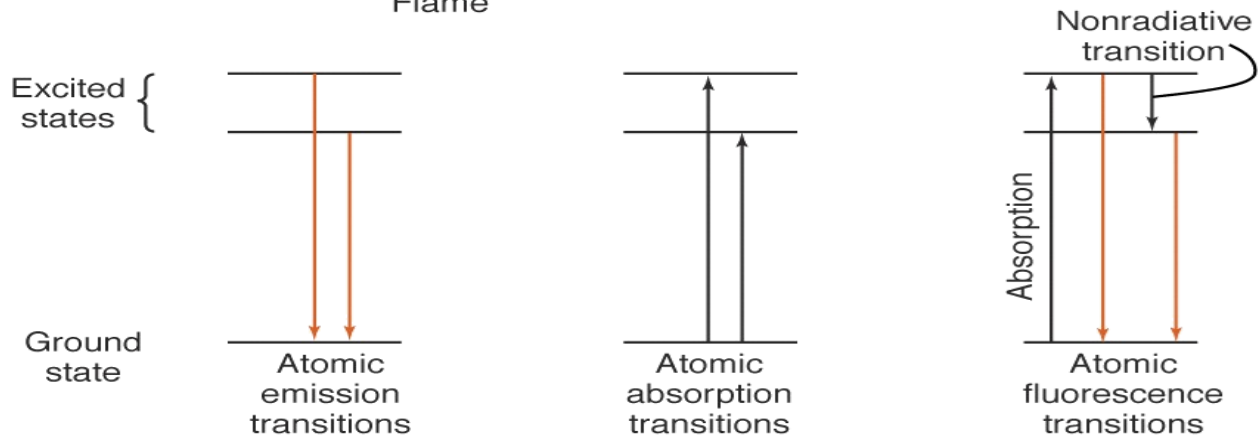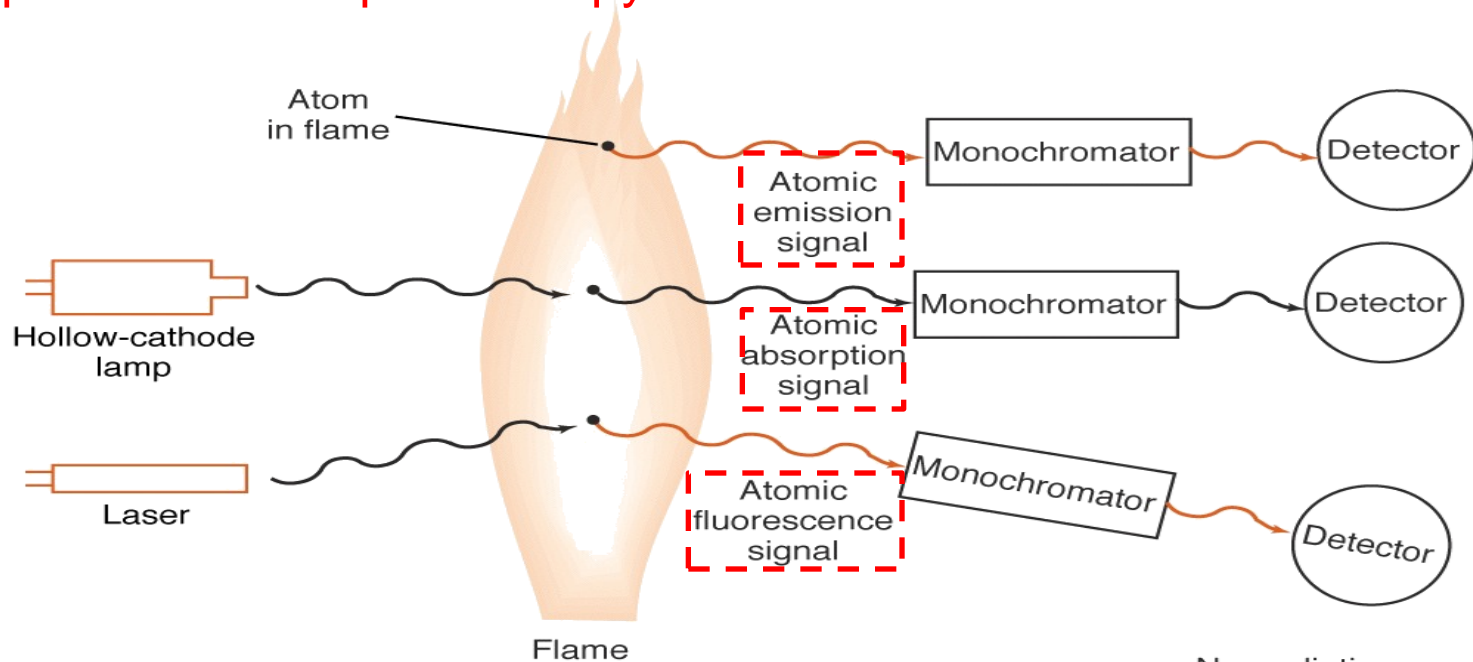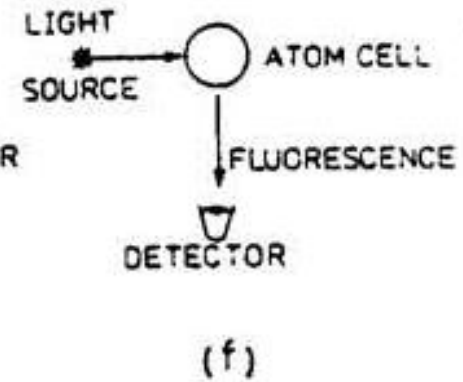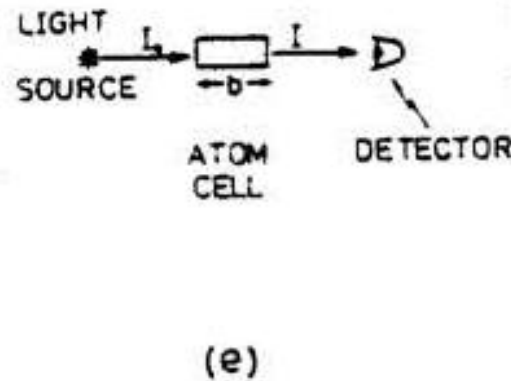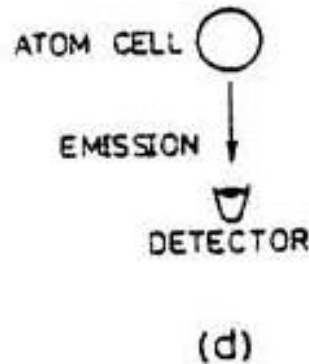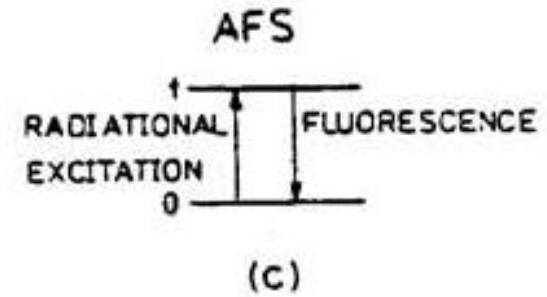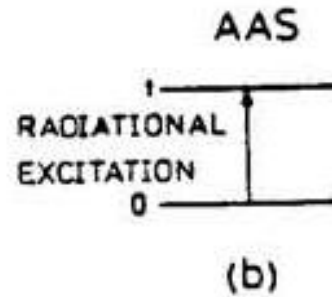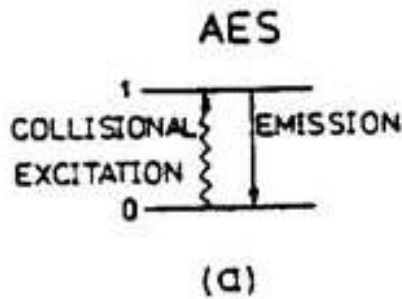
(a), (b) and (c) represent the simplest possible atomic transitions that are used for each technique.
(d), (e), (f) represent the basic experiment arrangement that allows the transition to be observed

Atom cell: device that provides a sufficiently high temperature to break down the sample into its constituent atom → flame

Outline

- **Atomic Absorption**
- Atomic Emission
- Atomic Fluorescence
- Use of X-rays

Atomic Absorption Spectroscopy (AAS)

- Quantitative determination of chemical elements employing the absorption of radiation (light) by free atoms in the gaseous state.

- Used for determining the concentration of a particular element (the analyte) in a sample.

AAS - Principle Operation

- Solution is aspirated into a flame and the sample element is converted to atomic vapor.

- Flame, contains atoms of that elements, some are thermally excited by the flame, but most remain in the ground state.

- Ground-state atom → absorb radiation of a particular wavelength .

Principle Operation of AAS
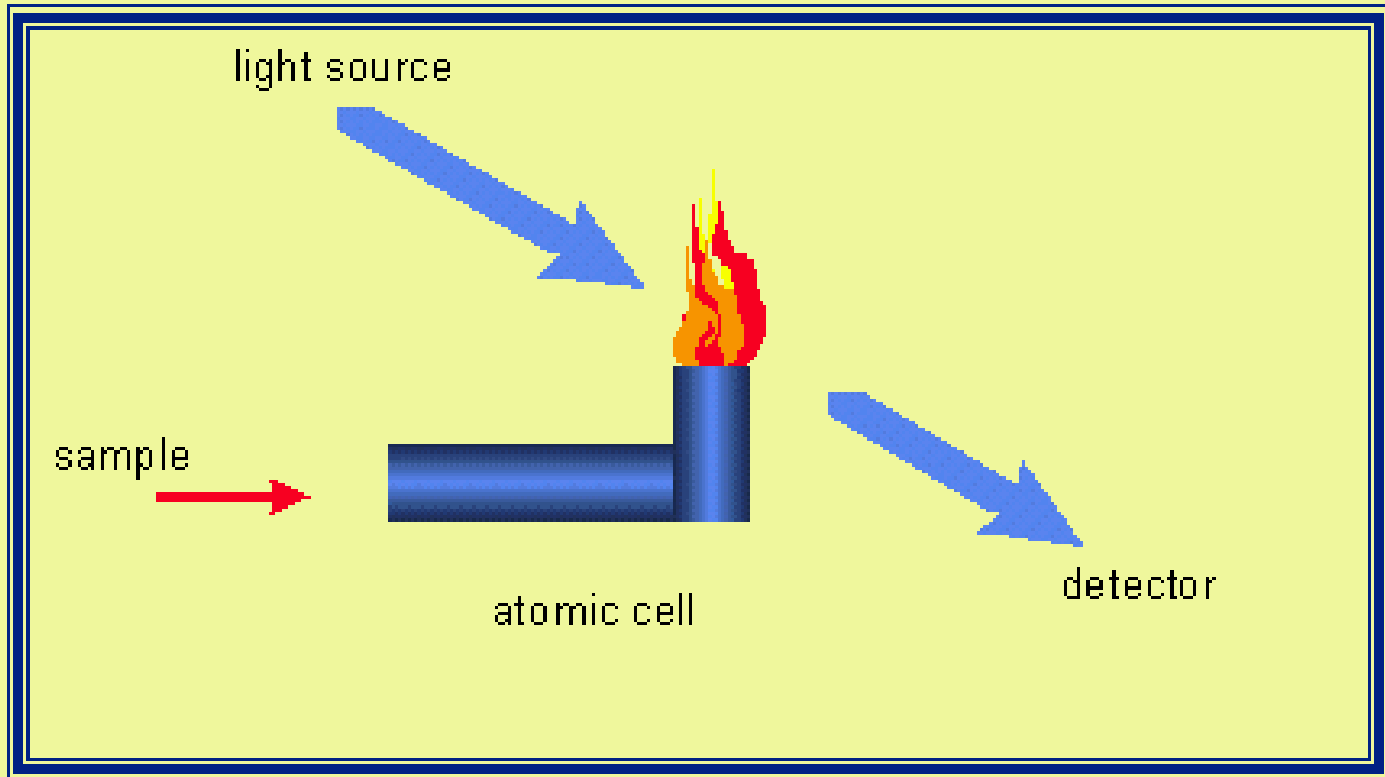
- The absorption follows <u>Beer's law</u>:

$$A = k. C$$

- <u>A is absorbance</u>, <u>C is concentration of atomic vapor</u> in the flame and *k is a specific coefficient* to each element at the given wavelength. The molar coefficient (ε) of absorption is not calculated in this case.

- Concentration of atomic vapor is directly proportional to the concentration of the analyte in the solution.

