ATOMIC ABSORPTION SPECTROSCOPY

Atomic Spectroscopy

- Atomic spectroscopy is used to determine the concentration of elements in a sample.
- Atomic spectroscopy has played a major role in the development of our current database for mineral nutrients and toxicants in foods.
- Atomic spectroscopic methods are used for the qualitative and quantitative determination of more than 70 elements.
- Typically, these methods can detect parts-per-million to parts-per-billion amounts, and in some cases, even smaller concentrations.
- Atomic spectroscopic methods are also rapid, convenient, and usually of high selectivity.
- There are several types of atomic spectroscopy. Atomic absorption spectroscopy (AAS), atomic emission spectroscopy (AES), and inductively coupled plasma-mass spectrometry (ICP-MS) are the most common.
- These three instrumental methods have largely replaced traditional wet chemistry methods for mineral analysis of foods, although traditional methods for calcium, chloride, iron and phosphorus remain in use today.

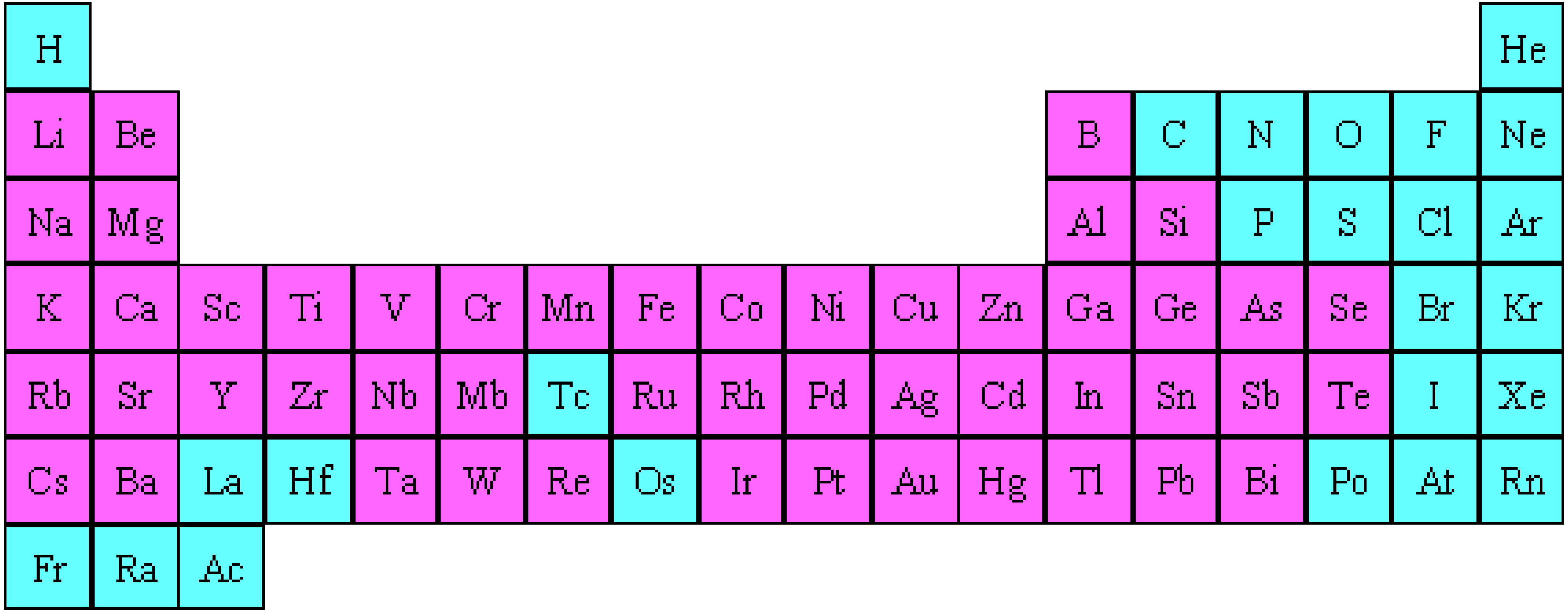
Atomic Spectroscopy

- In theory, virtually all of the elements in the periodic chart may be determined by AAS or AES.
- In practice, atomic spectroscopy is used primarily for determining mineral elements.

