

INSTRUMENTAL ANALYSIS II



Unit 5

Atomic Absorption and emission Spectroscopy

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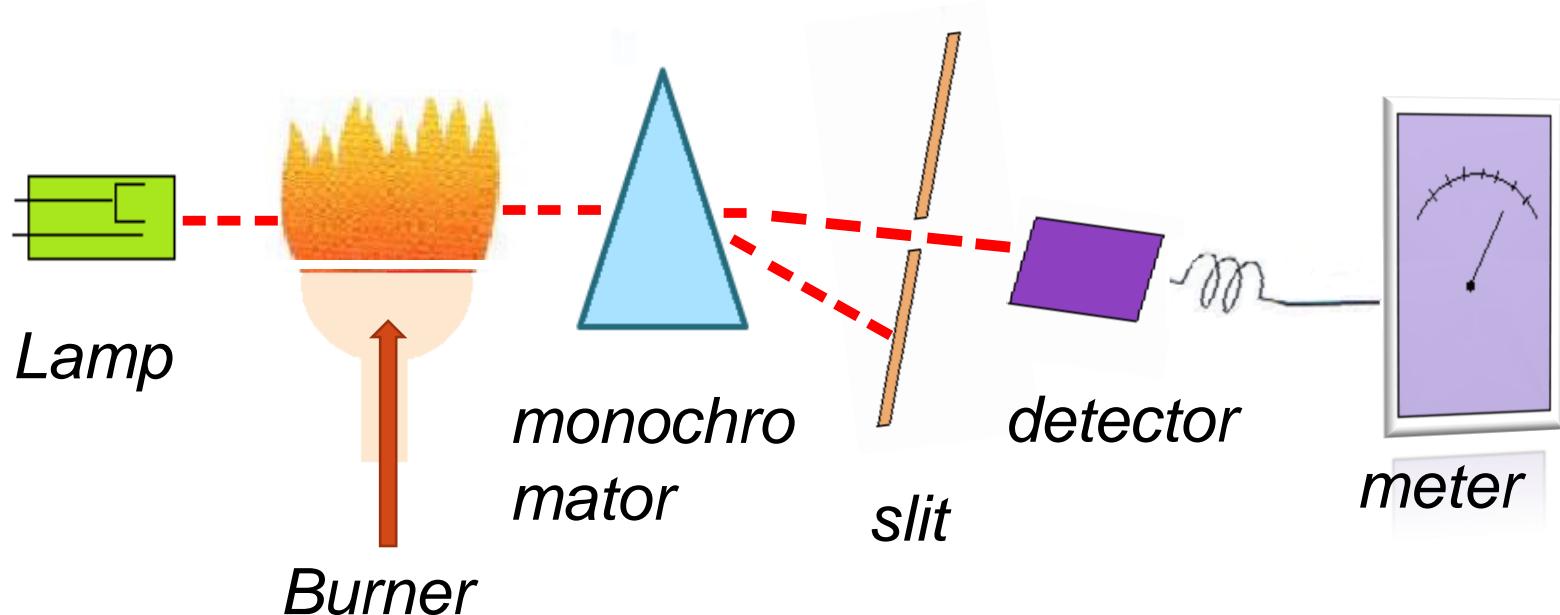
Atomic Absorption Spectroscopy

- ❖ AAS is based on the absorption of radiant energy by free gas phase atoms.
- ❖ AAS is an analytical technique that measures the concs of elements. It makes use of the absorption of light by these elements in order to measure their concentration .
- ❖ AAS quantifies the absorption of ground state atoms in the gaseous state .
- ❖ The atoms absorb UV /Vis light & make transitions to higher electronic energy levels.
- ❖ The analyte conc is determined from the amount of absorptⁿ.
- ❖ Conc measurements are usually determined from a working curve after calibrating the instrument with standards of known conc.
- ❖ AA is a very common technique for detecting metals & metalloids in environmental samples.

The Atomic Absorption Spectrometer

Atomic absorption spectrometers have 5 principal components

1. A light source (usually a hollow cathode lamp)
- 2 . An atom cell (atomizer)
3. A monochromator
4. A detector and
5. Read out device .

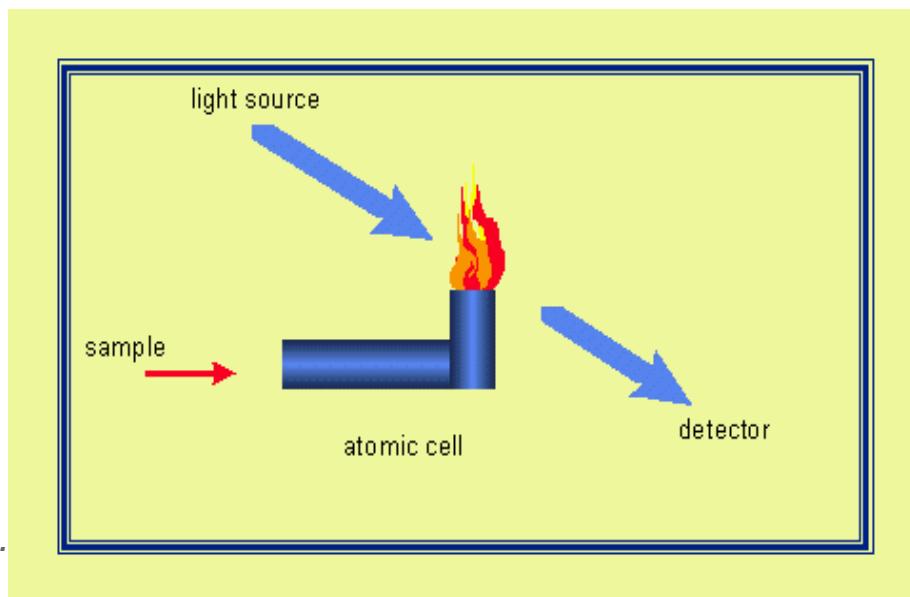


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Fig 3.1. Schematic Diagram of an AAS

Introduction to the Principles of Atomic Spectroscopy

- Liquid sample is aspirated to become aerosols of fine particles (nebulization)
- Flame vaporizes the aerosols (atomization)
- Elevated temperatures in a flame or furnace changes the chemistry of atoms
- Temperature affects the ratio of excited and unexcited atoms
- Beer's law is used to calculate concentration