- Calibration curve of absorbance versus concentration in the standard solution $\rightarrow$ determination of concentration of the unknown solution.
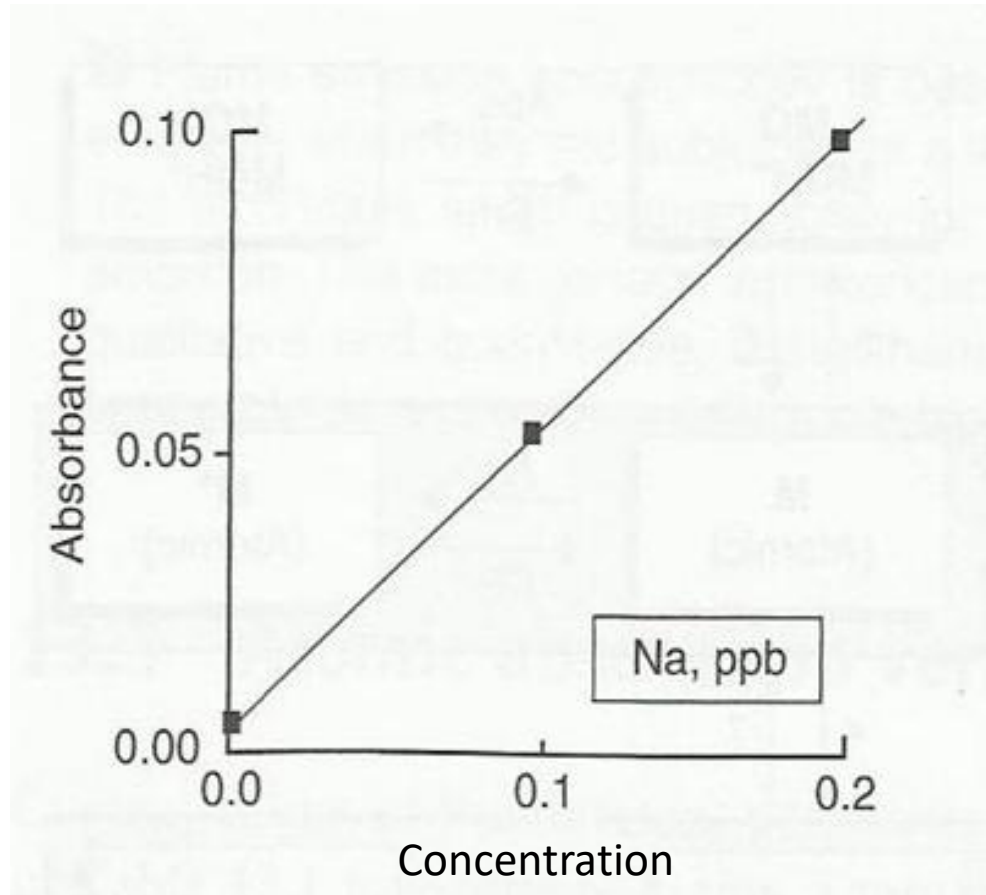
Example of calibration graph in AAS

AAS-Instrumentation
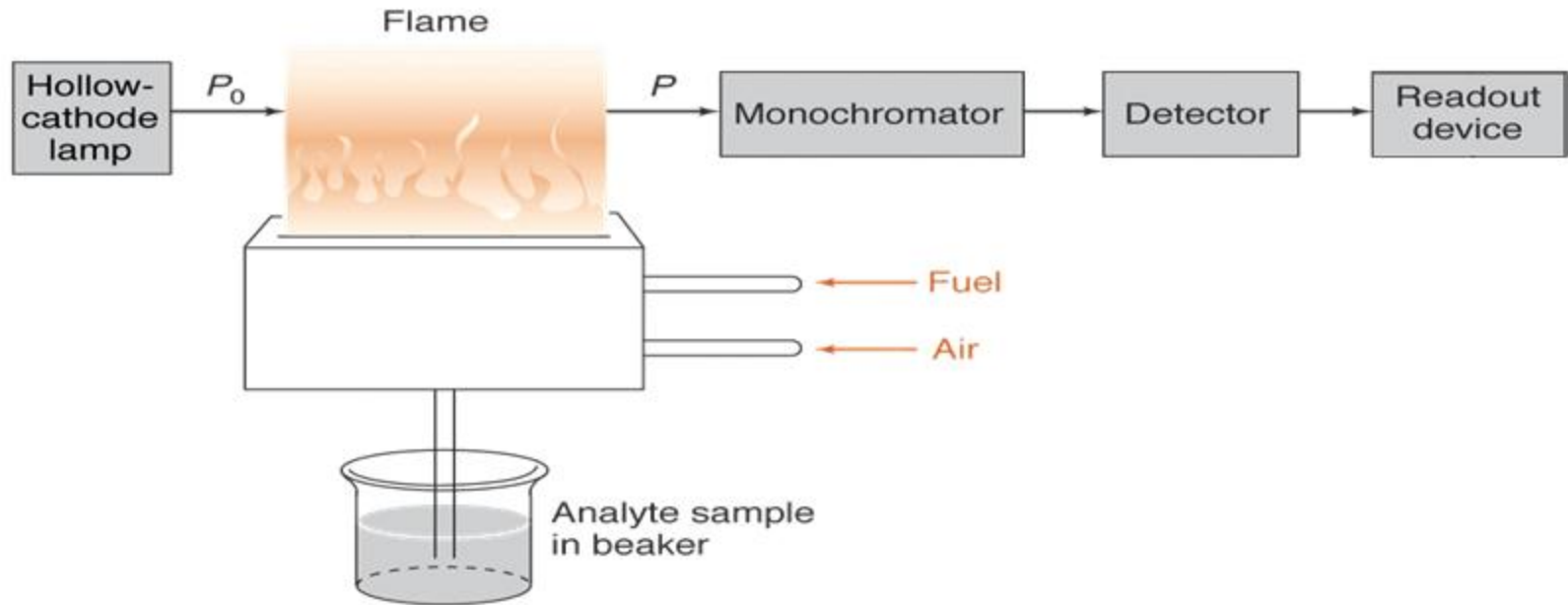
- It contains five principal components:
  (1) light source
  (2) burner/thermal device (element is brought to its atomic state)
  (3) monochromator
  (4) detector
  (5) Readout device

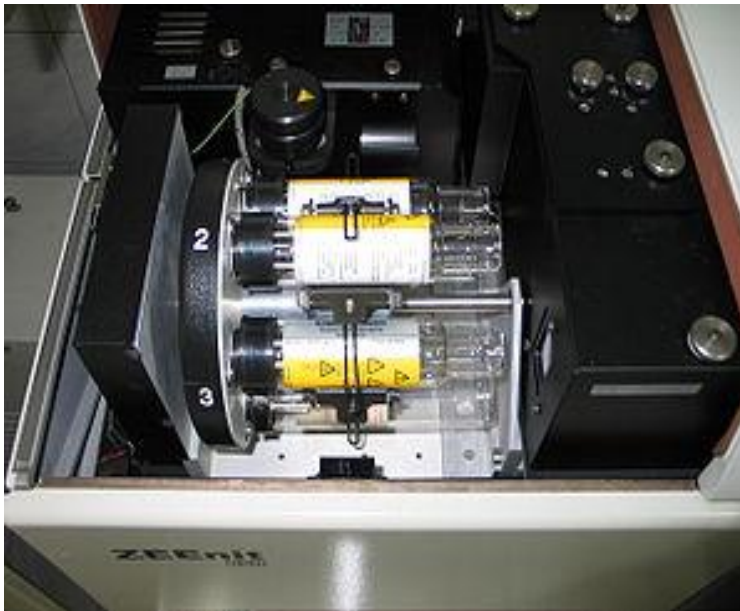# (1) Light source: Hollow-cathode Lamp (HCL)

Insulating disk

Quartz or glass window

(−)

(+)

Hollow cathode

Anode
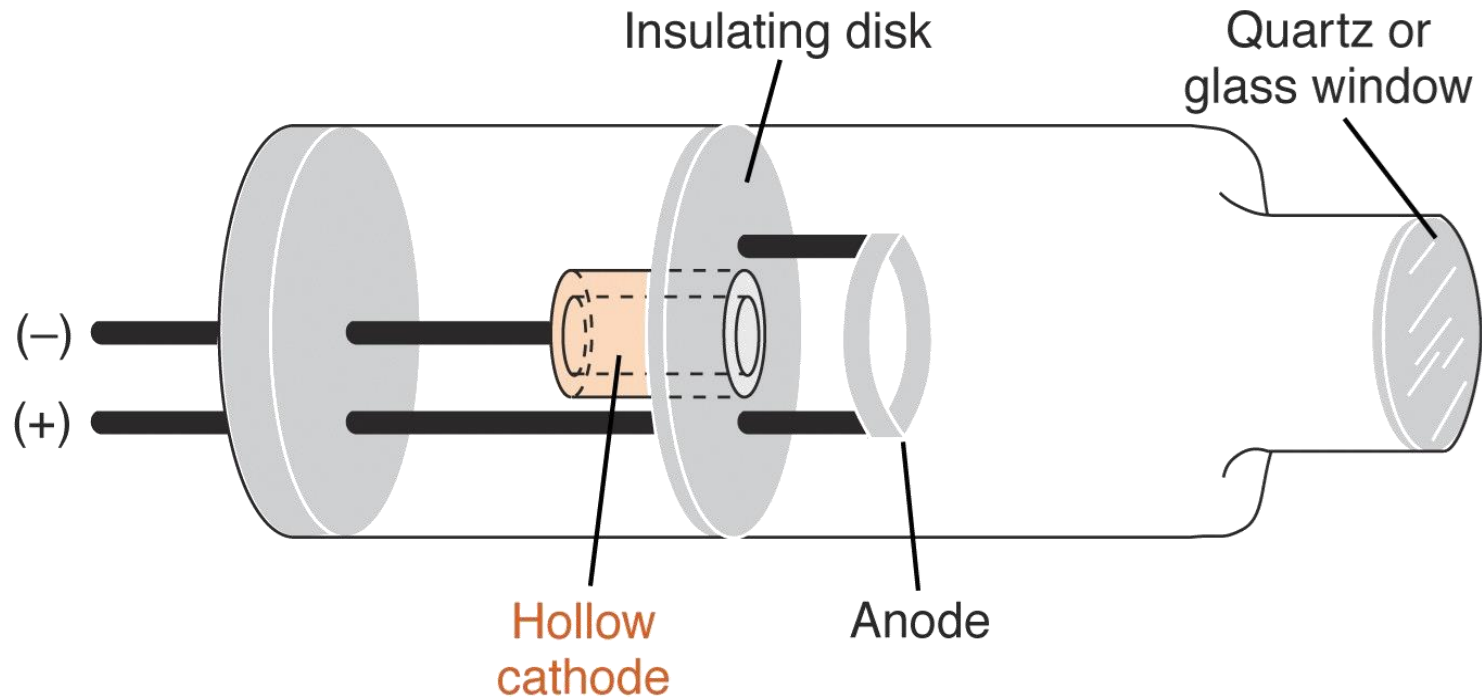
Hollow-cathode lamps from an
atomic absorption spectrometer

(1) Light source: Hollow-cathode Lamp (HCL)

- Filler gas is ionized → positive ions are accelerated toward the cathode → sputter metal atoms from the cathode into gas phase.

- The free atom are excited by collisions with high-energy electrons and then emit photons to return to the ground state.

- The emitted energy can passed through the flame and can become absorbed by the test element because they posses the right energy.

- Hollow cylinder cathode coated with element same as analyte.

- Drawback: different lamp is required for each element.

Principle of Ionization in HCL
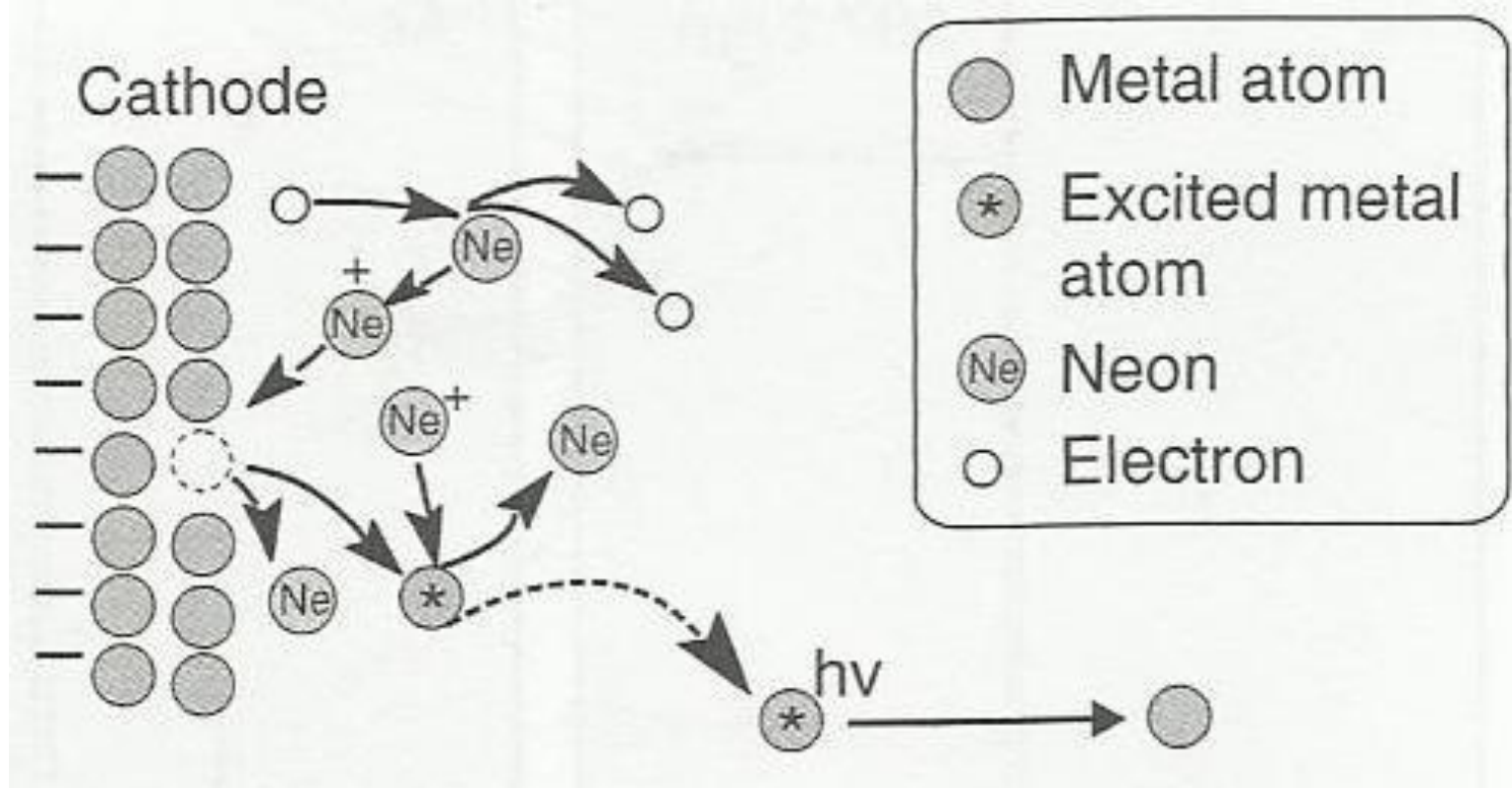
(2) Atomization: Burner / Thermal Device

