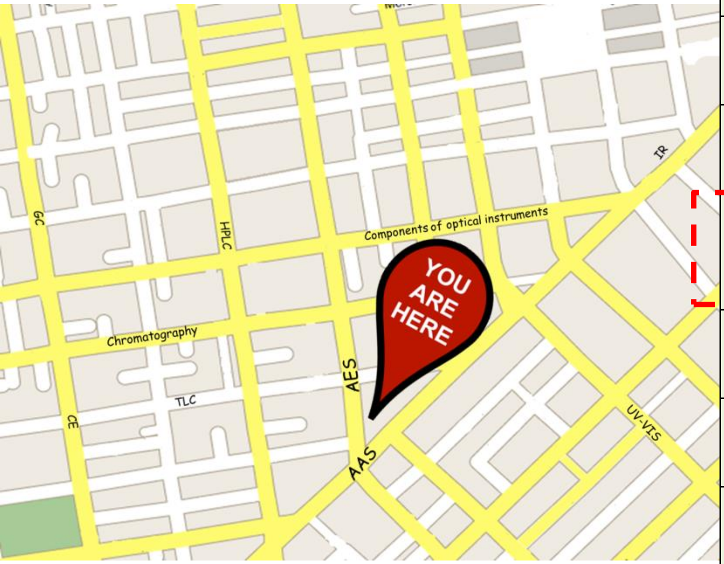
NEPHAR 201
Analytical Chemistry II

Chapter 4
Atomic absorption and emission spectrometry

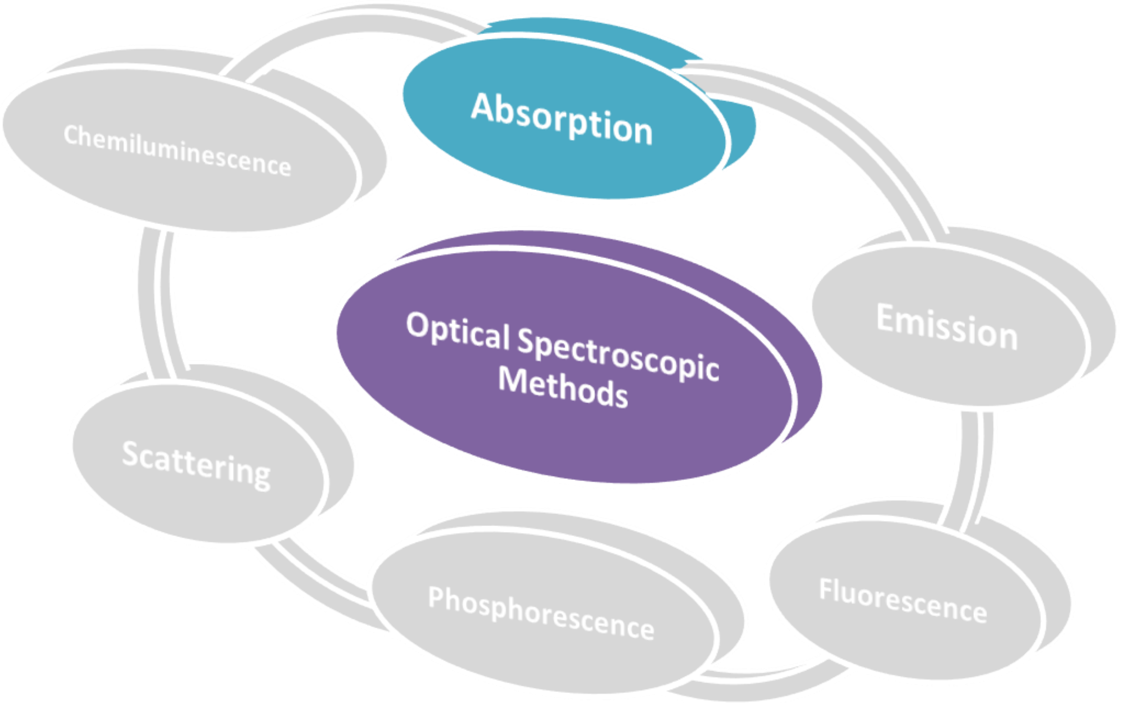
Assist. Prof. Dr. Usama ALSHANA



Week	Topic	Reference Material	Instructor
1 [14/09]	Introduction	Instructor's lecture notes	Alshana
2 [21/09]	An introduction to spectrometric methods	• Principles of Instrumental Analysis, Chapter 6, pages 116-142 • Enstrümantal Analiz- Bölüm 6, sayfa 132-163	Alshana
3 [28/09]	Components of optical instruments	• Principles of Instrumental Analysis, Chapter 7, pages 143-191 • Enstrümantal Analiz- Bölüm 7, sayfa 164-214	Alshana
4 [05/10]	Atomic absorption and emission spectrometry	• Principles of Instrumental Analysis, Chapter 9, pages 206-229, Chapter 10, pages 230-252 • Enstrümantal Analiz- Bölüm 9, sayfa 230-253, Bölüm 10 sayfa 254-280	Alshana
5 [12/10]	Ultraviolet/Visible molecular absorption spectrometry	• Principles of Instrumental Analysis, Chapter 13, pages 300-328 • Enstrümantal Analiz- Bölüm 13, sayfa 336-366	Alshana
6 [19/10]	Infrared spectrometry	• Principles of Instrumental Analysis, Chapter 16, pages 380-403 • Enstrümantal Analiz- Bölüm 16, sayfa 430-454	Alshana
7 [26/10]	Quiz 1 (12.5 %)		Alshana
	Chromatographic separations	• Principles of Instrumental Analysis, Chapter 26, pages 674-700 • Enstrümantal Analiz- Bölüm 26, sayfa 762-787	
8 [02-07/11]	MIDTERM EXAM (25 %)		
9 [09/11]	High-performance liquid chromatography (1)	• Principles of Instrumental Analysis, Chapter 28, pages 725-767 • Enstrümantal Analiz- Bölüm 28, sayfa 816-855	Alshana
10 [16/11]	High-performance liquid chromatography (2)		Alshana
11 [23/11]	Gas, supercritical fluid and thin-layer chromatography	• Principles of Instrumental Analysis, Chapter 27, pages 701-724, Chapter 29 pages 768-777 • Enstrümantal Analiz- Bölüm 27, sayfa 788-815, Bölüm 29 sayfa 856-866, Bölüm 28 sayfa 848-851	Alshana
12 [30/11]	Capillary electrophoresis	• Principles of Instrumental Analysis, Chapter 30, pages 778-795 • Enstrümantal Analiz- Bölüm 30, sayfa 867-889	Alshana
13 [07/12]	Quiz 2 (12.5 %)		Alshana
	Extraction techniques	Instructor's lecture notes	
14 [14/12]	Revision	Instructor's lecture notes and from the above given materials	Alshana
15 [21-31/12]	FINAL EXAM (50 %)		

Atomic Absorption

Optical spectroscopic methods are based upon six phenomena:



Atomic absorption:

A method that measures the concentration of atoms of an element by passing light, emitted by a hollow cathode lamp of that element, through a cloud of atoms from a sample. Only those atoms that are the same as those in the lamp will absorb the light from the lamp. A reduction in the amount of light reaching the detector is seen as a measure of the concentration of that element in the original sample.

Atomic Absorption Spectrometry (AAS)

- **AAS** is the **most widely used** technique for the determination of single elements in analytical samples.
- AAS can be used to determine **over 70 different elements** in solution or directly in solid samples mostly used for determination of metals but less for metalloids and non-metals.

Working Principle

- The analyte in the sample is converted to its elemental state (**atomization**),
- Electrons of the atoms in the atomizer can be promoted to higher orbitals (**excited state**) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength),
- This amount of energy (i.e., **wavelength**) **is specific** to a particular electron transition in a particular element, which gives the technique its elemental selectivity,
- The radiation flux without a sample and with a sample in the atomizer is measured using a **detector**,
- The ratio between the two values (**absorbance**) is converted to analyte concentration using Beer's Law.