The Atomic Absorption Spectrometer

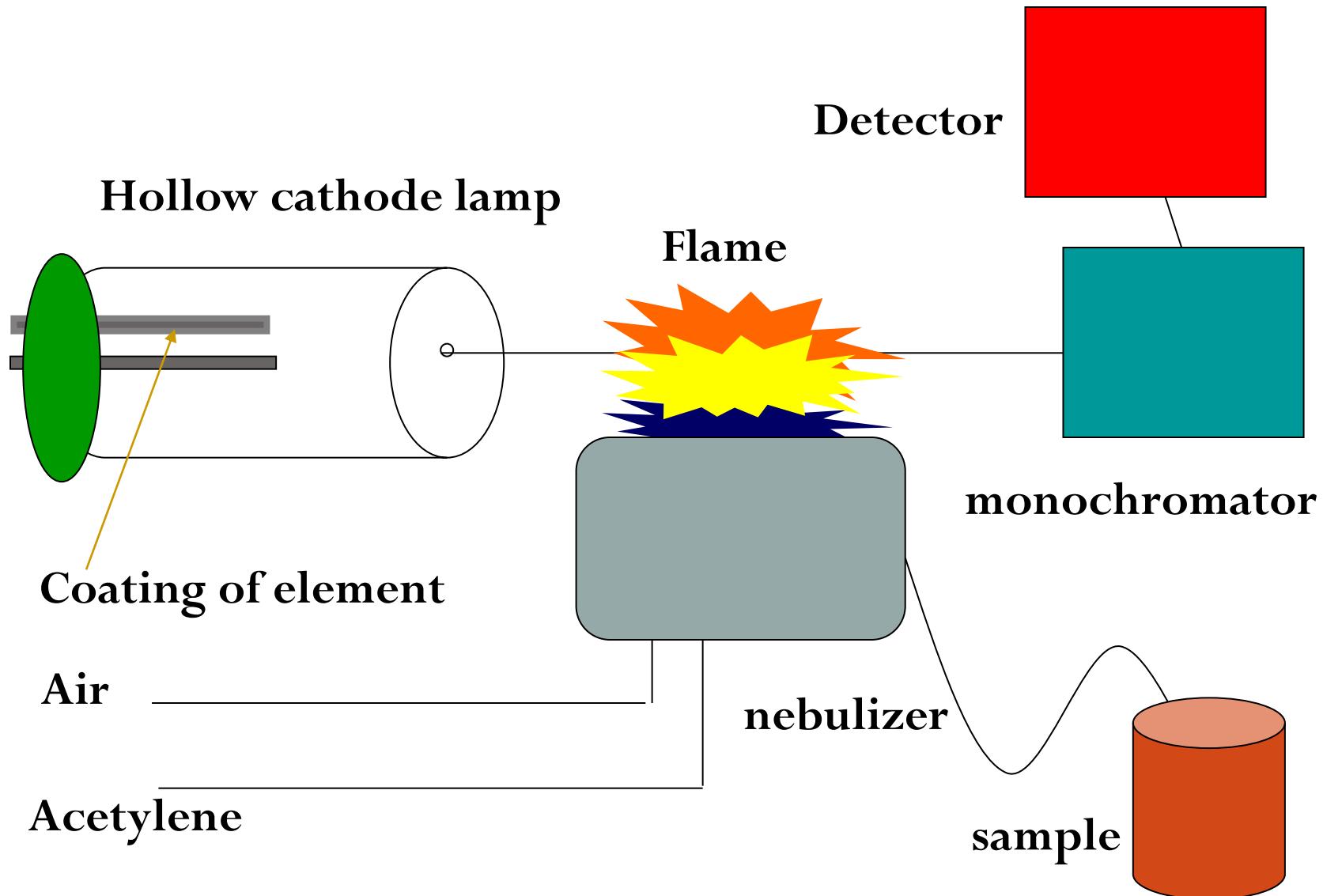


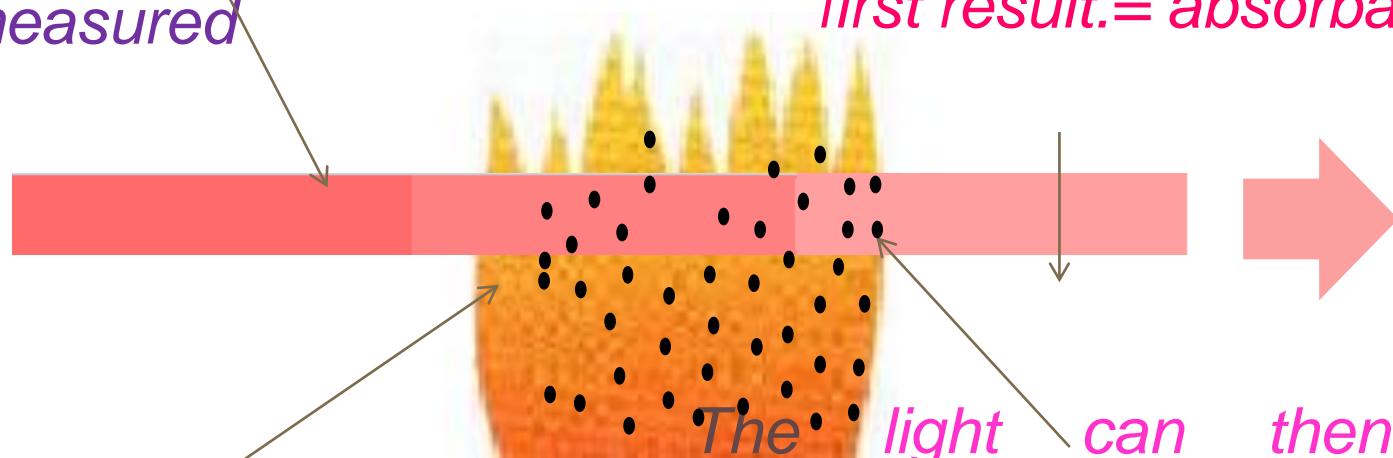
Fig 4.1. Schematic Diagram of an AAS

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How can we obtain the data?

The intensity of the light coming through the cathode lamp is measured

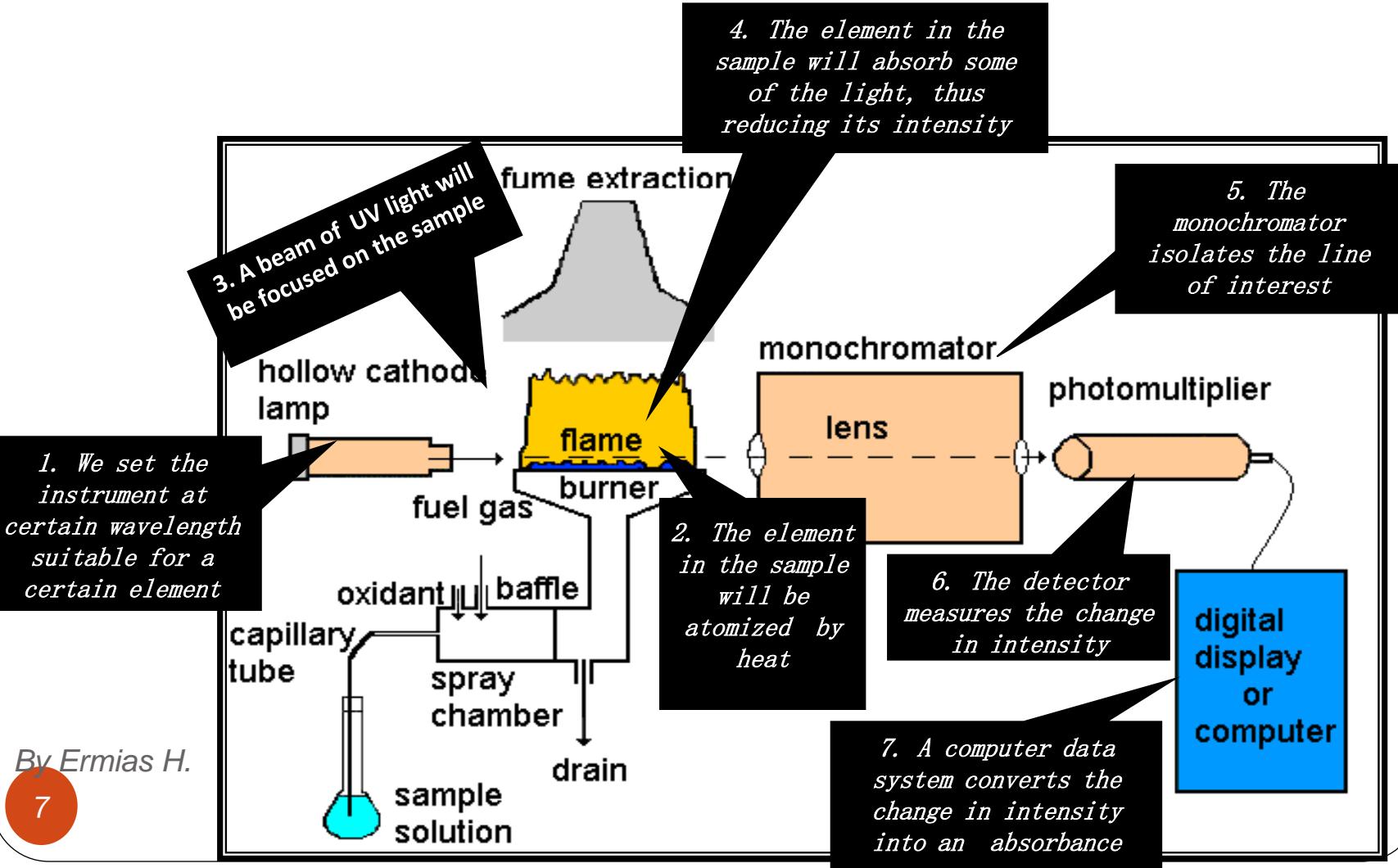
The intensity of the light is then again measured and compared to the first result.= absorbance



The higher the conc. of the metal that is being observe in the sample the greater the absorbance.

The light can then be absorbed by the atoms from the sample that has been vaporized in the flame. This wavelength can then promote the electrons to a higher Energy level = excited state

The simple diagram for the AAS



Overview of FAAS spectrometer.



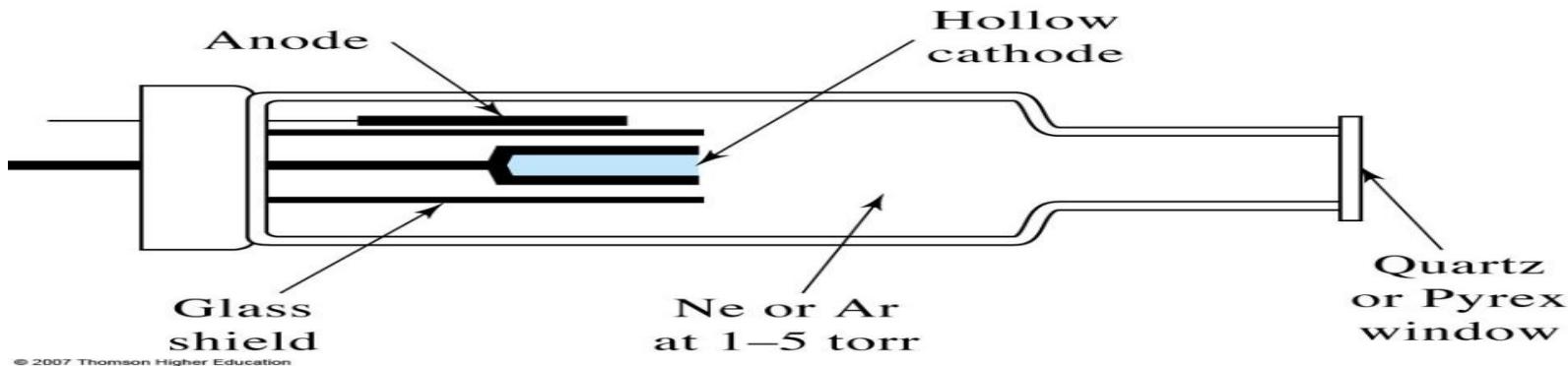
1 – Light Source

- Each element has its own unique lamp which must be used for that analysis.
- The light source is usually a HCL 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 Ne/Ar.

