

Bonga university

Instrumental Analysis II (Chem.2052)

Chapter 4

Principle, Instrumentation and Application
of Atomic Spectroscopy

2012 E.C

Introduction

- Atomic absorption, along with atomic emission, was first used by Guystav Kirchhoff and Robert Bunsen in 1859 and 1860, as a means for the qualitative identification and quantitative of atoms.
- Modern atomic absorption spectroscopy was introduced in 1955 as a result of the independent work of A. Walsh and C. T. J. Alkemade.¹⁸
- Commercial instruments were in place by the early 1960s, and the importance of atomic absorption as an analytical technique was soon evident.



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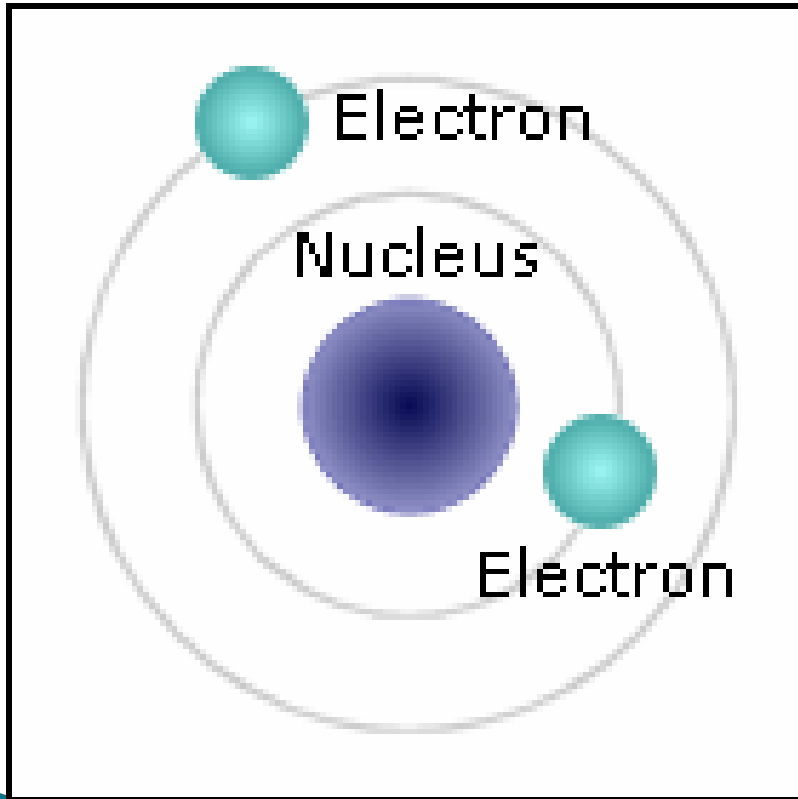
- ✓ An atomic absorption spectrometer is an instrument which is used to analyze the concentrations of metals in solution.
- ✓ Atomic absorption is so sensitive that it sixty eight elements can be determined directly over a wide range of concentrations from ppb to per cent in a sample.
- ✓ The technique makes use of the wavelengths of light specifically absorbed by an element.

Basic Principle

- ❖ Absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by atoms resulting in changes in electronic structure. Observed by passing radiation characteristic of a particular element through an atomic vapour of the sample.
- ❖ Sample vaporized by aspiration of solution into a flame or evaporation from electrically heated surface.

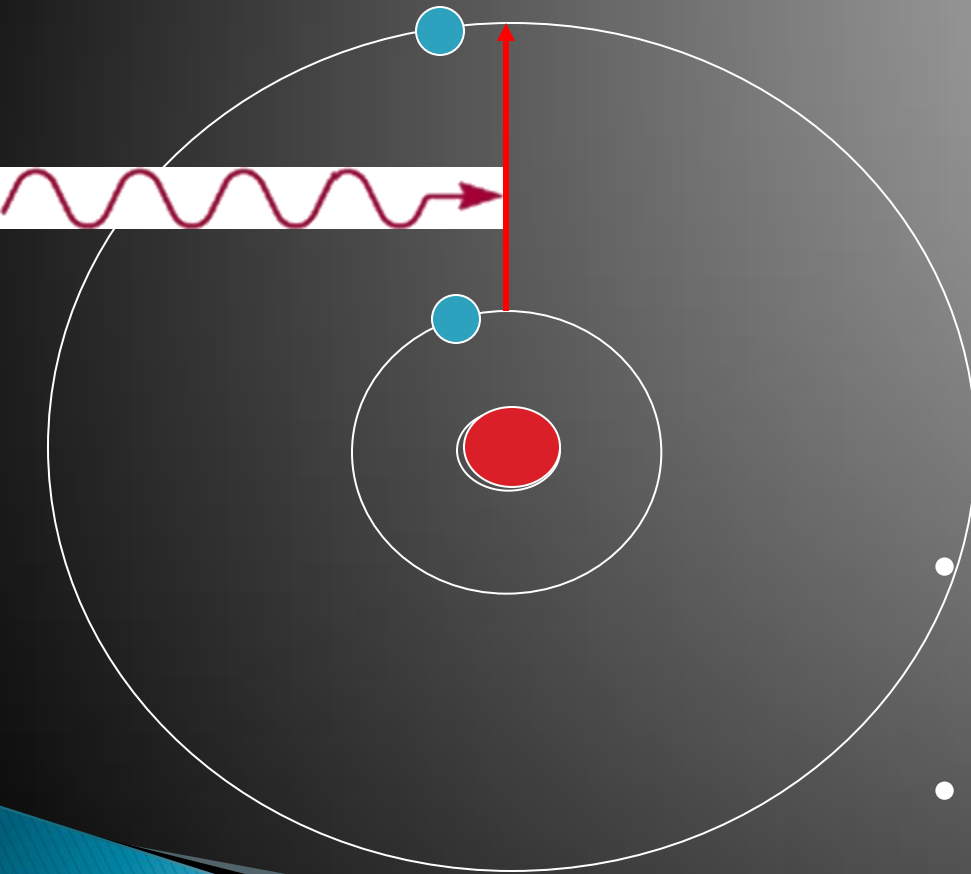
- AAS is an analytical technique that measures the **concentrations of elements or identify its identity**
- Applicable to many metals and few non metals
- It makes use of the absorption of light by these elements in order to measure their concentration
- Atomic-absorption spectroscopy quantifies the absorption of **ground state atoms** in the gaseous state.
- The atoms **absorb ultraviolet or visible light** and make transitions to **higher electronic energy levels**
- The analyte concentration is determined from the amount of absorption.