Instrumentation

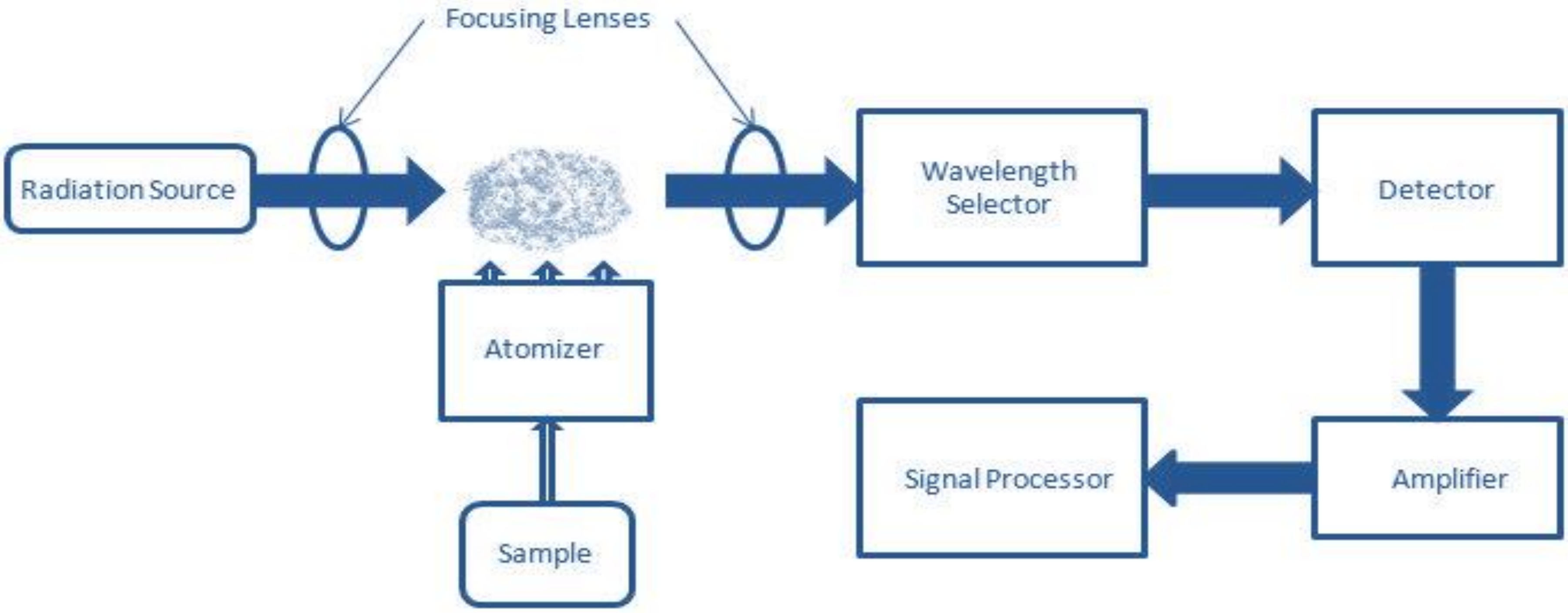
Source lamp

Sample holder

Wavelength selector

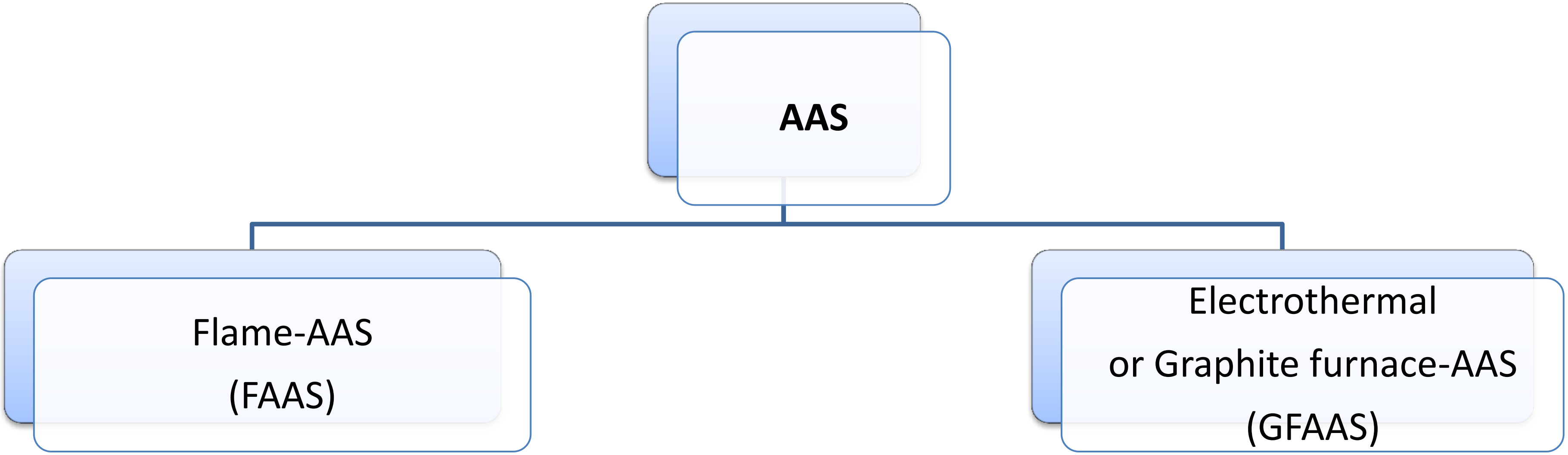
Detector

Signal processor



Atomic absorption spectrometer block diagram

- In order to analyze a sample for its atomic constituents, the element has to be **atomized**.
- The atomizers most commonly used nowadays are **flames** and **electrothermal** (graphite tube) atomizers.
- The atoms should then be irradiated by optical radiation. The radiation source could be **an element-specific line** radiation source or **a continuum radiation source**.
- The radiation then passes through a **monochromator** in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector.



AAS

Flame-AAS (FAAS)

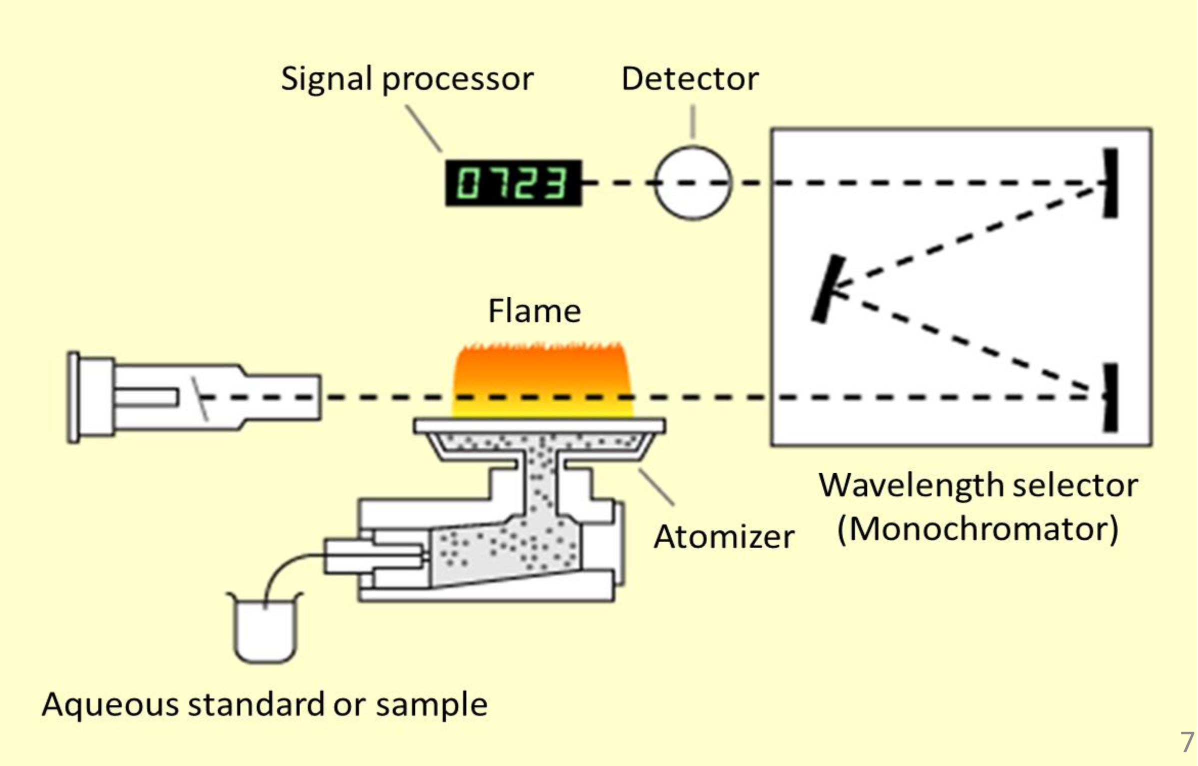
Electrothermal or Graphite furnace-AAS (GFAAS)

Sample Atomization Techniques

- **Atomizers**
  - Flame
  - Electrothermal or Graphite furnace

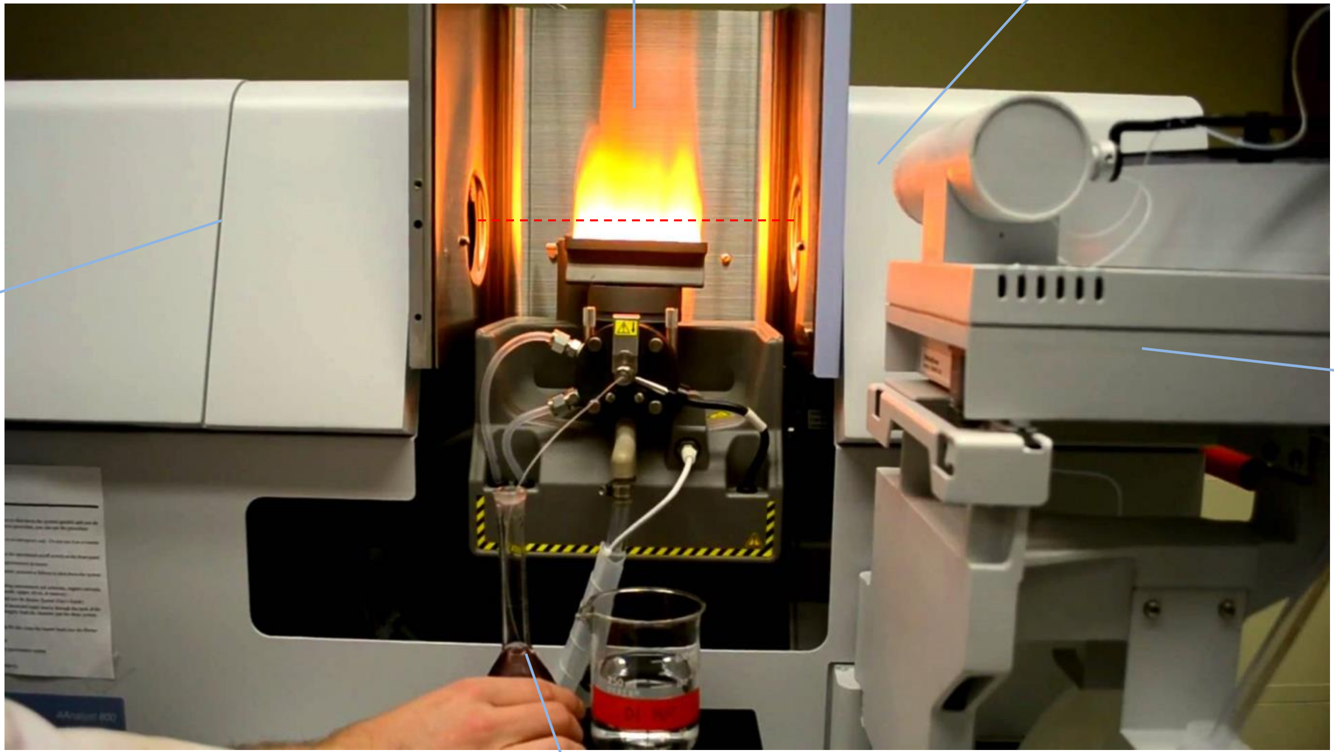
Flame Atomization

In a flame atomizer, a solution of the sample is **nebulized** (sprayed) by a gaseous mixture of an oxidant and a fuel and carried into a flame where **atomization** occurs.