Mineral elements in foods classified according to nutritional essentiality and potential toxic risk

Essential Nutrient	Toxicity Concern
Calcium	Lead
Phosphorous	Mercury
Sodium	Cadmium
Potassium	Nickel
Chlorine	Arsenic
Magnesium	Thallium
Iron	
Iodine	
Zinc	
Copper	
Selenium	
Chromium	
Manganese	
Arsenic	
Boron	
Molybdenum	
Nickel	
Silicon	

Elements detectable by atomic absorption spectroscopy are highlighted in pink color in periodic table



Atomic Spectroscopy-General Principles

- **AAS** quantifies the absorption of electromagnetic radiation by well-separated neutral atoms in the gaseous state, while **AES** measures emission of radiation from atoms excited by heat or other means.

- **Atomic spectroscopy** is particularly well suited for analytical measurements because atomic spectra consist of discrete lines, and every element has a unique spectrum.

- Therefore, individual elements can be identified and quantified accurately and precisely even in the presence of atoms of other elements.

Atomic Spectroscopy-General **Principles-** Atomization

- Atomic spectroscopy requires that atoms of the element of interest be in the **atomic state** (not combined with other elements in a compound) and that they be well separated in space.

- In foods, virtually all elements are present as compounds or complexes and, therefore, must be converted to neutral atoms (atomized) before atomic absorption or emission measurements can be made.

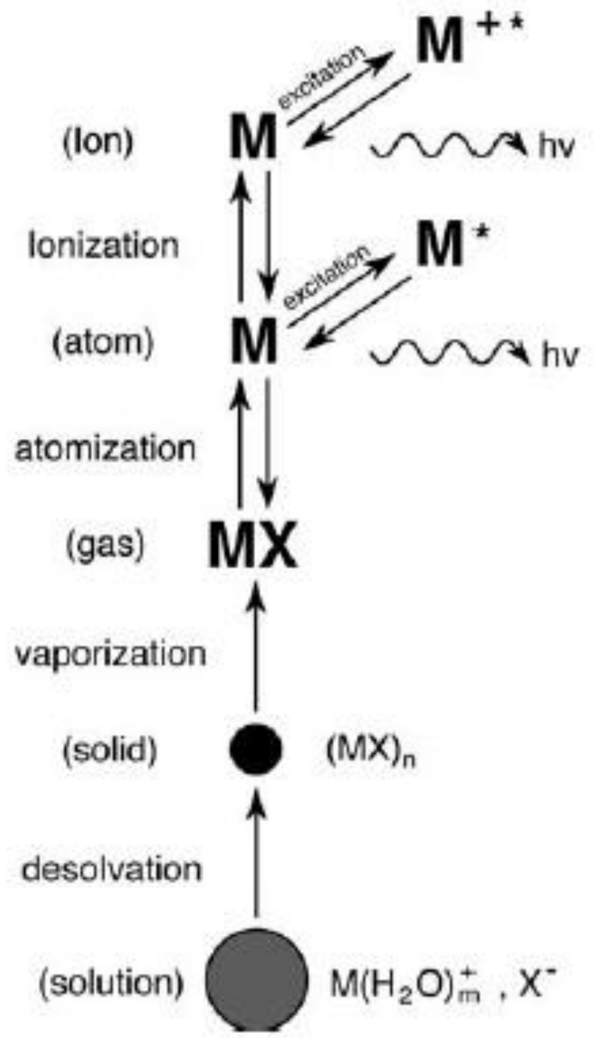
- **Atomization** involves separating particles into individual molecules (vaporization) and breaking molecules into atoms. It is usually accomplished by exposing the analyte (the substance being measured) to high temperatures **in a flame** or **plasma.**

Atomic Spectroscopy-General Principles-Atomization

[A schematic representation of the atomization of an element in a flame or plasma]().

(The large circle at the bottom represents a tiny droplet of a solution containing the element (M) as a part of a compound).

- **A solution containing the analyte is introduced into the flame or plasma as a fine mist.**
- **The solvent quickly evaporates, leaving solid particles of the analyte that vaporize and decompose to atoms that may absorb radiation (atomic absorption) or become excited and subsequently emit radiation (atomic emission).**



Atomic Spectroscopy-General Principles-Atomization

Methods for Atomization of Analytes

Source of Energy for Atomization	Approximate Atomization Temperature (˚C)	Analytical Method
Flame	1700-3150	AAS, AES
Electrothermal	1200-3000	AAS (graphite furnace)
Inductively Coupled Argon Plasma	6000-7000	ICP-AES, ICP-MS

Atomic Absorption Spectroscopy (AAS)

- **AAS** is an analytical method based on the absorption of ultraviolet or visible radiation by free atoms in the gaseous state.