Theory of Operation



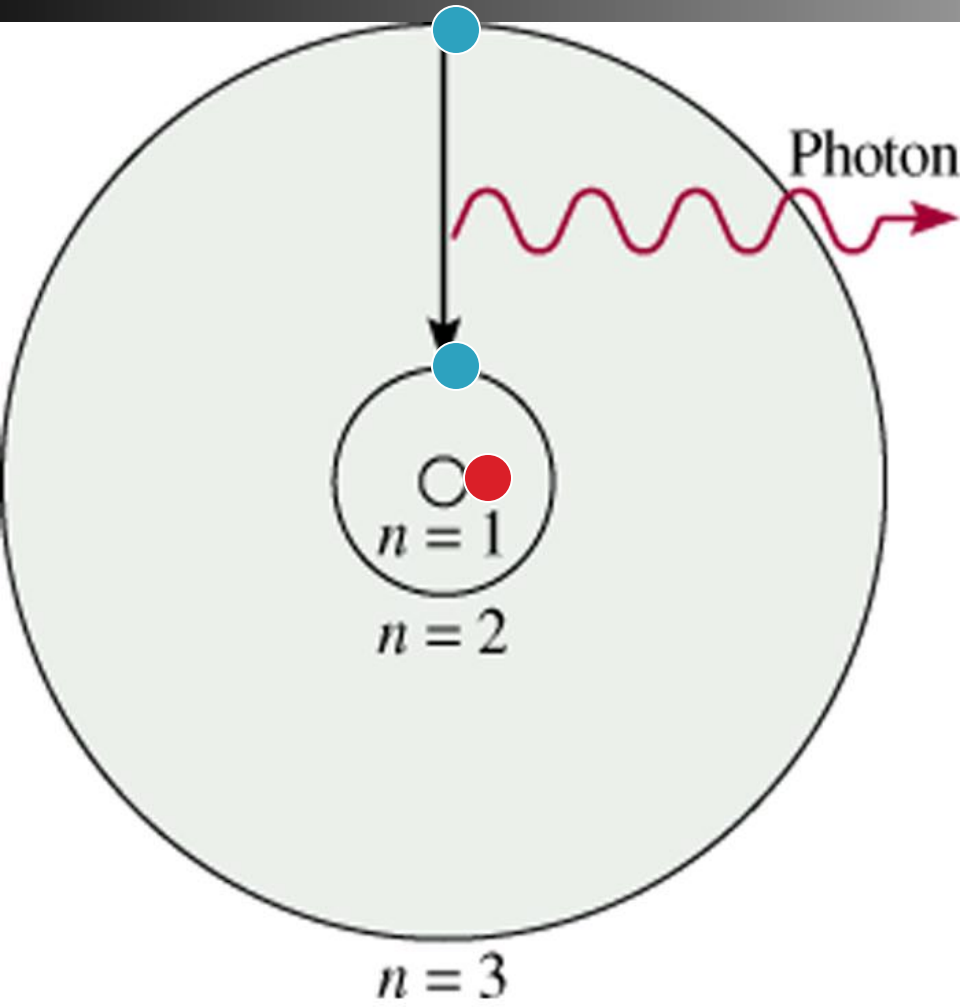
- ▶ Structure of an atom
 - Atoms consist of a nucleus and electrons.
 - The nucleus contains protons and neutrons.
 - The negatively charged electrons are located in orbitals around the nucleus.
 - When electrons occupy the innermost available orbital, their energy is at a minimum (ground state).

Theory of Operation



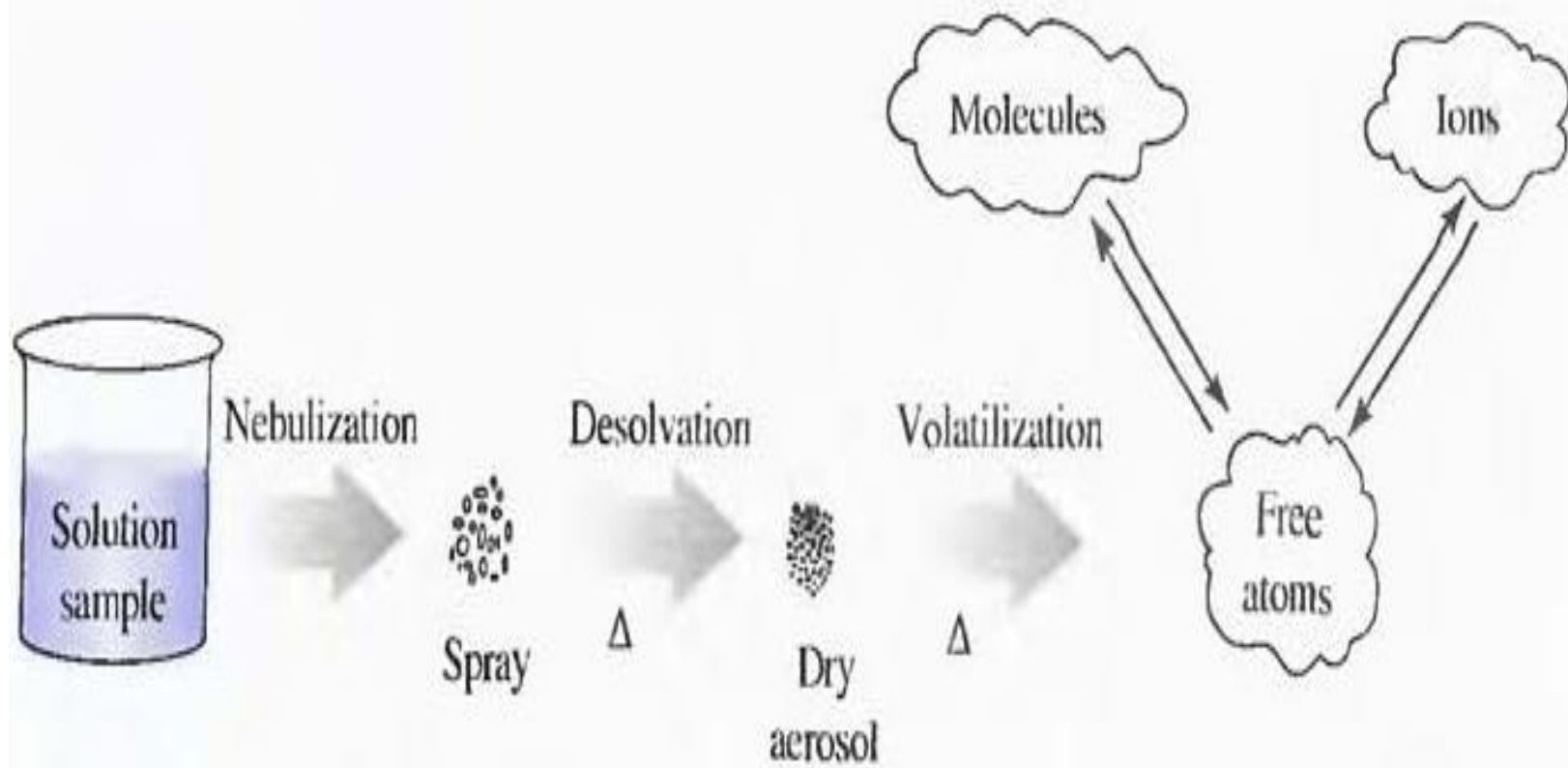
- When atoms are subjected to heat or some form of EMR, one or more electrons jump to a higher energy level, leaving a vacancy in the inner shell
- We say the electron is excited
- As this happens, energy is absorbed