Atomizer (flame)

Wavelength selector



Radiation source

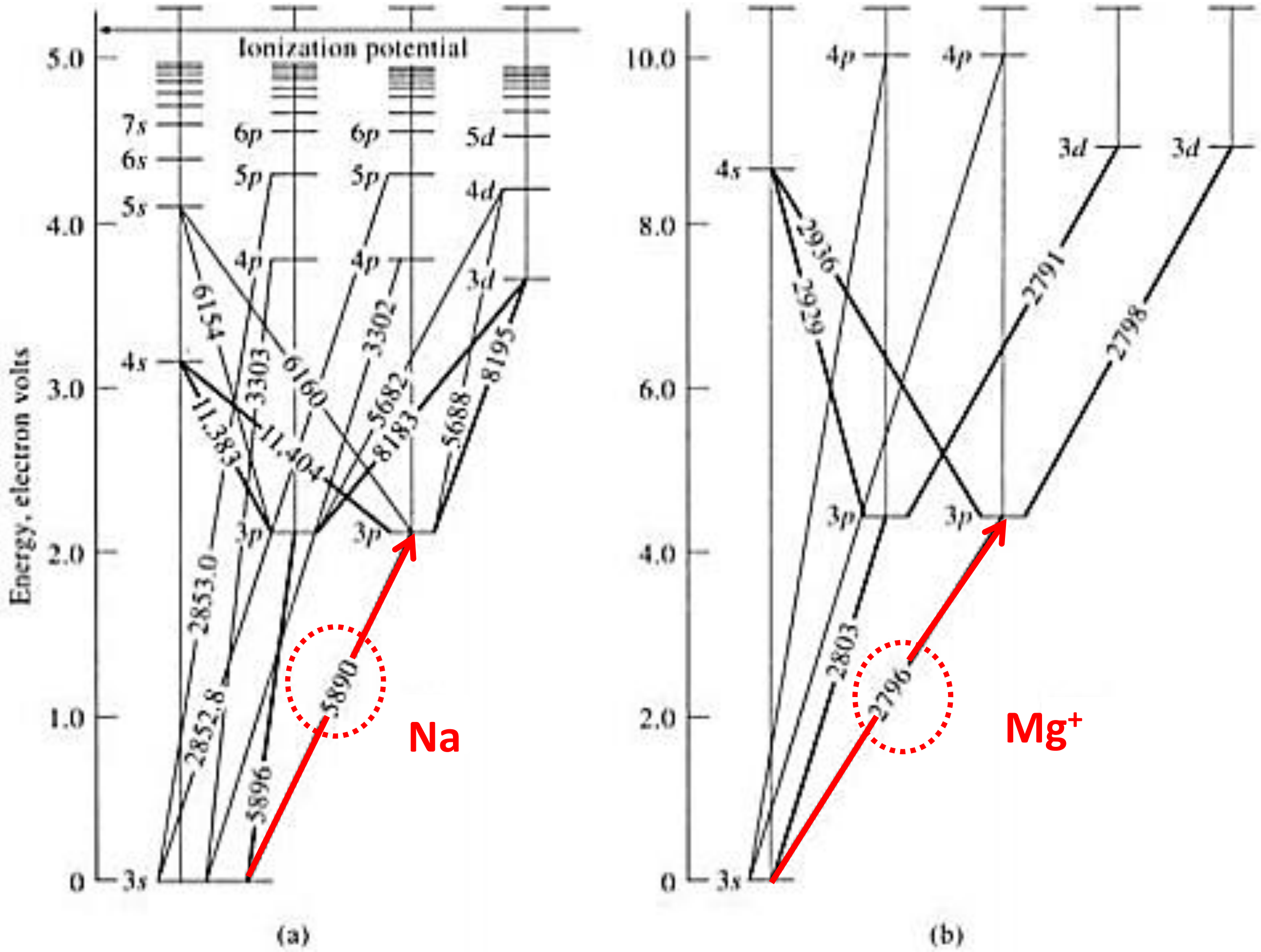
Detector

Aqueous sample

Flame Atomic Absorption Spectrometry (FAAS)

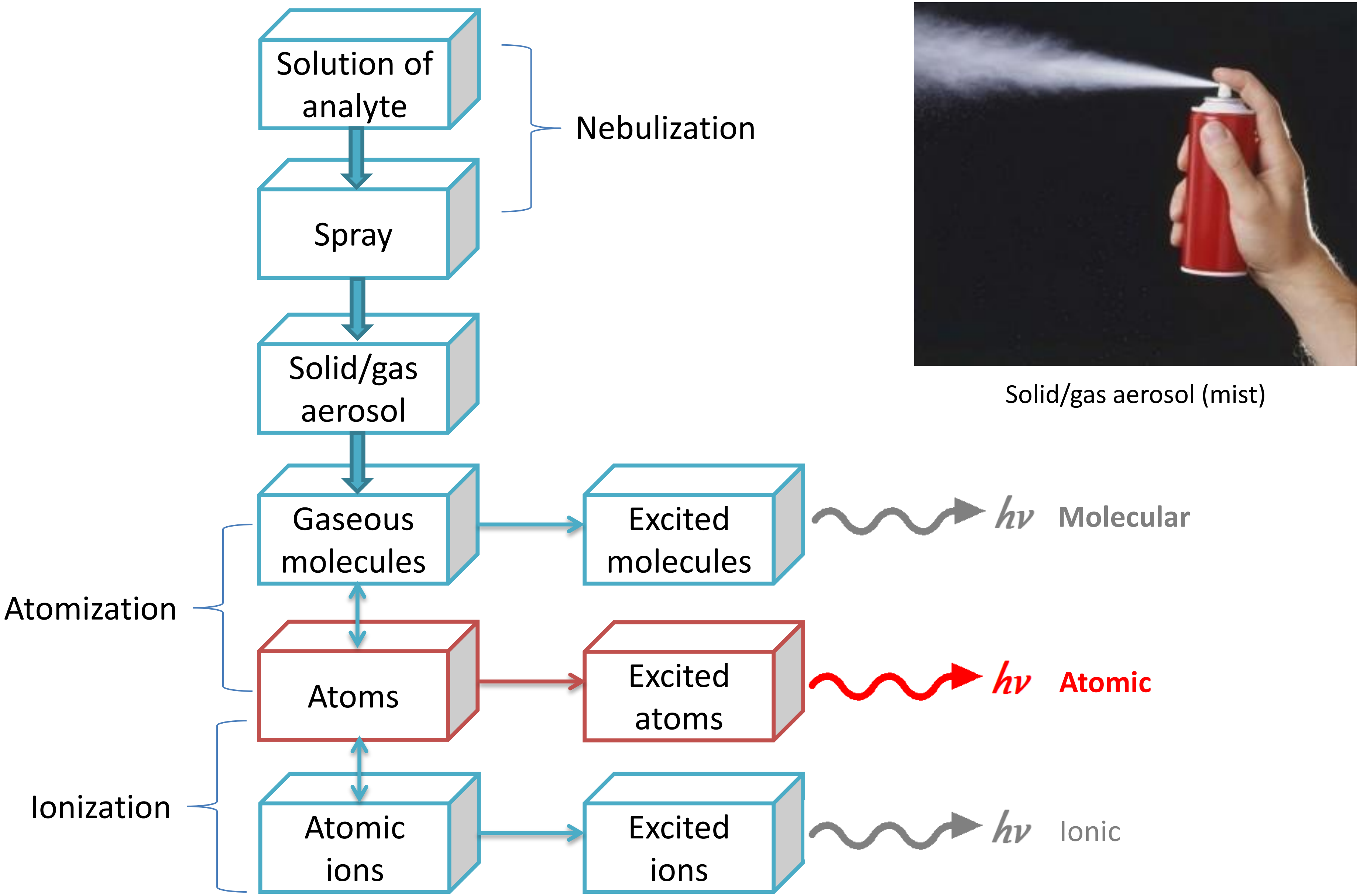
Energy Level Diagrams

- Energy diagrams for elements are helpful to understand the principle of absorption in AAS.



Energy diagrams for: (a) Sodium atom and (b) Magnesium ion

Processes Occurring During Atomization



Solution of analyte

Spray

Nebulization

Solid/gas aerosol

Gaseous molecules

Excited molecules

$h\nu$ Molecular

Atomization

Atoms

Excited atoms

$h\nu$ **Atomic**

Ionization

Atomic ions

Excited ions

$h\nu$ Ionic

Solid/gas aerosol (mist)

Sample Atomization

- The task of an atomizer is to **convert** elements and molecules in the sample **to atomic** analytes in the gaseous state. To do so, flame or electrothermal atomizers are used.

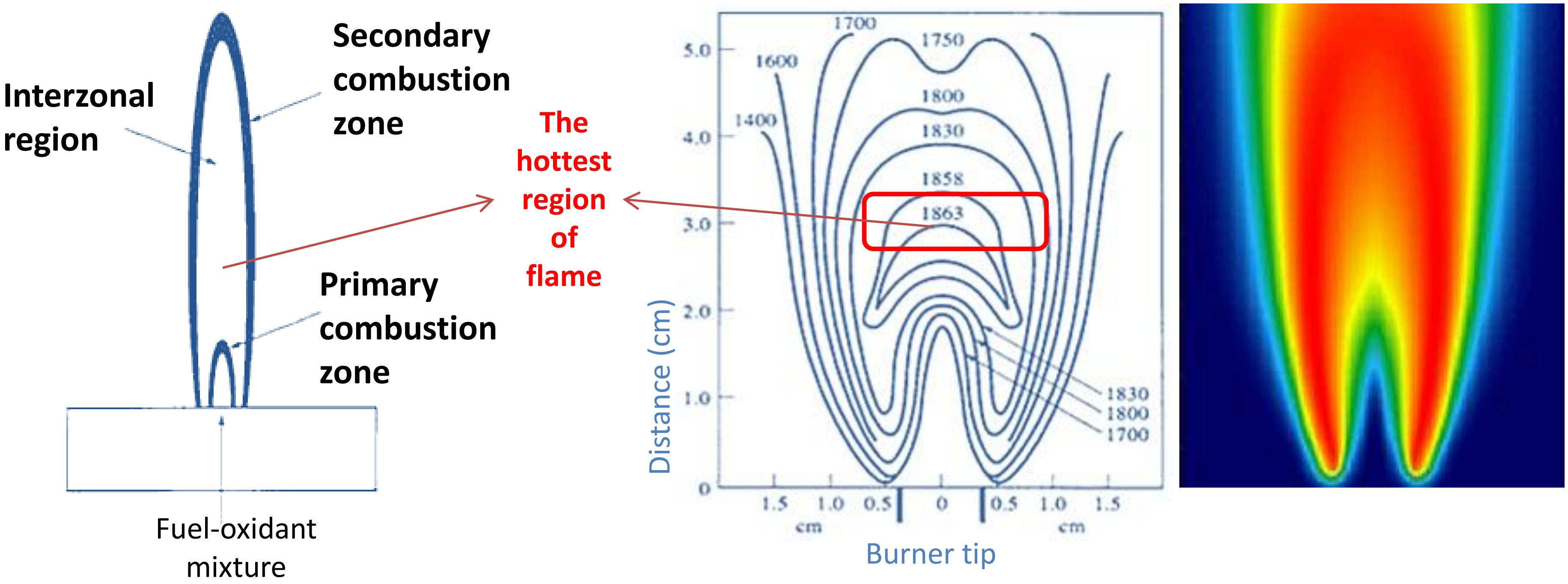
- In AAS, **a high population of atoms** in the ground state **is desired**; as the number of atoms increases, the probability of excitation of atoms and thus absorbance increases.