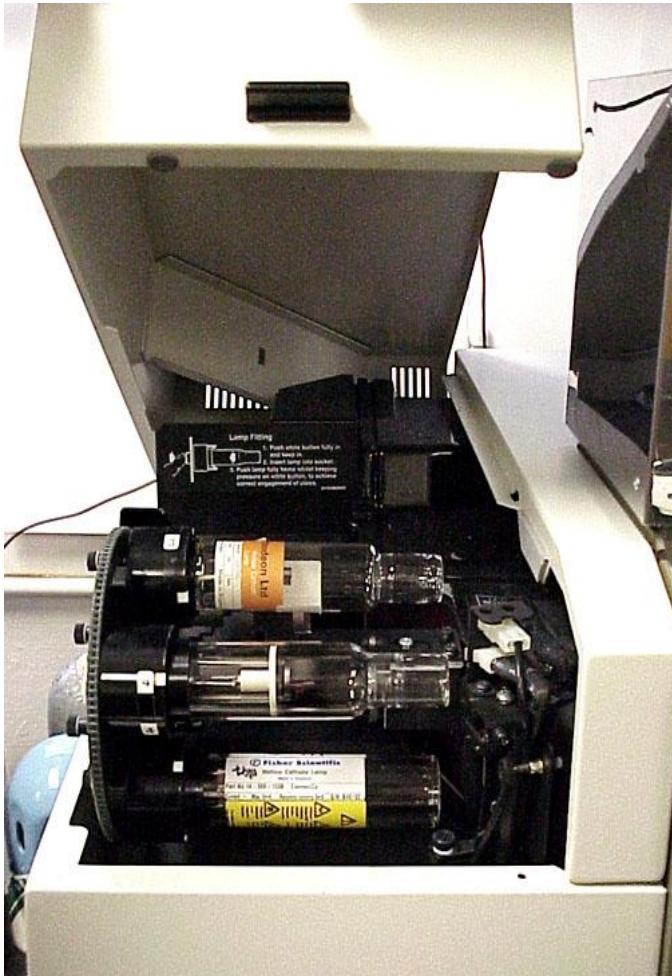
How it works

- Applying a potential difference between the anode & the cathode leads to the ionization of some gas atoms.
- These gaseous ions bombard the cathode & eject metal atoms from the cathode surface 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 d/t elements absorb characteristic λ_s of light.
- Analyzing a sample to see if it contains a particular element means using light from that element.
- E.g. with Pb, a lamp containing Pb emits light from excited lead atoms that produce the right mixture of λ_s to be absorbed by any lead atoms from the sample .
- A beam of the EMR emitted from excited lead atoms is passed through the vaporized sample.
- Some of the radiation is absorbed by the Pb atoms in the sample. The greater the number of atoms there in the vapor, the more radiation is absorbed .



- *The cathode lamps are stored in a compartment inside the AA spectrometer.*

- *The specific lamp needed for a given metal analysis is rotated into position for a specific experiment.*

2 – Atomizer

- ❖ The atomizer is the **sample cell** of the AAS system. The atomizer must produce the ground state free gas phase atoms necessary for the AAS process to occur.
- ❖ The analyte atoms are generally present in the sample as salts, molecular compounds, or complexes.
- ❖ The atomizer **must convert** these species to the reduced, **free gas phase atomic state**.
- ❖ The **two most common atomizers** are **flame atomizers** and **electrothermal** (furnace) atomizers.
- ❖ Atomization is separation of particles into individual molecules & breaking molecules(analyte) into gaseous atoms.
- ❖ This is done by exposing the analyte to high temp in a flame or graphite furnace . The role of the atom cell is to primarily dissolve a liquid sample and then the solid particles are vaporized into their free gaseous ground state form.

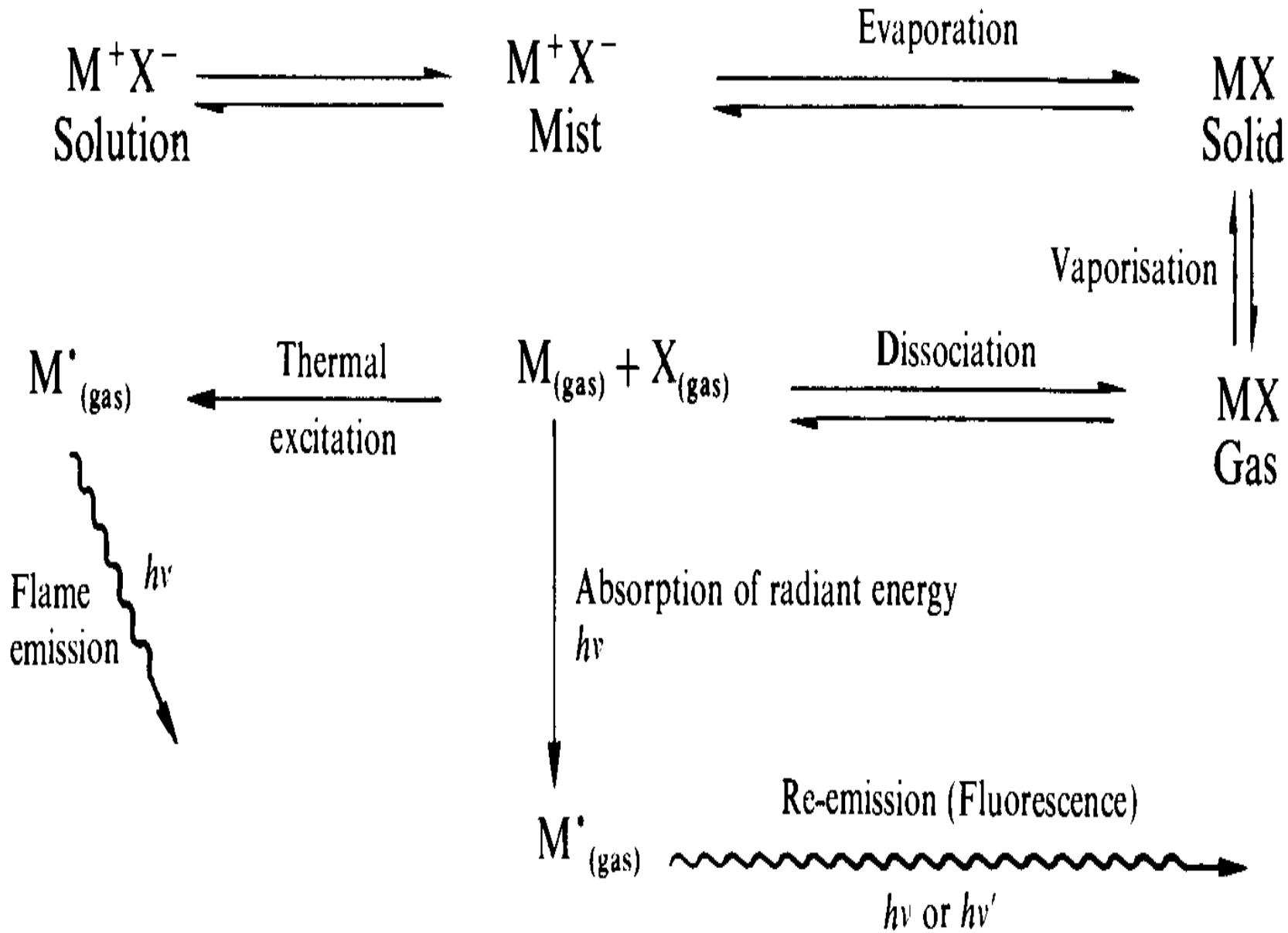
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- ✓ In this form atoms will be available to absorb radiation emitted from the light source & thus generate a measurable signal proportional to conc.
- ❖ There are 2 types of atomization: Flame & Graphite furnace