Theory of Operation



- When the excited electron in the outer orbital returns to the lower energy level of the inner, vacant orbital, energy is released in the form of a photon

❖ For work in atomic absorption spectrometry, a primary light source must be added, either a hollow-cathode lamp or an electrodeless discharge lamp



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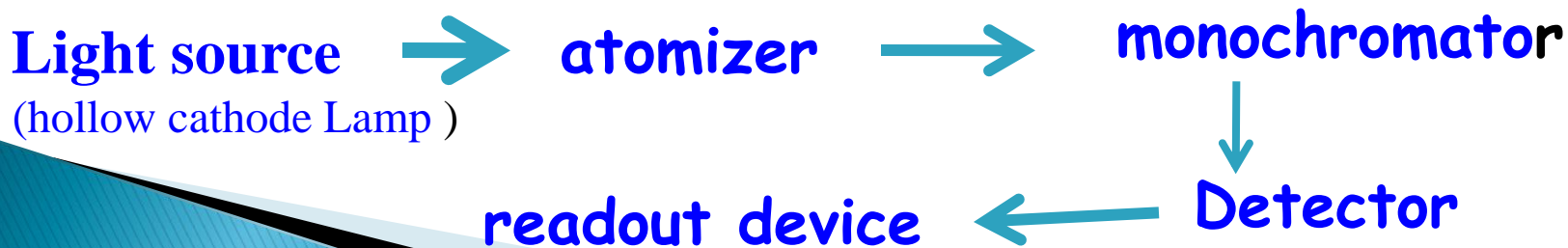
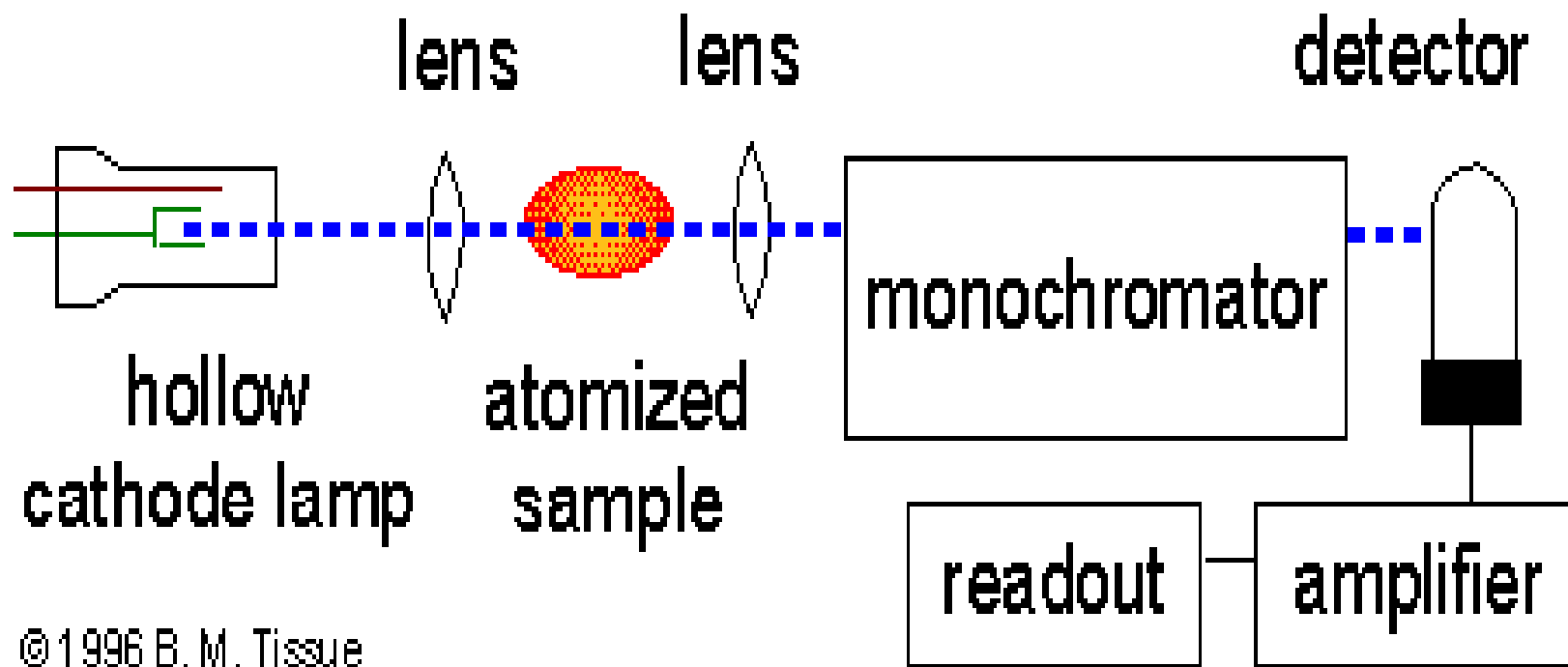
The solvent of the solution is evaporated and all materials present in the sample are vaporized and dissociated to atoms at the very high temperature.

- ❖ The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels.
- ❖ The analyte concentration is determined from the amount of absorption.

Cont...

- ✓ The sample is atomized at a very high temperature (2500-3000 °C) and the free atoms have line spectrum.
- ✓ It means that they can only absorb the energy of light at discrete energy levels according to the excitations of electrons.
- ✓ There are no vibration or rotation energy levels that would widen the lines to bands in the spectrum (like it happens in the case of UV-Vis).

Instrumentation for AAS



Group discussion

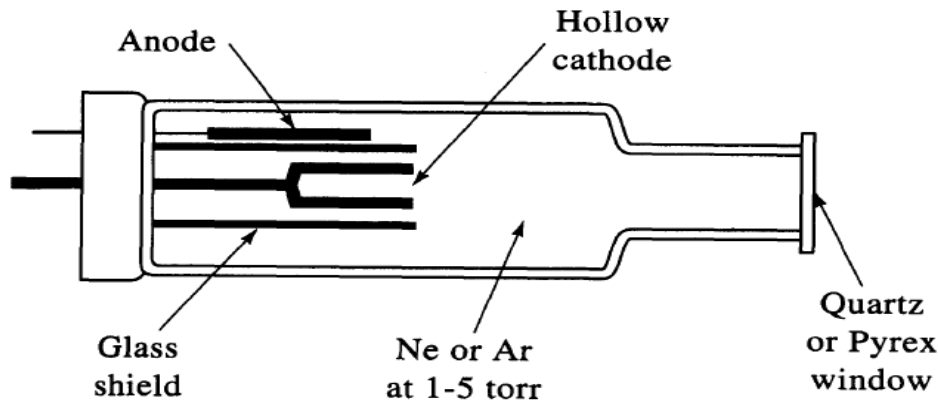
Briefly describe or define

- ❑ Atomic spectroscopy
- ❑ Basic principles of atomic spectroscopy
- ❑ Light sources
- ❑ Detector
- ❑ Atomized sample
- ❑ Wavelength selector
- ❑ readout device and
- ❑ Application of atomic spectroscopy

1 – Light Source

a) hollow cathode lamp

- ▶ The light source is usually a **hollow cathode lamp** of the element that is being measured. It contains a **tungsten anode** and a **hollow cylindrical cathode made of the element to be determined**. These are sealed in a glass tube filled with an inert gas (neon or argon)
- ▶ Each element has its own unique lamp which must be used for that analysis.