➢ **Types and properties of flames used in AAS**

Fuel	Oxidant	Temperature (°C)	Max. 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

- **Acetylene-oxygen** flame has the highest temperature and burning velocity,
- The burning velocity is important because:
  1. if the gas flow rate does not exceed the burning velocity, the flame propagates itself back into the burner, giving **flashback**.
  2. if the gas flow rate is equal to the burning velocity, the flame is **stable**,
  3. if the gas flow rate exceeds the burning velocity, the flame **blows off** of the burner.

Flame Structure



Interzonal region

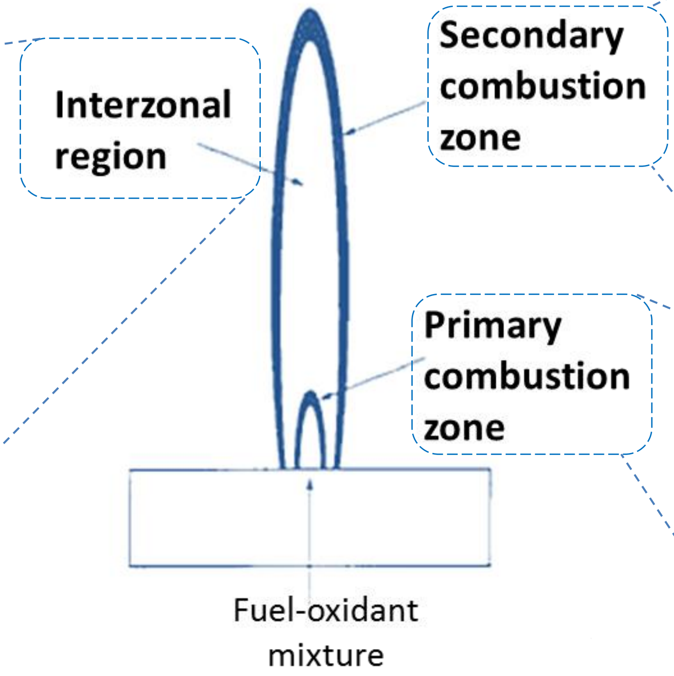
Secondary combustion zone

Primary combustion zone

Fuel-oxidant mixture

The hottest region of flame

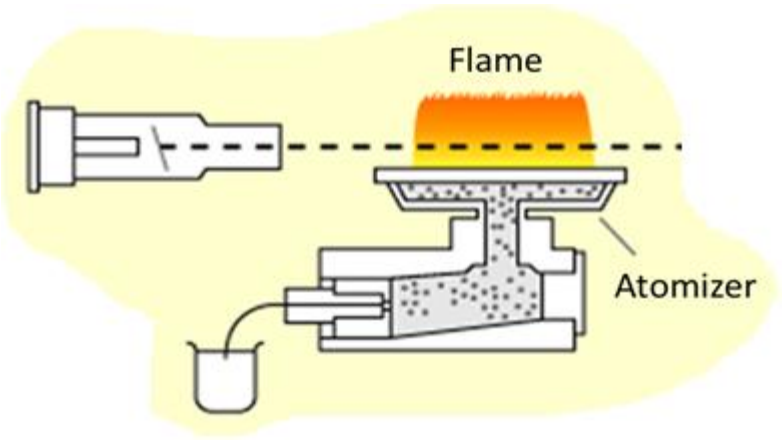
Why is the "Interzonal Region" most suitable for measurement of absorption?



This zone is rich in free atoms that can absorb that wavelength emitted by the source and be excited. This region is the most widely used one in AAS

Atoms are converted to stable oxides which escape into the surroundings. They do not absorb that wavelength

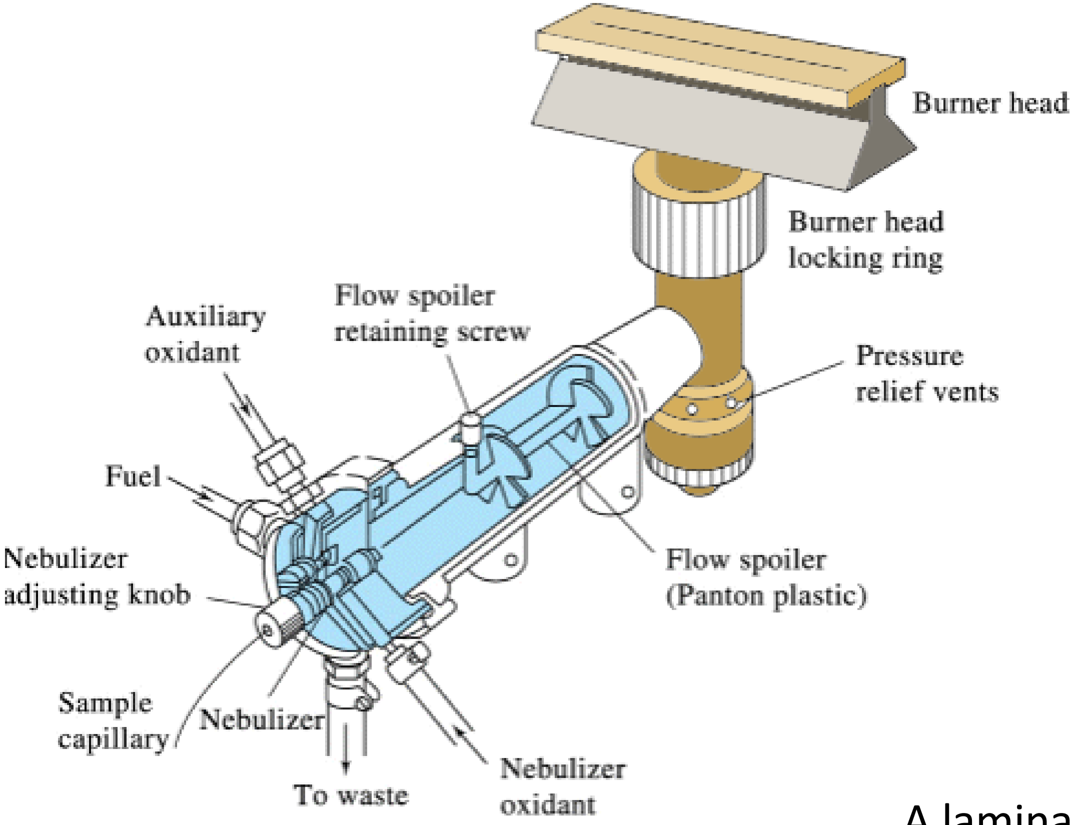
Thermal equilibrium is not reached in this region. Therefore, it is seldom used.



Laminar Flow Burners

- ☐ **Laminar flow burners:**

1. Provide a relatively quiet flame. → Increases reproducibility.
2. Provide a long path length. → Increases sensitivity.

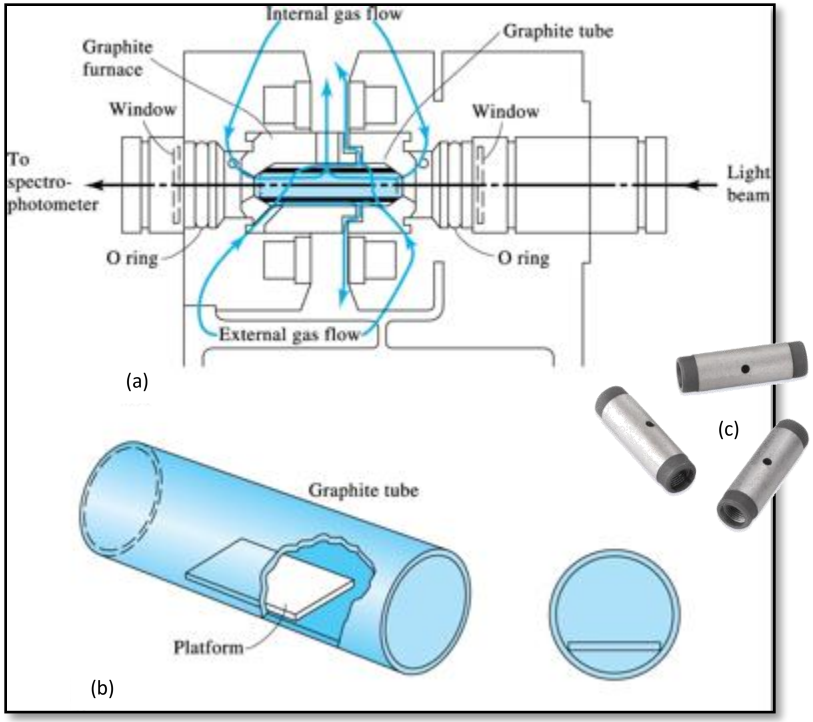


A laminar flow burner

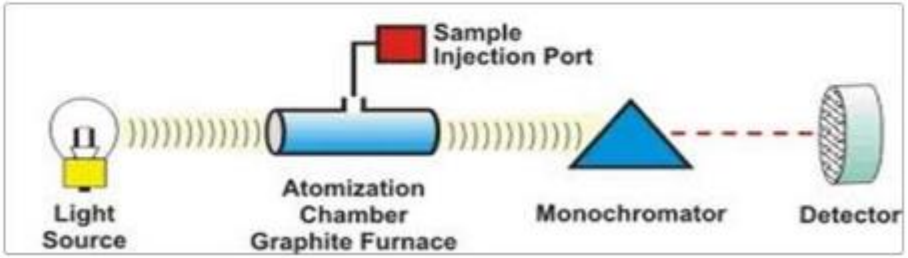
- **Reproducibility** is the ability of an entire experiment or study to be **duplicated**, either by the same researcher or by someone else working independently.

Electrothermal Atomization

- In graphite-furnace AAS, atomization occurs in a **graphite tube** that is open at both ends. Few microliters of the sample are injected onto the tube through a hole.
- As temperature of the tube is raised, the sample is **atomized**.
- Radiation passes from one end of the tube and excites the analytes. The absorbed fraction is measured by the detector at the other end.

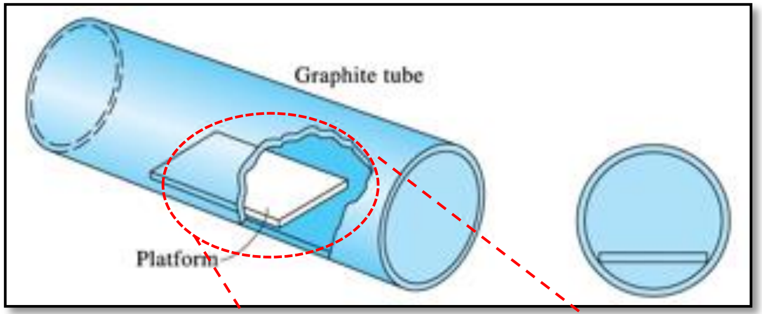


(a) A graphite furnace, (b) L'vov platform and (c) Graphite tubes.