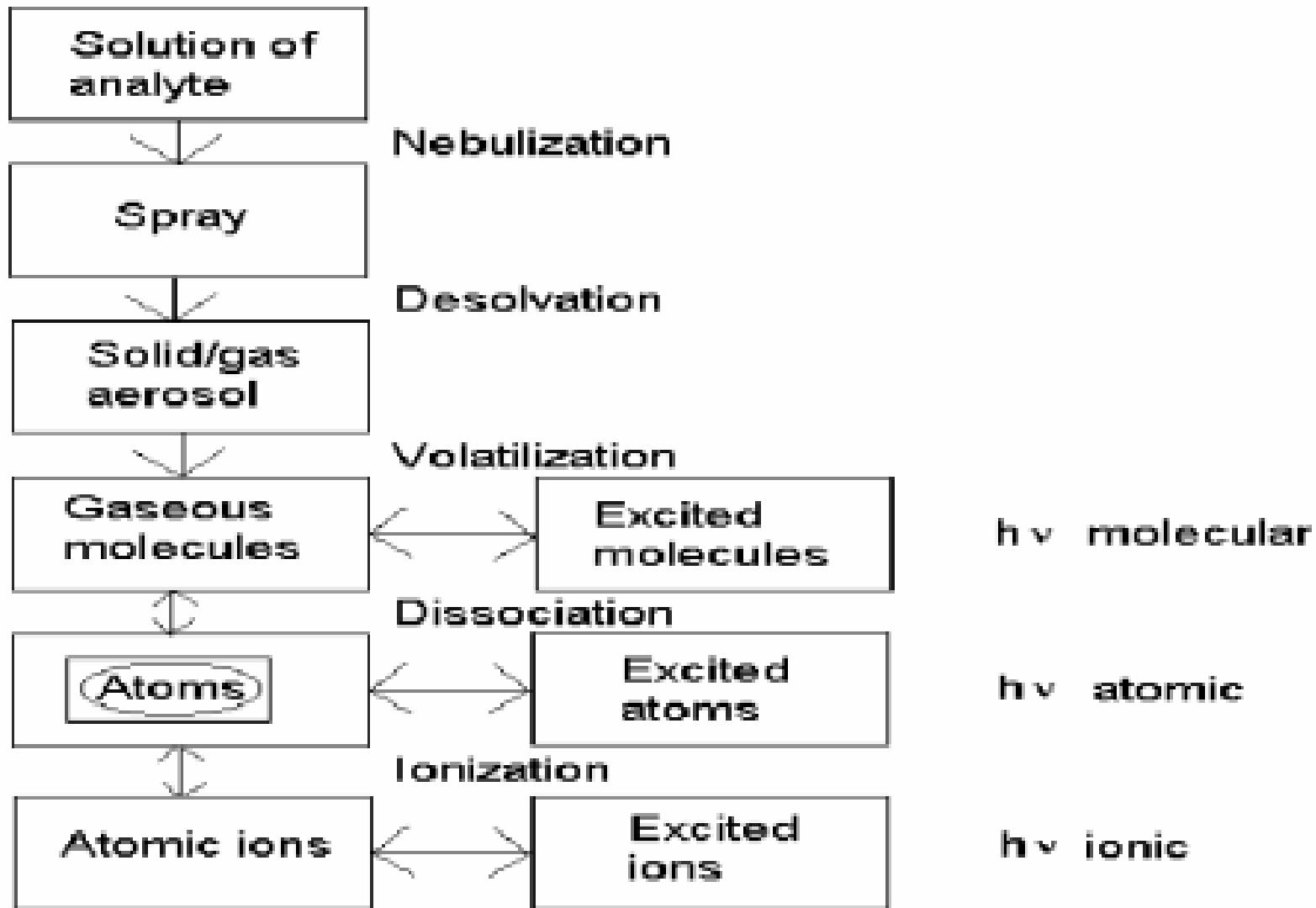
Steps in atomization

- 3 steps are involved in turning a liquid sample into an atomic gas:
 1. **Desolvation** – the liquid solvent is evaporated, and the dry sample remains
 2. **Vaporisation** – the solid sample vaporises to a gas
 3. **Volatilization** – the cpds making up the sample are broken into free atoms.

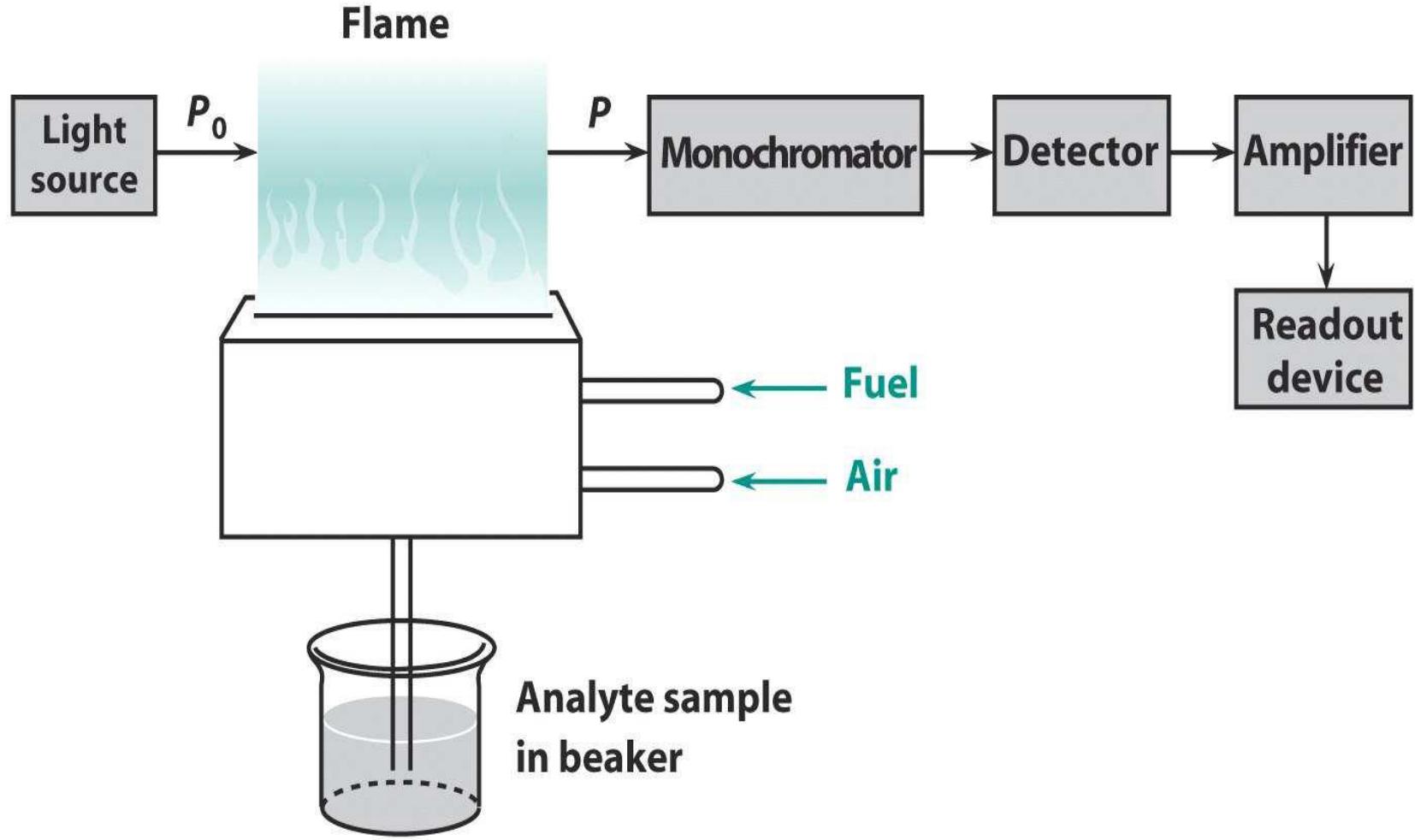
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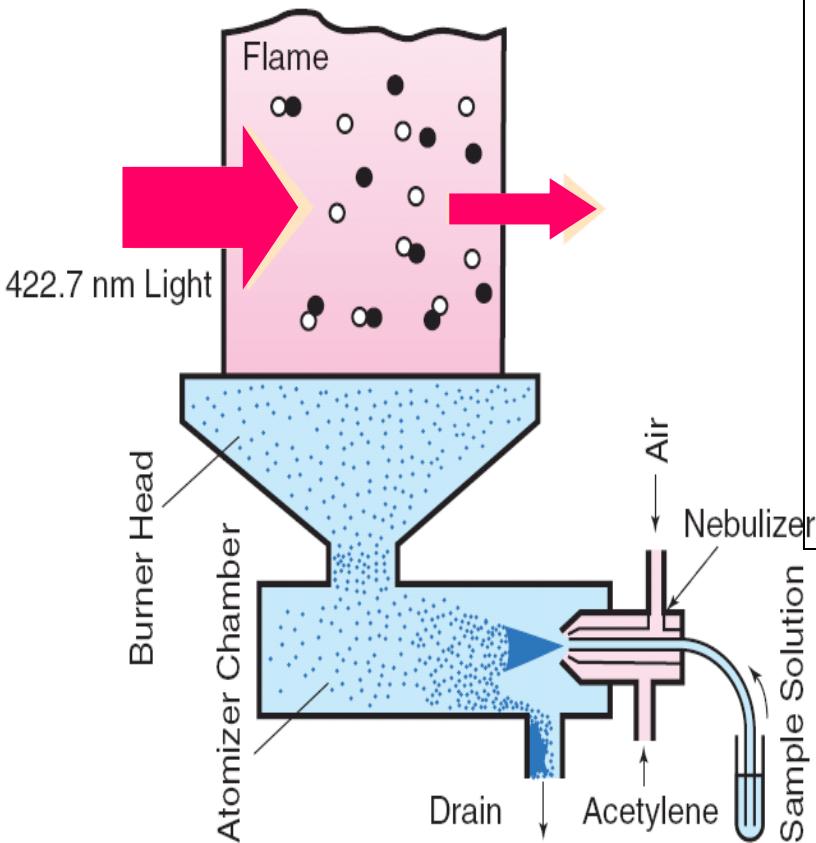
Processes that take place in flame