(i) Burner(Flame)

(a)
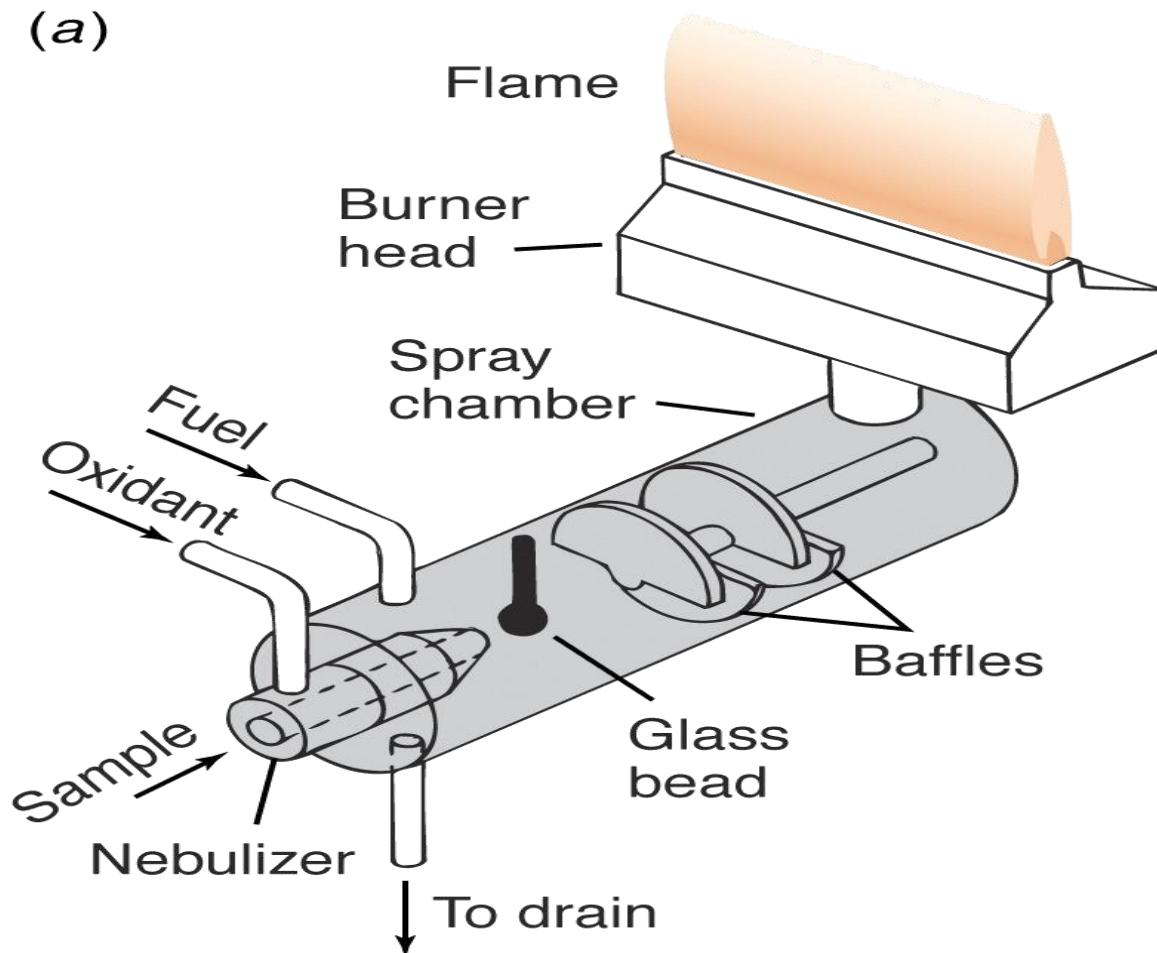
- Use a premix burner →fuel, oxidant and sample are mixed before introduce into flame.

- Solutions are aspirated with the gas flow into a nebulising/mixing chamber to form small droplets prior to entering the flame.

- Degree of atomization → temperature dependent

Fuel	Oxidant	Temperature (K)
Acetylene	Air	2400-2700
Acetylene	Nitrous oxide	2900-3100
Acetylene	Oxygen	3300-3400
Hydrogen	Air	2300-2400
Hydrogen	Oxygen	2800-3000
Cyanogen	Oxygen	4800

(ii) Furnace

- Graphite furnace comprising a tube of graphite with a small cavity that can hold a precise quantity of sample → requires less sample.

- Can attain 3000 K.

- Graphite tube→ surrounded by double sleeve
  1) inert gas (protect elements from oxidation)
  2) coolant (water).

- Flameless atomization → a very high atom density and a longer confinement period → greater sensitivity of 1000.

Sample port

Light in

Light out

Furnace wall

Curved L'vov platform

(a)
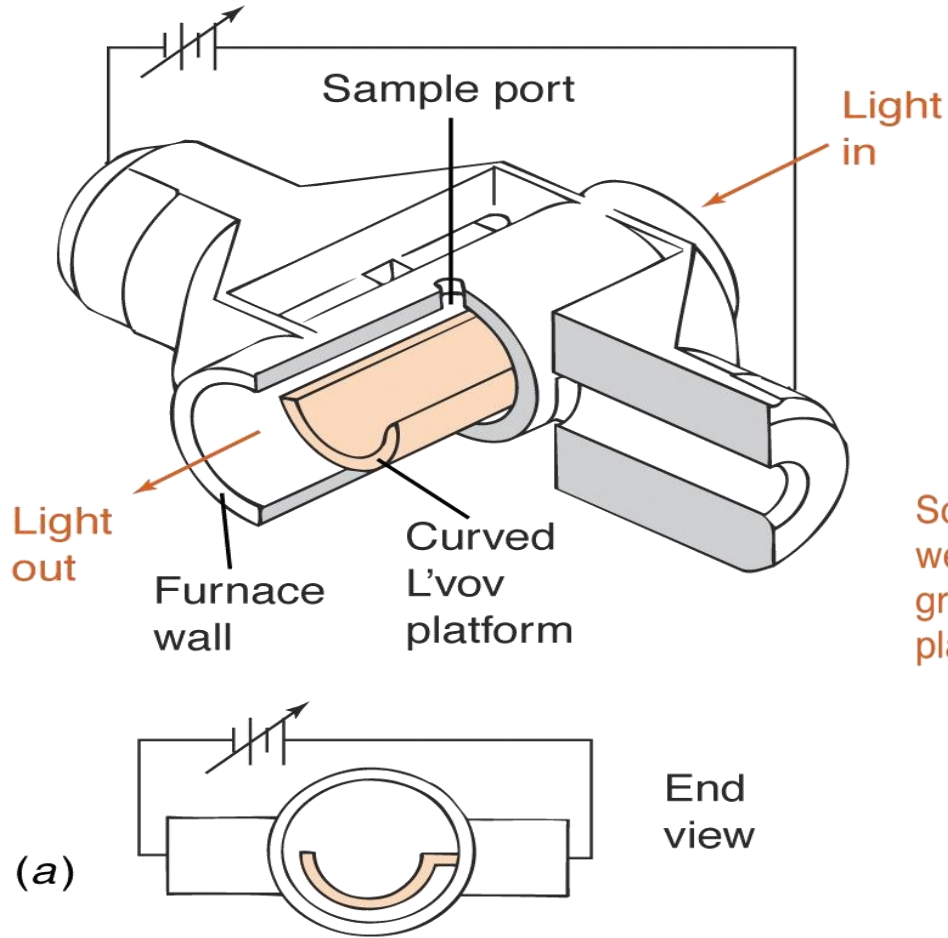
End view

Solid sample weighed onto graphite platform
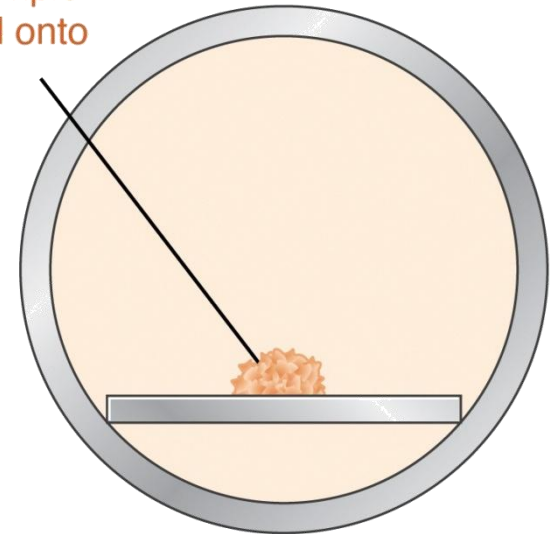
Direct solid sampling — end view of furnace

(3) Monochromator

- Enables the elimination of a large part of the stray light due to the hollow cathode lamp, and the selection of the most intense spectral line in order to obtain a better sensitivity.

Arsenic hollow cathode lamp
Filler gas: Neon
Window: quartz
Most sensitive line: 197.2 nm
Spectral bandwidth: 0.5 nm
Secondary line
(50% less intense): 193.7 nm
Spectral bandwidth: 1 nm.
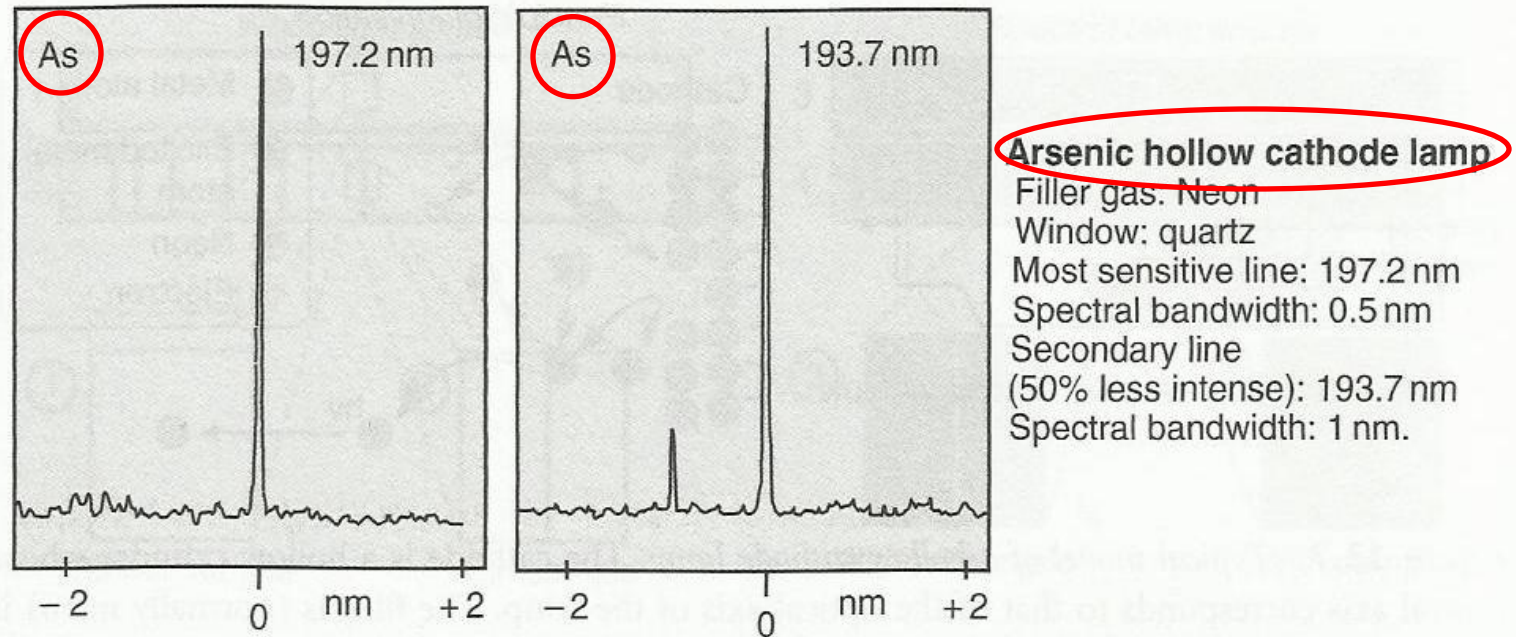
Interference in Atomic Spectroscopy

- Any effect that changes the signal while analyte concentration remain unchanged.

- Type of interferences:

  (1) Spectral interference
     → unwanted signals overlapping analyte solution.

  (2) Chemical interference
     → chemical reactions decreasing the concentration of analyte atoms.

  (3) Ionization interference
     → ionization of analyte atoms decreases the concentration of neutral atoms

Background Correction

- To **distinguish analyte signal** from **absorption, emission**, and **optical scattering** of the **sample matrix, the flame, plasma or furnace**.

- To avoid significant error.

- Instrument with burner→ low background noise.

