ATOMIC SPECROSCOPY (AS)

Atomic Absorption Spectroscopy

Flame Atomic Emission Spectroscopy

ICP Atomic Emission Spectroscopy

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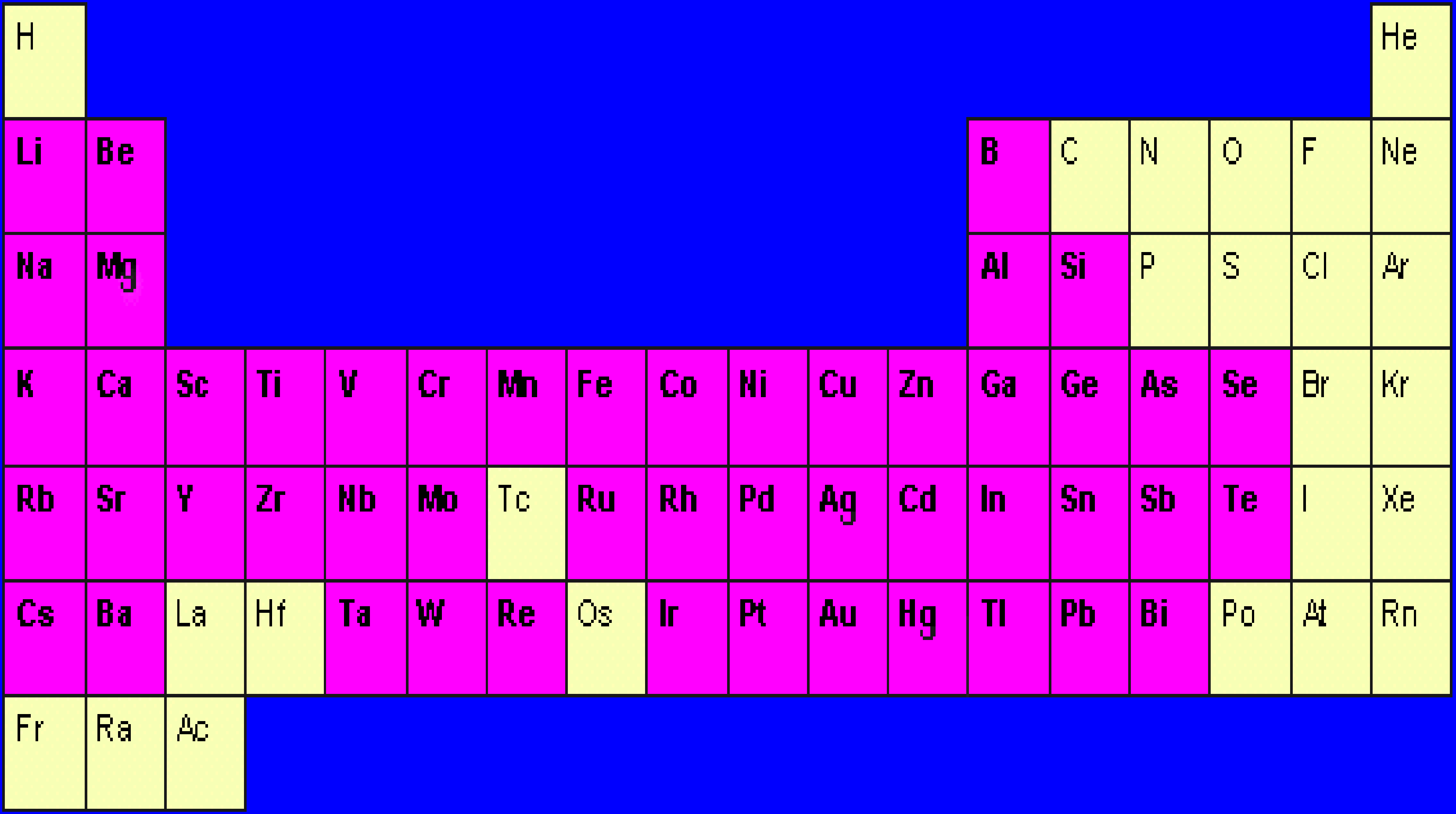
BASIC PRINCIPLE

ATOMIC ABSORPTION SPECTROSCOPY (AAS) is an analytical technique that measures the concentrations of elements. 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.

- Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

- Atomic absorption is a very common technique for detecting metals and metalloids in environmental samples.