Atomization



Flame Method



With the Flame Method, the sample solution is converted into mist-form using a nebulizer, and then introduced into the flame. It is atomized by the temperature of the flame.

Measurement time: A few dozen seconds

Flame Atomization Method

Types of Flames Used in FAAS

TABLE 9-1 Properties of Flames

Fuel	Oxidant	Temperature, °C	Maximum 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

1. Types of Flames

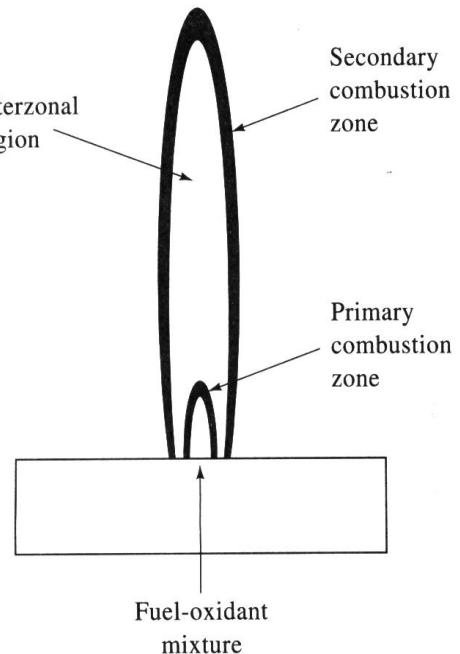
	<u>Fuel / Oxidant</u>	<u>Temperature</u>
$H-C\equiv C-H$	acetylene / air	2100 °C – 2400 °C (<i>most common</i>)
	acetylene / N_2O	2600 °C – 2800 °C
	acetylene / O_2	3050 °C – 3150 °C

- Selection of flame type depends on the volatilization temperature of the atom of interest.

2. Flame Structure

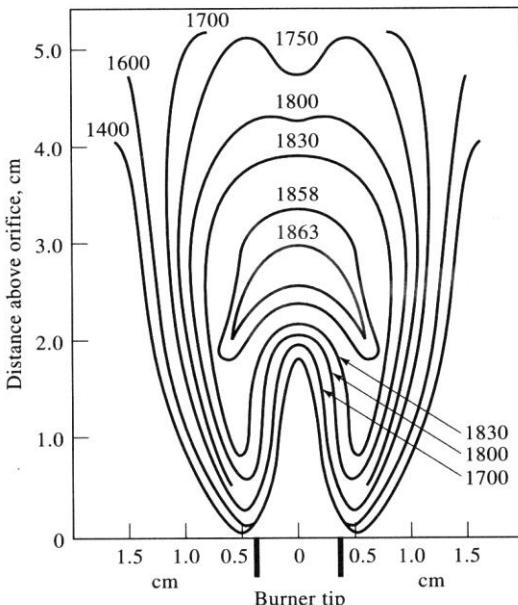
- *Interzonal region is the hottest part of the flame and best for atomic absorption.*
- *Fuel rich flames are best for atoms because the likelihood of oxidation of the atoms is reduced.*
- *Oxidation of the atoms occurs in the secondary combustion zone where the atoms will form molecular oxides and are dispersed into the surroundings.*

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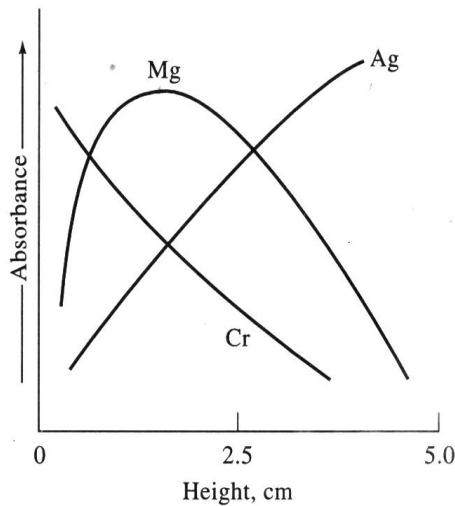
3. Temperature Profiles

- It is important to **focus** the entrance slit of the monochromator on the same part of the flame for all **calibration** and **sample** measurements.



4. Flame Absorption Profiles

- Mg - atomized by longer exposure to flame, but is eventually oxidized.
- Ag - slow to oxidize, **the number of atoms increases with flame height.**
- Cr - oxidizes readily, **highest concentration of atoms at the base of the flame.**

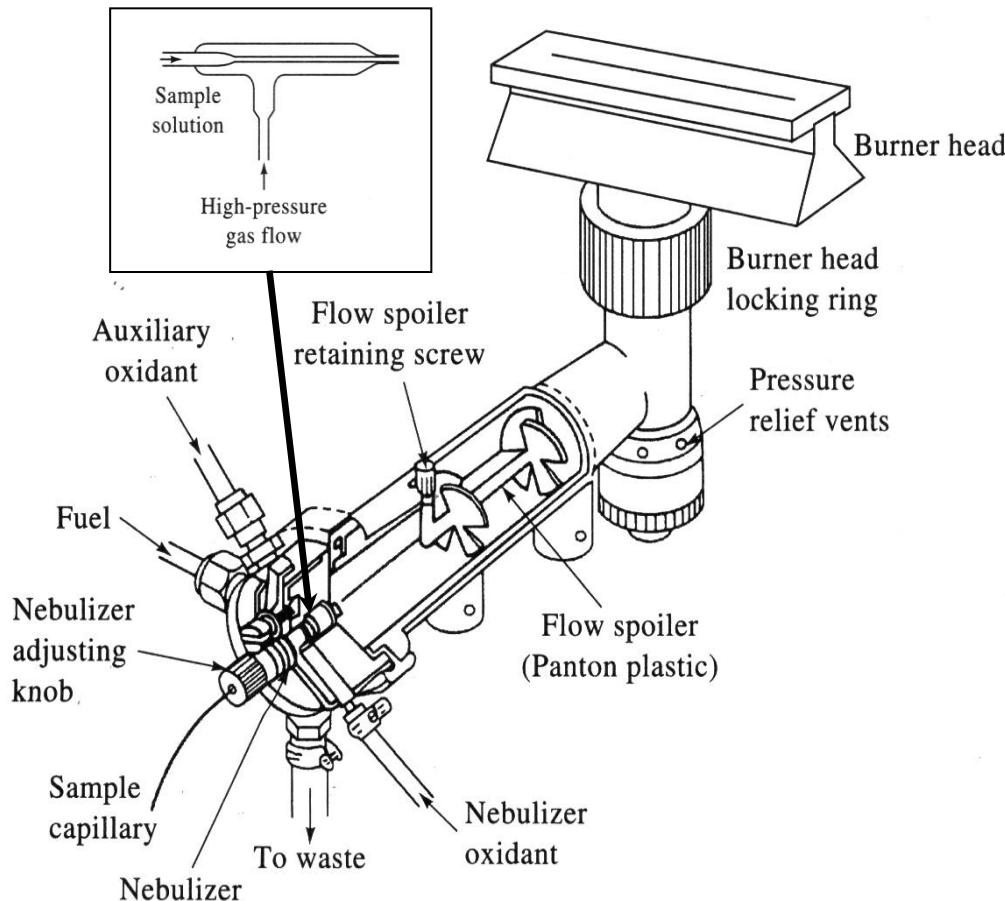


5. Flame Atomizers

Laminar Flow Burners

- Sample is “pulled” into the nebulization chamber by the flow of fuel and oxidant.