GF-AAS

Why is a L’vov platform used?



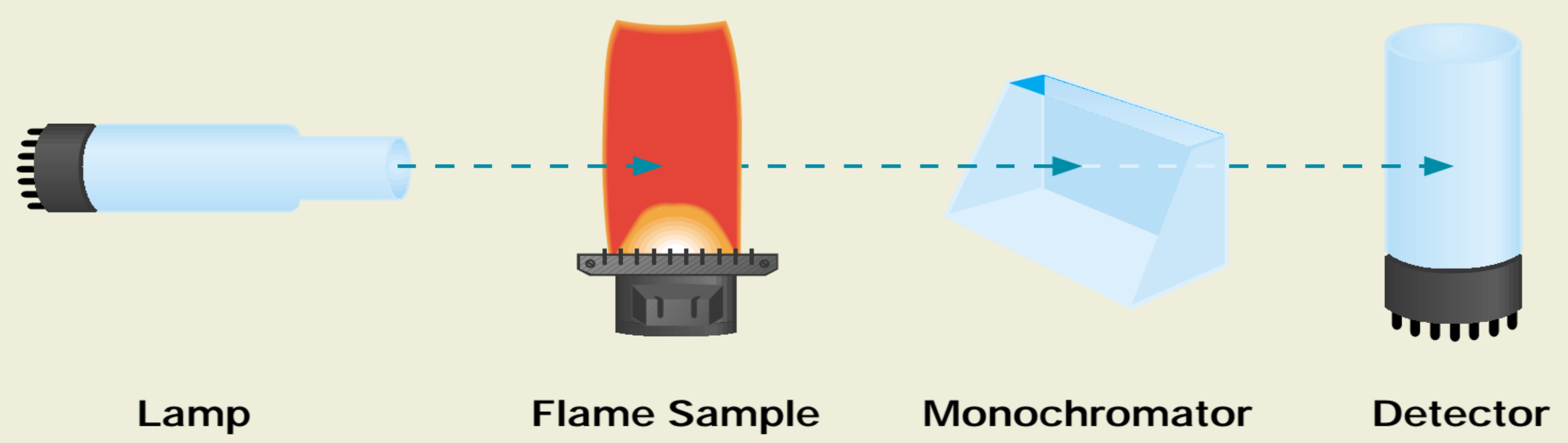

L’vov platform

- The L'vov platform is a small plate of solid pyrolytic graphite that is inserted into the graphite tube. It has a slight depression in the center which can accommodate up to **50 µL** of solution. The function of the L'vov platform is to isolate the sample from the tube walls to allow more reproducible atomization of the sample through indirect heating. The platform heats primarily by the radiation given off from the tube walls. Sample vaporization and atomization occur after the tube reaches a steady-state temperature.

Use of the L'vov platform provides:

1. Vaporization into a higher temperature gas atmosphere producing more free atoms, which **reduce interferences**.
2. **Longer tube life** through reduced attack by sample matrix and reagents.

A comparison between FAAS and GFAAS



Flame Atomic Absorption Spectrometry (FAAS)

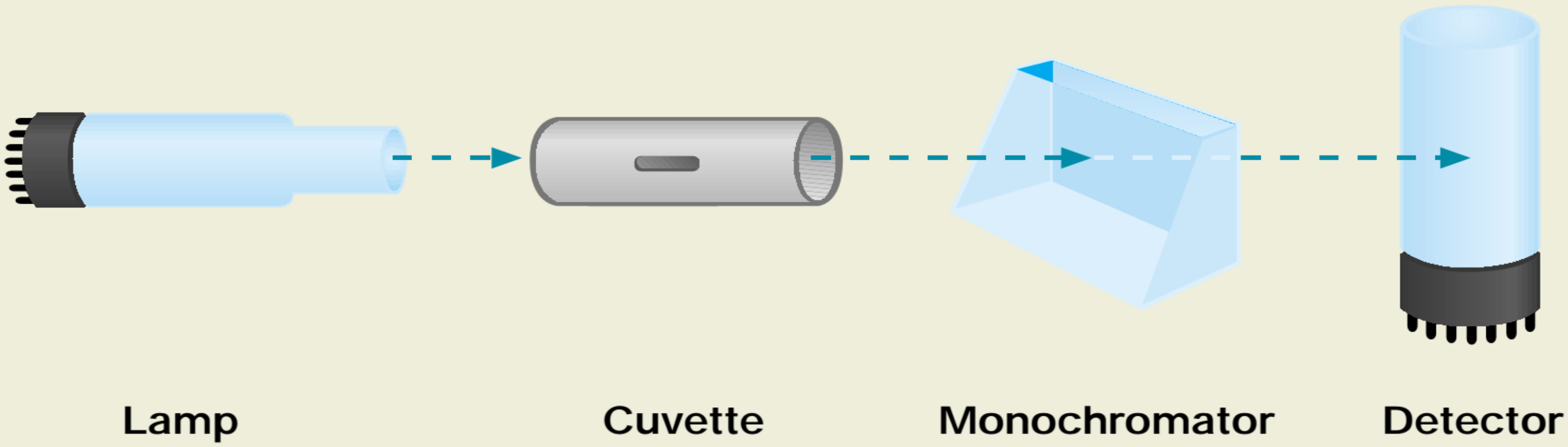
Strengths

- Easy to use
- Very fast
- Lowest capital cost
- Relatively few interferences
- Very compact instrument
- Good performance
- Robust interface

Limitations

- Moderate detection limits
- Element limitations
- 1-10 elements per determination
- No screening ability

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)



Strengths

- Very good detection limits
- Small sample size
- Moderate price
- Very compact instrument
- Few spectral interferences

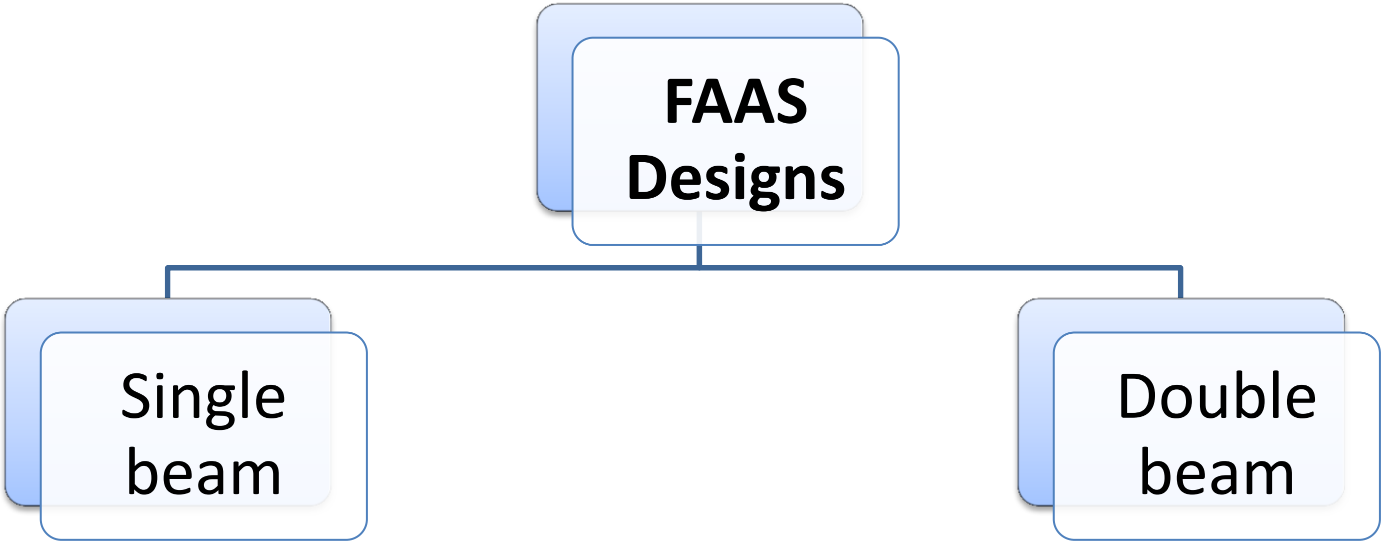
Limitations

- Slower analysis time
- Chemical interferences
- Element limitations
- 1-6 elements per determination
- No screening ability
- Limited dynamic range

Limits of detection (LOD) in FAAS and GFAAS

Element	Flame AAS (ppb)	GFAAS (ppb)	Element	Flame AAS (ppb)	GFAAS (ppb)
Nb	2000		Se	500	0.65
Nd	850		Si	200	0.8
Ni	10	0.24	Sm	750	
Os	100		Sn	95	0.6
P	4000	100	Sr	2	0.1
Pb	10	0.04	Ta	1500	
Pd	10	0.5	Tb	700	0.2
Pr	5000		Te	30	0.5
Pt	75	4.5	Th		
Rb	5	0.06	Ti	70	1.6
Re	800		Tl	20	0.75
Rh	3	0.4	Tm	20	
Ru	100	0.75	U	40000	

- **Limit of detection (LOD)** is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value).
- It can be concluded from the table that LODs in GFAAS are lower than those of FAAS. This means that **GFAAS is more sensitive than FAAS**.

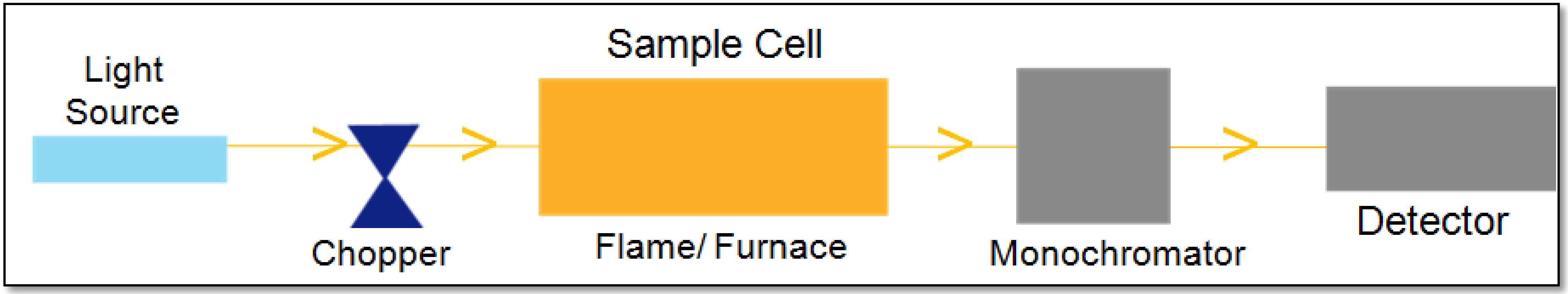


FAAS Designs

Single beam

Double beam

Single-Beam AAS



- The light source comprising of a hollow cathode lamp **(HCL) emits sharp atomic line** of the element whose determination is required.
- **The light is modulated** (switched on and off) rapidly by means of a rotating chopper located between the light source and the flame.
  - ✓ **"Modulation serves to differentiate the light coming from the source lamp from the emission from the flame."**
- The modulated light is led to the flame where ground state atoms of the element of interest are present and after **absorption** is led to the **monochromator** which isolates the wavelength of interest which is then led to the **detector**.