H																	He
Li	**Be**											**B**	C	N	O	F	Ne
Na	**Mg**											**Al**	**Si**	P	S	Cl	Ar
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	Br	Kr
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	Tc	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	I	Xe
Cs	**Ba**	La	Hf	**Ta**	**W**	**Re**	Os	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	Po	At	Rn
Fr	Ra	Ac															

Elements detectable by atomic absorption are highlighted in pink in this periodic table

The Atomic Absorption Spectrometer

- Atomic absorption spectrometers have 4 principal components

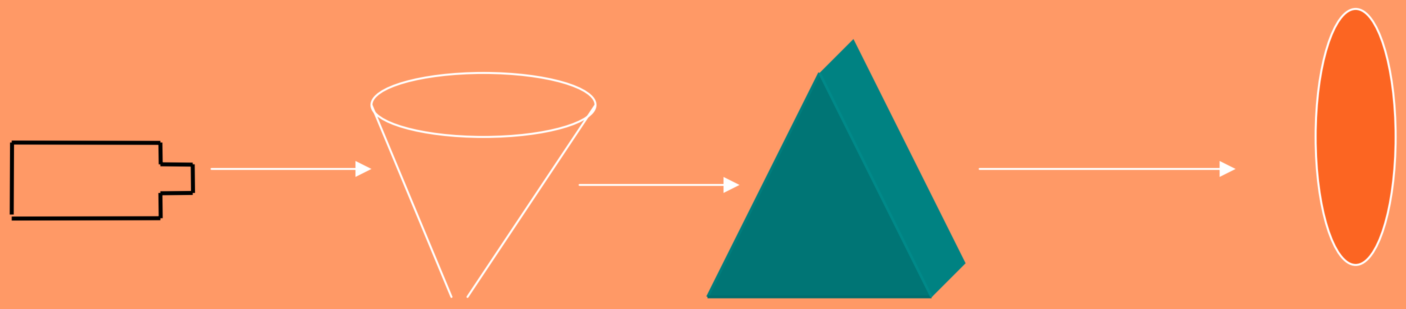
1 - A light source (usually a hollow cathode lamp)

2 – An atom cell (atomizer)

3 - A monochromator

4 - A detector , and read out device .

Schematic Diagram of an Atomic Absorption Spectrometer



Light source
(hollow cathode Lamp)