- Contains spoilers (baffles) to allow only the finest droplets to reach the burner head.
- Burner head has a long path length and is ideal for atomic absorption spectroscopy.



Nebulizer

- ❖ Sucks up the liquid sample (aspiration)
- ❖ Creates a fine aerosol (fine spray) for introduction into flame
- ❖ Mixes **aerosol**, fuel and **oxidant** thoroughly, creates a heterogeneous mixture
- ❖ The smaller the size of the droplets produced, the higher the element sensitivity

fuel  **acetylene**

oxidant  **air (or nitrous oxide)**

Graphite Furnace



- The atomizer for graphite furnace AA is a furnace.
- It is actually a small graphite tube that can be quickly electrically heated to a very high temperature.
- A relatively small vol of the sample so/n is placed in the tube either manually (with a micropipet) or drawn in with a vacuum mechanism.
- This furnace is then electrically brought to a very high temperature in order to atomize the sample inside.
- The light beam is directed through the tube, in which there is a cloud of atoms, and measured.
- Instruments that utilize a flame for the atomizer can also utilize the graphite furnace.
- It is a matter of replacing the flame module with the furnace module and lining it up with the light beam.

➤ The graphite furnace has several advantages over a flame.

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Advantages over FAAS:

- Solutions, slurries and solid samples can be analysed.
- Much more efficient atomizer than a flame.
- Greater sensitivity
- Smaller quantities of samples(typically 5 – 50 µL).
- 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.

Disadvantages

Expensive, Low sample throughput, Requires high level of operator skill

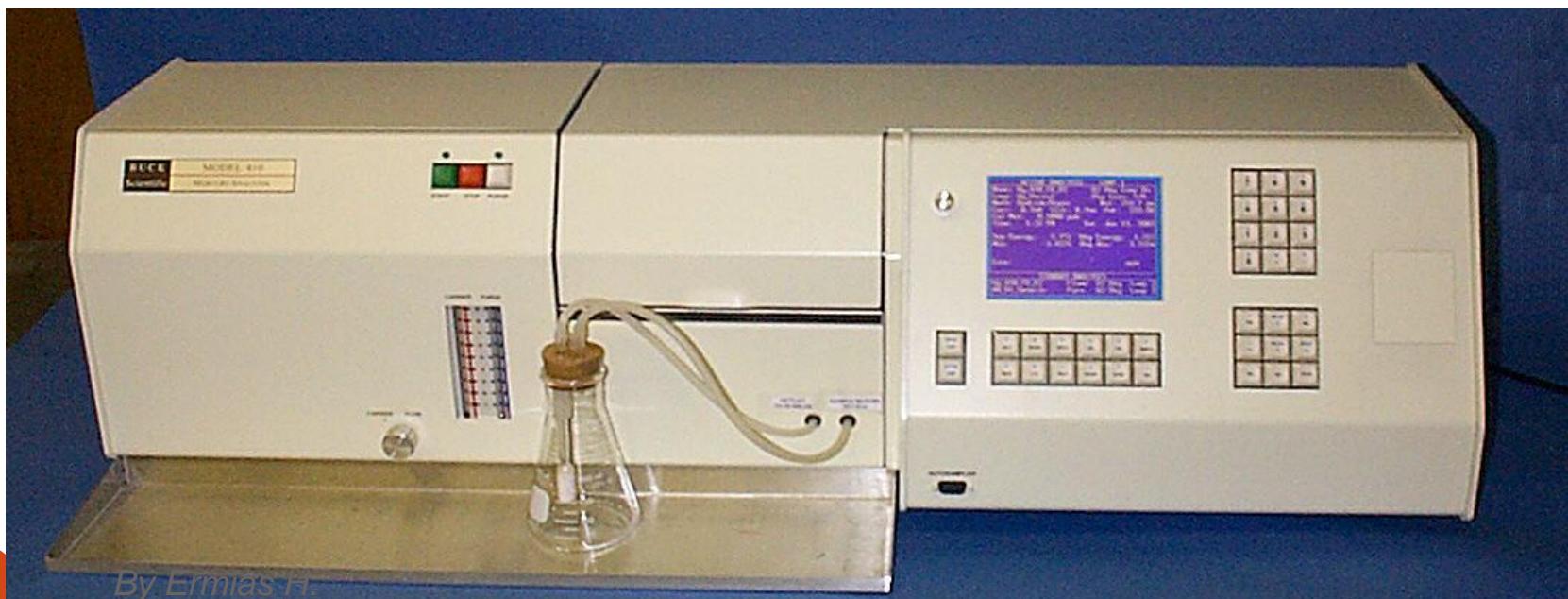
Low precision (because the high energy that is provided to atomize the sample particles into ground state atoms might excite the atomized particles into a higher energy level and thus lowering the precision) .

3- Monochromators

- ✓ This is a very important part in an AA spectrometer.
- ✓ A monochromator is required to separate the absorption line of interest from other spectral lines emitted from the HCL and from other elements in the atomizer that are also emitting their spectra.
- ✓ Because the radiation source produces such narrow lines, spectral interference is not common. Therefore the monochromator does not need high resolution.
- ✓ Without a **good monochromator, detection limits** are severely compromised.
- ✓ A monochromator is **used to select the specific λ of light** which is absorbed by the sample, & to exclude other λ s.
- ✓ Isolation of the absorption line from background light & from molecular emissions originating in the flame, i.e. tuned to a specific wavelength

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.



Experiment

- Prepare the sample (extraction, digestion, dilution)
- Insert the HCL of the metal to be analysed
- Adjust the wavelength
- Aspirate blank, set 100 % T
- Aspirate the standards
- Plot calibration curve
- Aspirate sample
- Calculate the concentration of the metal from the calibration curve equation

Calibration Curve

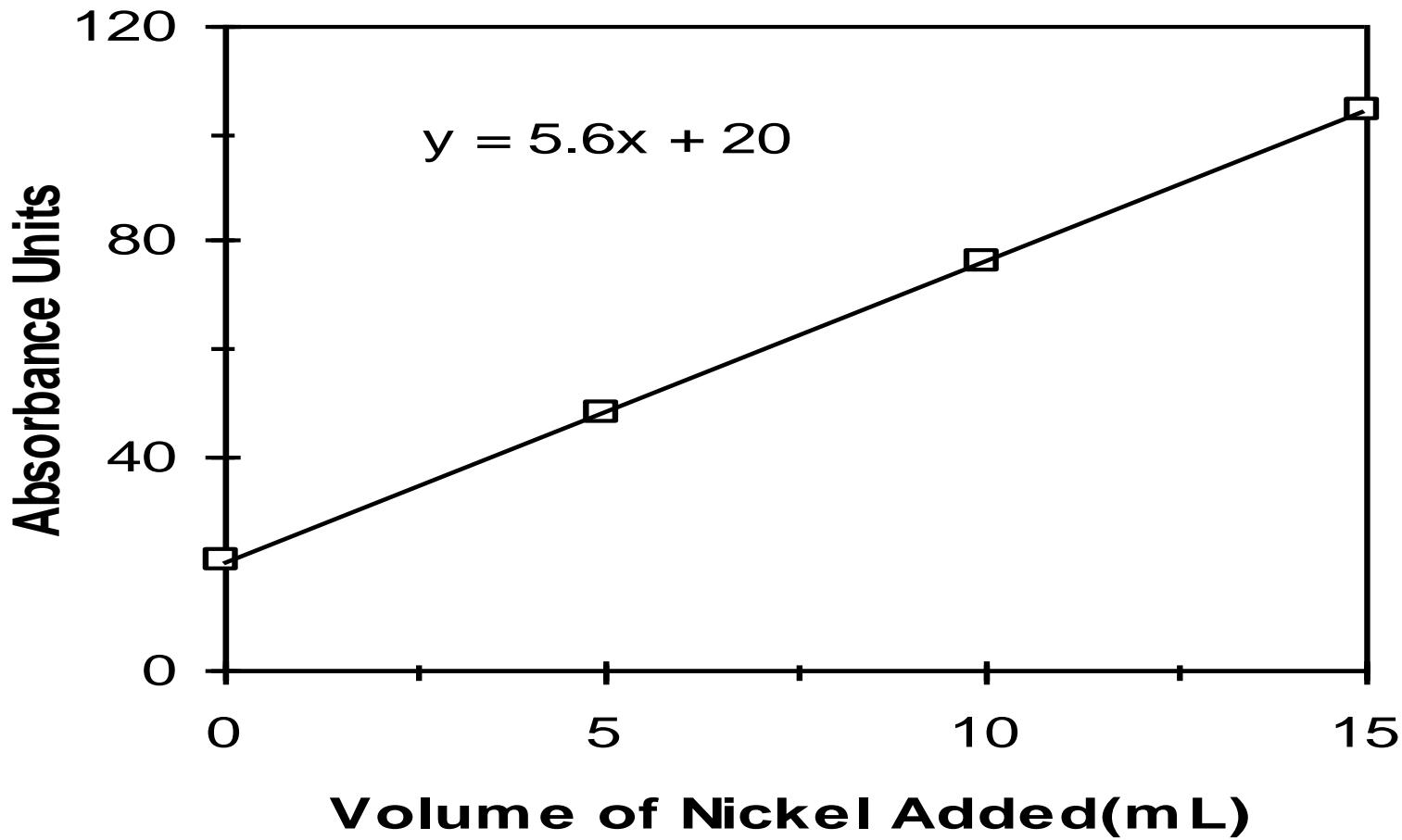
- A calibration curve is used to determine the unknown conc of an element in a solution.
- The instrument is calibrated using several solutions of known concentrations (standard solutions).
- The absorbance of each known solution is measured and then a calibration curve of conc vs absorbance is plotted.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

Qualitative and Quantitative Analysis

- Recall Beer's Law ($A = \log P_0/P = \epsilon b C$) is obeyed when line width small compared to absorption band.
- Atoms absorb radiation at discrete wavelengths.

