INTRODUCTION

Atomic absorption spectroscopy (AAS) currently is the most widely used of atomic spectroscopic techniques. AAS is a quantitative method of elemental analysis that is applicable to many metals and a few nonmetals. Atomic Absorption Spectrophotometry is widely applied for the analysis of samples, such as agriculture , clinical and biochemistry, minerals, food , drugs , environmental species and others .

AAS deals with atoms , Fe^{2+} and Fe^{3+}
will not be distinguished.

PRINCIPLES OF AAS

In AA spectroscopy, as in all atomic spectroscopic methods, the sample must be converted into an atomic vapor by a process known as **atomization**. In this process, the sample is volatilized and decomposed to produce atoms and perhaps some ions in the gas phase. Several methods are used to atomize samples. The two most important of these for AA spectroscopy are **flame** and **furnace atomization**.

The radiation of a line source of the analyte , typically a hollow cathode lamp, is directed through the flame containing the gaseous analyte atoms . These ground state atoms absorb some of the source radiation . The extend of this **absorption** will be proportional to the number of the ground state atoms in the flame i.e. the analyte's concentration .
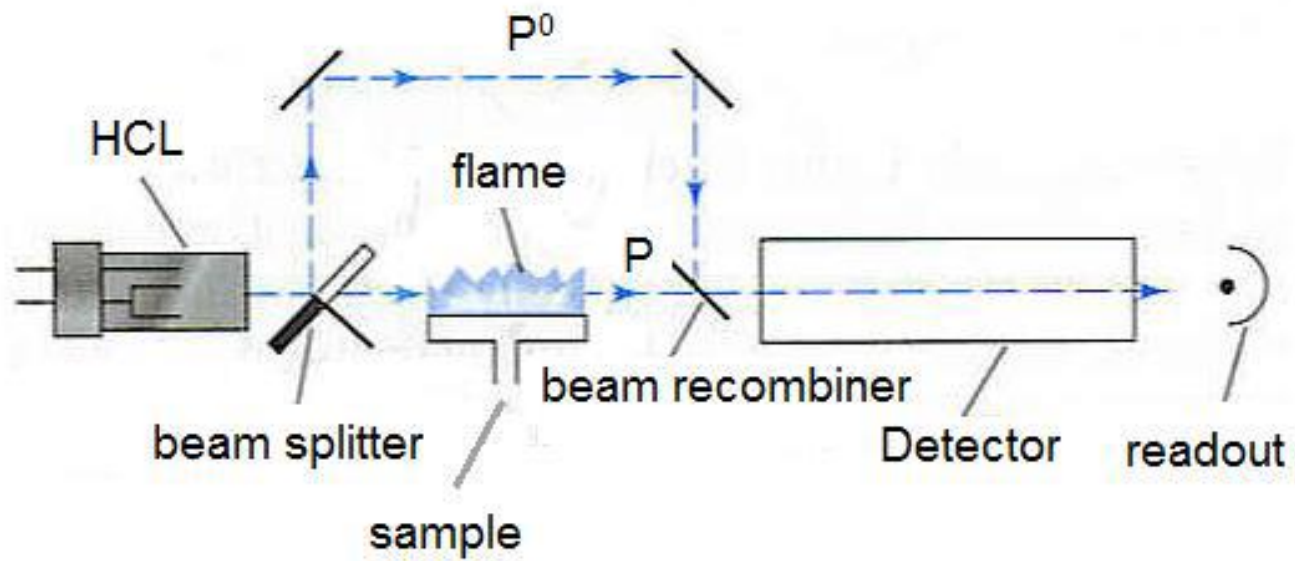
PRINCIPLES OF AAS … cont'd
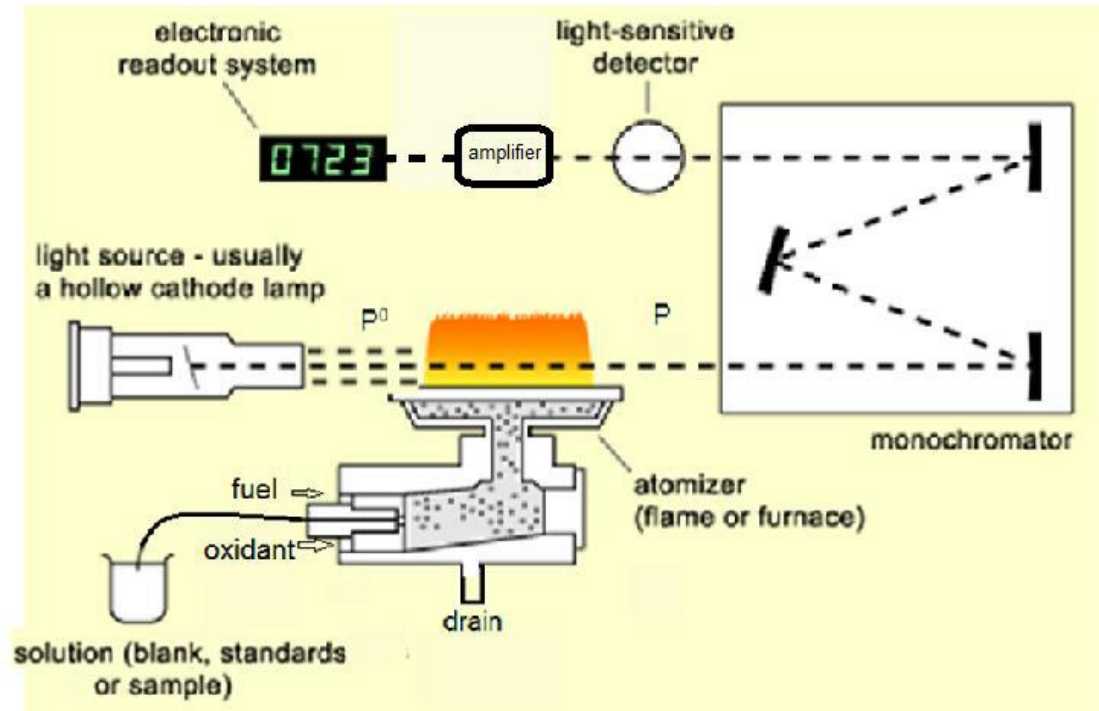
PRINCIPLES OF AAS … cont'd

Part of the energy of the incident radiation P_0 is absorbed.
The transmitted radiation P is given by

$P = P^0 e^{-(ab)},$ $A = \log P^0 / P = abc = -\log T$ (see Beer's law unit 4)

where a is the absorption coefficient of the analyte element and b is the horizontal path length of the radiation through the flame and the others as in Beer's law. Atomic absorption is determined by the difference in radiant power of the resonance line in the presence P and absence P^0 of analyte atoms in the flame. The width of the line emitted by the light source must be narrower than the width of the absorption line of the analyte in the flame.

PRINCIPLES OF AAS … cont'd

Solution samples are usually brought into the flame by means of a sprayer or nebulizer as mentioned in unit 7 and only 5% of the ground state atoms are excited and used by FAES and the remaining 95% will be used by AAS .

The use of a flame limits the excitation temperature reached by a

sample to a maximum of approximately 2600^oC .For many

elements this is not a problem . Compounds of the alkali metals, for example, and many of the heavy metals such as lead or cadmium and transition metals like manganese or nickel are all atomized with good efficiency in the flame , with typical detection limits in the sub-ppm range.

PRINCIPLES OF AAS … cont'd

However, there are a number of refractory elements like V, Zr, Mo and B which do not perform well with a flame source. This is because the maximum temperature reached in the flame, is insufficient to break down compounds of these elements. As a result, flame AAS sensitivity for these elements is not as good as other elemental analysis techniques .