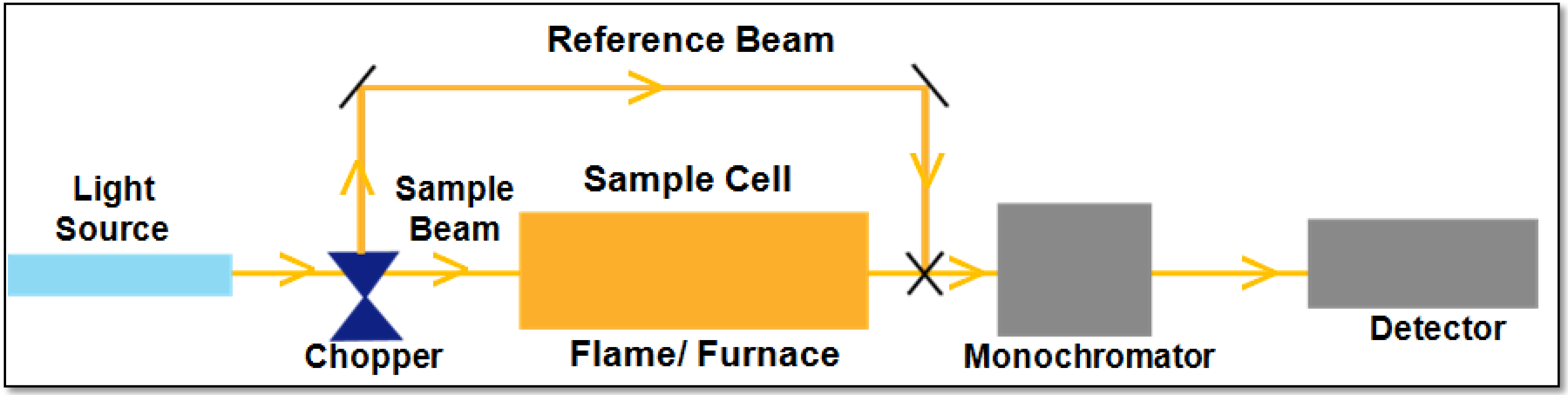
- **Advantages of Single-Beam Systems:**

1. Single beam instruments are **less expensive** than double-beam ones,
2. **High energy throughput** due to non-splitting of source beam results in high sensitivity of detection.

- **Disadvantages:**

  1. **Instability due to lack of compensation for disturbances** like electronic circuit fluctuations, voltage fluctuations, mechanical component's instability or drift in energy of light sources. Such drifts result in abnormal fluctuations in the results.

Double-Beam AAS



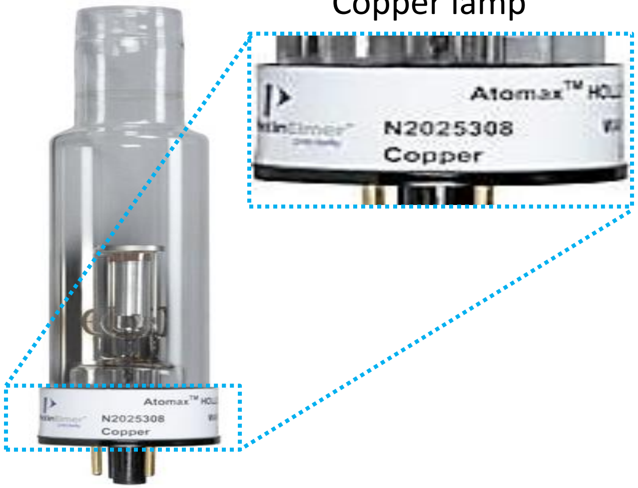
- **The light beam from the source is split** into sample beam and reference beam by the mechanical chopper.
- The **reference beam monitors the lamp energy** whereas the **sample beam reflects sample absorption**.
- The observed absorbance measurement is the ratio of the sample and reference beams which are recombined before moving to the **monochromator**.
- This arrangement **compensates the effects due to drift in lamp intensity**, electronic and mechanical fluctuations which affect both the sample and reference beams equally.

- **Advantages of Double-Beam Systems:**
  1. Modern improvements in optics permit high level of automation and offer the same or even better level of detection as compared to earlier single beam systems. **Instability** factors due to lamp drift, stray light, voltage fluctuations **do not affect the measurement** in real-time.
  2. Little or no lamp warm up time is required. This not only improves **throughput** of results but also **conserves lamp life**.

- **Disadvantages :**
  1. Double-beam instruments are **more expensive** than single-beam ones,
  2. **Lower energy throughput** due to splitting of source beam results in lower sensitivity of detection.

Sources of radiation for AAS

Line Sources



Copper lamp

Hollow Cathode Lamps (HCL)

Mercury lamp

Selenium lamp

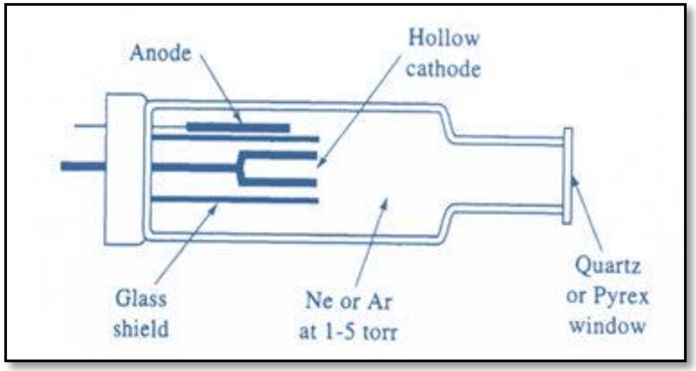
Zinc lamp

Electrodeless Discharge Lamps (EDL)

HOLLOW CATHODE LAMPS (HCL)

- HCL is the most commonly used lamp in AAS as a line source.

- As described earlier, an HCL usually consists of a glass tube containing a cathode, an anode, and a noble gas (e.g., Ar or Ne). The cathode material is constructed of the metal whose spectrum is desired. For example, if selenium is to be determined, the cathode would be made of selenium.

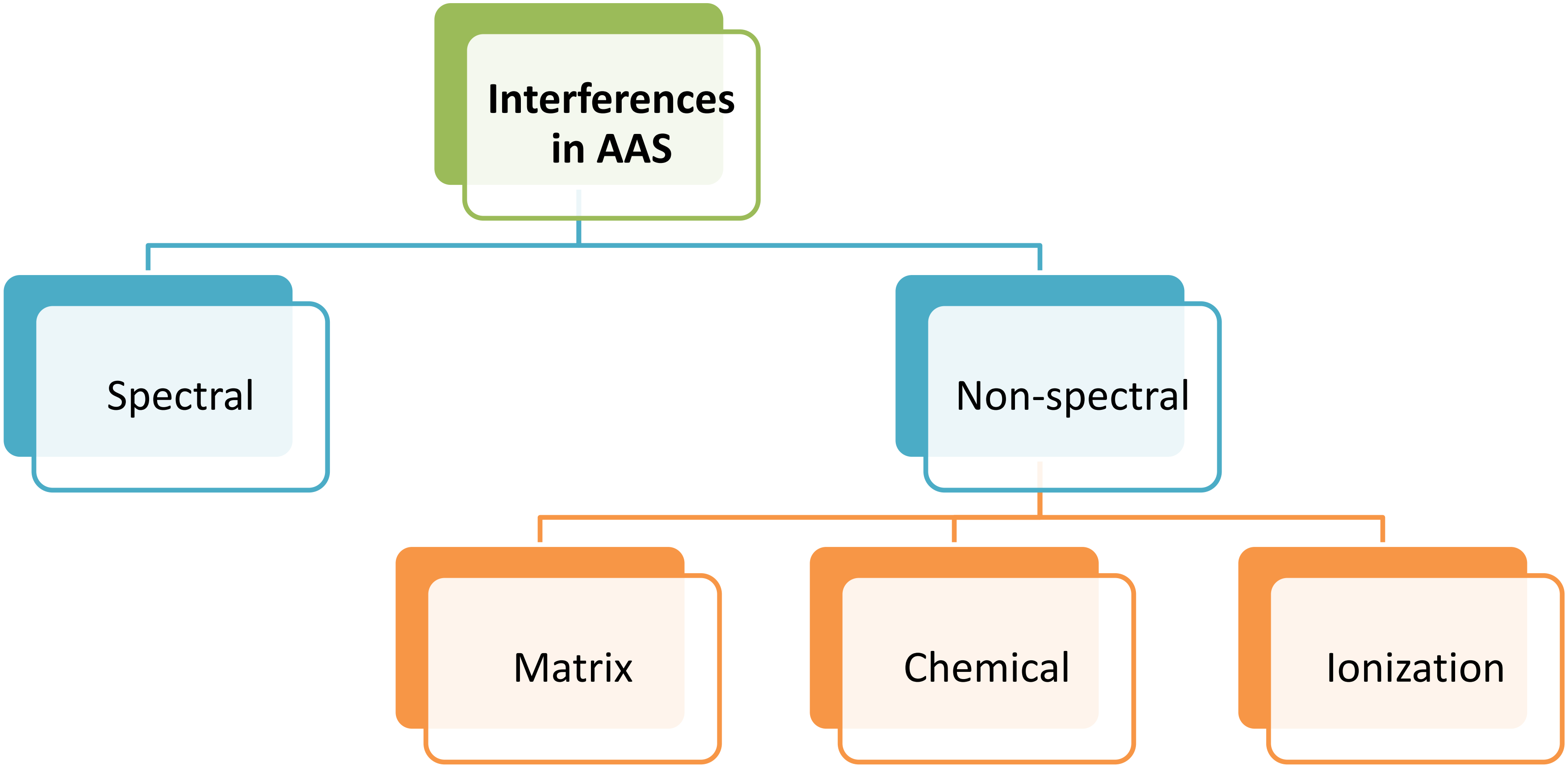


Schematic cross section of a hollow cathode lamp

- A large voltage causes the gas to ionize, creating a plasma. The gas ions will then be accelerated into the cathode, **sputtering** off atoms from the cathode. Both the gas and the sputtered cathode atoms will be excited by collisions with other atoms/particles in the plasma. As these excited atoms relax to lower states, they emit photons, which can then be absorbed by the analyte in the sample holder.