Determining conc from Calibration Curve

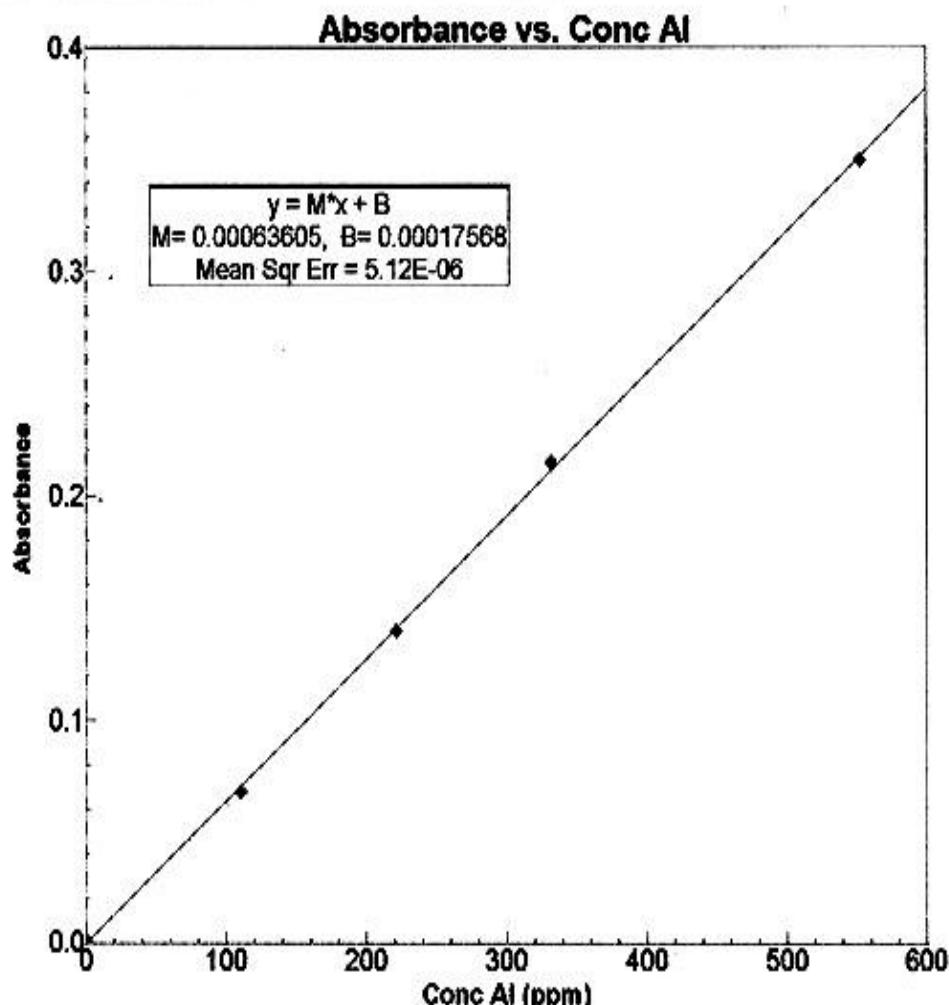
Determination of Nickel Content by AA



Determine the conc of a so/n from a calibration curve.

	Data Set 1: Data	
Row Num	Conc Al (ppm)	Absorbance ()
1	0.00	0.001
2	110.50	0.068
3	221.00	0.140
4	331.50	0.215
5	552.50	0.350
Number	5	5
Mean	243.10	0.155
Min	0.00	0.001
Max	552.50	0.350
Std Dev	212.55	0.135

Calibration Curve for the Determination of Aluminum by Atomic Absorption Spectroscopy



Calibration methods:

- A simple linear relation is

$$Y = a + bx$$

- where Y is the indication of the instrument (i.e., the **instrument response**),
 x is the independent variable, which in most cases for our purpose may be the **concentration of the measured**, and
 a and b are known as the **intercept** and slope

$$b = \frac{\sum_{i=1}^n [(x_i - \bar{x})(y_i - \bar{y})]}{\sum_{i=1}^n (x_i - \bar{x})^2}$$
$$a = \bar{y} - b\bar{x}$$

The product–moment correlation coefficient

- is the calibration plot linear? A common method of estimating how well the experimental points fit a straight line is to calculate the **product–moment correlation coefficient**, r . This statistic is often referred to simply as the ‘correlation coefficient’ because in quantitative sciences it is by far the most commonly used type of correlation coefficient.

Product–moment correlation coefficient,

$$r = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\left\{ \left[\sum_i (x_i - \bar{x})^2 \right] \left[\sum_i (y_i - \bar{y})^2 \right] \right\}^{1/2}}$$

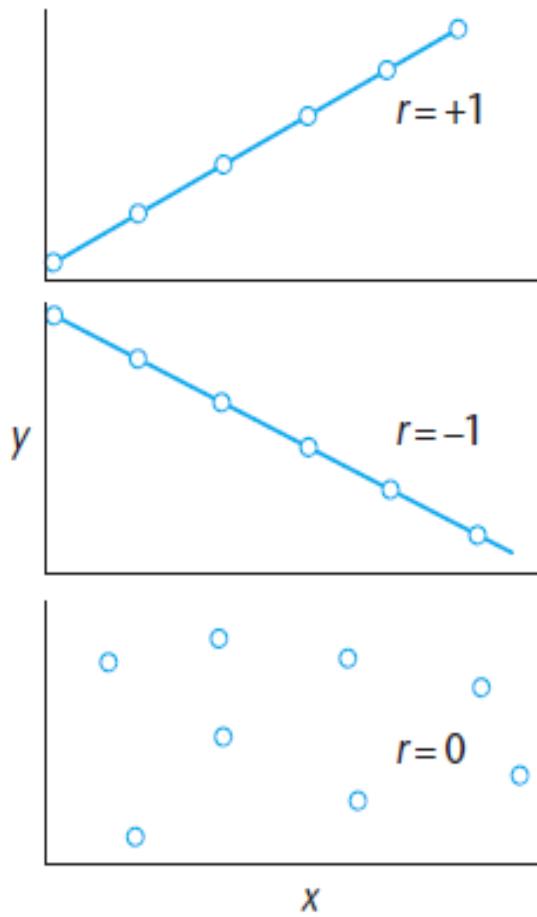


Figure. The product-moment correlation coefficient, r .

- It can be shown that r can take values in the range $-1 \leq r \leq +1$.
- As indicated in Figure an r -value of -1 describes perfect negative correlation, i.e. all the experimental points lie on a straight line of negative slope.
- Similarly, when $r = +1$ we have perfect positive correlation, all the points lying exactly on a straight line of positive slope.
- When there is no correlation between x and y the value of r is close to zero.
- In analytical practice, calibration graphs frequently give numerical r -values greater than 0.99, and r -values less than about 0.90 are relatively uncommon.
- A typical example of a calculation of r illustrates a number of important points.

Example

Standard aqueous solutions of fluorescein are examined in a fluorescence spectrometer, and yield the following fluorescence intensities (in arbitrary units):

Fluorescence intensities:	2.1	5.0	9.0	12.6	17.3	21.0	24.7
Concentration, pg ml^{-1}	0	2	4	6	8	10	12

Determine the correlation coefficient, r .