PRINCIPLES OF AAS … cont'd
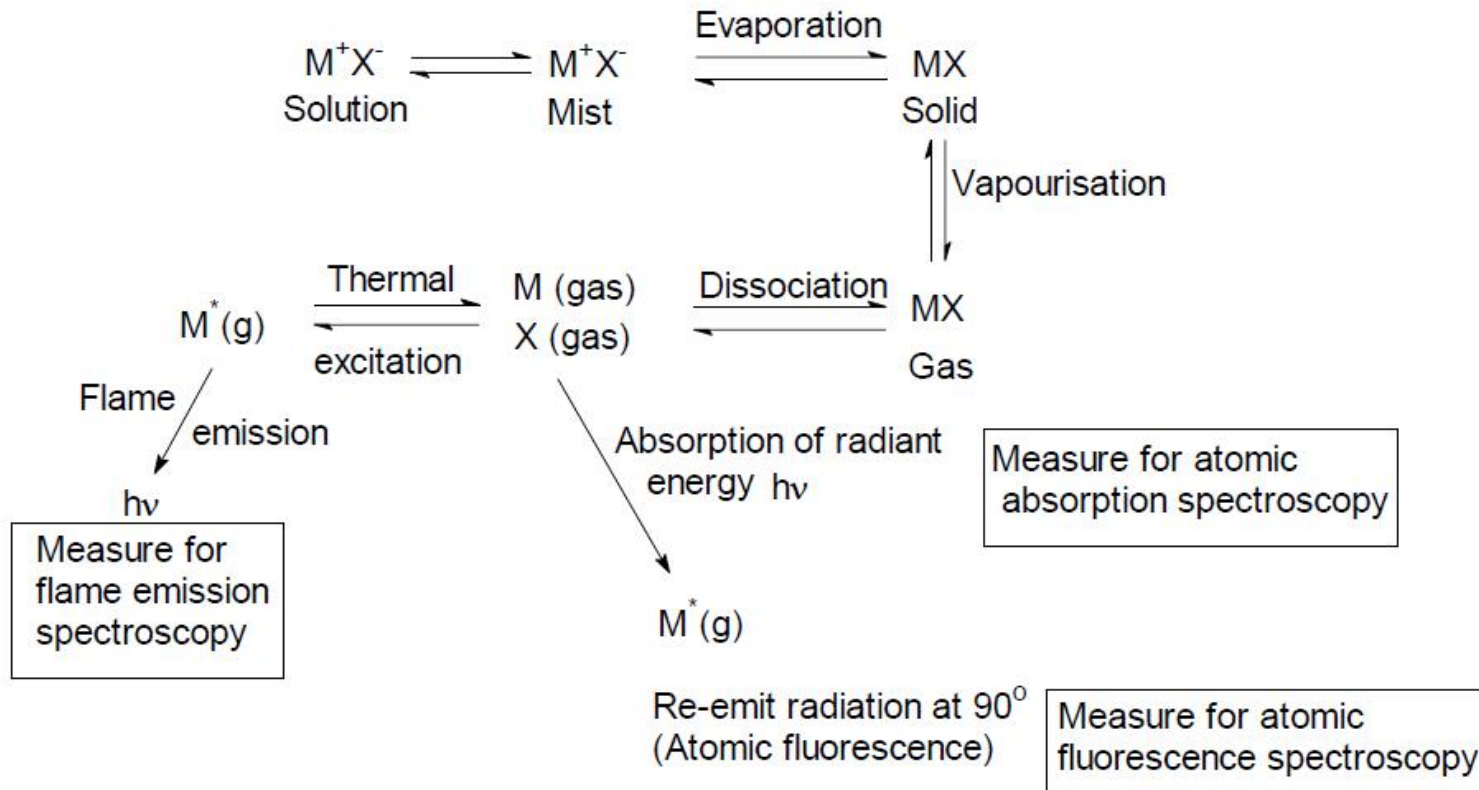
Process by which gaseous atoms are produced in flames
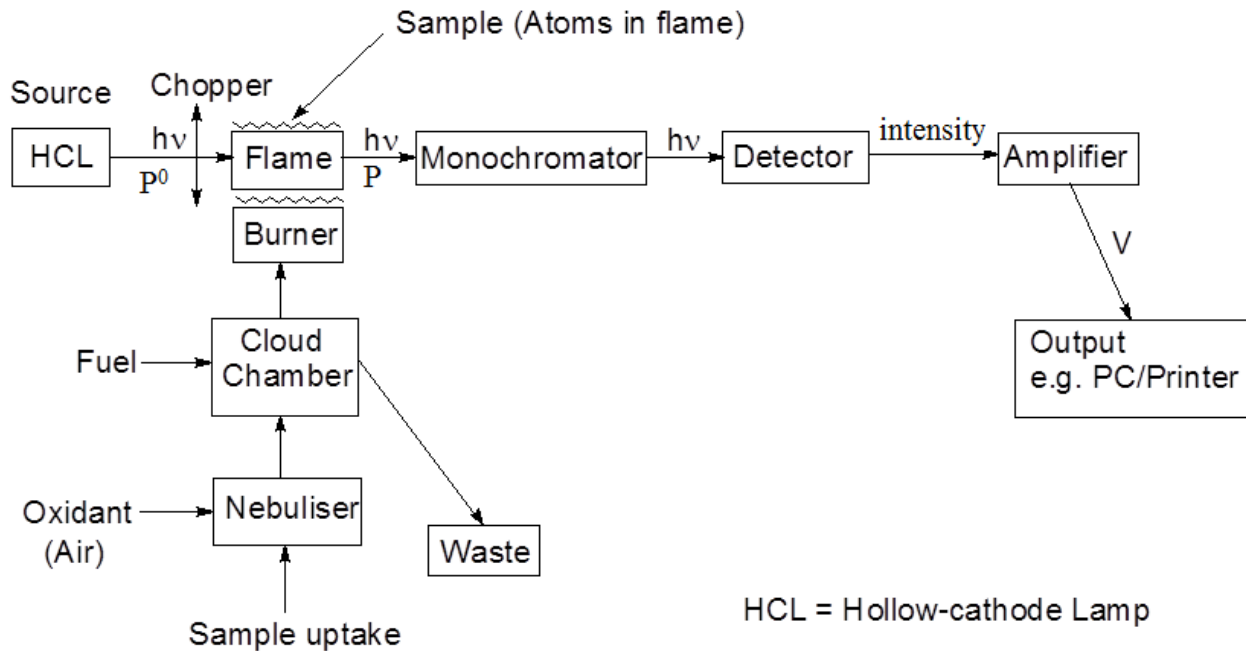
INSTRUMENTATION

Every AA spectrometer must have the following components :

1- **Radiation Source :** which emits the sharp atomic lines of the element to be determined is required (line source) . The most widely used source is the hollow cathode lamp. These lamps are designed to emit the atomic spectrum of the analyte .