Interferences in AAS

- **Interference** is a phenomena that leads to changes (either **positive or negative**) in intensity of the analyte signal in spectroscopy. Interferences in atomic absorption spectroscopy fall into two basic categories, namely, non-spectral and spectral.



Interferences in AAS

Spectral

Non-spectral

Matrix

Chemical

Ionization

Spectral Interference

- **Spectral interferences are caused by presence of:**
  1. **another atomic absorption line,**
  2. **or a molecular absorbance band close to the spectral line of element of interest.**

     Most common spectral interferences are due to molecular emissions from oxides of other elements in the sample.
- The main cause of background absorption is presence of **undissociated molecules** of matrix that have broad band absorption spectra and tiny solid particles, unvaporized solvent droplets or molecular species in the flame which may scatter light over a wide wavelength region. When this type of non-specific adsorption overlaps the atomic absorption of the analyte, background absorption occurs.

- The problem is overcome by:
    1. measuring and **subtracting the background** absorption from the total measured absorption to determine the true atomic absorption.
    2. by **choosing another line** for the analyte. For example, a vanadium line at 3082.11 Å interferes with aluminum line at 3082.15 Å. This interference is avoided by employing the aluminum line at 3092.7 Å.

Non-spectral Interference

Matrix Interference

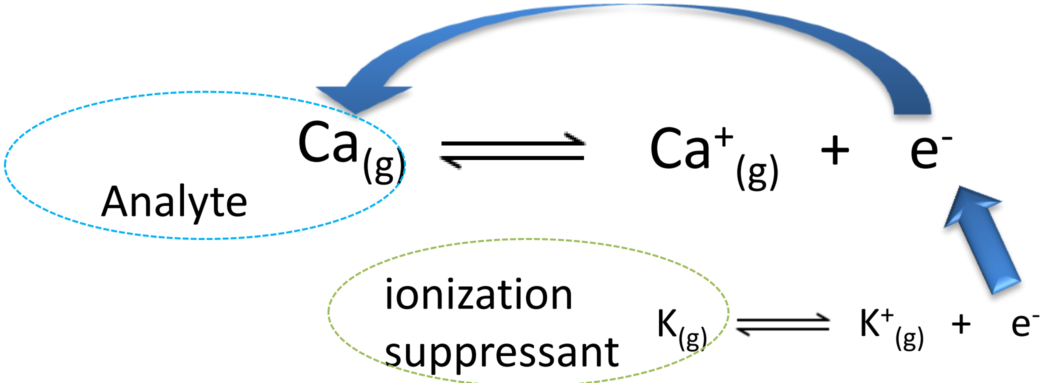
- When a sample is **more viscous** or has different surface tension than the standard, it can result in differences in sample uptake rate due to changes in nebulization efficiency.
- Such interferences are minimized by **matching** as closely as possible the **matrix composition** of standard and sample.

Chemical Interference

- If a sample contains a **species which forms a thermally stable compound with the analyte** that is not completely decomposed by the energy available in the flame then chemical interference exists.
- **Refractory elements** such as Ti, W, Zr, Mo and Al may combine with oxygen to form thermally stable oxides.
- Analysis of such elements can be carried out at **higher flame temperatures** using nitrous oxide – acetylene flame instead of air-acetylene to provide higher dissociation energy.
- Alternatively, an **excess of another element or compound can be added** e.g. Ca in presence of phosphate produces stable calcium phosphate which reduces absorption due to Ca ion. If an excess of lanthanum is added it forms a thermally stable compound with phosphate and calcium absorption is not affected.

Ionization Interference

- **Ionization interference is more common in hot flames**. The dissociation process does not stop at formation of ground state atoms. Excess energy of the flame can lead to **ionization of ground state atoms** by loss of electrons thereby resulting in depletion of ground state atoms.
- In cooler flames such interference is encountered with easily ionized elements such as alkali metals and alkaline earths.
- Ionization interference is eliminated by **adding an excess of an element which is easily ionized** thereby creating a large number of free electrons in the flame and suppressing ionization of the analyte. Salts of such elements as K, Rb and Cs are commonly used as **ionization suppressants**.



$Ca_{(g)} \rightleftharpoons Ca^+_{(g)} + e^-$

Analyte

ionization suppressant

$K_{(g)} \rightleftharpoons K^+_{(g)} + e^-$

Atomic Emission Spectrometry (AES)

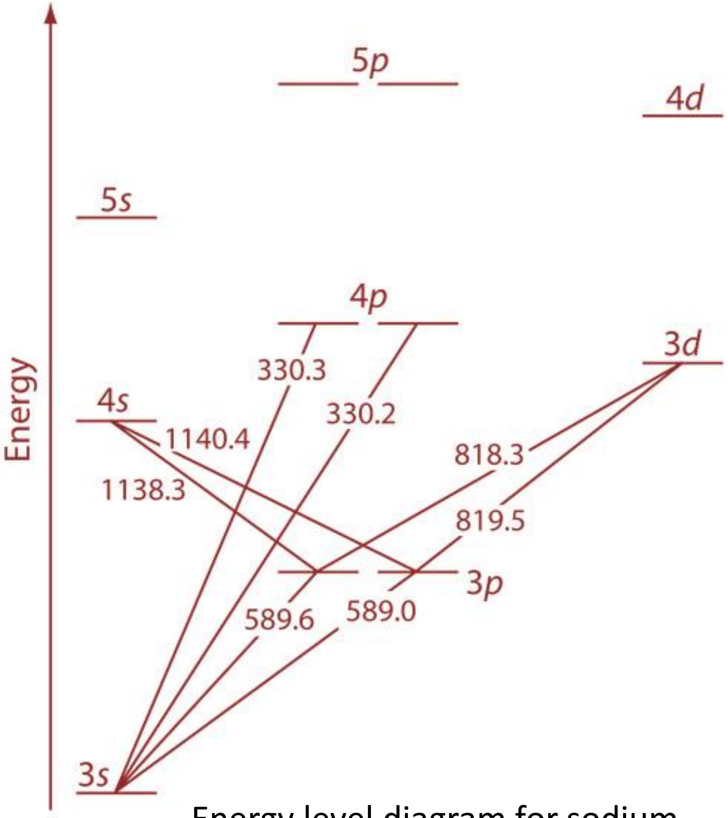
AES Instrument

- **Atomic emission spectrometry (AES)** is a technique that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample.
- The wavelength of the **atomic spectral line gives the identity** of the element while the intensity of the **emitted light is proportional to the number of atoms** of the element.

Working Principle

- The theory or working principle of Atomic Emission Spectrometry involves the examination of the wavelengths of photons discharged by atoms and molecules as they transit from a high energy state to a low energy state. A characteristic set of wavelengths is emitted by each element or substance which depends on its electronic structure. A study of these wavelengths can reveal the elemental structure of the sample.

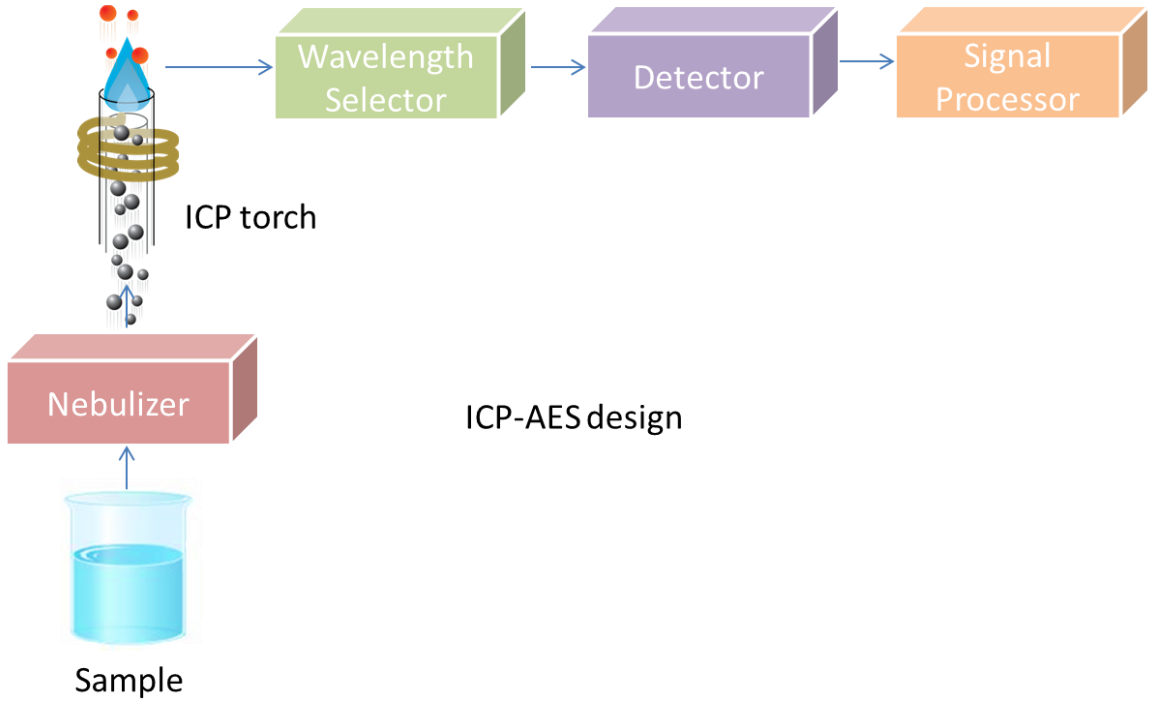
- Atomic emission occurs when a valence electron in a higher energy atomic orbital returns to a lower energy atomic orbital. The figure on the right shows a portion of the energy level diagram for sodium, which consists of a series of discrete lines at wavelengths corresponding to the difference in energy between two atomic orbitals.