atomizer

monochromator

Detector and
readout device

Atomic Absorption Spectrophotometer

1 – Light Source

- 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

Quartz window

Pyrex body

Anode

Cathode

cathode

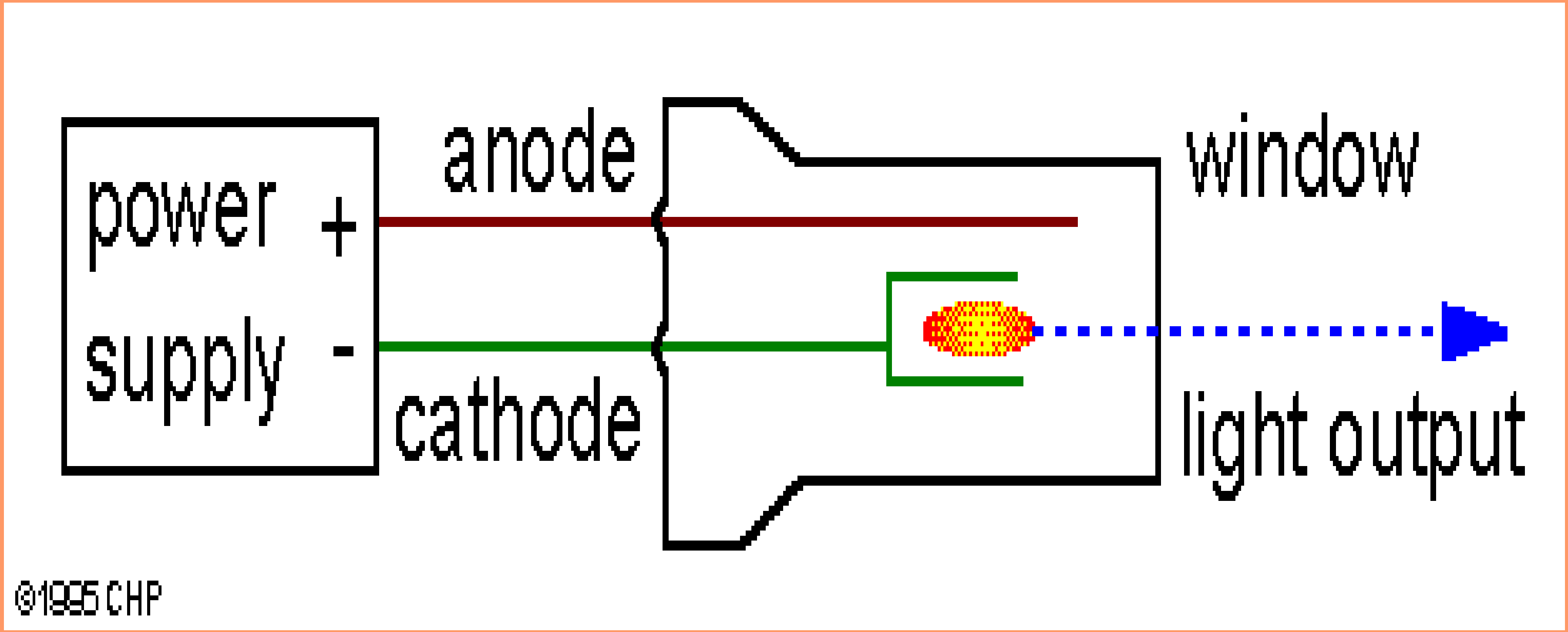
Anode

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 .

Scheme of a hollow cathode lamp



The shape of the cathode which is hollow cylindrical concentrates the emitted radiation into a beam which passes through a quartz window all the way to the vaporized sample.

Since atoms of different elements absorb characteristic wavelengths of light. Analyzing a sample to see if it contains a particular element means using light from that element .

For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample .

A beam of the electromagnetic radiation emitted from excited lead atoms is passed through the vaporized sample. Some of the radiation is absorbed by the lead atoms in the sample. The greater the number of atoms there is in the vapor , the more radiation is absorbed .