- It is relatively a simple method and was the most widely used form of atomic spectroscopy. However, it is being gradually replaced by inductively coupled plasma (ICP) spectroscopy and inductively coupled plasma-mass spectrometry.

- The process of **AAS** involves two steps:

1) Atomization of the sample
2) The absorption of radiation from a light source by the free atoms

(The sample, either a liquid or a solid, is atomized in either **a flame** or **a graphite furnace**. Upon the absorption of ultraviolet or visible light, the free atoms undergo electronic transitions from the ground state to excited electronic states).

- Two types of atomization are commonly used in AAS:
  - Flame atomization
  - Electrothermal (graphite furnace) atomization

Atomic Absorption Spectroscopy (AAS)-Principle

- The technique uses basically the principle that free atoms (gas) generated in an atomizer can absorb radiation at specific frequency.
- AAS quantifies the absorption of ground state atoms in the gaseous state.
- The atoms absorb UV or visible light and make transitions to higher electronic energy levels.
- The analyte concentration is determined from the amount of absorption.
- Concentration measurements are usually determined from a working (calibration) curve after calibrating the instrument with standards of known concentration.
- AAS is a very common technique for detecting and measuring the concentration of metals in a sample at very low levels and with great accuracy.
- In comparison with traditional wet chemistry methods, measurements with AAS are extremely rapid.

Principles of Flame Atomic Absorption Spectroscopy

The amount of radiation absorbed by the sample is given by Beer's law:

$A = \log(I_0/I) = abc$

where:
A = absorbance
I_0 = intensity of radiation incident on the flame
I = intensity of radiation exiting the flame
a = molar absorptivity
b = path length through the flame
c = concentration of atoms in the flame

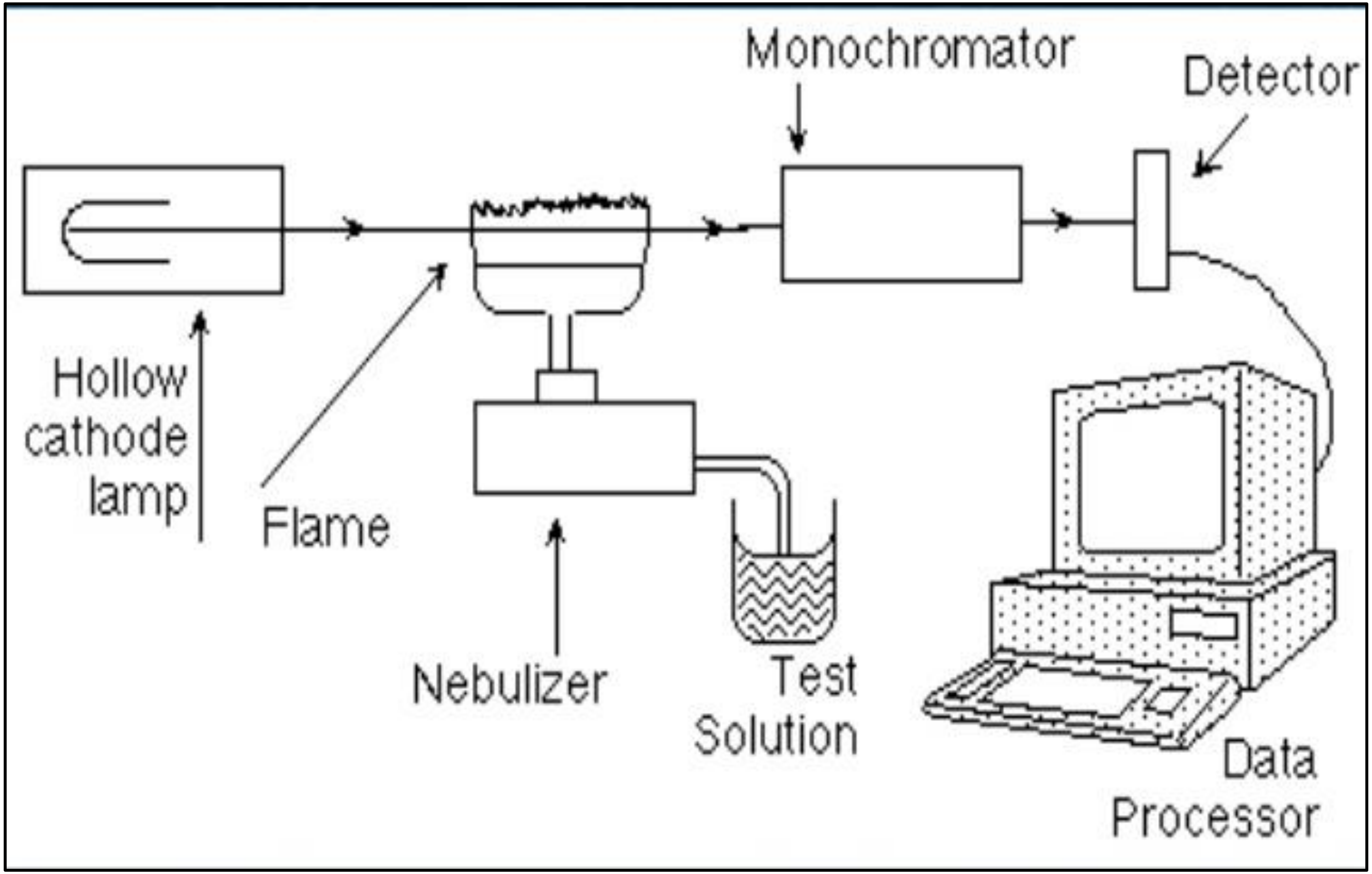
Absorbance is directly related to the concentration of atoms in the flame.