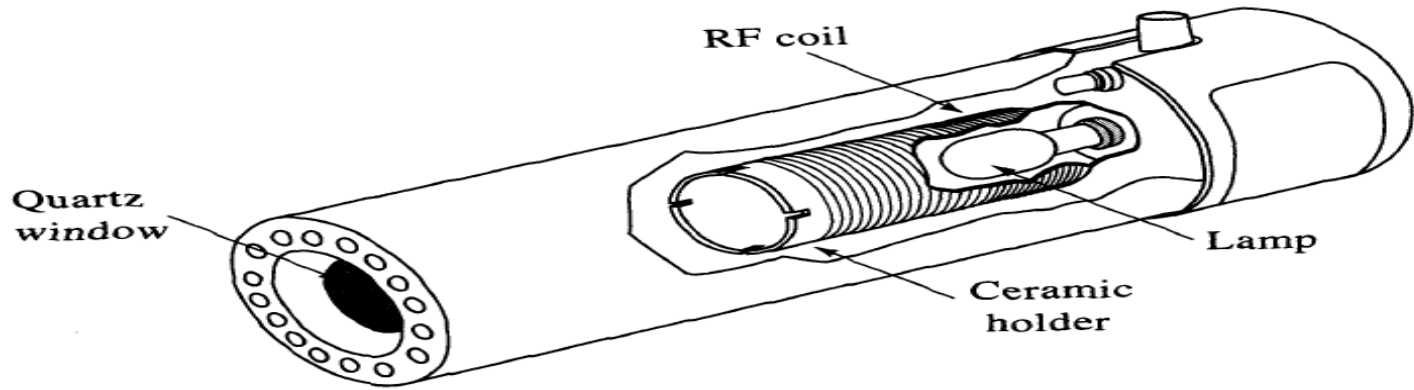
hollow cathode lamp

N.B there also exist a Multi element lamps are available

How it works?

- Applying a potential difference between the anode and the cathode leads to the ionization of some gas atoms .
- These gaseous ions bombard the cathode and eject metal atoms from the cathode in a process called **sputtering**. Some sputtered atoms are in excited states and emit radiation characteristic of the metal as they fall back to the ground state .

b) Electrodeless Discharge Lamp (EDL)



How it works ?

- ❖ Electrodeless discharge lamps (EDLs) consist of an element or a salt of the element sealed in a quartz bulb that contains an inert-gas atmosphere.
- ❖ The bulb is contained in a ceramic cylinder on which RF coil is wound.

- ▶ When RF field of sufficient power is applied, the inert gas is ionized and the coupled energy vaporizes the element and excites the atoms inside the bulb, resulting in the emission of the characteristic spectrum. EDLs and amounts usually are interchangeable with hollow-cathode lamps.
- ▶ EDLs are typically **much brighter** and, in some cases, provide **better sensitivity** than comparable hollow-cathode lamps, and they are preferred for **certain volatile elements**. They offer better **precision and lower detection limits** and are preferred for analyses that are noisy due to weak hollowcathode emission.
- ▶ Lamps are available for these elements: As, Bi, Cd, Cs, Ge, Hg, K, P, Pb, Rb, Sb, Se, Sn, Te, Ti, Tl, and Zn.

How it works ?

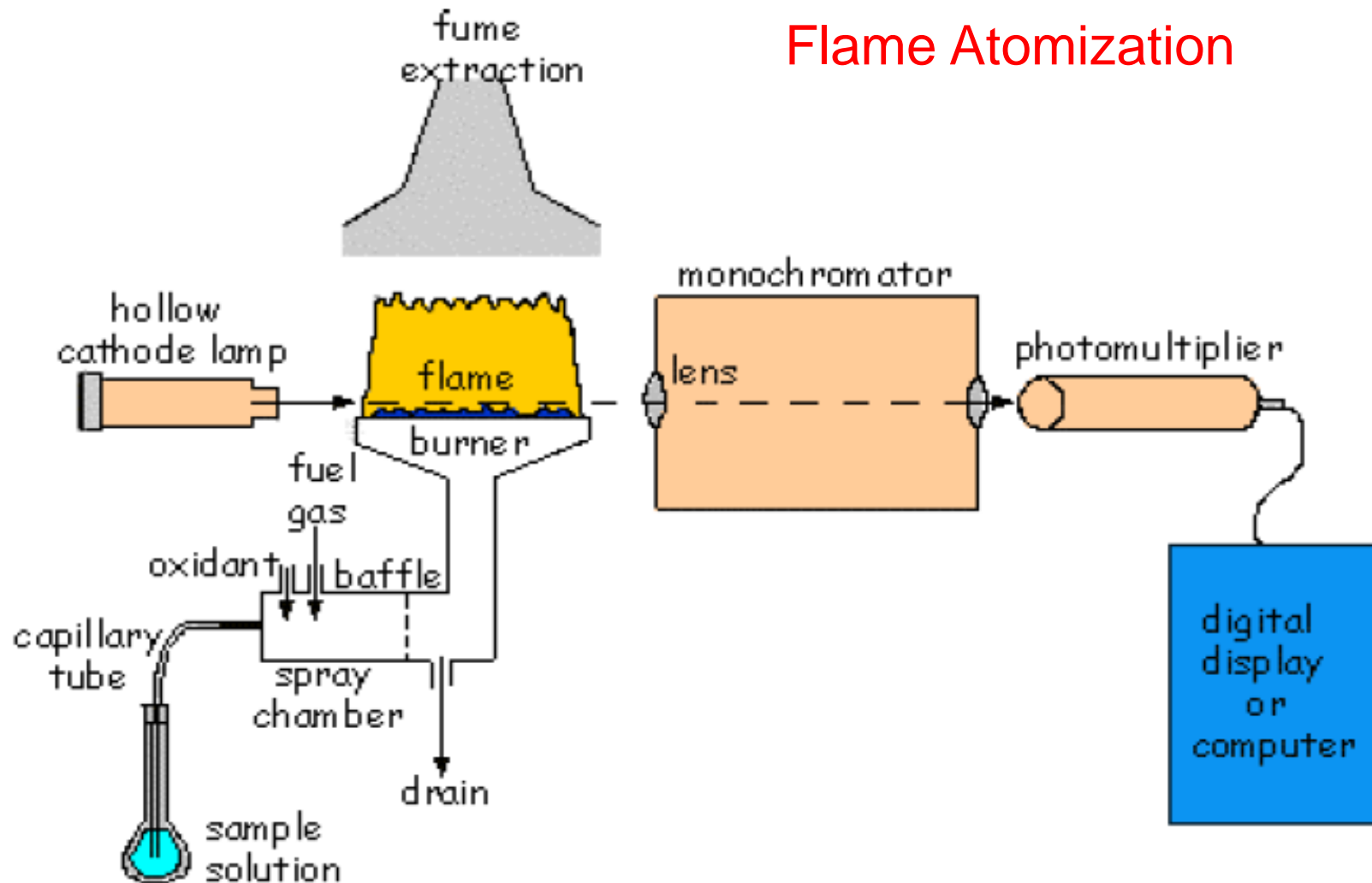
- ▶ 300 V applied between anode (+) and metal cathode (-)
- ▶ Ar ions bombard cathode and sputter cathode atoms
- ▶ Fraction of sputtered atoms excited, then fluoresce
- ▶ Cathode made of metal of interest (Na, Ca, K, Fe...)
 - ✓ different lamp for each element
 - ✓ restricts multielement detection
- ▶ Hollow cathode to maximize probability of redeposition on cathode restricts light direction.