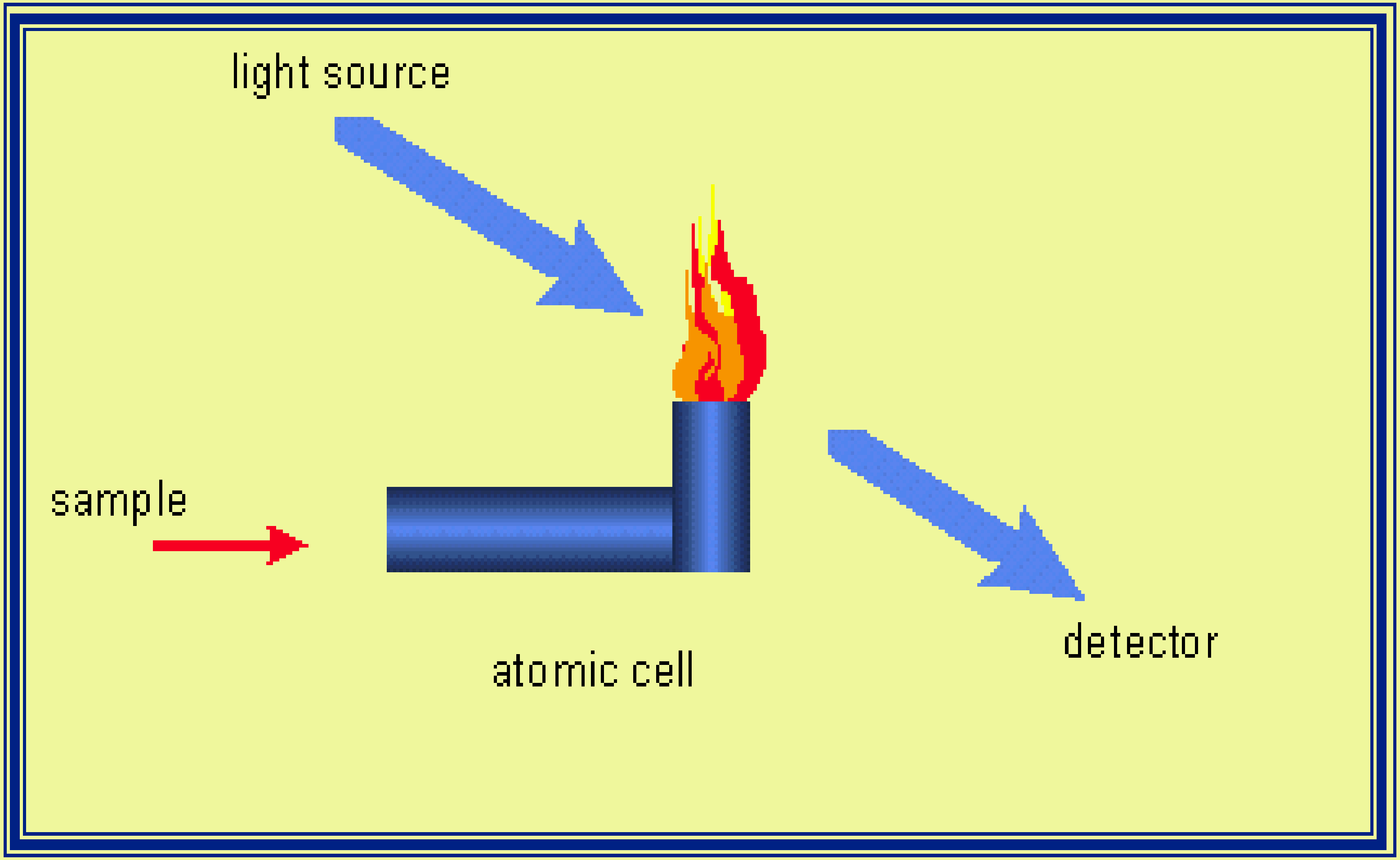
2 – Atomizer

Elements to be analyzed needs to be in atomic sate

Atomization is separation of particles into individual molecules and breaking molecules into atoms .This is done by exposing the analyte to high temperatures in a flame or graphite furnace .

The role of the atom cell is to primarily dissolvate a liquid sample and then the solid particles are vaporized into their free gaseous ground state form . In this form atoms will be available to absorb radiation emitted from the light source and thus generate a measurable signal proportional to concentration .

There are two types of atomization : Flame and Graphite furnace atomization .


light source
sample
atomic cell
detector

Flame

- Flame AA can only analyze solutions , where it uses a slot type burner to increase the path length, and therefore to increase the total absorbance .

  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.

FLAME ATOMIZERS

- Used in all Atomic Spectroscopic techniques
- Converts analyte into free atoms in the form of vapor phase free atoms
- Heat is required
- Routes for sample introduction

ATOMIZATION DEVICES

- **ATOMIZATION :**
- **A process of forming free atoms by heat**
- **Atomizers are devices that carry out atomization:**

- **Continuous**
- **Non-continuous**

- **Continuous: (Constant temperature with time)**
- **Flame**
- **Plasma**

- **Non-Continuous: (temperature varies with time)**
- **Electrothermal**
- **Spark discharge**

SAMPLE INTRODUCTION SYSTEMS

➢In continuous atomizers sample is constantly introduced in form of droplets, dry aerosol, vapor

➢**Nebulizer :** A device for converting the solution into fine spray or droplets

➢Continuous sample introduction is used with continuous nebulizers in which a steady state atomic population is produced. Sample is introduced in fixed or discrete amounts.

➢Discontinuous samplers are used with continuous atomizers

1- **Discrete** samples are introduced into atomizers in many ways:
Electrothermal atomizers
a syringe is used
a transient signal is produced as temperature changes with time and sample is consumed

2- **Indirect insertion** (Probe)
sample is introduced into a probe (carbon rod) and mechanically moved into the atomization region
vapor cloud is transient because sample introduced is limited

3-Flow Injection

The analyte is introduced into the carrier stream into a nebulizer as mist

4-Hydride Generation

the volatile sample is stripped from the analyte solution and carried out by a gas into the atomizer. This strip is followed by chemically converting the analyte to hydride vapor form.

5- With Arc Spark

Solids are employed

6- Laser Microbe Technique

A beam of laser is directed onto a small solid sample, gets vaporized, atomized by relative heating. Either sample is probed by encoding system or vapor produced is swept into a second absorption or fluorescence

- Nebulization gas is always compressed, usually acts as the oxidant; it is oxygen (O_2) in flame and argon (Ar) in plasma

- Nebulization chambers produce smaller droplets and remove or drain larger droplets called aerosol modifiers

- Aspiration rate is proportional to compressed gas pressure. The pressure drops through capillary, here 1/4 capillary diameters are recommended. This is inversely proportional to viscocity of the solution