a) **Hollow Cathode Lamp (HCL) :**

This lamp consists of a cylindrical metallic cathode (made from the same element being analyzed) and tungsten anode sealed in
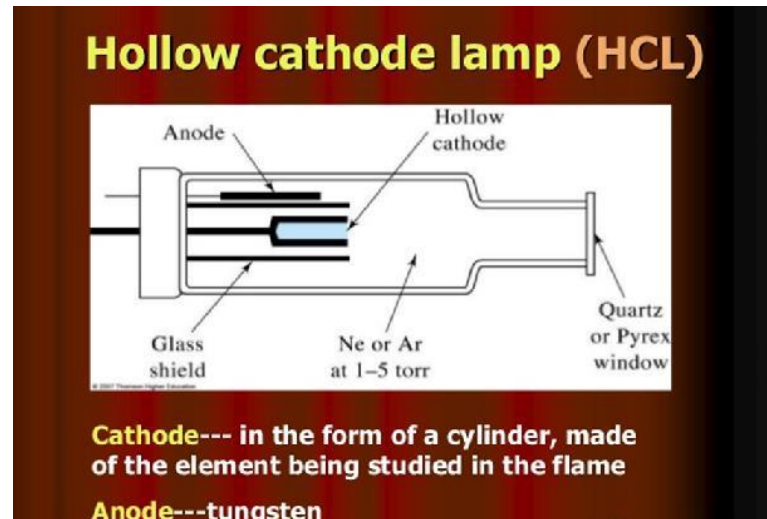
INSTRUMENTATION … cont'd

Schematic Diagram of an Atomic Absorption Spectrophotometer

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INSTRUMENTATION …. continued

a glass tube containing neon or argon. When high voltage is applied between the anode and cathode, the filler gas is ionized and positive ions are accelerated toward the cathode.

Hollow cathode lamp (HCL)

Anode

Hollow cathode

Glass shield

Ne or Ar at 1–5 torr

Quartz or Pyrex window

Cathode--- in the form of a cylinder, made of the element being studied in the flame

Anode---tungsten

Hollow Cathode Lamp (Cont'd)

They strike the cathode with enough energy to "sputter" metal atoms from the cathode surface into the gas phase. The free atoms are excited by collisions with high-energy electrons and then emit photons to return to the ground state. This radiation has the same frequency as that absorbed by analyte atoms in the flame .
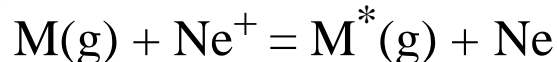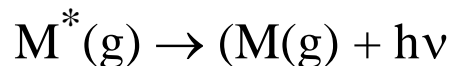
(1) Ionization of the filler gas:

$$Ne + e^- = Ne^+ + 2e^-$$

(2) Sputtering of the cathode element(M):

$$M(s) + Ne^+ = M(g) + Ne$$
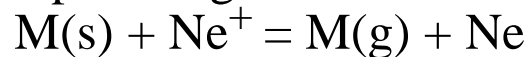
(3) Excitation of the cathode element(M):

$$M(g) + Ne^+ = M^*(g) + Ne$$

(4) Emission of radiation

$$M^*(g) \rightarrow (M(g) + h\nu$$
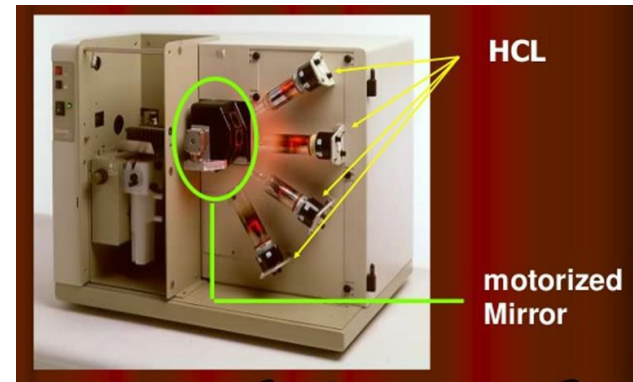
Hollow Cathode Lamp (Cont'd)

The main disadvantage of HCL is that each element has it's own unique lamp because the cathode is made from the analyte . This can be also considered an advantage due to less spectral interferences .

The linewidth from the HCL is to (comparednarrowrelatively linewidths of atoms in the flame or furnace i.e. absorption line) because of low pressure and lower temperature in lamp (less Doppler broadening).

Hollow Cathode Lamp (Cont'd)

Atomic absorption of a narrow emission line from a source.

Atomic absorption of a narrow emission line from a source. The source lines in (a) are very narrow. One line is isolated by a monochromator. The line is absorbed by the broader absorption line of the analyte in the flame (b) in resulting reduction (c) of the source radiation.
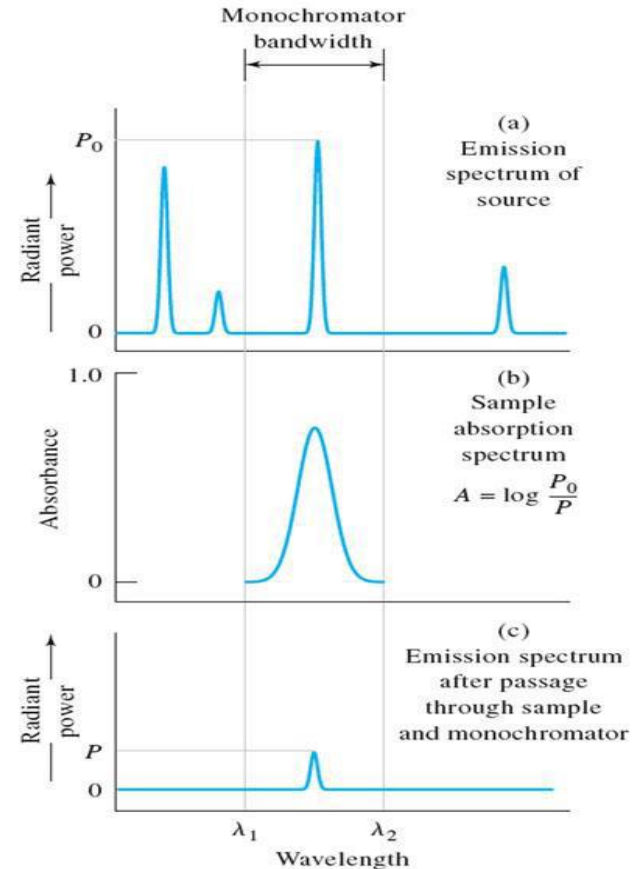
© 2007 Thomson Higher Education

Doppler broadening :

The linewidth of the source must be narrower than the linewidth of the atomic absorption for Beer's law to be obeyed .

The line bandwedth of radiation emitted or absorbed by a fast moving atom decreases or increases as a result of the rapid motion of the atoms . This is called Dopplerbroadening .

Collisional broadening :

Collisional , broadening arises from collisions of emitting or absorbing species with other atoms or ions in the heated medium which leads to deactivation of the excited state and thus broadening the spectral lines .

b- Electrodeless Discharge Lamps (EDL) :

Constructed from a sealed quartz tube containing an inert gas such as argon and a small quantity of the metal analyte (or its salt).The lamp does not contain an electrode but instead is energized by a field of radio-frequency or microwave radiation. Radiant intensities greater than HCL.The main drawbacks of EDL are their performance does not appear to be as reliable as that of the HCL lamps (signal instability) and they are only commercially available for some elements.

C- Lasers:
They are intense enough to excite atoms to higher energy levels.

Why we don't use continuum source in AAS ?