2 – Atomizer

Elements to be analyzed needs to be in atomic state

- ▶ The process of converting an analyte in solid, liquid, or solution form to a free gaseous atom is called **atomization**.
- ▶ Atomization is usually performed by:
 - Flames- **uses flame as atomizer**
 - Furnaces- **uses electrically heated furnace**
 - Plasmas- **uses ionized argon gas**

Flame Atomization



- Sample solutions are usually introduced into a nebuliser by being sucked up a capillary tube . In the nebuliser the sample is dispersed into tiny droplets , which can be readily broken down in the flame.

a) Flame Atomization

Degree of atomization is temperature dependent.

Table 1. Vary flame temperature by fuel/oxidant

Fuel	Oxidant	Temperature (K)
Acetylene	Air	2,400 - 2,700
Acetylene	Nitrous Oxide	2,900 - 3,100
Acetylene	Oxygen	3,300 - 3,400
Hydrogen	Air	2,300 - 2,400
Hydrogen	Oxygen	2,800 - 3,000
Cyanogen	Oxygen	4,800

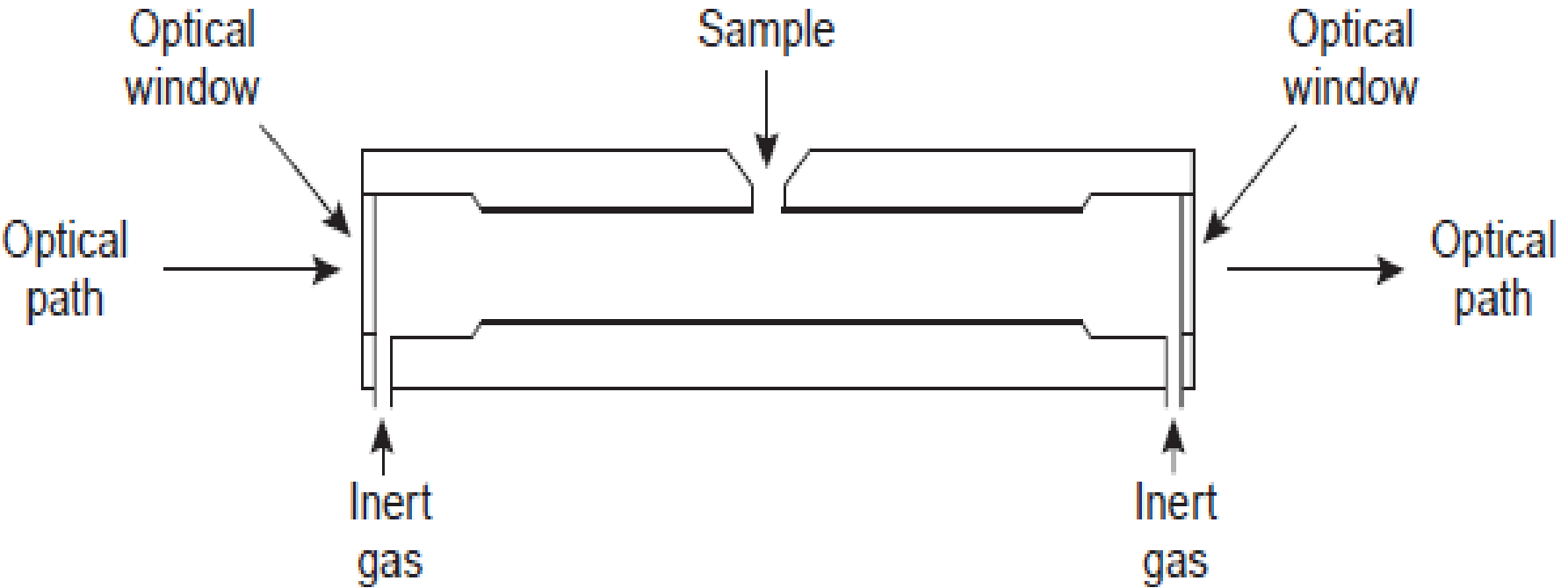
Table 2 Degree of ionization of elements in flames

Element	Air-propane 2200 K	Oxygen-hydrogen 2450 K	Oxygen-acetylene 2800 K	Nitrous oxide-acetylene 3230 K
Li	<0.01	0.9	16	68
Na	0.3	5.0	26	82
K	2.5	32	82	98
Rb	13.5	44	90	99
Cs	28.3	70	96	100
Be				0
Mg				3
Ca	<0.01	1.0	7.3	43
Sr	<0.1	2.7	17	71
Ba	1.0	8.6	43	92
Al				17

- ▶ A significant **disadvantage** to flame atomizers is that the efficiency of atomization may be quite poor. This may occur for two reasons.
- First, the majority of the aerosol mist produced during nebulization consists of droplets that are too large to be carried to the flame by the combustion gases. Consequently, as much as 95% of the sample never reaches the flame.
- the large volume of combustion gases significantly dilutes the sample.
- ▶ ppm concentration (part per million, that is mg kg^{-1} or mg/L in case of dilute solutions