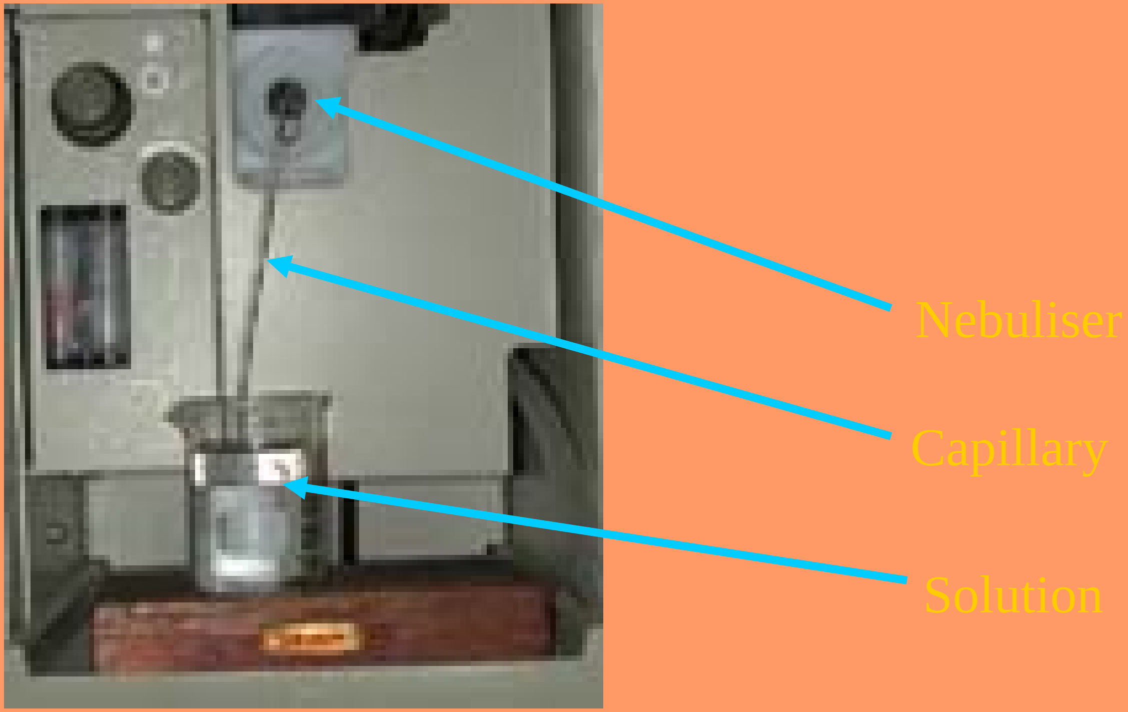
- Peristaltic and/or syringe pumps could be used

- Oxidant and fuel are usually brought into the nebulization chamber through a separate port. They mix and pass the burner head called premixed burner system.

- Add organic solvents to reduce the size of the drop

The Atomic Absorption Spectrometer

Sample Introduction System



- The fine mist of droplets is mixed with fuel (acetylene) , and oxidant (nitrous oxide) and burned.

The flame temperature is important because it influences the distribution of atoms. It can be manipulated by oxidant and fuel ratio.

Graphite Furnace

- The graphite furnace has several advantages over a flame. First it accept solutions, slurries, or solid samples.
- Second it is a much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidized elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyte atoms.
- It accommodates smaller samples but it's a difficult operation, because the high energy that is provided to atomize the sample particles into ground state atoms might excite the atomized particles into a higher energy level and thus lowering the precision .

3- Monochromators

This is a very important part in an AA spectrometer. It is used to separate out all of the thousands of lines. Without a good monochromator, detection limits are severely compromised.

A monochromator is used to select the specific wavelength of light which is absorbed by the sample, and to exclude other wavelengths. The selection of the specific light allows the determination of the selected element in the presence of others.

4 - Detector and Read out Device

The light selected by the monochromator is directed onto a detector that is typically a photomultiplier tube , whose function is to convert the light signal into an electrical signal proportional to the light intensity.