Atomic absorption bandwidths are so narrow, with an inherent linewidth of 0.0001 nm. Due to Doppler effect and collisional broadening,linewidths of atoms in a flame are typically 0.001 – 0.01 nm.The narrowest band of wavelengths that can be isolated from a continuum with best monochromator is about 0.5 *nm.* Therefore, we require a source having a linewidth of less than 0.01 nm . At a proper conditions, the bandwidth of emitted radiation with hollow cathode lamp is even narrower than the atomic absorption bandwidth.
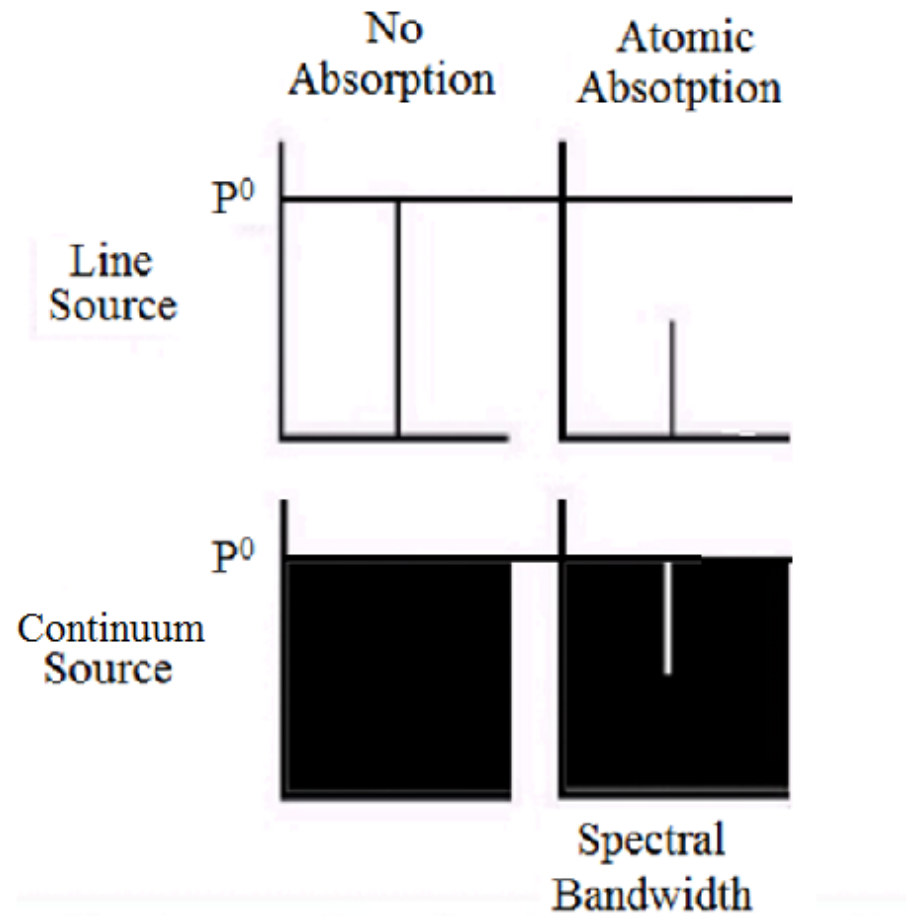
Atomic and background absorption with
a line source and a continuum source .
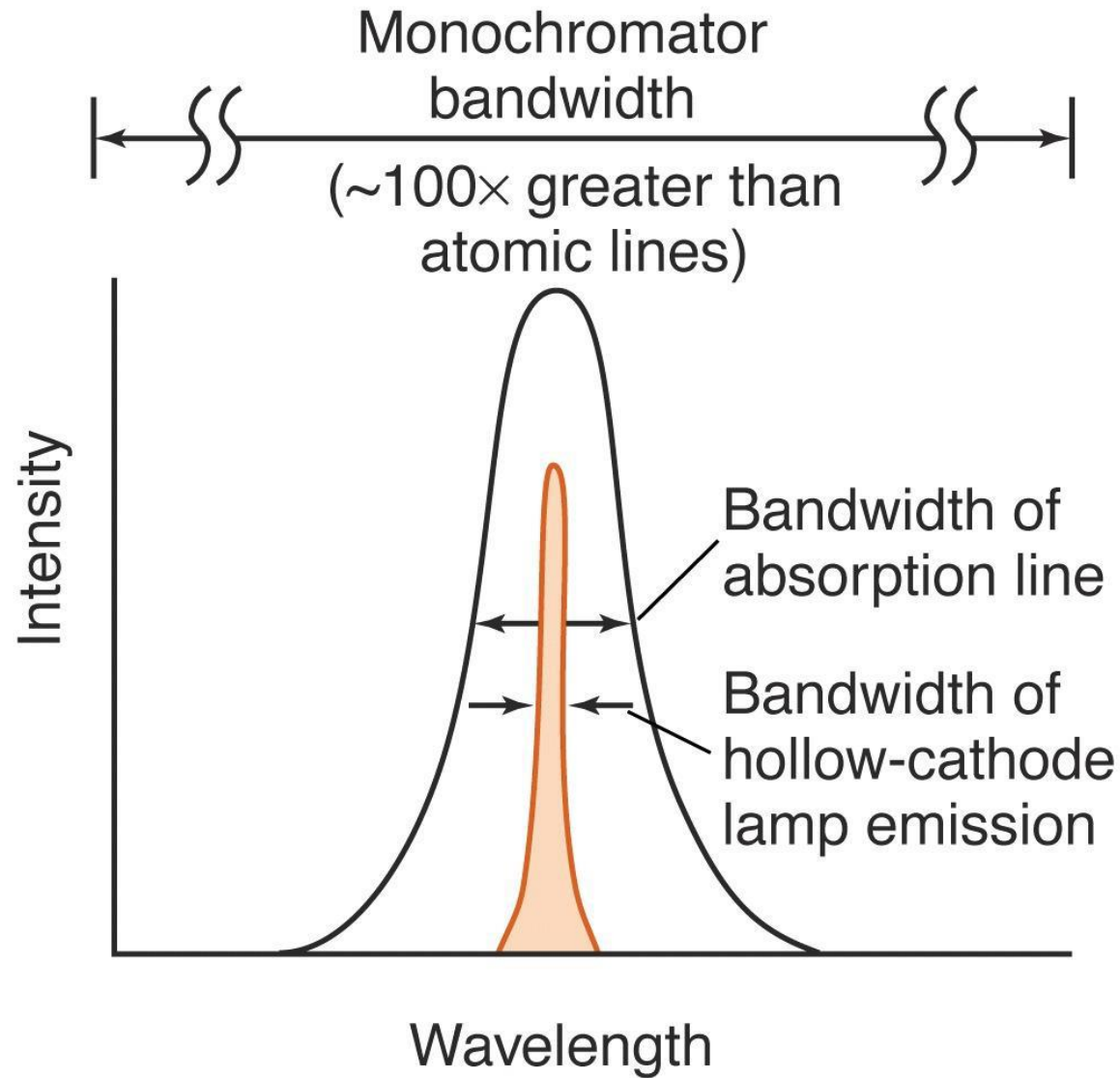
INSTRUMENTATION …cont'd

2- Nebulizer to transfer analyte solution into the flame atomizer. By breaking the sample solution into small droplets. Most (>99%) are collected as waste , only small fraction reach the flame . The flame path is about 10 – 12 cm in AAS to increase the absorption and consequently the sensitivity while in FAES it is rounded .