- Most critical for graphite furnace (incomplete atomization).
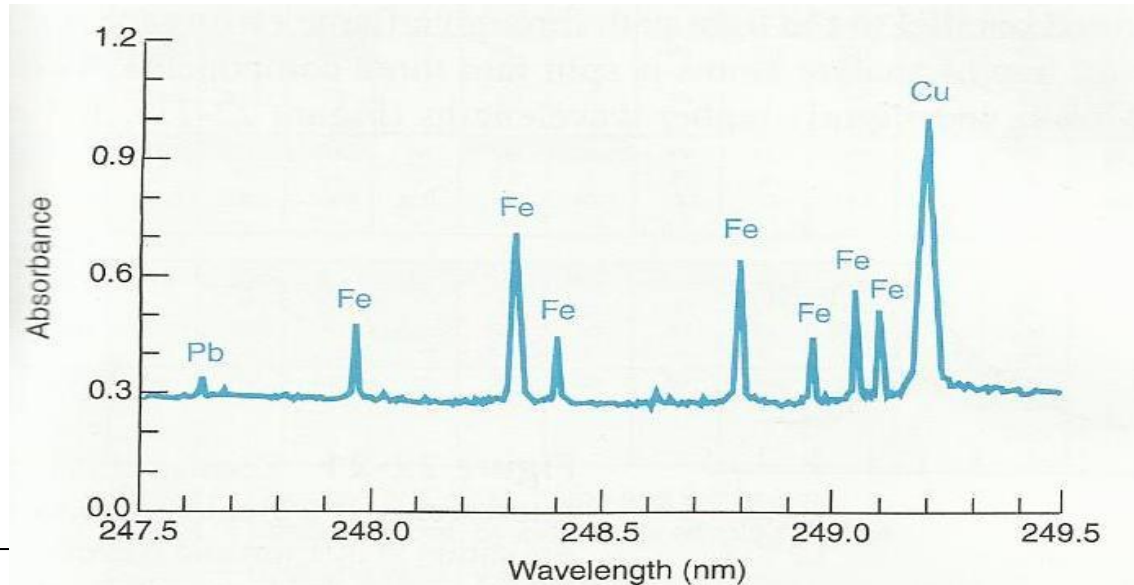
Example of graphite furnace absorption spectrum

Correction Methods

(1) <u>Beam Chopping (correct beam for flame emission)</u>

- HCL (pulsing it on and off) → distinguish the signal of the flame from the desired atomic line at the same wavelength.

- the lamp being periodically blocked by the rotating chopper.

- while the beam is blocked, signal → from the flame emission.

- when the beam is not blocked, signal → from the lamp and the flame.

- difference between these signals → desired signal.
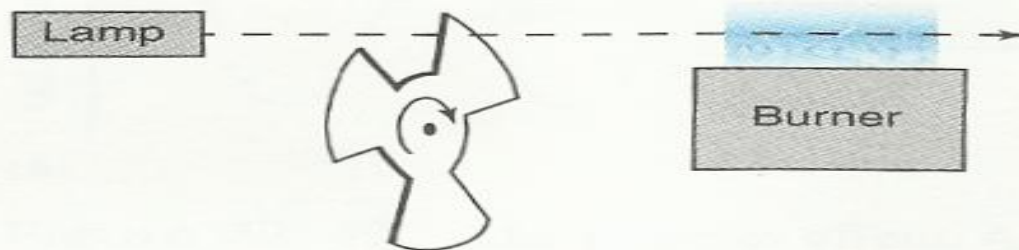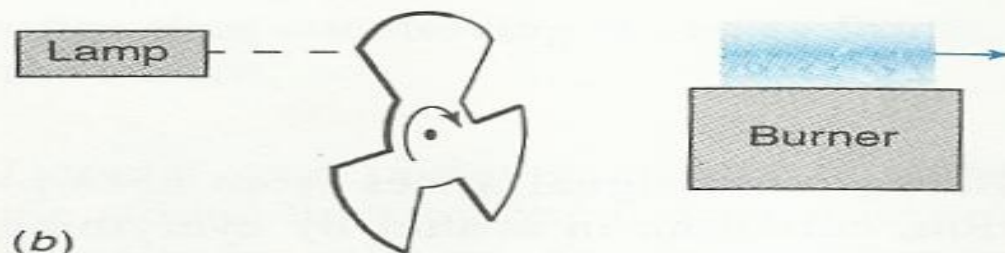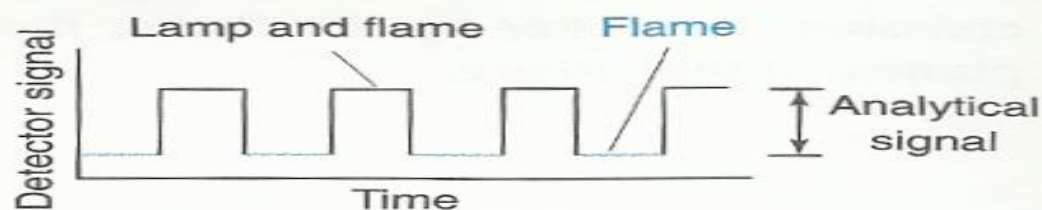
Figure 22-19 Operation of a beam chopper for subtracting the signal due to flame background emission. (*a*) Lamp and flame emission reach detector. (*b*) Only flame emission reaches detector. (*c*) Resulting square wave signal.

(2) Deuterium Lamp Background Correction

- Additional D_2 lamp passed through the flame in alternation with HCL.

- Light from HCL is absorbed analyte and absorbed scattered by background.

- Light from D_2 lamp is absorbed and scattered only by background.

- Difference between absorbance measured $\rightarrow$ absorbance due to analyte.

Disadvantage: uses more complex optical assembly including a second source
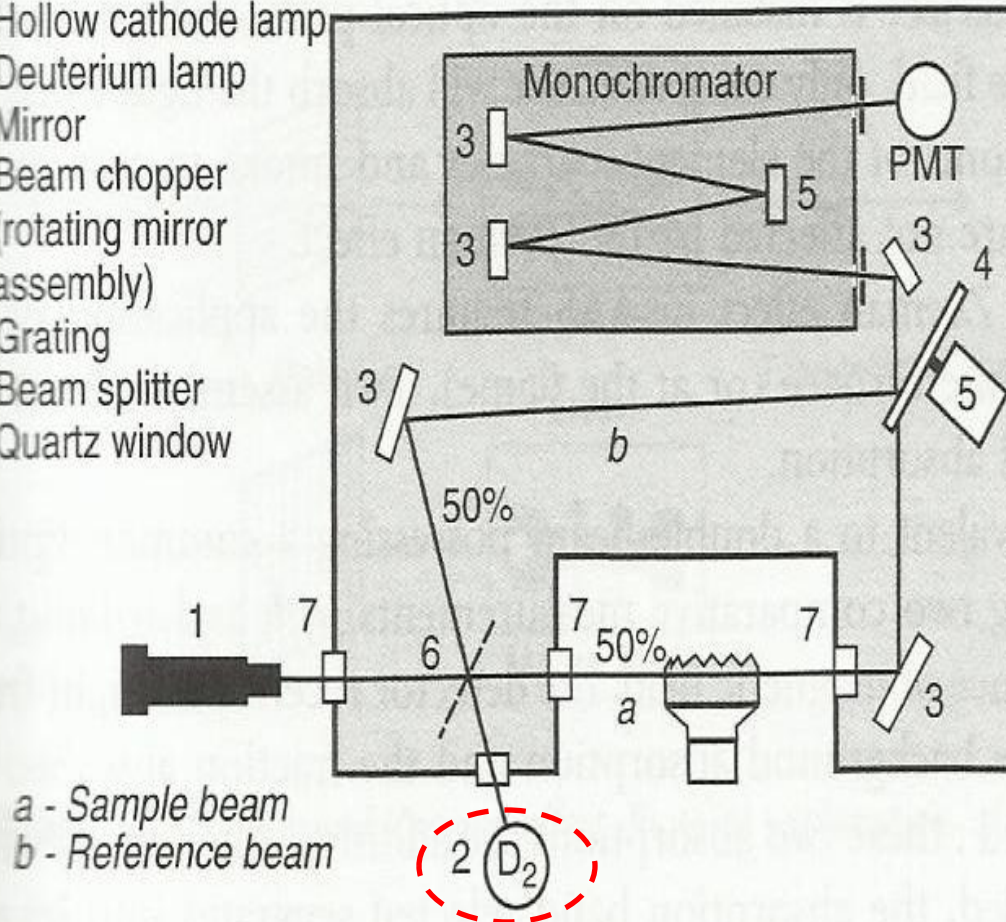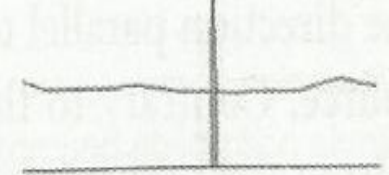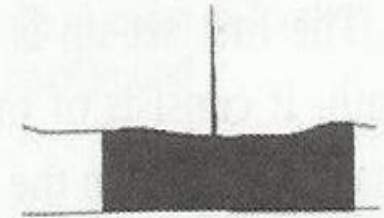
AAS with deuterium lamp background correction (double-beam AAS)

(3) Smith-Hieftje (pulsed HCL) Correction

- When HCL run at high current → output is broadened.
- The lamp is first run at low current, and pulsed at high current to measure absorbance.
- Difference between absorbances measured before and after → absorbance due to analyte.
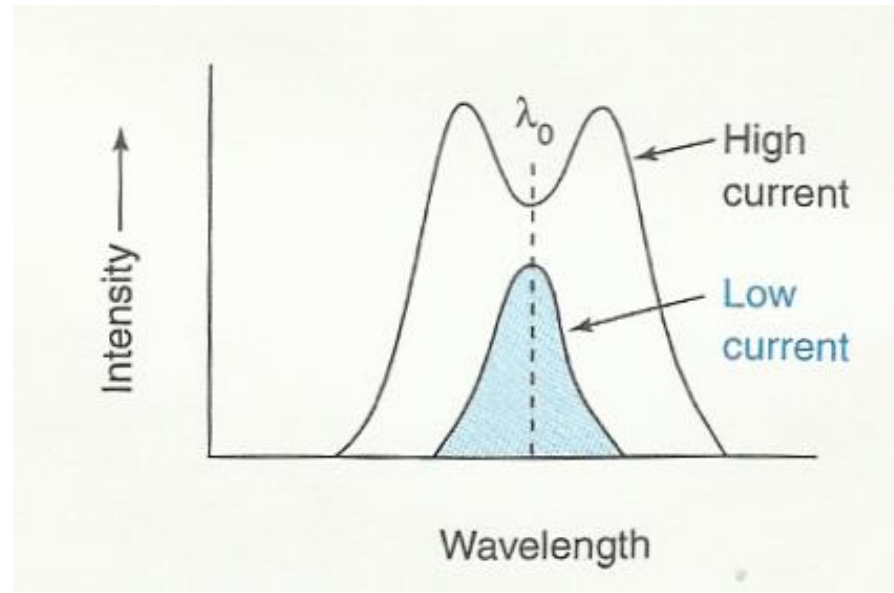
Disadvantage: high-current pulses reduce lamp lifetime

(4) Zeeman Effect

- Shifting of energy levels of atoms and molecules in a magnetic field.

- Sample and background are observed when magnetic field is off.

- Background alone is observed when magnetic field is on.