b) Graphite furnace/electrothermal atomizer

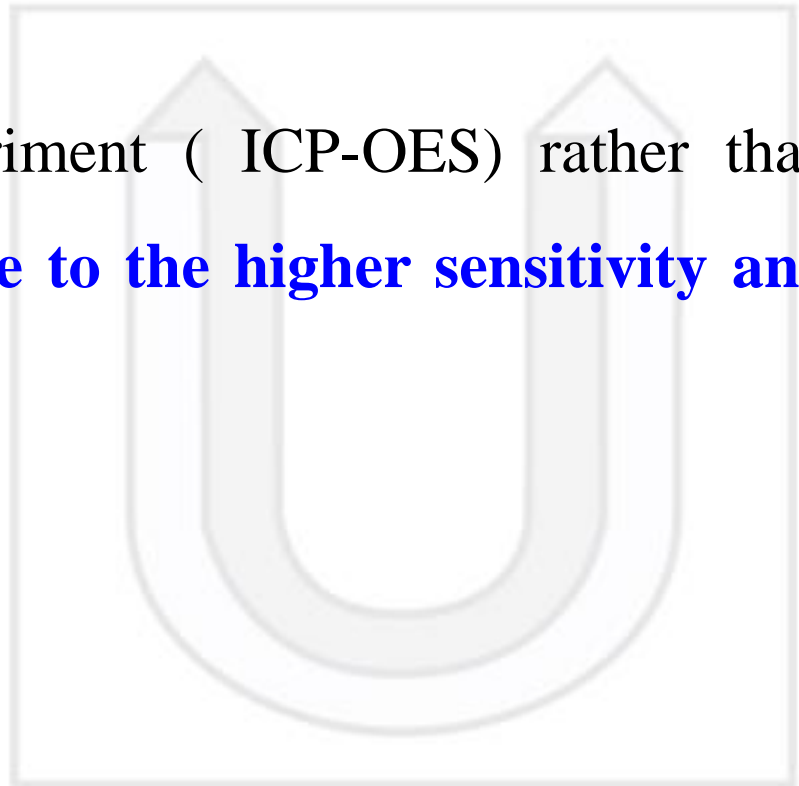
- **A significant improvement in sensitivity is achieved by using resistive heating in place of a flame.**
- **A typical electrothermal atomizer, also known as a graphite furnace, consists of a cylindrical graphite tube approximately 1–3 cm in length, and 3–8 mm in diameter**
- **The assembly also allows for the passage of a continuous stream of inert gas, protecting the graphite tube from oxidation, and removing the gaseous products produced during atomization.** A power supply is used to pass a current through the graphite tube, resulting in resistive heating.



- Improved sensitivity over flame sources. (Hence) less sample is required.
- Measurements could be done at ppb level (part per billion, $\text{ppb} = 10^{-3} \text{ ppm}$, that is $\mu\text{g kg}^{-1}$ or $\mu\text{g L}^{-1}$)

c) Inductively Coupled Plasmas

- ✓ Enables much higher temperatures to be achieved. Uses Argon gas to generate the plasma.
- ✓ **Temps ~ 6,000-10,000 K.**
- ✓ Used for emission experiment (ICP-OES) rather than absorption experiment **due to the higher sensitivity and elevated temperatures.**



ICP-MS

- ▶ An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer.

Cont....

- ✓ ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICP-AES).
- ✓ Detection limits for most elements equal to or better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
- ✓ Higher throughput than GFAAS
- ✓ The ability to handle both simple and complex matrices with **a minimum of matrix interferences** due to the high-temperature of the ICP source
- ✓ Superior detection capability to ICP-AES with the same sample throughput

Sample Preparation:

- ❖ A disadvantage of flame spectroscopic methods is the requirement that the sample be introduced into the excitation source in the form of a solution, most commonly an aqueous one.
- ❖ Unfortunately, many materials of interest, such as soils, animal tissues, plants, petroleum products and minerals are not directly soluble in common solvents, and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization.

- ❖ Indeed, the decomposition and solution steps are often **more time consuming and introduce more error than the spectroscopic measurement itself**. Some of the common methods used for decomposing and dissolving samples for atomic absorption methods include
 - **treatment with hot mineral acids; oxidation with liquid reagents, such as sulfuric, nitric, or perchloric acids.**
 - **Alkaline fusion**
 - ❖ **Graphite furnace AAS can take solid samples directly.**

For metals extraction

- ▶ Dry ashing
- ▶ Wet digestion using mixture of acids
- ✓ Digestion on a hot plate
- ✓ Kjeldahal digestion fitted with a reflux condenser
- ✓ Microwave digestion

Interferences in AAS

❖ Matrix interference

- ✓ acid concentration
- ✓ Viscosity of the sample
- ✓ Incomplete digestion of the organic matter

❖ Chemical interference

- ✓ Insufficient temperature to dissociate molecular form of the analyte
- ✓ Effect of phosphate on Ca and Mg

❖ Ionization Interference

- ✓ which is often encountered in hot flames
- ✓ the dissociation process does not necessarily stop at the ground state atom rather it may ionize if additional energy is applied
- ▶ common with the hotter nitrous oxide-acetylene flame

Application of Atomic Absorption Spectrometry

1. Qualitative detection

2. For the quantitative determination of more than 60 metals elements

Parameters used for digestion

- Heating temperature
- Reagent volume
- Time

Analysis of samples

Optimization of the working procedure

✚ analyst need to develop an **Optimum working procedure** in order to **get a reliable result** from an analytical experiment.

Example:

- ✚ To get **clear colorless sample solution** different working procedures were assessed using **HNO₃** and **HClO₄** acid mixtures.
- ✚ For this parameters such as volume of the acid mixture, digestion time and digestion temperature were used.
- ✚ Nineteen trials were made to identify optimum conditions.

Digestion of the Fruit Samples

- ✦ 0.5 g of the dried and grounded fruit sample was accurately weighed on a digital analytical balance.
- ✦ This is transferred quantitatively in to a 100 mL round bottom digestion flask.
- ✦ To the fruit samples, 5 mL of freshly prepared 4:1 mixture of 69-72% of conc. HNO_3 and 70% of conc. HClO_4 was added, respectively.

Cont...,

- ⊕ The mixture was then heated on **Kjeldah heating apparatus** fitting the flask to a **reflux condenser** for the first **30 min** by setting the temperature (**120 °C**) and followed by (**270 °C**) as maximum temperature for the other **2:00** hours.



Table 4. Different methods tested during the optimization of procedures for Croton leaves infusion samples.

No	^a Volume of ^b CLI (mL)	Reagent volumes (mL)			Maximum temperature (°C)	Time (min)	Result
		HClO ₄	HNO ₃	Total volume			
1	25	1	2	3	300	180	Yellowish
2	25	2	2	4	300	180	Yellowish and turbid
3	25	1	3	4	300	180	Yellowish with no turbidity
4	25	1	4	5	300	180	Clear and colorless
5	25	2	3	5	300	180	Clear and colorless
6	25	3	3	6	350	180	Clear but yellowish
7	25	2	4	6	300	180	Clear and yellowish
8	25	1	4	5	240	150	Clear and colorless
9	25	1	4	5	240	120	Clear and turbid
10	25	1	4	5	210	120	Clear but yellowish
11	25	1	4	5	270	210	Clear but yellowish
12	25	1	4	5	350	180	Clear and turbid

^a Volume of the sample was reduced to about 3 mL by evaporating.


^b Croton leaves infusion.

Cont...,

- ⊕ The **digested solutions** were allowed **to cool** for **20 min** without **dismantling the condenser** from the flask and for **10 min** after removing the condenser.