premix burner

High-pressure gas flow

Sample solution

(b)
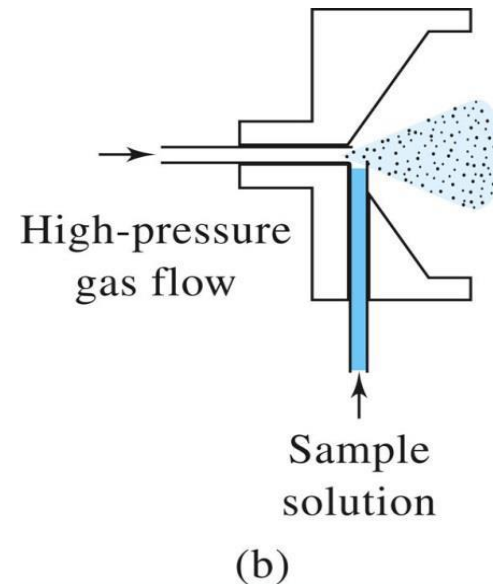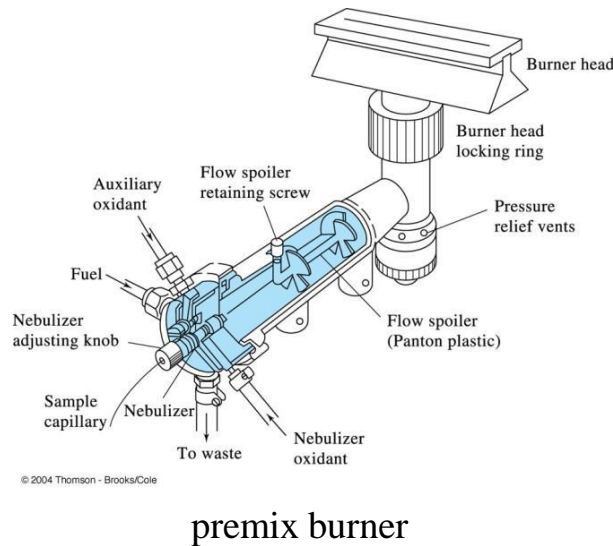
INSTRUMENTATION …cont'd

3- Atomizer : to convert the analyte to ground state free atoms . For this purpose we use either flame or graphite furnace or tube.

(a) Flame atomizer (FAAS) : In most cases air or nitrous oxide – acetylene flames are used . Different flames can be achieved using different mixtures of gases, depending on the desired temperature and burning velocity. Some elements can only be converted to atoms at high temperatures. Some metals form oxides that do not re-dissociate into atoms. To inhibit their formation, conditions of the flame may be modified to achieve a reducing, non-oxidizing flame.

INSTRUMENTATION …cont'd

Small changes in flame temperature have little effect in atomic absorption but have significant effects in atomic emission spectroscopy . The flame has been previously discussed in unit 7. Other atomizers are graphite furnace and hydride generation system will be discussed later .

ADVANTAGES AND DISADVANTAGES OF FLAME AAS

Advantages :

1- equipment relatively cheap .

2- easy to use (training easy compared to furnace) .

3- good precision .

4- cheap to run .

Disadvantages :

1- lack of sensitivity (compared to furnace) .

2- problems with refractory elements .

3- require large sample size .

4- sample must be in solution .

(b) Electrothermal Atomzer (ETA)   :

The sample is contained in a heated, graphite furnace.The furnace is heated by passing an electrical current through it (thus, it is electro thermal). To prevent oxidation of the furnace, it is sheathed in gas (Ar usually) .There is no nebulization ,the sample is introduced as a drop (usually 5-20 µL) or solid (rare). The furnace goes through several steps .
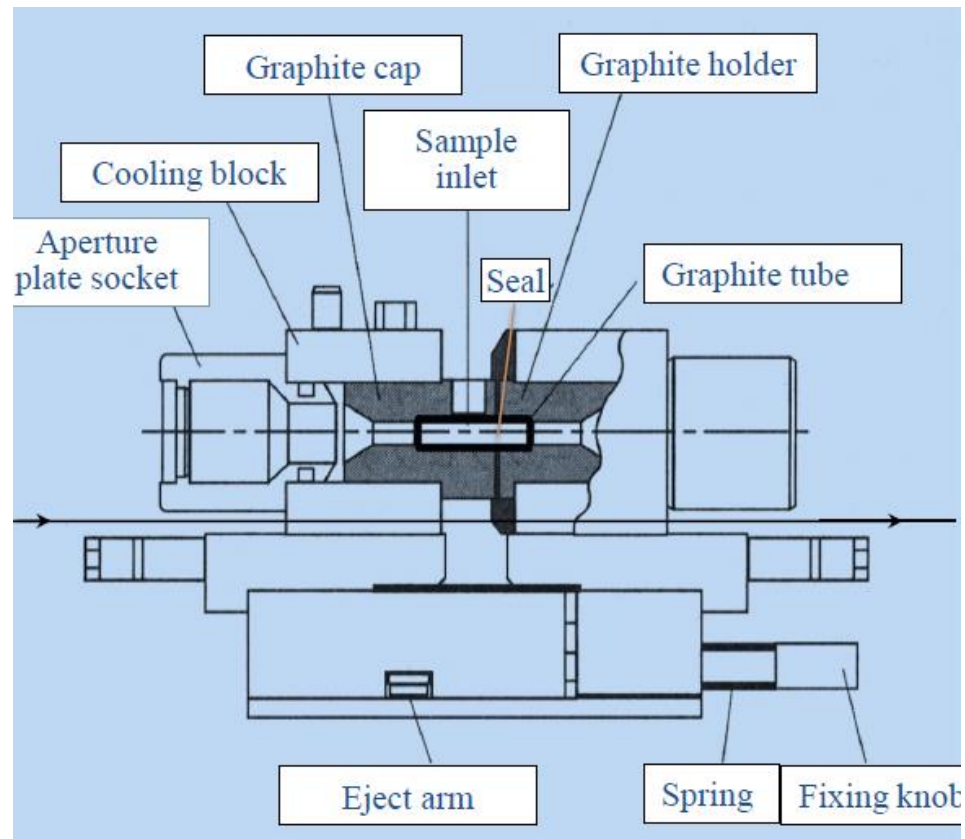- Drying (usually just above 110 deg. C.)
- Ashing (up to 1000 deg. C)
- Atomization (Up to 2000-3000 C)
 Waste is blown out with a blast of Ar.
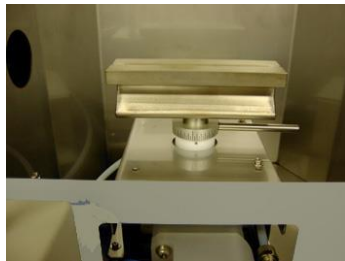
b) Electrothermal Atomzer : … cont'd

The light from the source (HCL) passes through the furnace and absorption during the atomization step is recorded over several seconds. This makes ETA more sensitive than flame for most elements.

Graphite tube

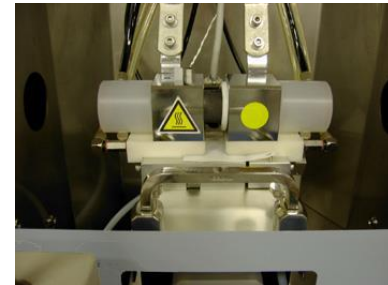## **Easy switching between flame and furnace**

Flame -> Furnace: All that is involved is to remove the burner head, place the furnace unit, and fix it with the screw. No tools are required.

Remove the burner head.

Fit the furnace.

Fit the burner head.

Remove the furnance

Advantages and disadvantages of electrothermal atomization

Advantages :

1- Very sensitive for many elements (10^{-14} g compared to

10^{-10}g for flame) .

2- Small sample size .

3- Less chemical interferences due to very high temperature .

4- Direct analysis of solid samples (rare) .

5- less physical interferences because there is no nebulization .

Advantages and disadvantages of electrothermal atomization .. Cont'd

Disadvantages

1- poor precision 5 – 10% compared to 1% for the flame .