- The difference → signal

Disadvantage: expensive
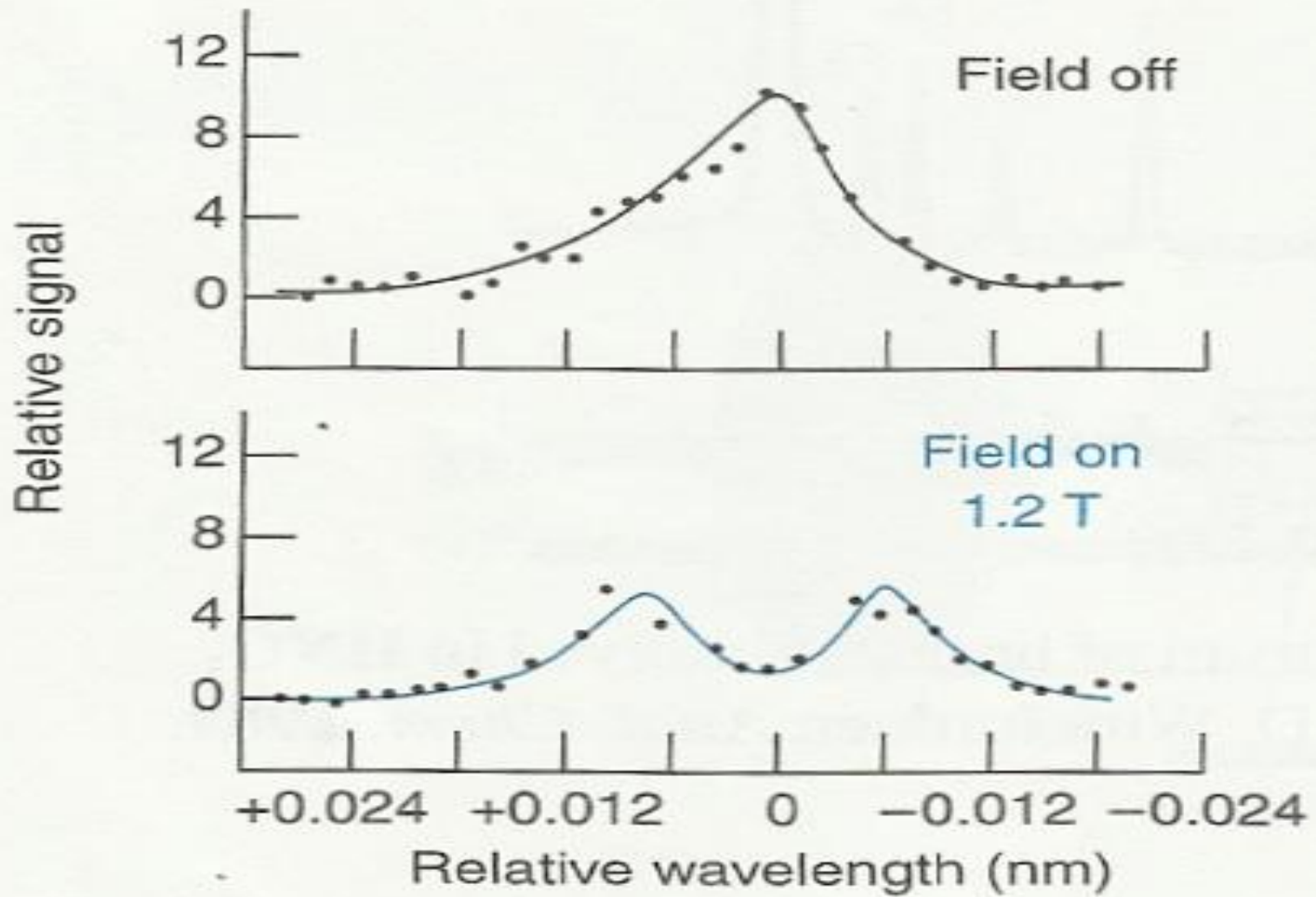
Modern AAS with background correction
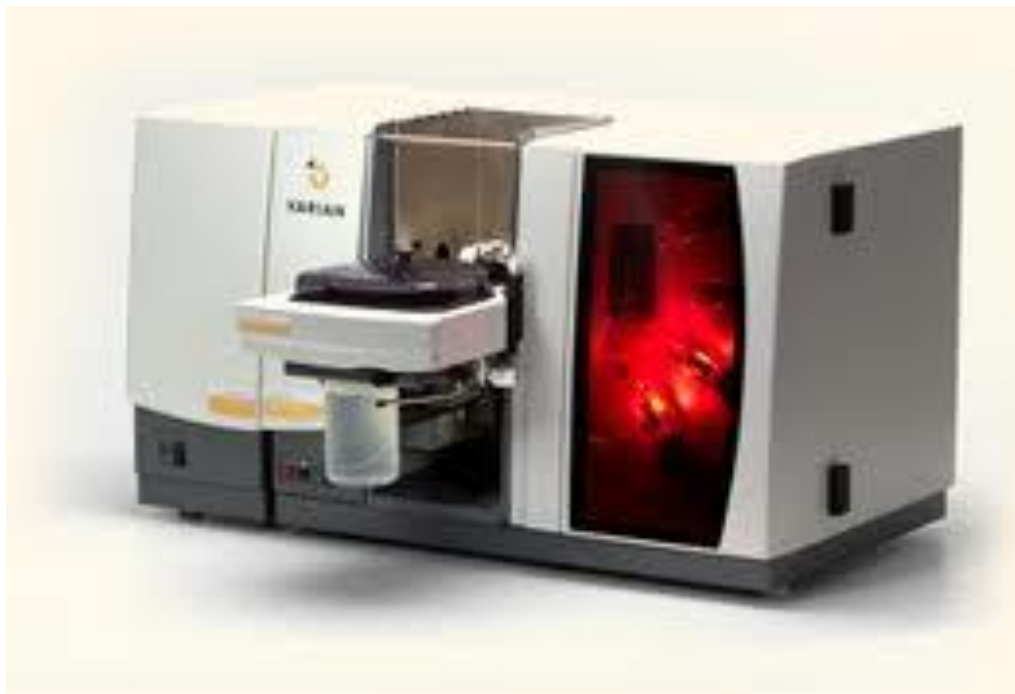
Outline

- Atomic Absorption
- **Atomic Emission**
- Atomic Fluorescence
- Use of X-rays

Atomic Emission Spectroscopy (AES)

- method of chemical analysis that uses the intensity of light emitted from plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample.

Advantages:

- Lower susceptibility to chemical interferences.

- Good emission spectra → multi-element analysis for small sample.

- Energetic plasma source→ determination of low concentration of element and nonmetal such as Cl, Br, I and S.

Recall:
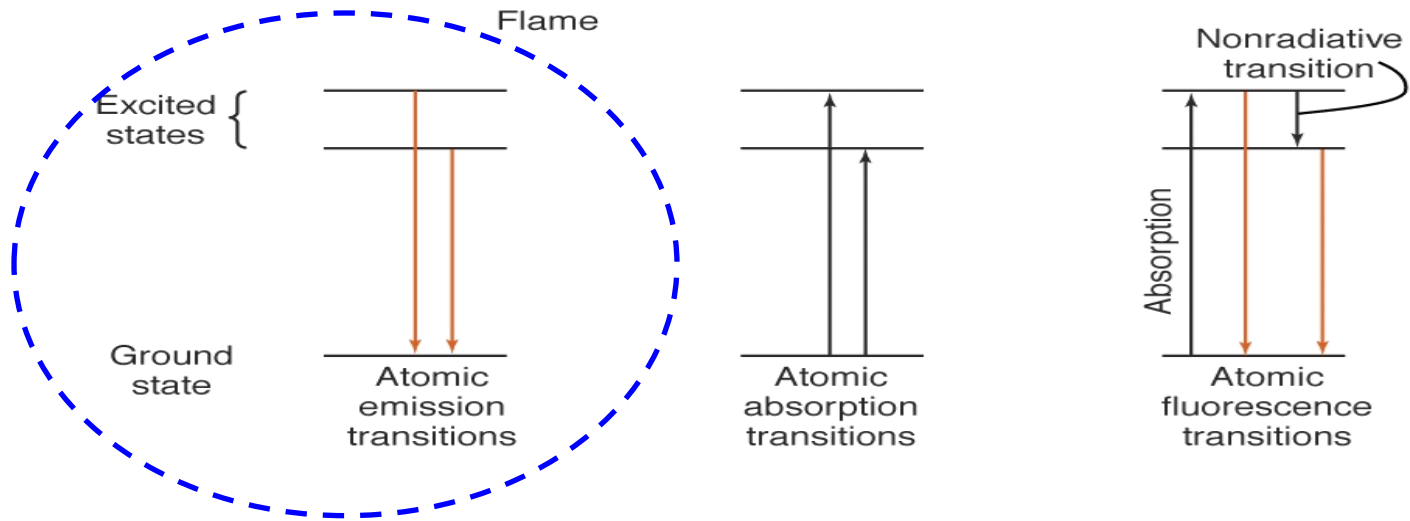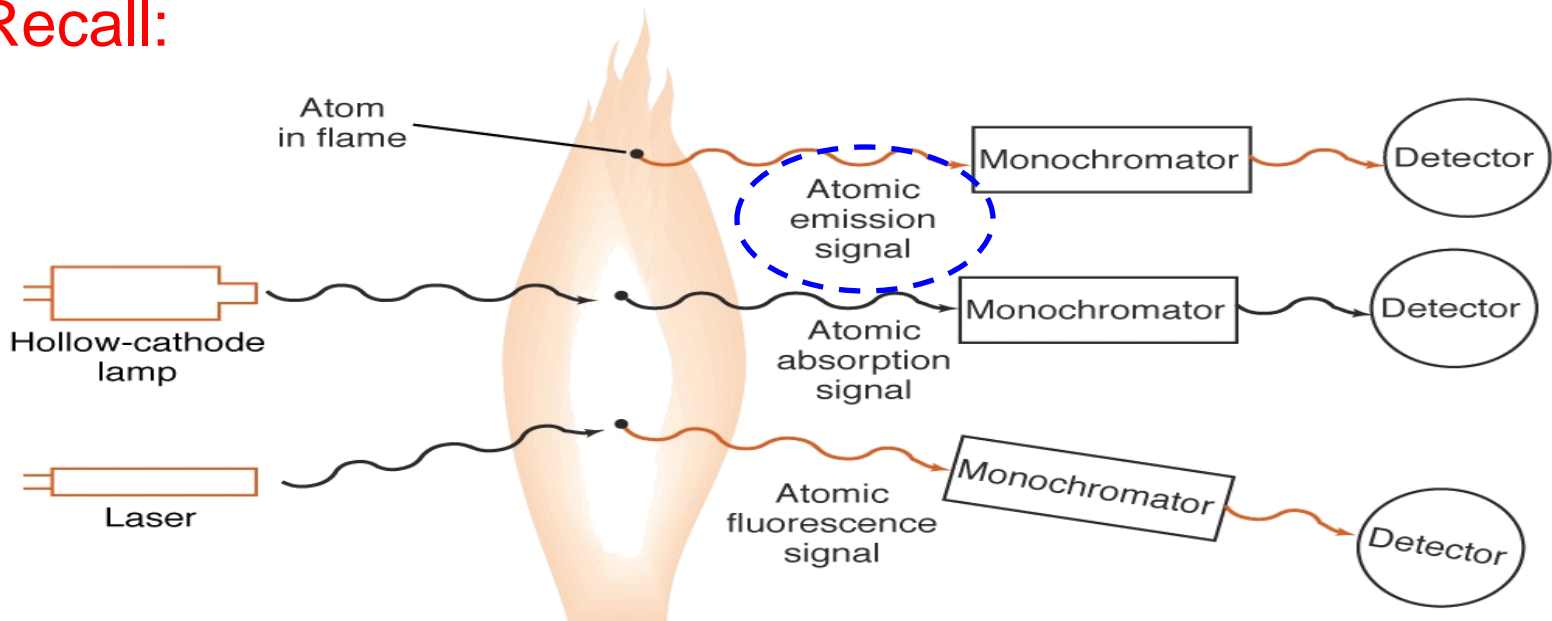
AES-Principal

Atomic Emission Spectroscopy
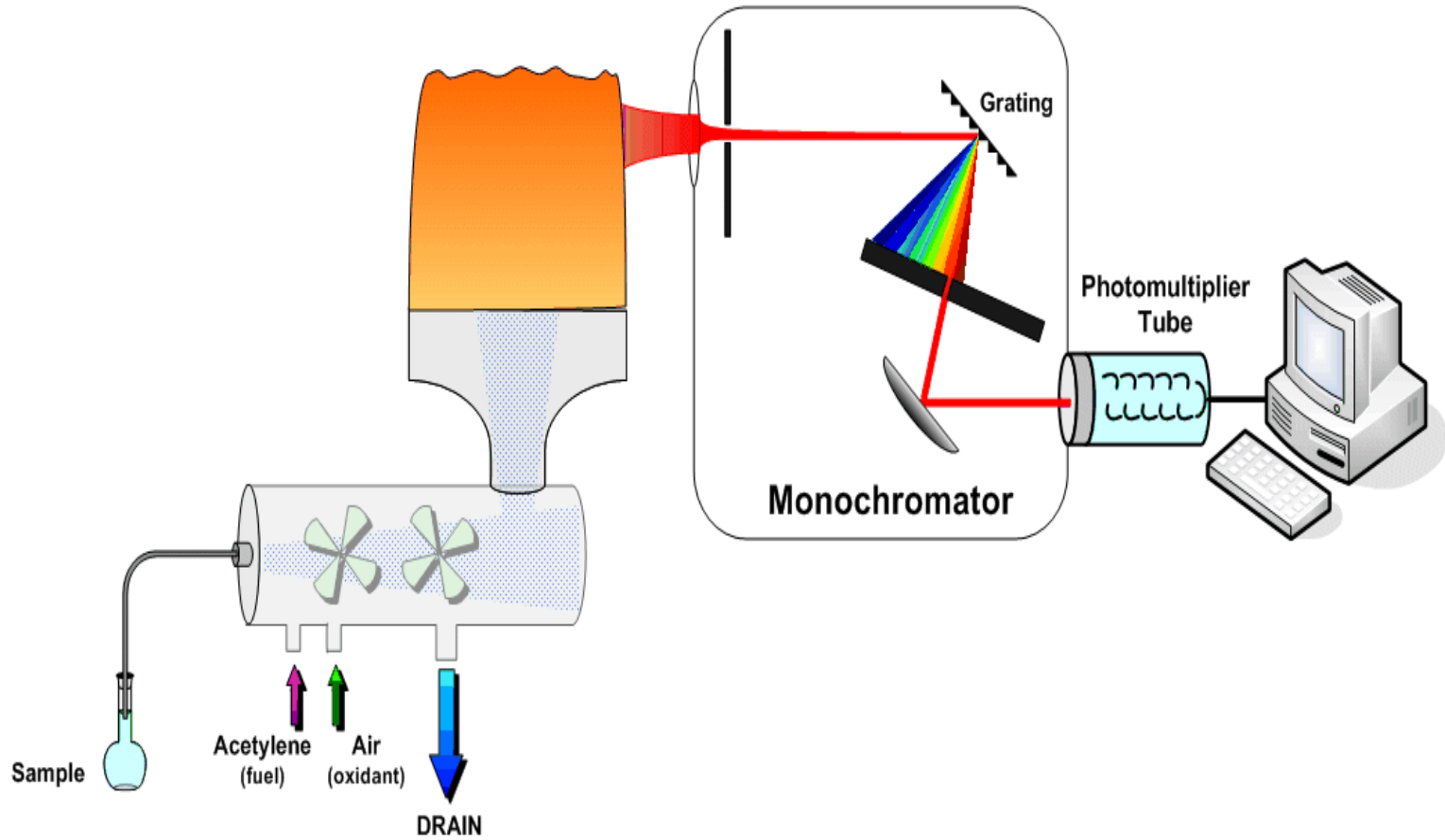
Disadvantages:

- Emission spectral → made up hundreds or even thousands of lines → increase the probability of spectral interferences in quantitative analysis.

- Require higher resolution and more expensive optical equipment that needed for AAS.

AAS

- simpler and less expensive
- lower operating cost
- greater precision
- require less operator

AES- based on Arc and Spark

- Based on excitation of emission spectra of elements with electric arcs or high voltage sparks (Temp = 3000 - 6000 K).