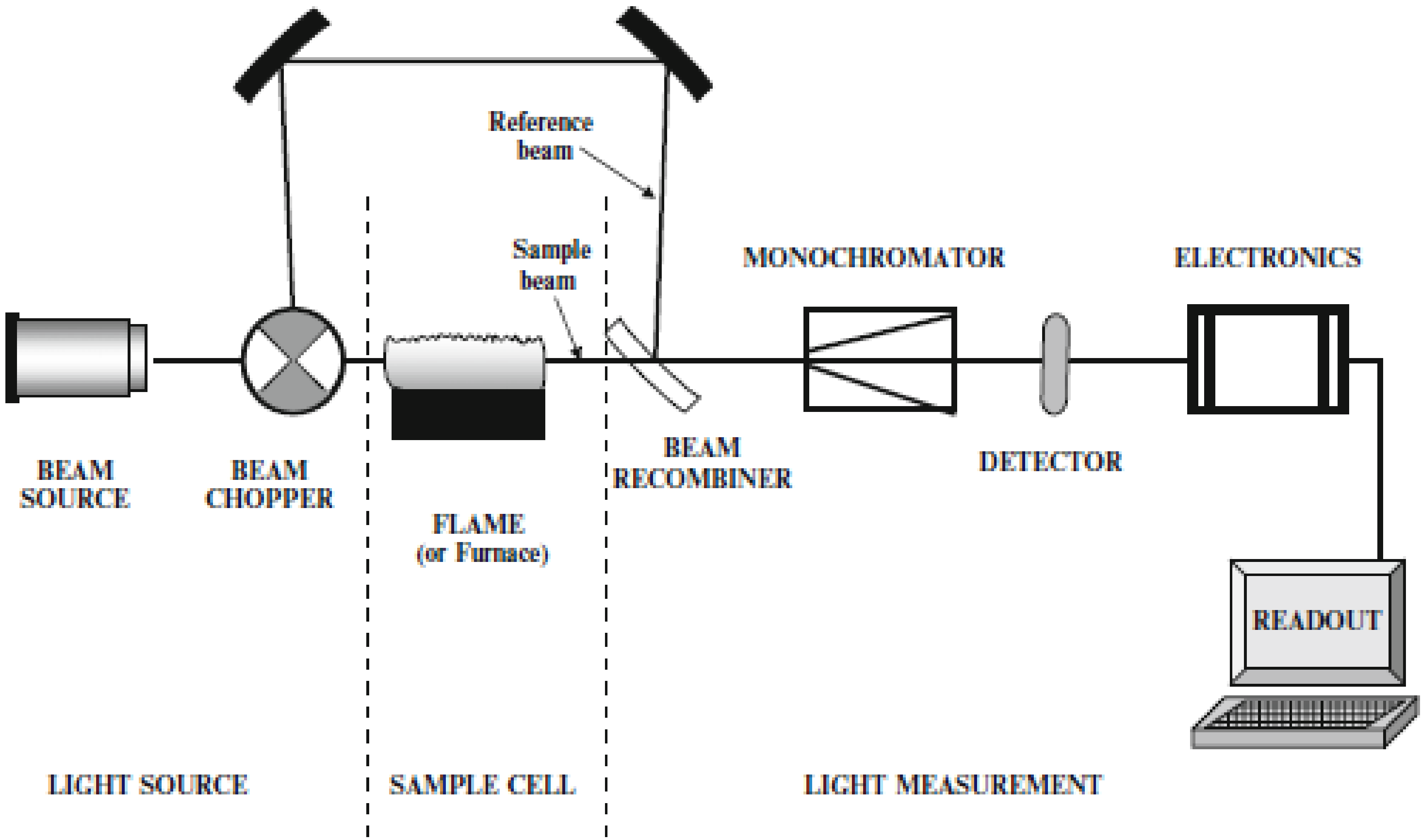
Atomic Absorption Spectroscopy (AAS)-Instrumentation