2- high ionization interferences due to high temperature.

2- Expensive to purchase and run (argon, tubes) .

3- Requires background correction .

4- Requires a high degree of operator skill (compared to flame AAS) .

5- The linearity range is relatively narrow .

NSTRUMENTATION …. Cont'd

4- Monochromators :

The operation and sensitivity of the atomic absorption spectrometer depends on the spectral band width of the resonance line emitted by the line source (the hollow cathode lamp).The function of the monochromator is to isolate the resonance line from other lines close to it in the source spectrum and from background continua and molecular emissions originating in the flame . Hollow cathode lamps emit a number of lines, in the case of multi-element lamps, the number can be quite large and it is necessary to isolate the line of interest.A prism or a grating can be used for this purpose . These also have been previously discussed in unit 3 .

INSTRUMENTATION …. Cont'd

5- The **detector** is normally a photomultiplier tube, which produces an electrical current which is amplified and processed by the instrument electronics to produce a signal which can be further processed to produce an instrument readout directly in concentration units .

The photomultiplier tube has been investigated in unit 3 .

Therefor we will limit our investigation to the components that have not been discussed before .
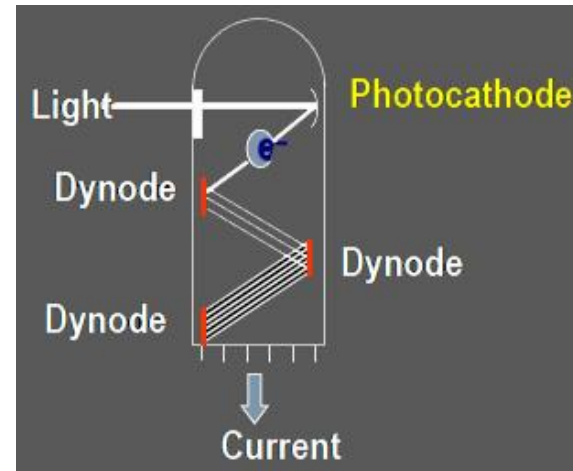
AAS INTERFERENCES

What do we mean with interference ?

Any factor that affects the ground state population of the analyte element in the atomizer . In other words any increase or decrease in the signal obtained from the analyte as a result of the presence of some other component in the sample or in the atomizer .

Also factor that may affect the ability of the instrument to read this parameter . There are five important types of interferences :

A) Spectral interferences:

This refers to <mark>overlap</mark> of analyte line with lines originating from other elements in the sample or with lines or bands due to the flame or furnace .e.g. flame background emission . The presence of <mark>Al and V in the same solution will interfere with each other :</mark>

308.216 nm Al

308.211 nm   V

Solution:

Use a different line (which may be less sensitive) or
Separate these elements .

Background correction

Background signal arises from absorption, emission, or scatter by everything in the sample besides analyte ((the matrix), as well as by the flame, the furnace, or the plasma.

Background correction methods :

1- Beam chopping

In order to eliminate the unwanted emissions from the atomizer, the light source is modulated by a chopper which is located between the hollow cathode lamp and the atomizer . The amplifier which modifies the signal from the photomultiplier is tuned in to the same frequency .
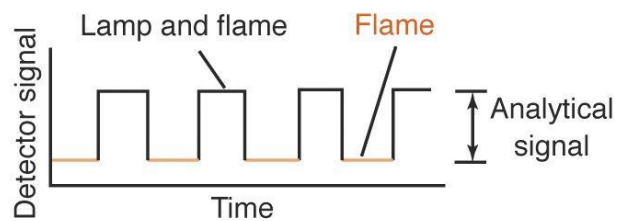(Alternatively, the hollow cathode lamp may be modulated by applying an AC voltage at say 50 Hz .
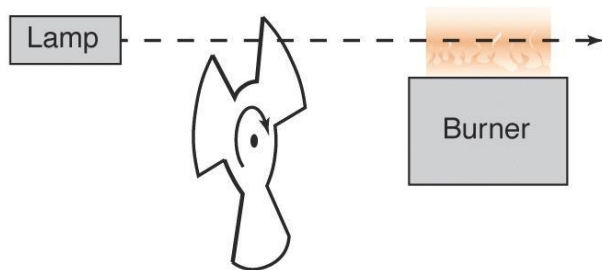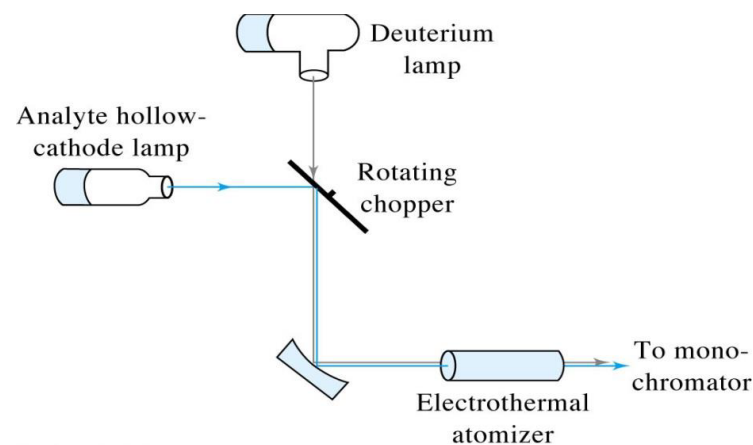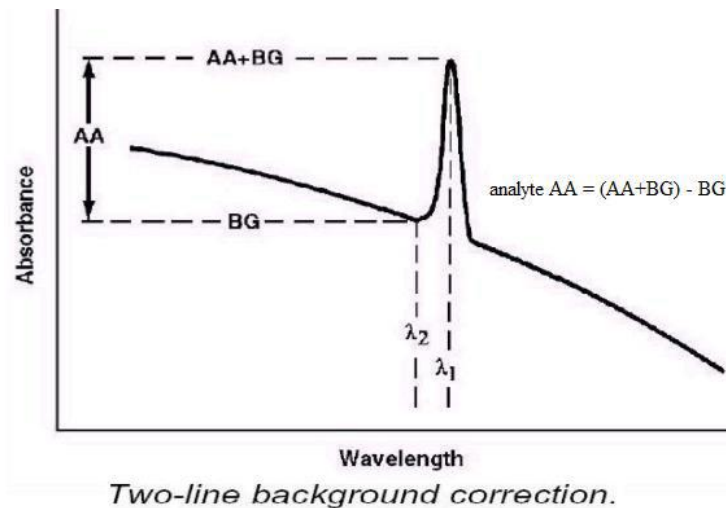
(a)   Rotating chopper
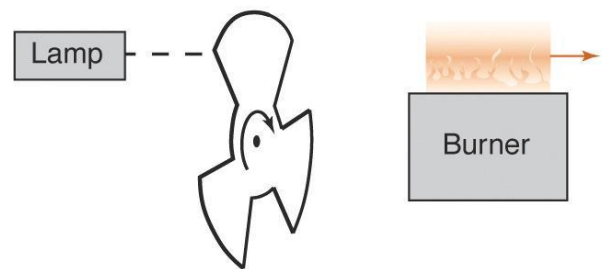
(b)

(c)

A beam chopper for subtracting the signal due to flame background emission. Resulting square-wave signal.

2- Using continuum source : The difference between absorbance measured with the hollow cathode and absorbance measured with the continuum source is the absorbance due to analyte.

Two-line background correction.