General operation:

- An electric arc or spark is passed through the sample → heating it to a high temperature to excited the atoms within it.

- The excited analyte atoms emit light at characteristic wavelengths that can be dispersed with a monochromator and detected.

AES-based on Plasma Source

- Most common – Inductively Coupled Plasma (ICP-AES)

- Plasma- is a gas that is hot enough to contain ions and free electrons.

- Temperature up to 8000 K→ high enough to excite most elements
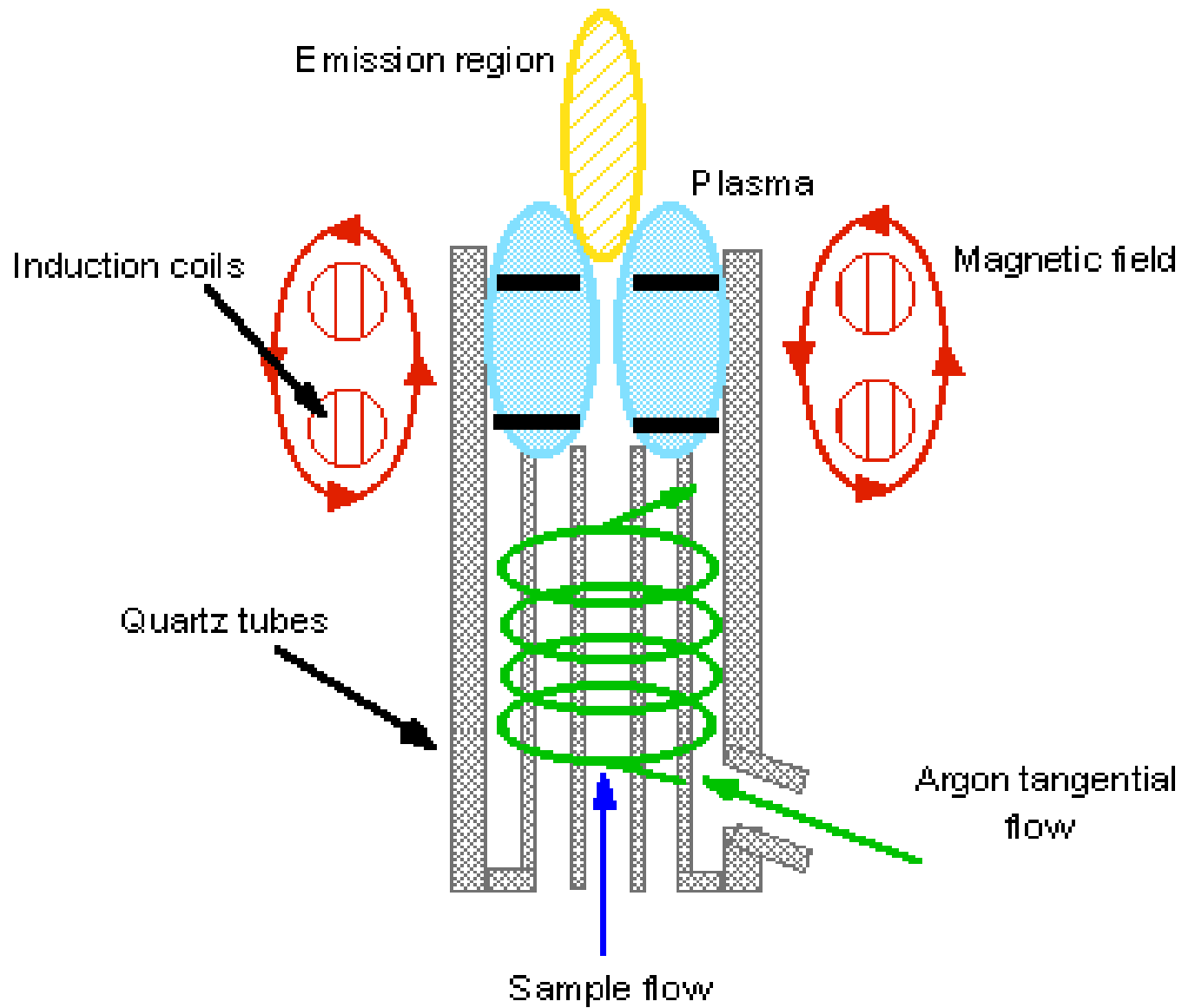
A typical ICP source
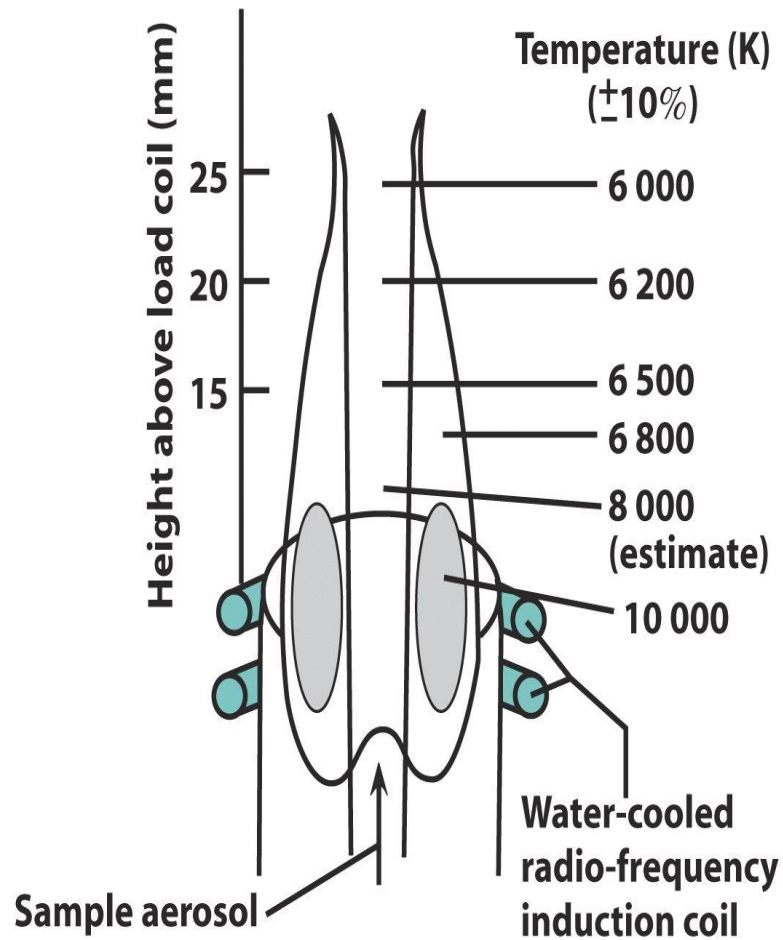
Temperature profile of ICP

Photo of argon plasma in operation

Modern ICP-AES

Outline

- Atomic Absorption
- Atomic Emission
- **Atomic Fluorescence**
- Use of X-rays

Atomic Fluorescence Spectroscopy (AFS)
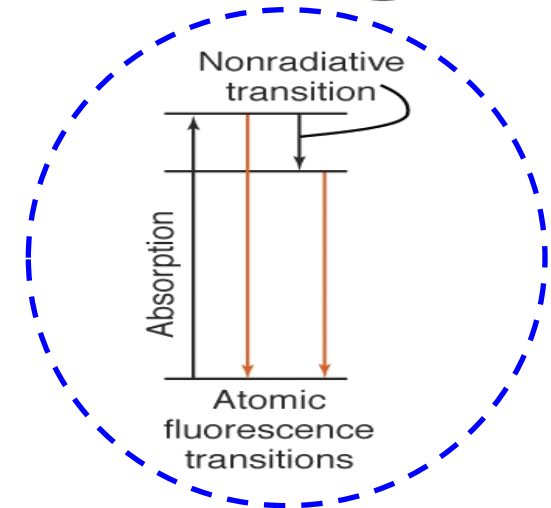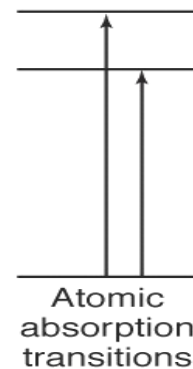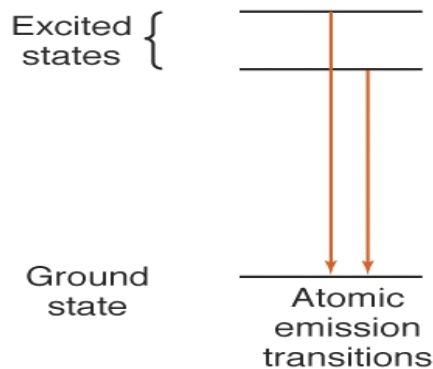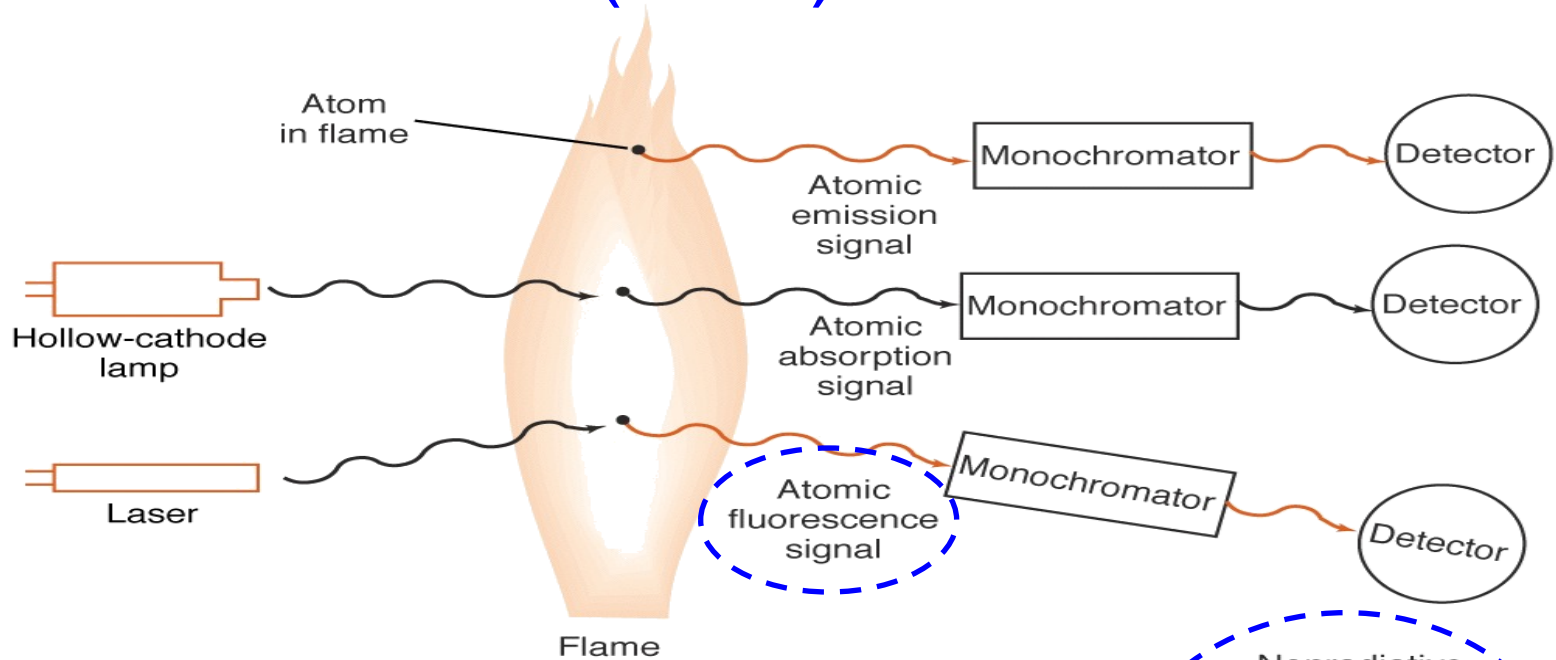
Atomic Fluorescence Spectroscopy (AFS)

- can be considered a combination of AAS and AES in that the excitation from the ground state to the upper state is carried out radiationally (as in AAS), but the measurement is made by detection of radiation emitted by the atom as it relaxes back from the excited state to the ground state (as in AES).

- In AES, the atoms are excited only by the collisional energy inherent in the high temperature of the atom cell.

- In AAS and AFS, the atoms are excited primarily by radiation from a light source.

Advantages:

- Lower detection limit → small quantity of fluorescence light can be more easily measured.

- Greater sensitivity achievable because the fluorescence signal has a very low background.

Disadvantages:

- High cost and operational complexity in AFS; and great success and widespread application in AAS →discouraged further development in AFS.

Modern AFS

Detection Limit for Atomic Spectroscopy

Element	AAS Flame	AAS Electro-thermal	AES Flame	AES ICP	AFS Flame
Al	30	0.1	5	0.2	5
As	200	0.5	—	2	15
Ca	1	0.25	0.1	0.0001	0.4
Cd	1	0.01	2000	0.07	0.1
Cr	4	0.03	5	0.08	0.6
Cu	2	0.05	10	0.04	0.2
Fe	6	0.25	50	0.09	0.3
Hg	500	5	—	—	5
Mg	0.2	0.002	5	0.003	0.3
Mn	2	0.01	—	0.01	1
Mo	5	0.5	100	0.2	8
Na	0.2	0.02	0.1	0.1	0.3
Ni	3	0.5	600	0.2	0.4
Pb	8	0.1	200	1	5
Sn	15	5	300	—	200
V	25	1	200	0.06	25
Zn	1	0.005	50000	0.1	0.1

Application of Atomic Spectrometry

- Widely used in many laboratories→ when trace element analyses are required.