- ⊕ To the cooled solution, two **10 mL** of **deionized water** were added to dissolve the **precipitate** formed on cooling and **gentle swirled** to reduce **dissolution** of the filter by digest residue.

Cont...,

- ⊕ The cooled digested samples were filtered into a 50 mL standard flask with a Whatman filter paper (110 mm, diam.) to remove any suspended or turbid matter.
 - ⊕ Subsequent rinsing the filtrate with 5 mL deionized water followed until the volume reaches the mark.
 - ⊕ For each bulk samples, triplicate digestions were carried out.
 - ⊕ Then the solutions will be stored in tightly capped polyethylene bottles and kept in refrigerator.
- 

Cont...,

- ✦ Intermediate standard solutions containing 10 mg/L were prepared from the atomic absorption spectroscopy standard stock solutions that contained 1000 mg/L.
- ✦ These intermediate standards were diluted with distilled-deionized water to obtain four working standards for each metal of interest.
- ✦ Three replicate determinations were carried out on each sample by optimizing different FAAS condition as shown in Table 7.

Instrumental operating conditions

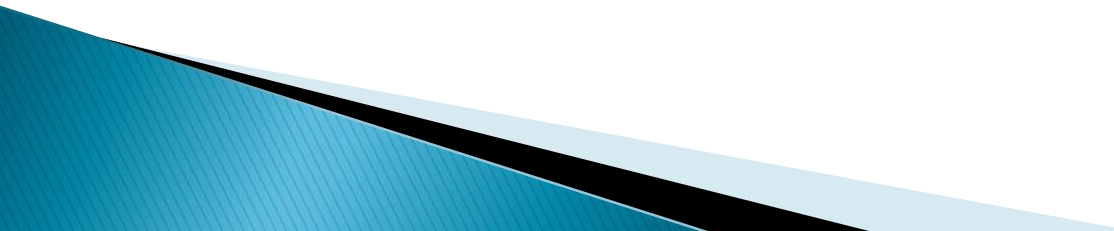
Table 7: Instrumental operating conditions for the determination of metals in fruit samples using flame atomic absorption spectrophotometer

Element	Wavelength (nm)	Detection limit (mg/L)	Slit width (nm)	Energy (eV)
Ca	422.7	0.01	0.7	3.606
Mg	285.2	0.001	0.7	3.994
Fe	248.3	0.03	0.2	3.256
Mn	279.5	0.001	0.7	3.971
Zn	213.9	0.005	0.7	3.047
Cu	324.7	0.02	0.7	3.327
Co	240.7	0.05	0.2	2.746
Cr	357.9	0.05	0.7	3.536
Ni	341.5	0.04	0.2	2.928
Cd	228.9	0.005	0.7	3.129
Pb	217.0	0.1	0.7	3.490

Calibration Curve

- A calibration curve is used to determine the unknown concentration of an element in a solution. The instrument is calibrated using several solutions of known concentrations. The absorbance of each known solution is measured and then a calibration curve of concentration vs absorbance is plotted.
- The sample solution is fed into the instrument, and the absorbance of the element in this solution is measured. The unknown concentration of the element is then calculated from the calibration curve either by extrapolation or using line equation ($Y = mx + b$)

Instrument calibration

- ② Calibration curves were prepared to determine the concentration of the metals in the sample solution.
 - ② The instrument was calibrated using **four series of working standards**.
 - ② The **working standard solutions** of each metal were prepared from the **10 mg/L intermediate standard solutions** of their respective metals.
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Determining concentration from Calibration Curve

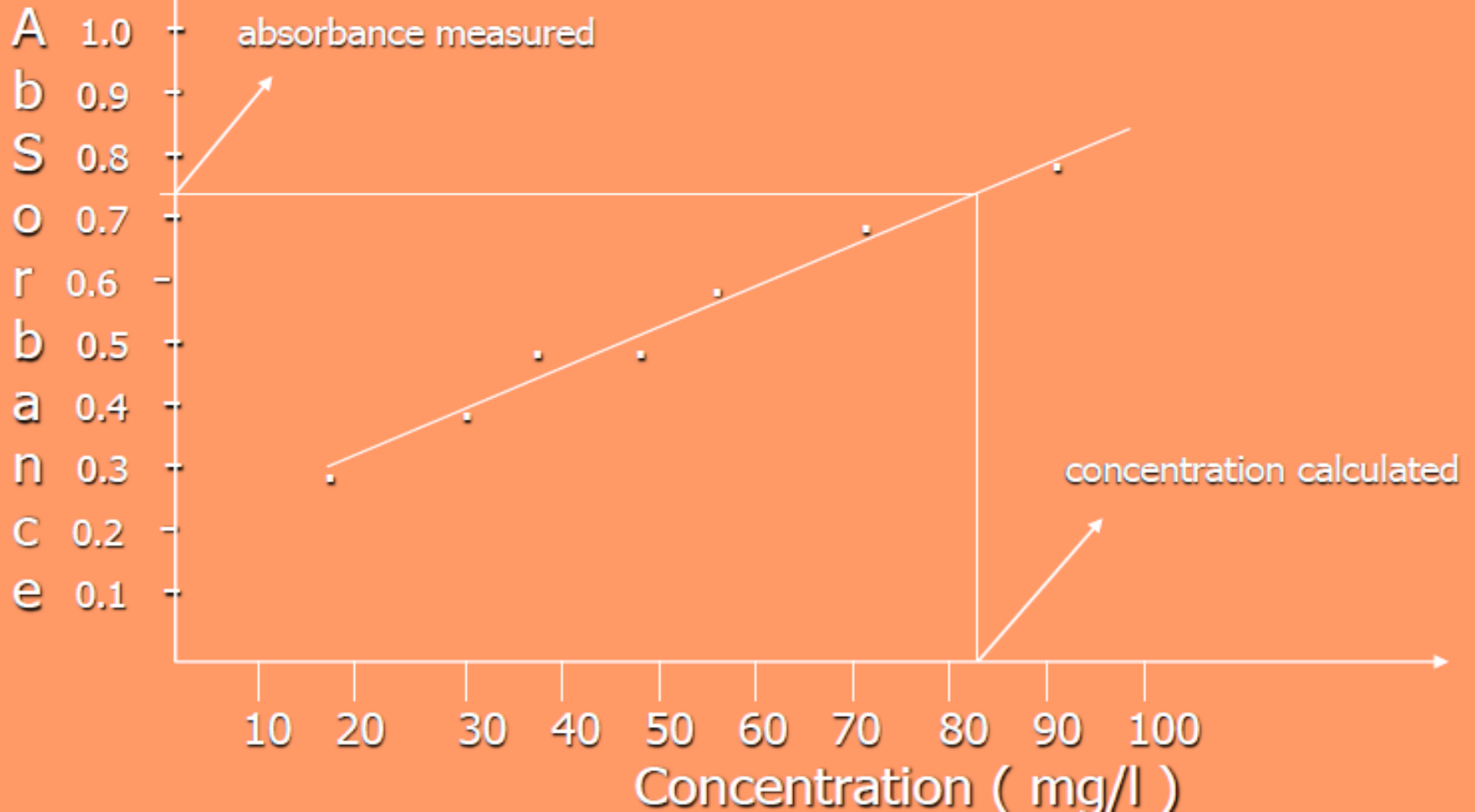


Table 6. Concentrations of working standard solutions and correlation coefficients of the calibration curves.