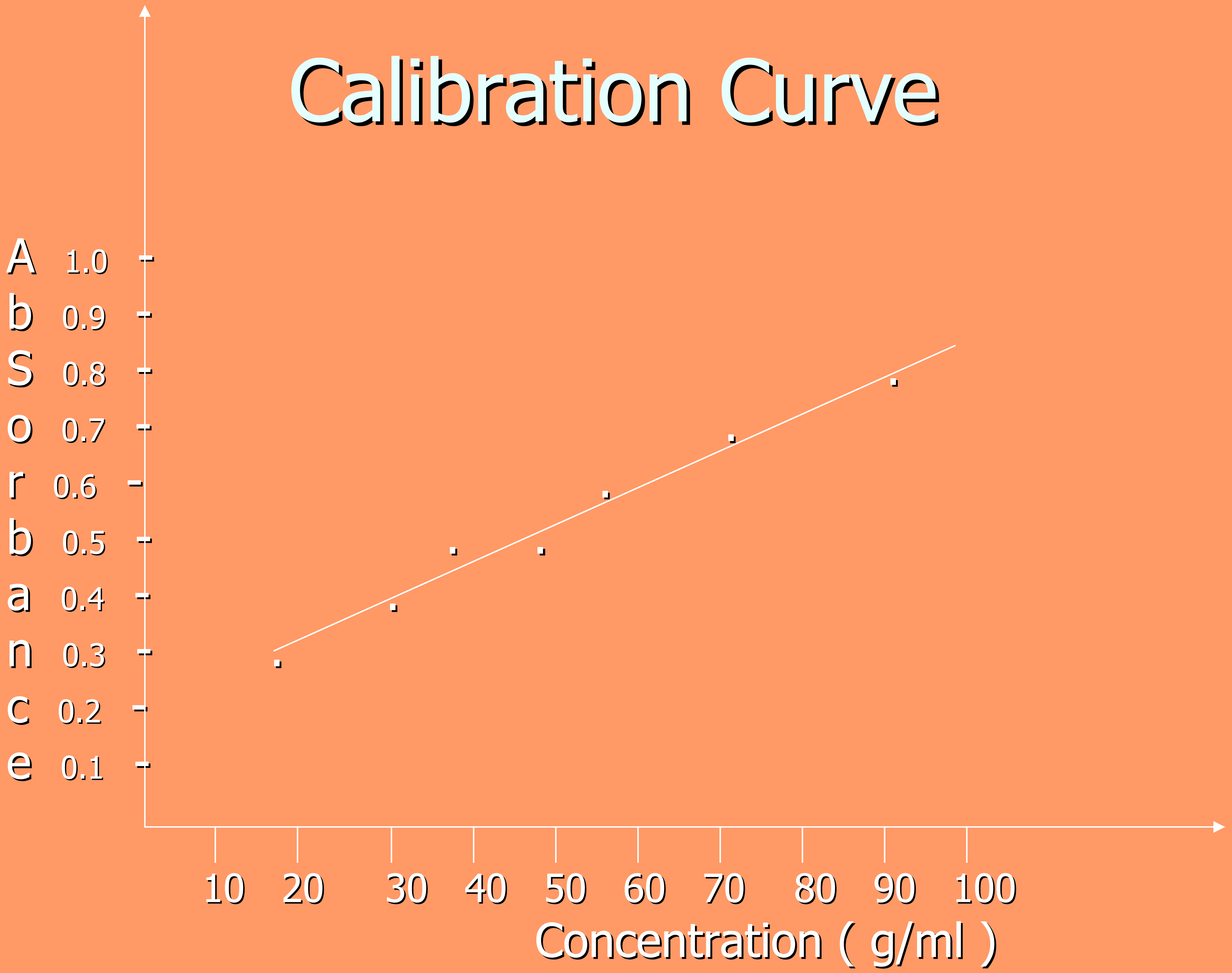
The processing of electrical signal is fulfilled by a signal amplifier . The signal could be displayed for readout , or further fed into a data station for printout by the requested format.

Calibration Curve

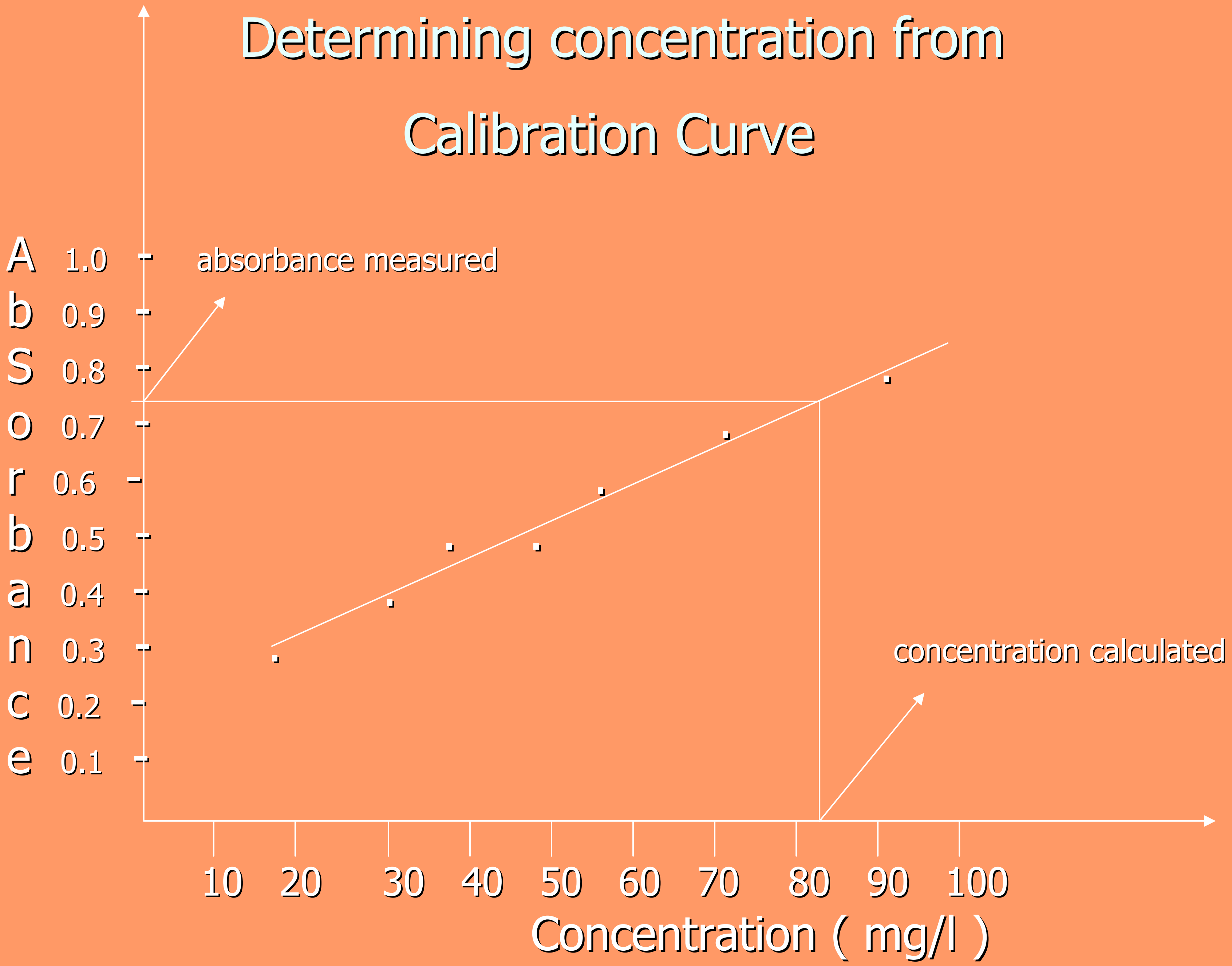
A calibration curve is used to determine the unknown concentration of an element in a solution. The instrument is calibrated using several solutions of known concentrations. The absorbance of each known solution is measured and then a calibration curve of concentration vs absorbance is plotted.