- Environmental samples for heavy –metal contamination.

- Pharmaceutical samples → analyzed for metal impurities.

- Steel industry → determine minor and major components.

Choice of atomic spectrometry method → Depend on the sensitivity required, number of samples, single-element or multi-element measurements.

Example 1

Five standard solutions were prepared for measuring the lead concentration in two solutions, A and B. The two solutions A and B contain the same concentration of magnesium used as an internal standard. The following data were obtained.

Conc. (mg/L)	Signal of Pb	Signal of Mg
0.10	13.86	11.88
0.20	23.49	11.76
0.30	33.81	12.24
0.40	44.50	12.00
0.50	53.63	12.12
Sol A	15.50	11.80
Sol B	42.60	12.40

From the data, calculate the lead concentration (mg/L) in the two sample solutions, A and B.

Solution

Construct the calibration graph of the ratio of the signal emission Pb/Mg against concentration

Conc. (mg/L)	Signal of Pb	Signal of Mg	Ratio Pb/Mg
0.10	13.86	11.88	1.17
0.20	23.49	11.76	2.00
0.30	33.81	12.24	2.76
0.40	44.50	12.00	3.71
0.50	53.63	12.12	4.42
Sol A	15.50	11.80	1.31
Sol B	42.60	12.40	3.44
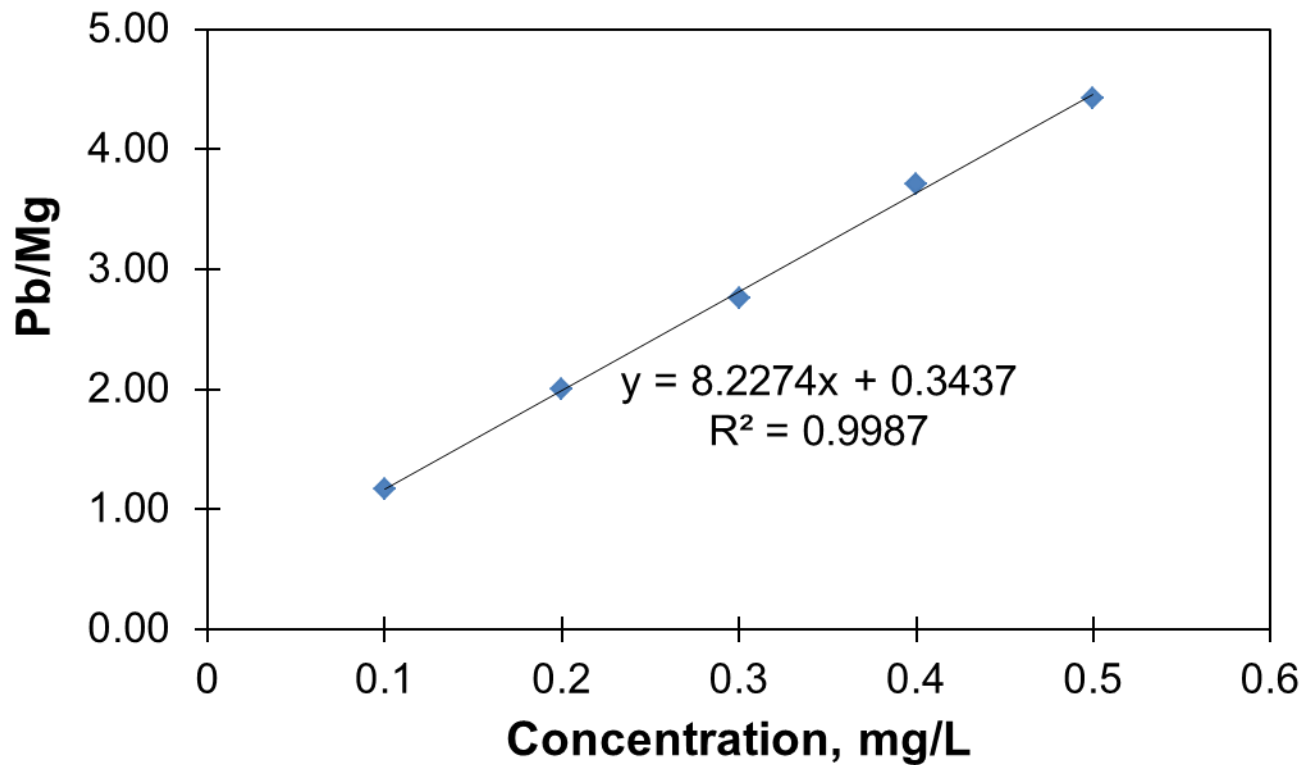
Ratio Pb/Mg, y = 8.2274 x +0.3437,
    whereby x = Pb concentration of solution in mg/L

For Solution A, Ratio Pb/Mg = 1.31

$$1.31 = 8.2274 \, x + 0.3437$$
$$x = 0.12 \text{ mg/L}$$

Therefore, concentration of Pb in Solution A = 0.12 mg/L

For Solution B, Ratio Pb/Mg = 3.44

$$3.44 = 8.2274 \, x + 0.3437$$
$$x = 0.38 \text{ mg/L}$$

Concentration of Pb in Solution B = 0.38 mg/L

Example 2

A stock solution of calcium ions was prepared by dissolving 1.834 g of $CaCl_2.2H_2O$ in 1.00 L of distilled water and then further diluting by a factor of ten.

From this new solution, three standard solutions were prepared by further dilutions of five, ten and twenty times, respectively. The unknown sample is itself diluted twenty-five times.

Sufficient strontium chloride was then introduced to eliminate any interference due to phosphate ions. An analytical blank containing the same concentration of strontium was the first solution to be examined by the air/acetylene flame. The results were as follows:

Standard	Signal
Blank	1.50
1:20	10.6
1:10	20.1
1:5	38.5
Unknown	29.6

MW:
Ca = 40.1 g/mol
Cl = 35.5 g/mol

What is the concentration (in ppm) of the calcium in the unknown sample?

Solution

1) The molar mass of $CaCl_2.2H_2O$

   $= (40.1 + (35.5 \times 2) + (18 \times 2) = 147.1$ g

2) The concentration of the parent solution (in 1.00 L solution)

   $= 1.834/147.1 = 0.01247$ mol/L

3) Solution diluted 10 times $= 0.01247/10 = 0.001247$ mol/L

4) Tabulated the data

Standard	Signal	Concentration (mol/L)
Blank	1.50	0
1:20	10.6	0.6234×10^{-4}
1:10	20.1	1.2468×10^{-4}
1:5	38.5	2.4935×10^{-4}
Unknown	29.6	?

5) Plot signal versus concentration

$$y = 148635x + 1.46$$
$$R^2 = 1$$
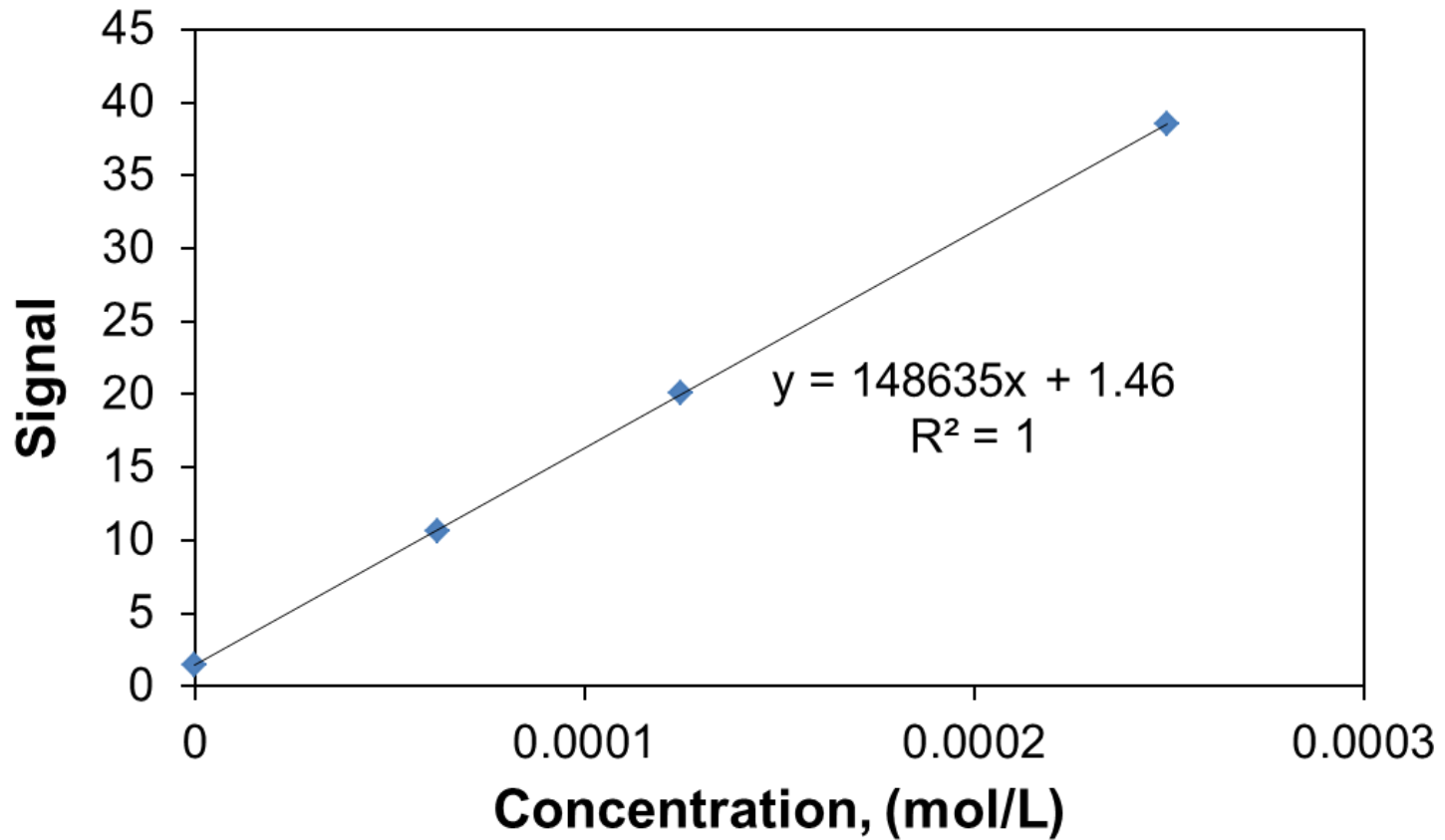
6) Concentration of unknown sample (after dilution)
   Given signal of the unknown sample y = 29.6
   x = (29.6 – 1.46)/148635 = 1.8932 x 10⁻⁴ mol/L

7) The parent solution has a concentration twenty-five times greater, therefore the concentration of unknown solution

= 1.8932 x 10^{-4} mol/L x 25 = 4.7331 x 10^{-4} mol/L

8) Concentration of Ca^{2+}

= 4.7331 x 10^{-4} mol/L x 40.1 g/mol = 0.19 g/L

In ppm = 0.19 g/L x 1L/1000 mL x 10^6 μg/g

= 190 μg/mL = 190 ppm = 1.90 x 10^2 ppm

Example 3

An AAS method is employed for the determination of lead (Pb) in a sample of adulterated paprika by the introduction of lead oxide (of same colour). An electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect is used.

0.0100 g of the paprika powder is placed in the tube of the graphite furnace. The determination of the area peak absorbance was made at λ = 283.3 nm first in the absence and later in the presence of a magnetic field. The value of the peak absorption following background correction was 1220 (arbitrary units).

Under the same conditions, 0.0100 mL of a solution of 10.0 g/L Pb led to a value of 1002 in the same units.

Calculate the % mass of lead in the sample of paprika under study.

Solution

The signal of absorbance of the sample extracted from paprika = A_x and the sample solution = A_S,

m_X = mass of lead in the paprika

m_S = mass of lead in the sample solution

We have: $A_X/A_S = m_X/m_S$, therefore $m_X = m_S A_X/A_S$

Given: $A_X = 1220$, $A_S = 1002$,

m_S = 10.0 g/L x 0.0100 mL x (1L/1000 mL) = 0.0001 g

m_X = (0.0001 g x 1220/1002) = 0.000122 g

The % mass in the paprika sample is therefore = (0.000122/0.01) x 100% = 1.22 %

Exercise 1

Magnesium is determined in a river water sample using electrothermal AAS, using multiple standard additions. Four 25.0 mL aliquots are pipetted into 50.0 mL volumetric flasks, and aliquots of a 2.50 ppm standard are added in the amounts of 0.00, 1.00, 2.00, 3.00 mL, respectively. Fixed volumes of each solution are measured, giving net absorbance signals of 0.10, 0.18, 0.24, 0.31, respectively. Calculate the concentration of magnesium in the sample.

Outline

- Atomic Absorption
- Atomic Emission
- Atomic Fluorescence
- Uses of X-rays

Atomic X-rays Spectroscopy

- X-rays are short-wavelength of electromagnetic radiation produced by the deceleration of high energy electrons or by electronic transitions in the inner orbitals of atoms.

- Based on measurement of emission, absorption, fluorescence and diffraction of electromagnetic radiation.

- The wavelength range: 10^{-5} Å to 100 Å. Conventional X-ray spectroscopy: 0.1 Å to 25 Å

- X-ray methods are widely used for the qualitative and quantitative determination of elements in the periodic table.