B) Chemical Interferences :

Elements that form very stable compounds are said to be <mark>refractory</mark> because they are not completely atomized at the temperature of the flame or furnace.
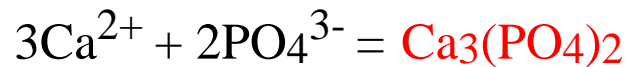
Solution

Use a higher flame temperature (nitrous oxide/acetylene)

Use a release agent

Use protective chelation

For example in the determination of calcium in the presence of sulfate or phosphate , the ground state calcium atoms will be reduced due to formation of thermally stable difficult to atomize compounds :

$$3Ca^{2+} + 2PO_4^{3-} = Ca_3(PO_4)_2$$

(stable compound)

This can be solved by either adding a release agent to free Ca from the stable compound e.g. $LaCl_3$

$$2LaCl_3 + Ca_3(PO_4)_2 = 3CaCl_2 + 2La(PO_4)$$
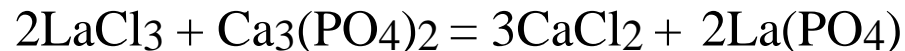
$CaCl_2$ readily dissociates

Or by adding chelating agent such as EDTA :

$$Ca_3(PO_4)_2 + 3EDTA = 3Ca(EDTA) + 2PO_4^{3-}$$
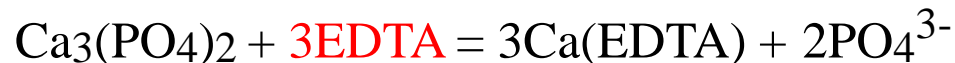
Ca(EDTA) dissociates readily.

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CHEMICAL INTERFERENCES

Decrease in calcium absorbance is observed with increasing concentration of sulfate or phosphate

Interfrences of Phosphate on Calcium
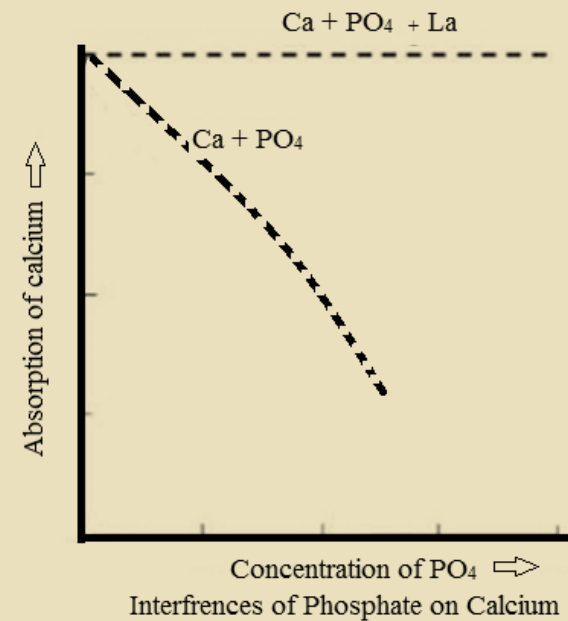
C) Ionization Interferences :

$$M(g) \rightarrow M^+(g) + e^-$$

A problem in the analysis of very low excitation potential metals such as alkali metal and particularly at higher temperatures. These metals are most extensively ionized in flames.

At 2450 K , sodium is 5% ionized.

Potassium is 33% ionized under the same conditions.

Ionized atoms emit radiation different from the radiation emitted by the excited atoms . Therefore the analytical signal from the ground state atoms (atomic absorption) is reduced.

To reduce the ionization interferences we add an ionization suppressor which is easily ionized element such as Cs e.g. adding Cs when analysing Na or K. Cs is more readily ionized than either Na or K.This produces a high concentration of electrons in the flame and reduce the ionization of Na or K according to Le Châtelier's principle.

$$K = \frac{[M^+][e^-]}{[M]}$$

$$[M] = \frac{[M^+][e^-]}{K}$$

Ionization interferences can be minimized by lowering the atomizer's temperature .

D) Self-absorption Interferences :

It is a process observed when a HCL lamp is operated at high currents where sputtering of a large number of atoms takes place. Most atoms do not get enough excitation energy in this process and thus absorb emitted radiation from other excited atoms within the lamp causing lower sensitivity and negative deviation in the calibration curve with the increasing concentration .This can be overcome by using only the lamp current suitable to the analyte . Also the ground state atoms in the outside cool parts of the flame can absorb the emission from the excited atoms in the hot meddle of the flame for the same elements resulting in reducing intensity in FAES and also FAAS . This can be reduced by reducing the length of the flame as in the following figure and avoiding high concentration .
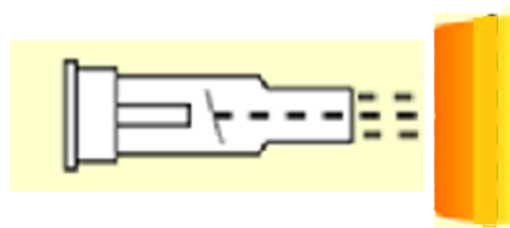
E) Physical interference

Spray efficiency fluctuations due to difference in physical properties e.g. viscosity , density and surface tension between the standards and sample . In other words The amount of sample reaching the flame and the droplet's size are dependent on the physical properties of the solution .

To avoid differences in the amount of sample and standard reaching the flame, it is necessary that the physical properties of both be matched as closely as possible . Example analysis of blood .

The increased signal In presence of ethanol is due to lower surface tension in presence of ethanol which produces smaller droplets.

SENSITIVITY :

the concentration of an element which will reduce the transmission by 1%

$$Abs = -\log\left(\frac{P}{P^0}\right) = -\log\left(\frac{99}{100}\right) = 0.00436$$

This corresponds to an absorption of 0.00436

DETECTION LIMIT :

The concentration of an element that gives a signal equal to three times the blank signal .

APPLICATIONS

A calibration curve is used to <mark>determine the unknown concentration of an element in a solution</mark>. 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 founded from the calibration curve
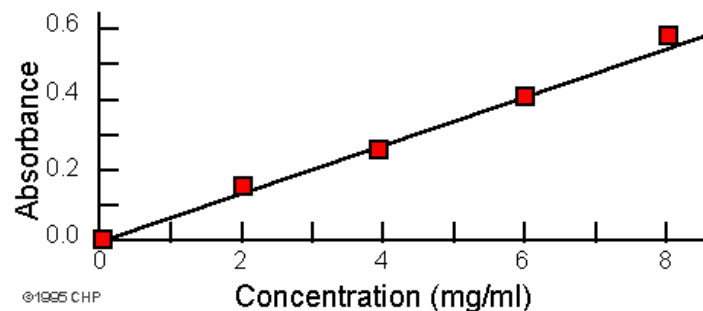
APPLICATIONS …. Cont'd

Standard addition method can also be used instead of the calibration method if necessary .

There 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, soil , and petrol.

- Pharmaceuticals. Analysis of drugs .

- 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. Analysis of trace elements in food and in cosmetics .

- 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 calciu is
a major constituent,

the lead level should be low because it is toxic . 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 .