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

Calibration Curve



Determining concentration from Calibration Curve



absorbance measured

concentration calculated

Interferences

The concentration of the analyte element is considered to be proportional to the ground state atom population in the flame ,any factor that affects the ground state atom population can be classified as an interference .

Factors that may affect the ability of the instrument to read this parameter can also be classified as an interference .

The different interferences that are encountered in atomic absorption spectroscopy are :

- Absorption of Source Radiation : Element other than the one of interest may absorb the wavelength being used.

- Ionization Interference : the formation of ions rather than atoms causes lower absorption of radiation .This problem is overcome by adding ionization suppressors.

- Self Absorption : the atoms of the same kind that are absorbing radiation will absorb more at the center of the line than at the wings ,and thus resulting in the change of shape of the line as well as its intensity .

- Back ground Absorption of Source Radiation :

  This is caused by the presence of a particle from incomplete atomization .This problem is overcome by increasing the flame temperature .

- Transport Interference :

  Rate of aspiration, nebulization, or transport of the sample (e g viscosity, surface tension, vapor pressure , and density) .

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Atomic Emission Spectroscopy

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 .

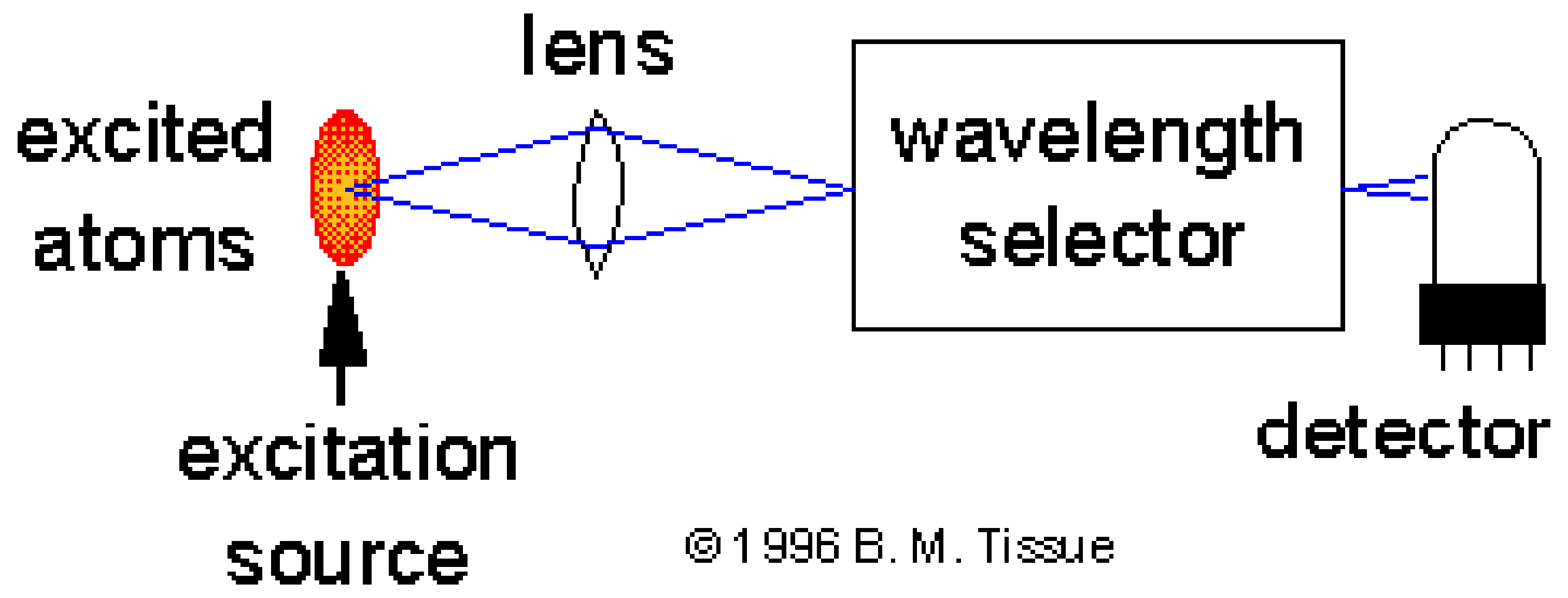
The analyte atoms are promoted to a higher energy level by the sufficient energy that is provided by the high temperature of the atomization sources .