Recall

← Increasing Frequency (ν)

10^{24} 10^{22} 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2} 10^{0} ν (Hz)

γ rays | X rays | UV | IR | Microwave | FM | AM | Long radio waves

Radio waves

10^{-16} 10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{0} 10^{2} 10^{4} 10^{6} 10^{8} λ (m)

Increasing Wavelength (λ) →

Visible spectrum

400   500   600   700

Increasing Wavelength (λ) in nm →
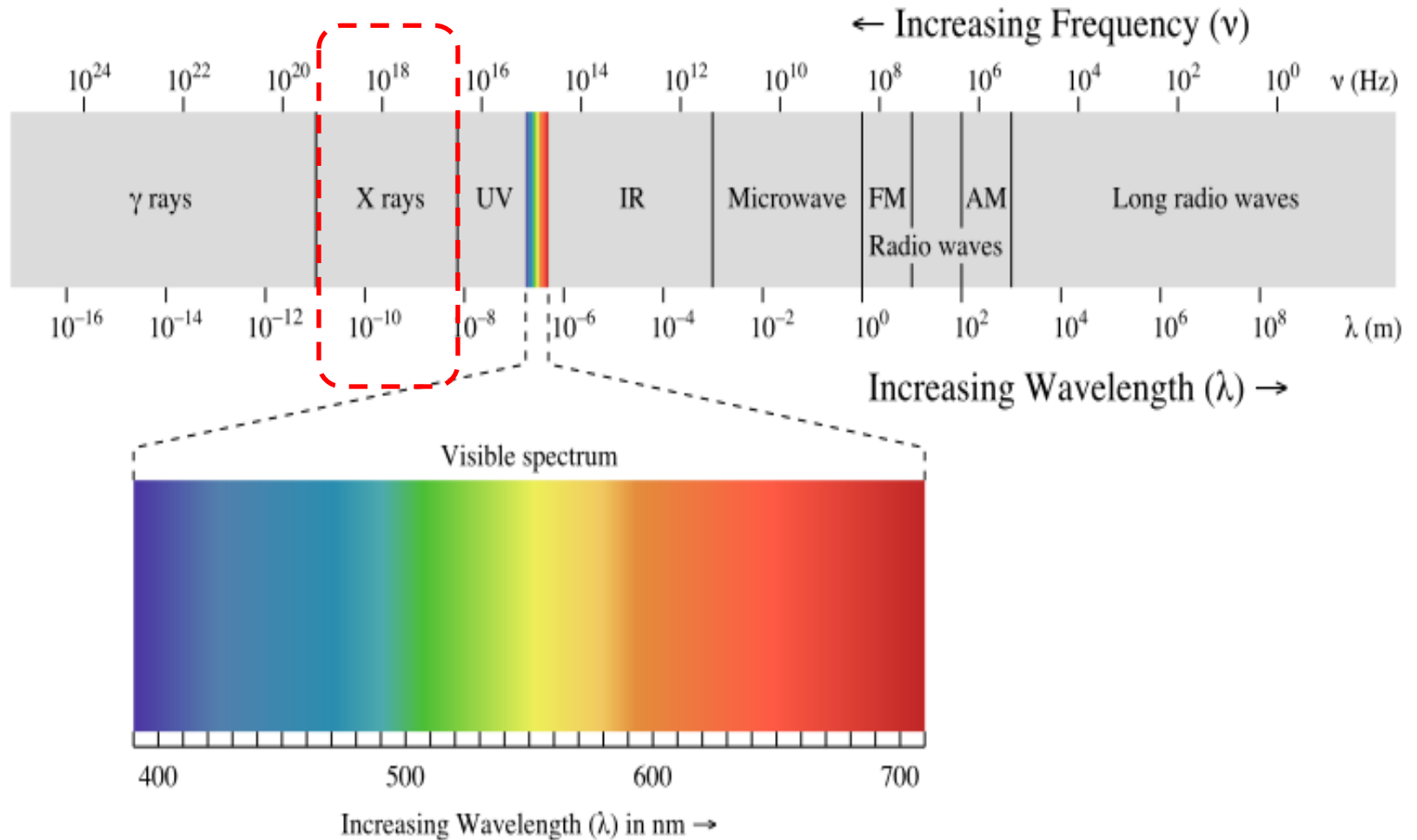
X-ray

- <u>X-rays are generated:</u>

(1) By bombardment of a metal target with a beam of high-energy electron

(2) By exposure of a substance to a primary beam of X-rays to generate a secondary beam of X-ray fluorescence.

(3) By use of a radioactive source whose decay process results in X-ray emission.

X-rays Instrumentation

- Generally consists of five main components:

(1) source→ tubes, radioisotopes and secondary fluorescence.

(2) monochromator (collimators) →restricting the wavelength range of incident radiation.

(3) sample holder

(4) radiation detector/transducer→ convert radiant energy to electrical signal.

(5) signal processor and readout

X-ray Fluorescence (XRF)

- The elements in the sample excited by absorption of the primary beam and emit their own characteristic fluorescence X-rays.
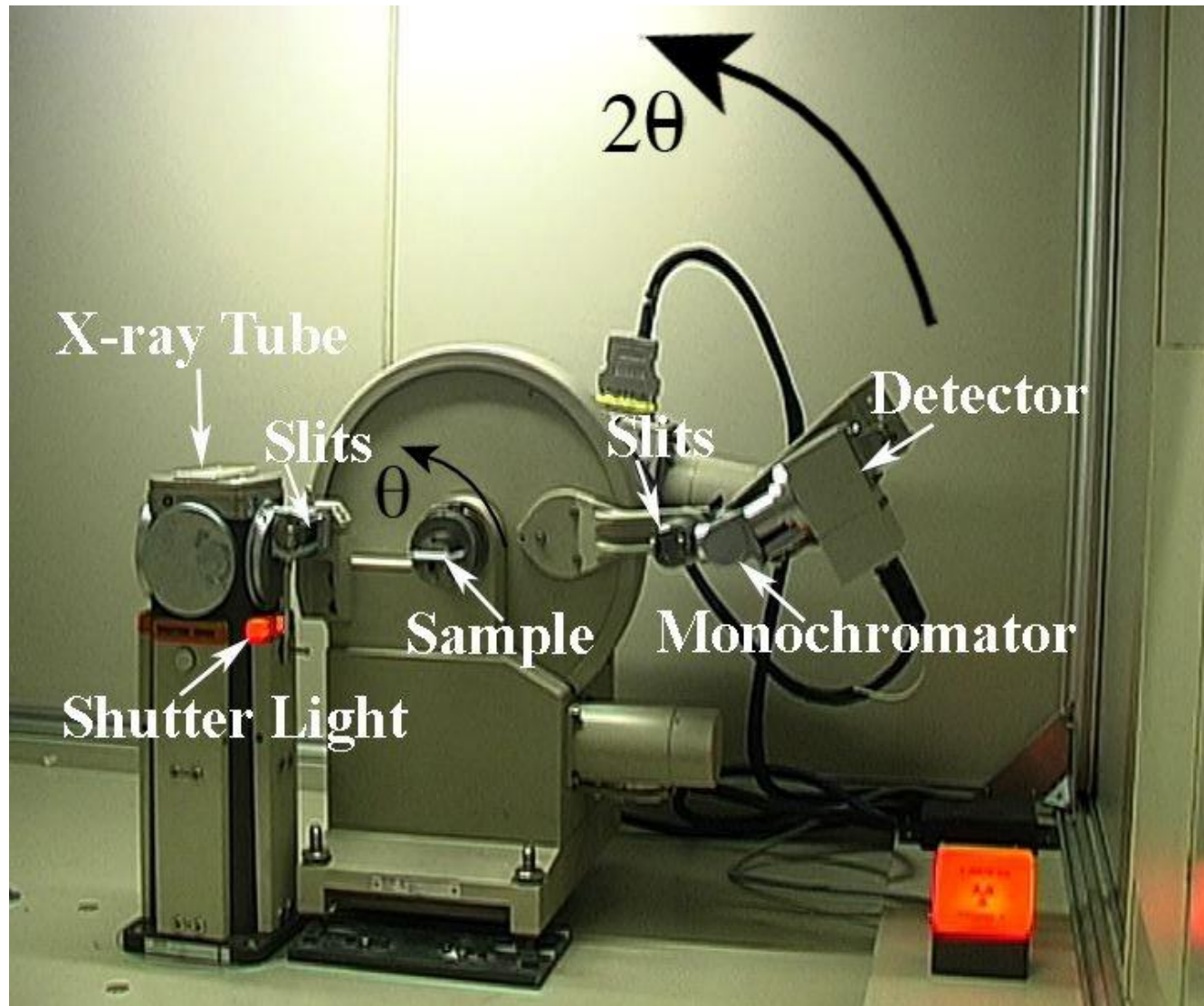
Use of X-ray Fluorescence (XRF)

- Quality control in the manufacture of metal and alloys.

- Correct the composition of the alloy during its manufacture.

- Easily adapted to liquid sample → direct quantitative determination of lead and bromine in aviation fuel sample.

- Determination of Ca, Ba and Zn in the lubricating oils.

- Determination of pigment paint.

- Analysis of pollutant.

- Determination of elements heavier than Na in rocks and soil.

Use of X-ray Absorption

- Widely-used technique for determining the local geometric and/or electronic structure of matter.

- Determination of lead in gasoline and sulfur or halogen in hydrocarbons.

- General useful only when a single element with high atomic number.

- Relatively limited when compared with XRF procedure.

- Cumbersome and time-consuming.

Use of X-ray Diffraction (XRD)

- Important information to science and industry.

- Determine the arrangement and the spacing of atoms in crystalline materials.

- Understanding of physical properties of metals, polymeric materials, and other solids.

- Determine the structures of such complex natural products such as steroids, vitamins and antibiotics.

- Qualitative identification of crystalline compounds → each crystalline substance has a unique X-ray diffraction.

- X-ray powder diffraction →providing qualitative and quantitative information about the compounds present in a solid sample

X-ray Diffractometer

X-ray Diffraction Spectrum
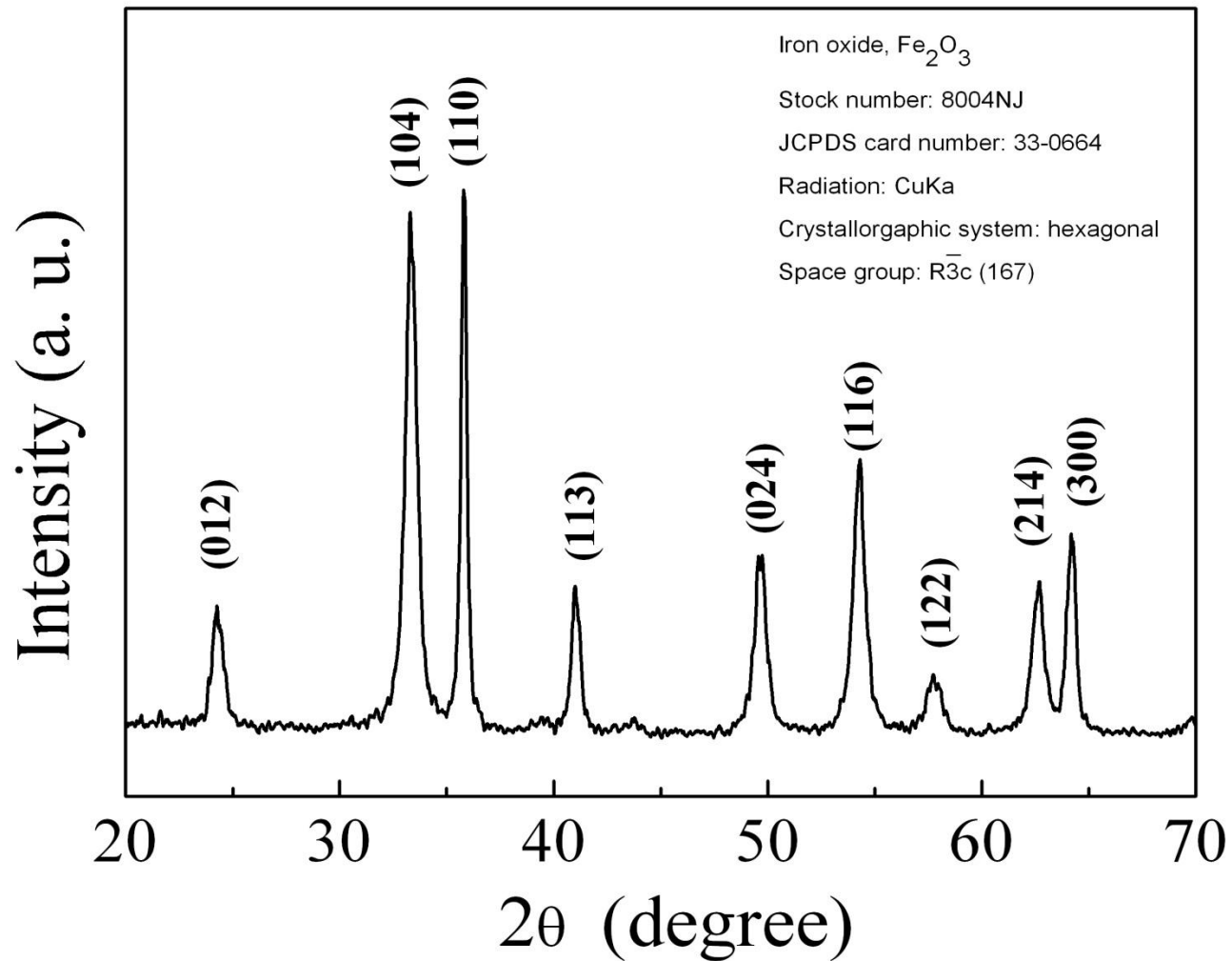
X-ray source: XR50

X-ray monochromator

X-ray Fluorescence Spectrometer

X-ray Absorption Spectrometer

X-ray Emission Spectrometer

X-ray Diffraction Spectrometer

END OF ATOMIC SPECTROSCOPY