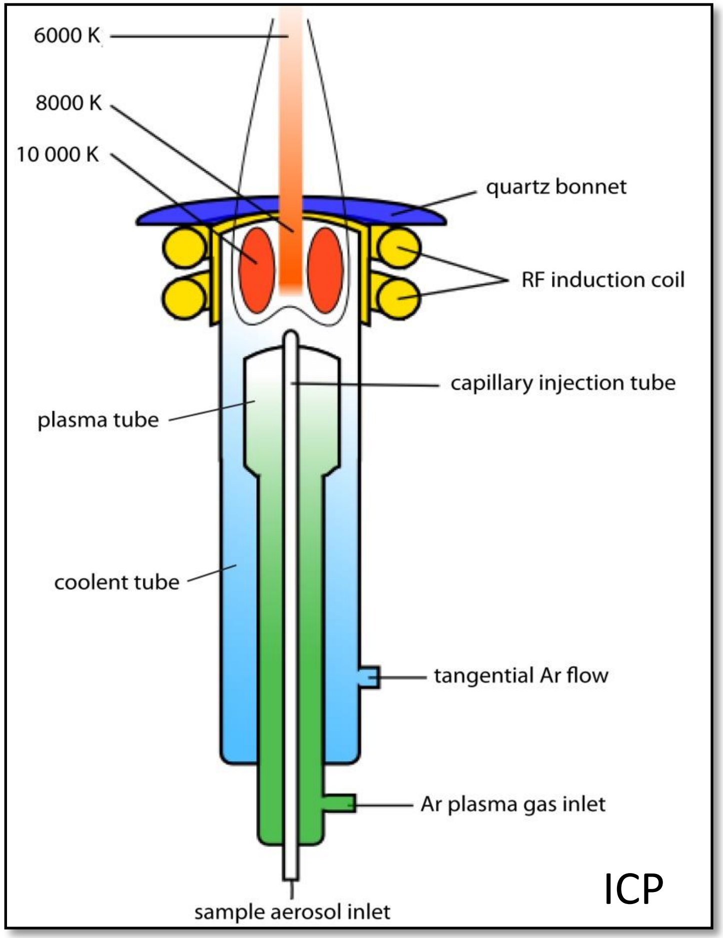
Energy level diagram for sodium

ICP-AES

- **Inductively coupled plasma (ICP)** are the most widely used atomizers in emission spectrometry.
- **A plasma** is a hot, partially ionized gas that contains cations and electrons.
- The plasmas used in atomic emission are formed by ionizing a flowing stream of argon gas, producing argon ions and electrons.
- Because plasmas operate at much higher temperatures than flames, they provide **better atomization** and a higher population of excited states.



ICP-AES design

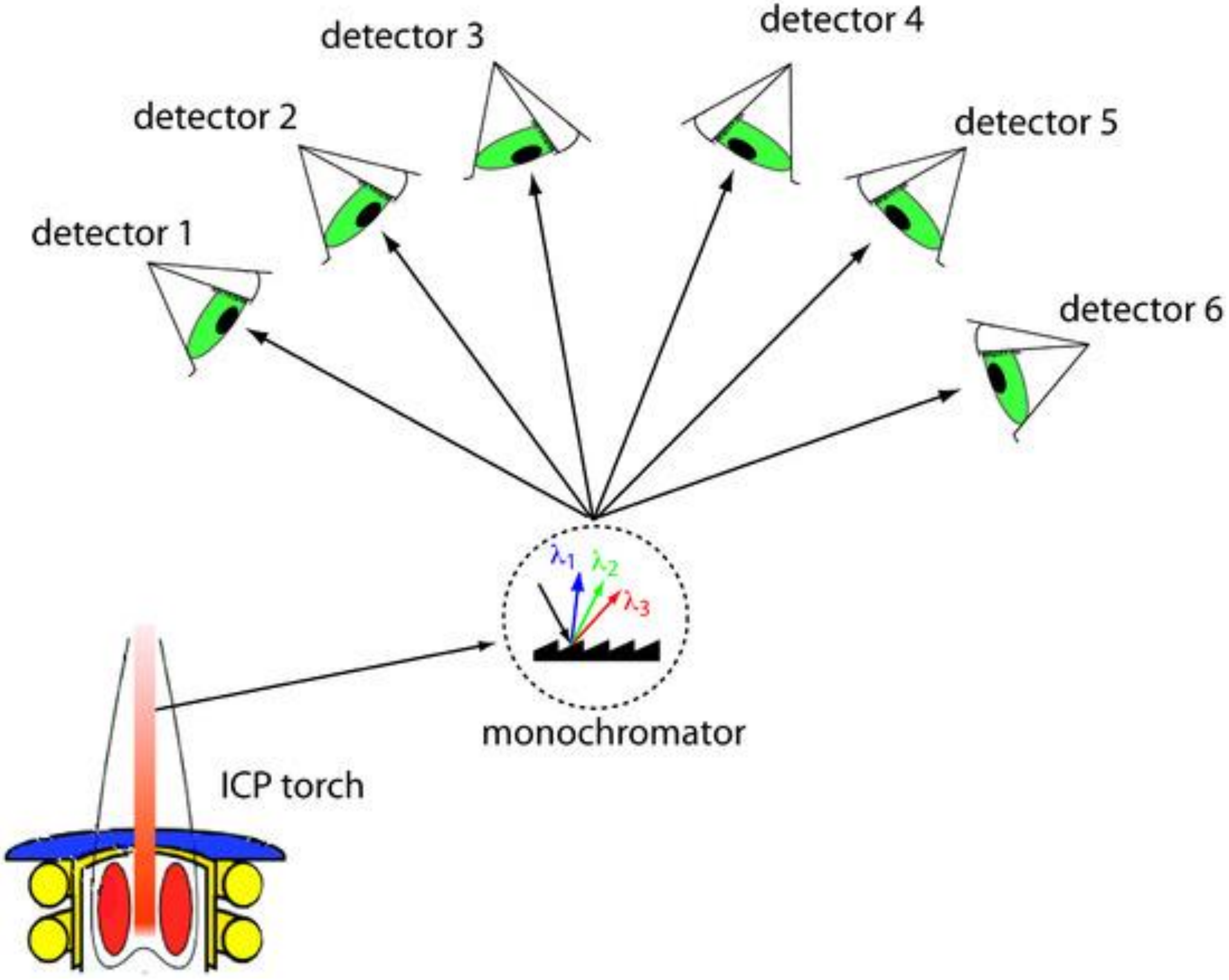


- The **ICP torch** consists of three concentric quartz tubes, surrounded at the top by a radio-frequency induction coil. The sample is mixed with a stream of Ar using a nebulizer, and is carried to the plasma through the torch's central capillary tube.
- Plasma formation is initiated by a spark from a Tesla coil. An alternating radio-frequency current in the induction coils creates a fluctuating magnetic field that induces the argon ions and the electrons to move in a circular path. The resulting collisions with the abundant unionized gas give rise to resistive heating, providing temperatures as high as **10000 K** at the base of the plasma, and between 6000 and 8000 K at a height of 15–20 mm above the coil, where emission is usually measured.
- At these high temperatures the outer quartz tube must be thermally isolated from the plasma. This is accomplished by the tangential flow of argon shown in the schematic diagram.

Multielemental Analysis in ICP-AES

- **AES is ideally suited for multielemental analysis because all analytes in a sample are excited simultaneously.** If the instrument includes a scanning monochromator, we can program it to move rapidly to an analyte's desired wavelength, pause to record its emission intensity, and then move to the next analyte's wavelength. This sequential analysis allows for a sampling rate of 3–4 analytes per minute.

- Another approach to a multielemental analysis is to use a **multichannel instrument** that allows us to simultaneously monitor many analytes. A simple design for a multichannel spectrometer couples a monochromator with multiple detectors that can be positioned in a semicircular array around the monochromator at positions corresponding to the wavelengths for the analytes



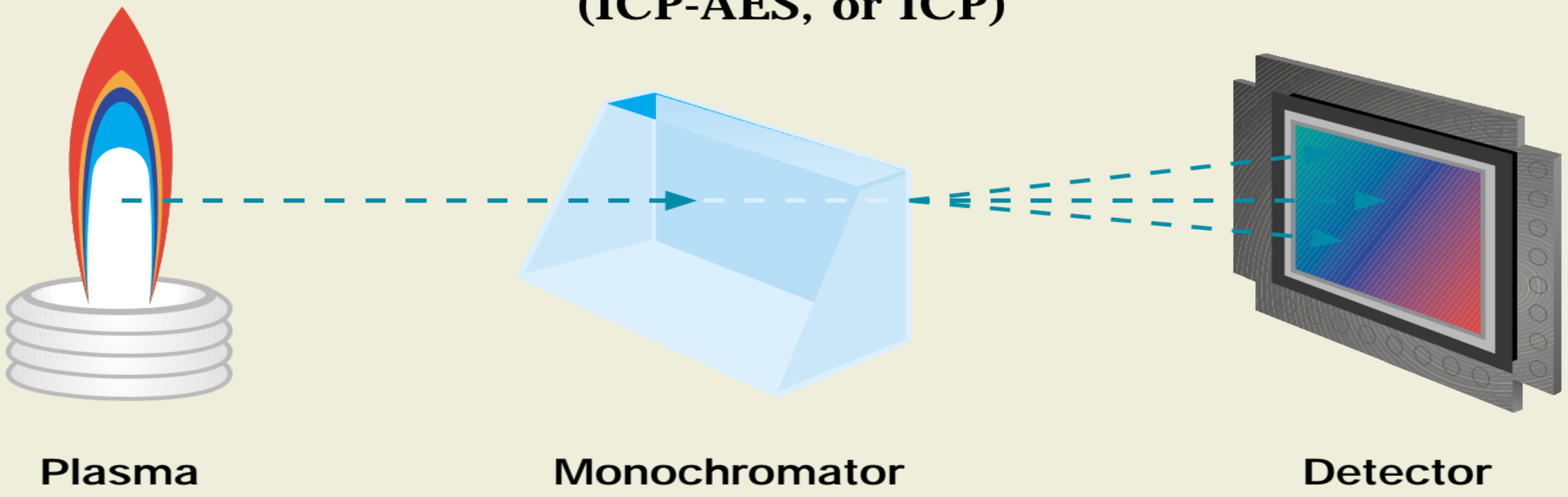
Schematic diagram of a multichannel AES for the **simultaneous determination of several elements**. Instruments may contain as many as 48–60 detectors.

Limits of detection (LOD) of ICP-AES

Element	LOD (μg/L)
Ca	0.0001
Mg	0.003
Zn	0.01
Mn	0.02
Na	0.02
Fe	0.09
Pb	1
As	2
Hg	10
Au	40

Typical limits of detection (LOD) in μg/L with ICP-AES

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, or ICP)



Strengths

- Easy to use
- Multi-element
- High productivity
- Very economical for many samples and/or elements
- Few chemical interferences
- Robust interface
- Excellent screening abilities

Limitations

- Moderate to low detection limits (but often much better than FAAS)
- Spectral interferences possible
- Some element limitations