Atomic absorption spectrometers consist of 5 main components:

1. **Radiation source:** a hollow cathode lamp (HCL) or an electrode-less discharge lamp (EDL)
2. **Atomizer:** a nebulizer-burner system or an electrothermal furnace
3. **Monochromator:** an ultraviolet-visible (UV-Vis) grating monochromator
4. **Detector:** a photomultiplier tube (PMT) or a solid-state detector (SSD)
5. **Computer**

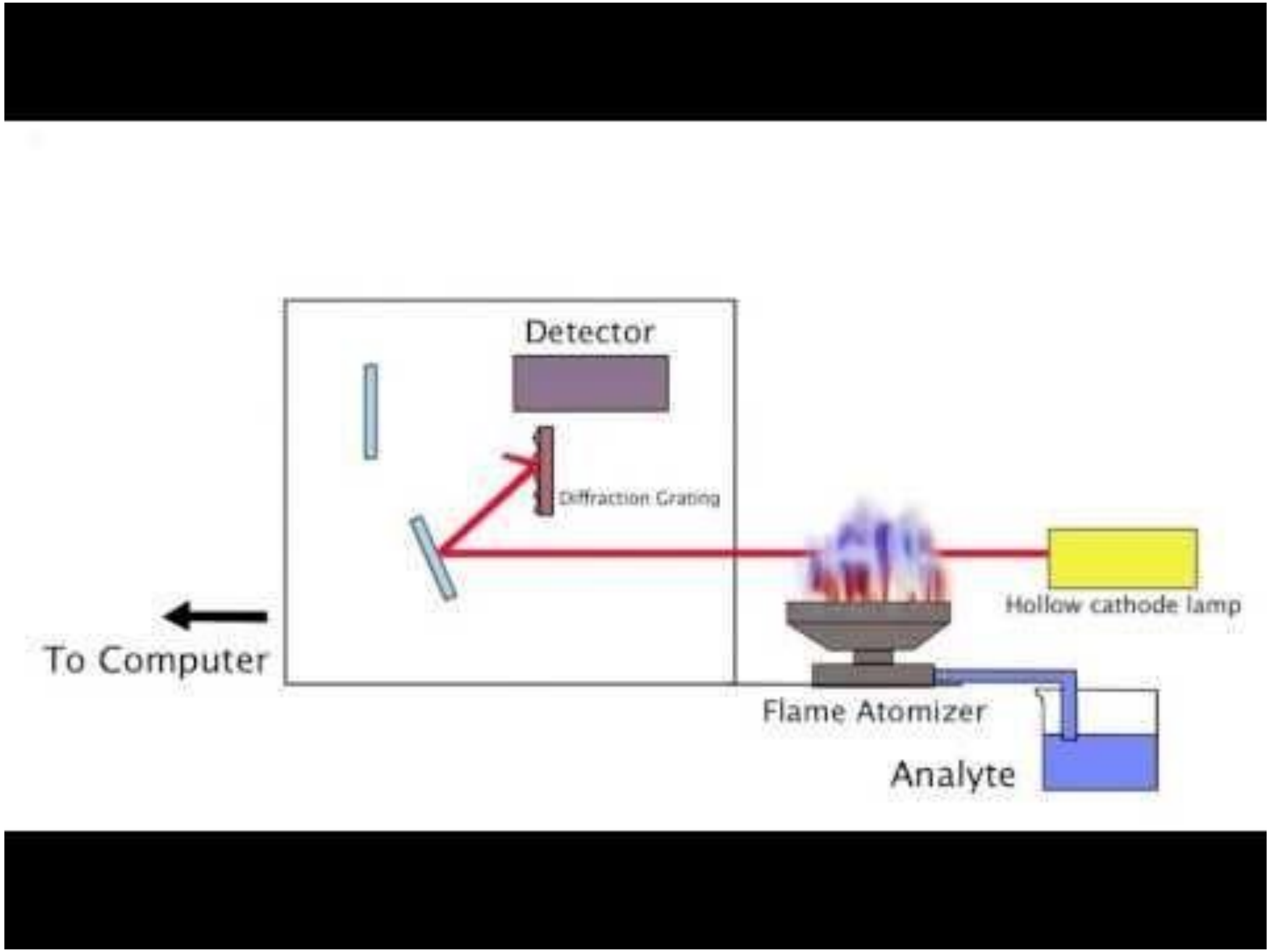
Simplified schematic diagram of AAS





Schematic representation of a double-beam atomic absorption spectrophotometer

Access link:
https://www.youtube.com/watch?v=_KZjb9G3hB8



Sample Preparation in AAS

- Sample preparation is relatively simple.

- In principle, any food may be analyzed with any of the atomic spectrocopy methods (AAS, ICP-AES). In most cases, it is necessary to ash the food the food to destroy organic matter and to dissolve the ash in a suitable solvent (usually water or dilute acid) prior to analysis.

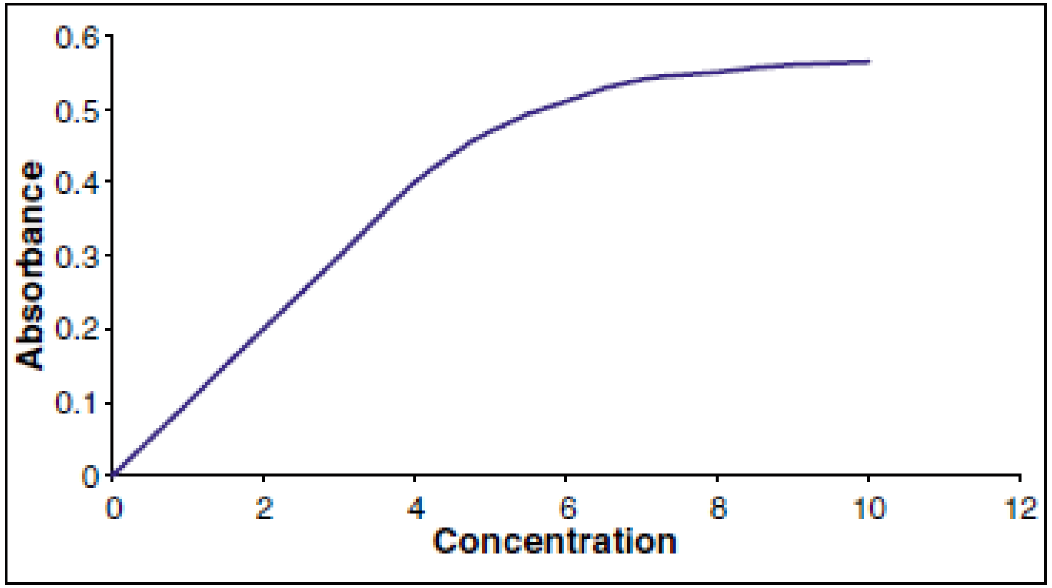
- Sample preparation for AAS technique involves destruction of organic matter by ashing, followed by dissolution of the ash in an aqueous solvent, usually a dilute acid.

- Proper ashing is critical to accuracy. Some elements may be volatile at temperatures used in **dry ashing (**heating the sample to about 500◦C to burn off the organicmatter) procedures. Volatilization is less of a problem in **wet ashing (**heating the sample in nitric acid and perchloric acid), except for the determination of boron, which is recovered better using a dry ashing method.

- However, ashing reagents may be contaminated with the analyte. It is therefore wise to carry blanks throughout the ashing procedure.

Results and Calibration Curves

- According to Beer's law, absorbance is directly related to concentration. However, a plot of absorbance vs. concentration will deviate from linearity when concentration exceeds a certain level.



A plot of absorbance vs. concentration showing nonlinearity above a certain concentration