The excited atoms decay back to lower levels by emitting light . Emissions are passed through monochromators or filters prior to detection by photomultiplier tubes.

The instrumentation of atomic emission spectroscopy is the same as that of atomic absorption ,but without the presence of a radiation source .

In atomic Emission the sample is atomized and the analyte atoms are excited to higher energy levels all in the atomizer .

Schematic Diagram of an Atomic Emission spectrometer



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 oC) is most useful for elements with relatively low excitation energies like sodium potassium and calcium .

- The ICP (6000 – 8000 oC) has a very high temperature and is useful for elements of high excitation energies .

Similar to an atomic absorption spectrometer ,the monochromator is simply a wavelength selector that separates all different wave lengths and select the desired one .

The selected wave length is passed on to a detector that converts the light signal into an electrical signal .

Comparison Between Atomic Absorption and Emission Spectroscopy

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

- It measures the radiation absorbed by the ground state atoms.	- It measures the radiation emitted by the excited atoms .
- Presence of a light source (HCL) .	- Absence of the light source .
- The temperature in the atomizer is adjusted to atomize the analyte atoms in the ground state only.	- The temperature in the atomizer is big enough to atomize the analyte atoms and excite them to a higher energy level.

3

AAS APPLICATIONS

The are many applications for atomic absorption:

- **Clinical analysis :** Analyzing metals in biological fluids such as blood and urine.
- **Environmental analysis :** Monitoring our environment – *e g* 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 – *e g* in concrete, where calcium is a major constituent, the lead level should be low because it is toxic.

- **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

Paper 1
Determination of lead in dialysis concentrates using FI – HG AAS

- Dialysis is a medical treatment that is given to patients with abnormal function of the kidney .
- Washing the kidney from the various trace elements that the kidney itself should have done .

- One of the elements that is present in a dialysis concentrate is lead ,which is very toxic and become fatal if it exceeds the level of 380 กg / l in our body .

- In order to determine the pb concentration in a dialysis concentrate, a flow injection hydride generation atomic absorption spectroscopy was proposed .

- The hydride generation is very applicable since its is a reducing agent and for some metals with high oxidation state the atomization energy is high ,so the hydride simply reduces the oxidation sate and thus the atomization energy .

- Lead hydride is usually unstable but in an acidic medium of Hcl with the presence of a mild oxidant k3 Fe (CN)6 it showed high precision and freedom from interferences .

- Sample is injected in an HCl , k3 Fe (CN) 6 carrier solution and then combined with with NaBH4 to mix in the mixing coil .

- An Argon gas carrier is used to sweep out the lead hydride carrier all the way to the atomizer .
- Comparison was done with an electro thermal AAS ,and the results were close but in FI HG AAS interference was absent .
- Finally FI HG AAS showed to be easy ,simple ,and low cost compared to ICP ; and it is applicable to all hydride standards .

paper 2

Online separation for the speciation of mercury in natural waters by flow injection Atomic Absorption Spectrometry ratio

- Nowadays methyl mercury is considered as the most toxic mercury compound .

- In this application separation of inorganic mercury Hg + from methyl mercury CH3Hg+ will be performed in an ion exchanger in a FIA apparatus ,and then followed by detection of CH3Hg+ in an atomic absorption spectrometer .

- An ion exchanger is used to take out the Hg+ since at pH < 10 Hg+ is completely anionic (HgCl)4-2 while CH3HgCl remains neutral .
- The left CH3Hgcl is detected by an atomic absorption Spectrometer .
- This application is very interesting because it used AAS , and FIA techniques to do both separation and detection .