AAS vs ICP

The basic difference between the two techniques is that AAS relies upon an atomic absorption process while ICP is an atomic/ionic emission spectroscopic technique. The next essential difference is the means by which the atomic or ionic species are generated. A combustion flame or graphite furnace is typically used for AAS while ICP-AES uses a plasma.
The typical maximum temperature for an air/acetylene flame is 2300 °C while for nitrous oxide acetylene, it is 2 900 °C. Temperatures as high as 10 000 K can be reached in an argon plasma.
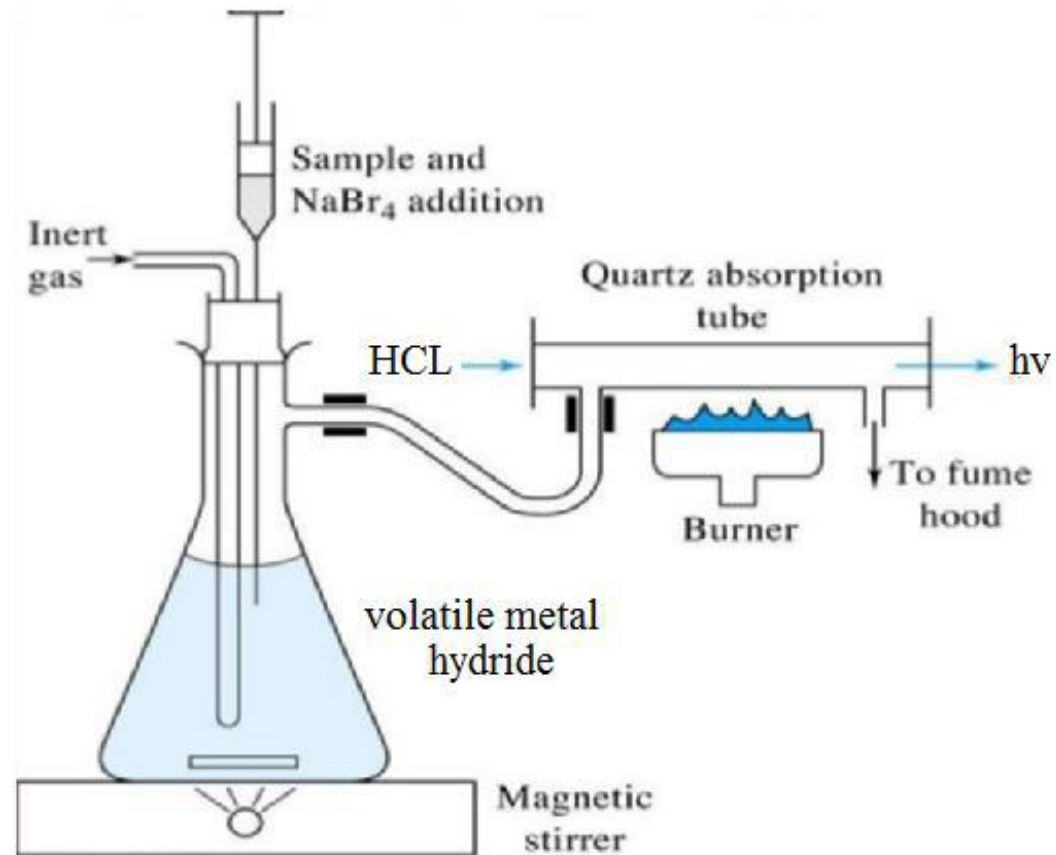
Non metals such as sulfur, nitrogen, carbon, and the halogens (e.g. I, Cl, Br) can only be determined by ICP.
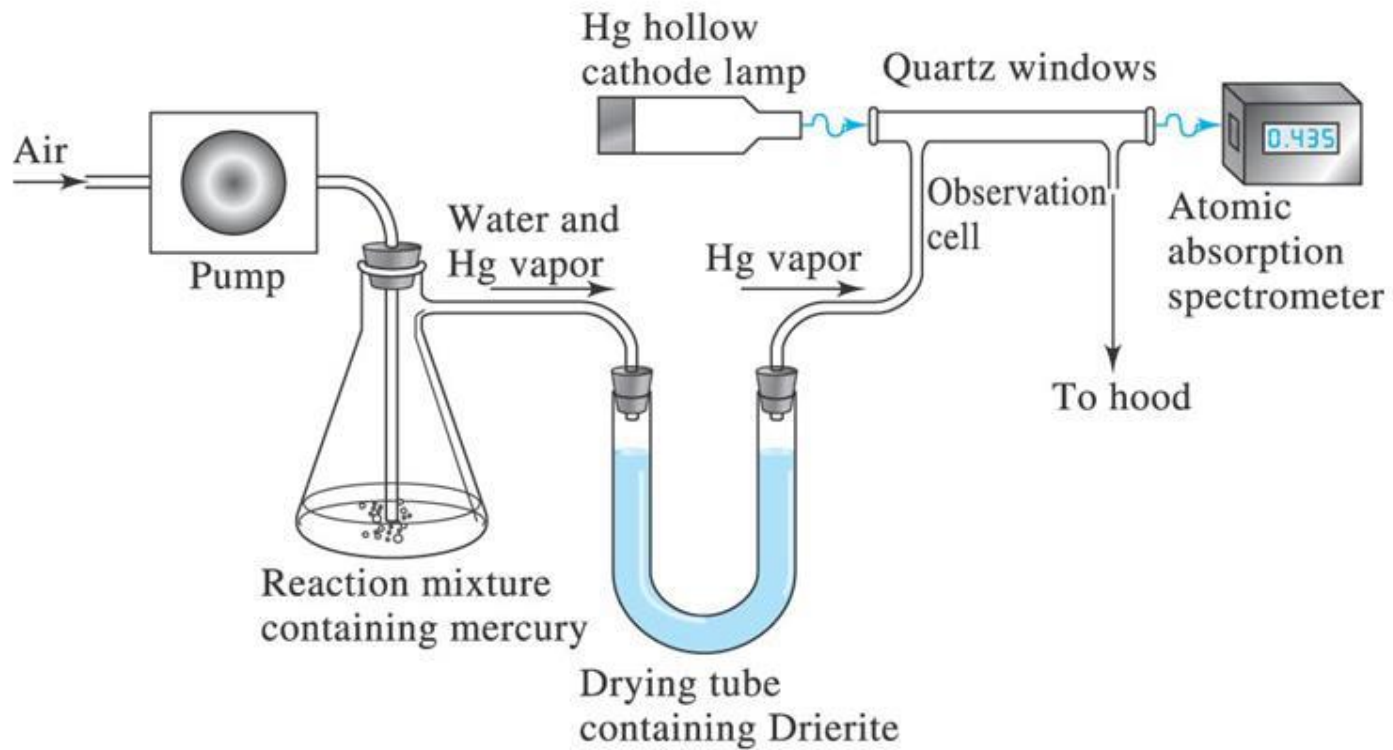
Determination of mercury by AAS without the use of atomizer

Determination of some elements by converting them to volatile hydrides

Sample and
NaBr$_4$ addition

Inert gas

Quartz absorption tube

HCL → hv

volatile metal hydride

Burner

To fume hood

Magnetic stirrer

Detection limits

COMPARISON OF DETECTION LIMITS FOR SELECTED ELEMENTS[a]

Element	AAS		AES	
	Flame	Electrothermal	Flame	ICP
Al	30	0.005	5	2
As	100	0.02	0.0005	40
Ca	1	0.02	0.1	0.02
Cd	1	0.0001	800	2
Cr	3	0.01	4	0.3
Cu	2	0.002	10	0.1
Fe	5	0.005	30	0.3
Hg	500	0.1	0.0004	1
Mg	0.1	0.00002	5	0.05
Mn	2	0.0002	5	0.06
Mo	30	0.005	100	0.2
Na	2	0.0002	0.1	0.2
Ni	5	0.02	20	0.4
Pb	10	0.002	100	2
Sn	20	0.1	300	30
V	20	0.1	10	0.2
Zn	2	0.00005	0.0005	2

[a]Parts per billion ($\mu g/L$). AAS, atomic absorption spectroscopy; AES, atomic emission spectroscopy.