Metal	Wavelength (nm)	Conc. of intermediate standard solution (mg/L)	Conc. of working standard (mg/L)	Correlation coefficient
Ca	422.7	10	0.50, 1.0, 2.0	0.99994
Mg	285.2	10	0.25, 0.50, 1.0	1.0
Fe	248.3	10	0.50, 1.0, 1.5	0.99997
Mn	279.5	10	0.25, 0.50, 1.0	0.99993
Cu	324.8	10	0.50, 1.0, 1.5	0.99952
Zn	213.9	10	0.20, 0.40, 0.80	0.99924
Co	240.7	10	0.25, 0.50, 1.0	0.99953
Ni	341.5	10	0.25, 0.50, 1.0	0.99999
Cr	357.9	10	0.50, 1.0, 1.5	0.99933
Cd	228.9	10	0.25, 0.5, 1.0	0.99981
Pb	217.0	10	0.2, 0.4, 0.8	0.99999

Method validation

- The efficiency of the **optimized procedure** was checked by spiking known standards of metals dividing the **11 metals** in to **two** groups.
- The spiked samples were digested in triplicate following the same digestion procedure developed for our sample.
- The digested spiked samples were finally analyzed for their respective metals using FAAS.
- Then the **percentage recovery** of the analyte was calculated by:
$$\% \text{Recovery} = \frac{\text{CM in spiked sample} - \text{CM in non spiked Sample}}{\text{CM added for spiking}} \times 100$$

Table 8. Recovery test values for Croton leaves sample.

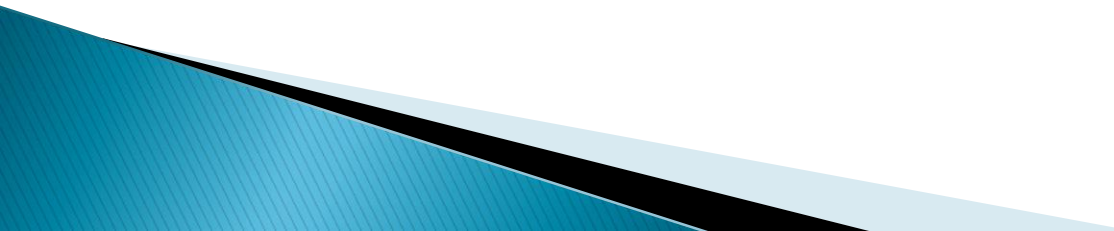
Metal	^a Conc. in sample ($\mu\text{g/g}$)	Amount added ($\mu\text{g/g}$)	^b Conc. in spiked sample ($\mu\text{g/g}$)	^c Recovery (%)
Ca	7040	1408	8406 \pm 12	97 \pm 7
Mg	2961	592	3511 \pm 8	93 \pm 2
Fe	581	116	698 \pm 5	102 \pm 3.5
Mn	283	56	335 \pm 3	98 \pm 2.5
Zn	60.5	12	71.3 \pm 1.5	94 \pm 1.4
Cu	18.6	10	27.6 \pm 0.8	96 \pm 0.25
Co	21.8	12	71.4 \pm 4	95 \pm 4.3
Cr	87.5	18	104 \pm 5	92 \pm 8
Ni	26.2	10	35.8 \pm 0.3	98 \pm 5.1
Cd	1.08	1.08	2.19 \pm 0.4	103 \pm 6.2
Pb	21.9	8.8	30.2 \pm 5.1	94 \pm 2.6

^a Mean concentration of samples analyzed in triplicate.

^b Mean concentration \pm SD of samples spiked in triplicate.

^c Mean recovery \pm SD of percentage recoveries of triplicate analyses.

Statistical Analysis

- ✦ As the sample means vary from one sample to another, **ANOVA** tests whether there is a **difference** between the **samples means** and thus enabling to explain the **cause of error**.
 - ✦ For the present study, the **significance of variation** between samples was analyzed using **one-way ANOVA** using origin 6.1.
- 

Atomic emission spectroscopy

Cont....

- Atomic emission spectroscopy is also an analytical technique that is used to measure the concentrations of elements in samples.
- It uses quantitative measurement of the emission from excited atoms to determine analyte concentration.

Cont....

- The analyte atoms are promoted to a higher energy level by the sufficient energy that is provided by the high temperature of the atomization sources .
- The excited atoms decay back to lower levels by emitting light. Emissions are passed through monochromators or filters prior to detection by photomultiplier tubes.

Cont....

- The instrumentation of atomic emission spectroscopy is the same as that of atomic absorption.
- In atomic Emission the sample is atomized and the analyte atoms are excited to higher energy levels all in the atomizer.

Cont...

- ❖ The source of energy in Atomic Emission could be a flame like the one used in atomic absorption ,or an inductively coupled plasma (ICP) .
- **The flame** (1700 – 3150 °C) is most useful for elements with relatively low excitation energies like sodium, potassium and calcium.
- **The ICP** (6000–8000 °C) has a very high temperature and is useful for elements of high excitation energies .

Comparison Between Atomic Absorption and Emission Spectroscopy

Absorption

- Measure trace metal concentrations in complex matrices .
- Atomic absorption depends upon the number of ground state atoms .

Emission

- Measure trace metal concentrations in complex matrices .
- Atomic emission depends upon the number of excited atoms .

- It measures the radiation absorbed by the ground state atoms.
- Presence of a light source (HCL) .
- The temperature in the atomizer is adjusted to atomize the analyte atoms in the ground state only.

- It measures the radiation emitted by the excited atoms .
- Absence of the light source .
- The temperature in the atomizer is big enough to atomize the analyte atoms and excite them to a higher energy level.

APPLICATIONS OF AAS

There are many applications for atomic absorption:

- **Clinical analysis:** Analyzing metals in biological fluids such as blood and urine.
- **Environmental analysis:** Monitoring our environment example finding out the levels of various elements in rivers, seawater, drinking water, air, and petrol.

- **Pharmaceuticals.** In some pharmaceutical manufacturing processes, minute quantities of a catalyst used in the process (usually a metal) are sometimes present in the final product. By using AAS the amount of catalyst present can be determined.
- **Industry :** Many raw materials are examined and AAS is widely used to check that the major elements are present and that toxic impurities are lower than specified example in concrete, where calcium is a major constituent, the lead level should be low because it is toxic.

Cont.....

- **Mining:** By using AAS the amount of metals such as gold in rocks can be determined to see whether it is worth mining the rocks to extract the gold .
- Trace elements in food analysis
- Trace element analysis of cosmetics
- Trace element analysis of hair

Thank you!