In practice, such calculations will almost certainly be performed on a calculator or computer, alongside other calculations covered below, but it is important

and instructive to examine a manually calculated result. The data are presented in a table, as follows:

	x_i	y_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$	$y_i - \bar{y}$	$(y_i - \bar{y})^2$	$(x_i - \bar{x})(y_i - \bar{y})$
	0	2.1	-6	36	-11.0	121.00	66.0
	2	5.0	-4	16	-8.1	65.61	32.4
	4	9.0	-2	4	-4.1	16.81	8.2
	6	12.6	0	0	-0.5	0.25	0
	8	17.3	2	4	4.2	17.64	8.4
	10	21.0	4	16	7.9	62.41	31.6
	12	24.7	6	36	11.6	134.56	69.6
Sums:	42	91.7	0	112	0	418.28	216.2

The figures below the line at the foot of the columns are in each case the sums of the figures in the table: note that $\sum(x_i - \bar{x})$ and $\sum(y_i - \bar{y})$ are both zero. Using these totals in conjunction with equation (5.2), we have:

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$$r = \frac{216.2}{\sqrt{112 \times 418.28}} = \frac{216.2}{\sqrt{216.44}} = 0.9989$$

Example:

Calculate the slope and intercept of the regression line for the data given in the previous example. we calculated that, for this calibration curve:

$$\sum_i (x_i - \bar{x})(y_i - \bar{y}) = 216.2; \quad \sum_i (x_i - \bar{x})^2 = 112; \quad \bar{x} = 6; \quad \bar{y} = 13.1$$

$$b = \frac{\sum_{i=1}^{i=n} [(x_i - \bar{x})(y_i - \bar{y})]}{\sum_{i=1}^{i=n} (x_i - \bar{x})^2}$$

we calculate that

$$a = \bar{y} - b\bar{x}$$

$$b = 216.2 / 112 = 1.93$$

$$a = 13.1 - (1.93 \times 6) = 13.1 - 11.58 = 1.52$$

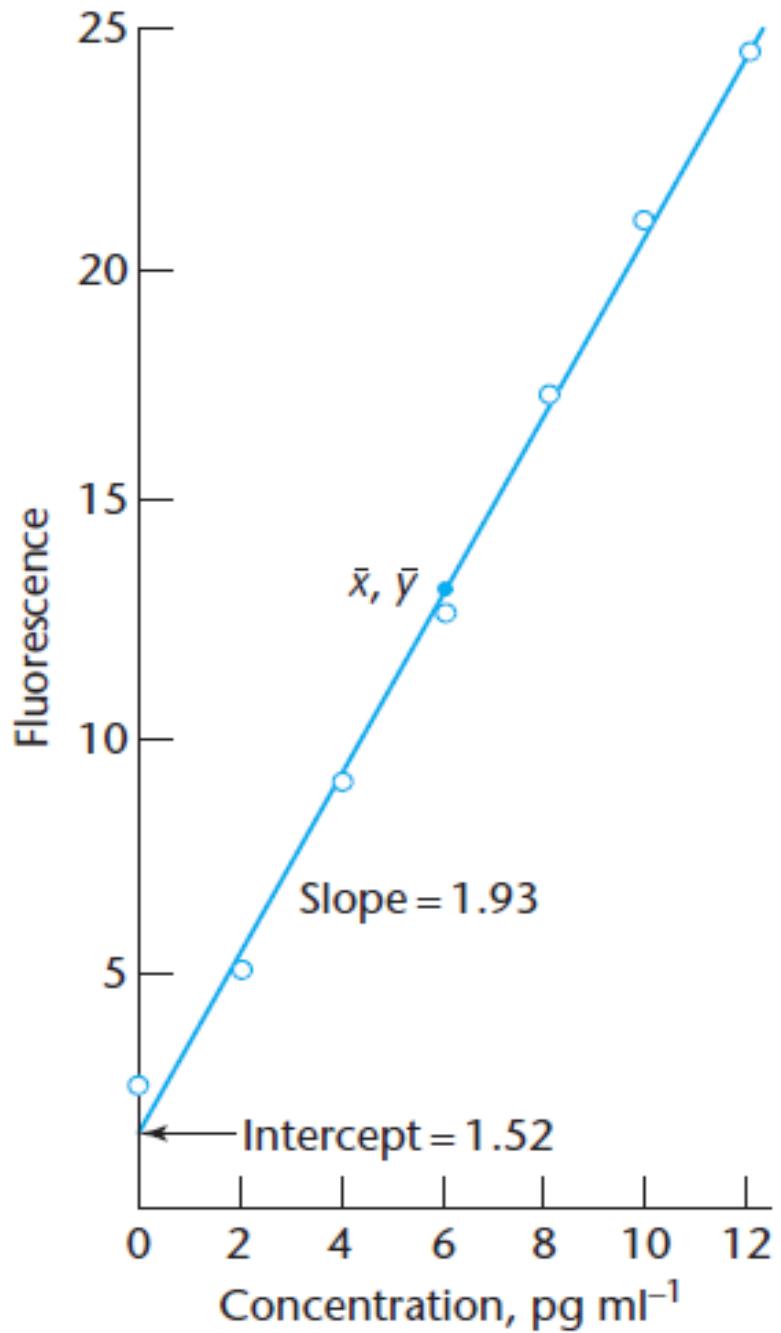


Figure : Calibration plot for the data in Example

Example :

- Using the data from the above example, determine the unknown conc. for solutions with fluorescence intensities of 2.9, 13.5 and 23.0 units.
- The x_0 values are easily calculated by using the regression equation determined in the above example,

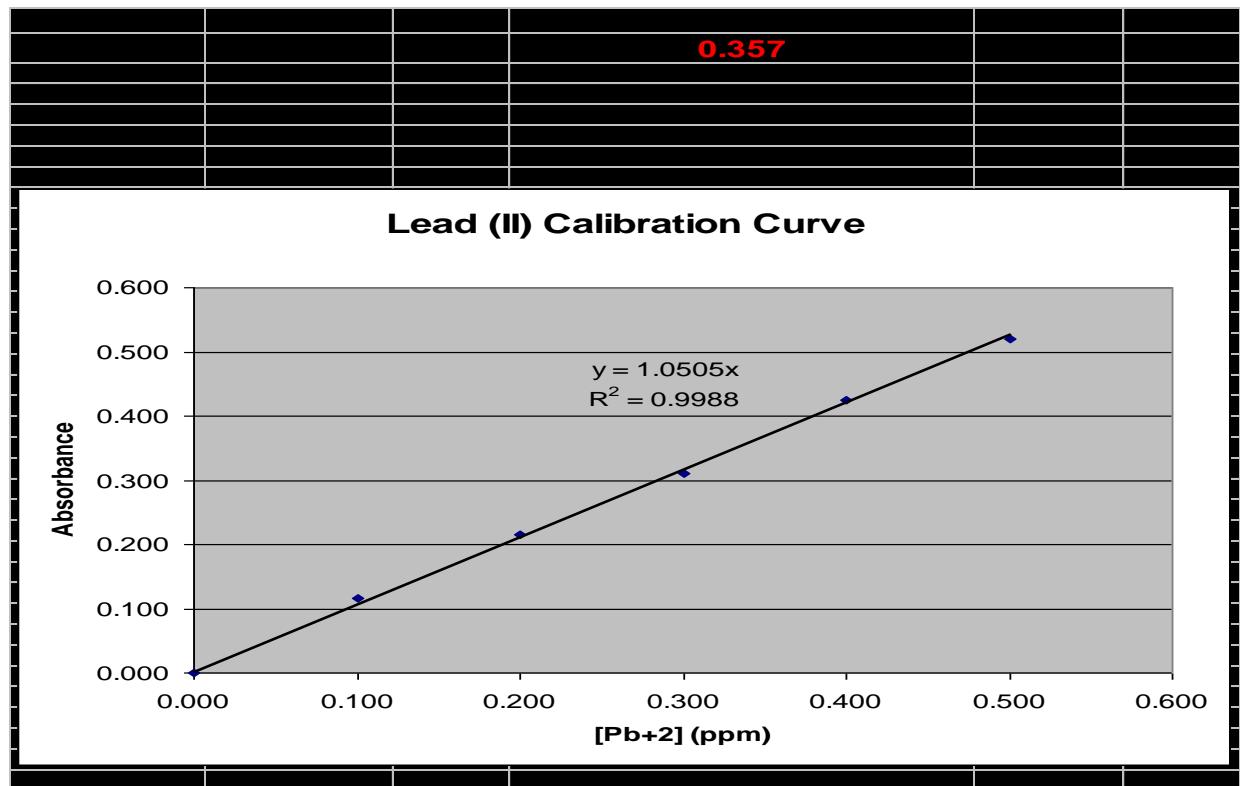
$$y = 1.93x + 1.52.$$

- Substituting the y_0 -values 2.9, 13.5 and 23.0,
- we obtain x_0 -values of 0.72, 6.21 and 11.13 pg ml⁻¹ respectively.

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Problem

Pb is extracted from a sample of blood & analyzed at 283 nm & gave an absorbance of 0.340 in an AAS. Using the data provided and calibration curve find the conc of Pb(II) in the blood sample.



The graph is used to calculate the best fit line. The equation is then used to calculate the conc of Pb (II) ions with an A of 0.340.

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 AAS 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 wing ,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 temp.
- **Transport Interference:** Rate of aspiration, nebulization, or transport of the sample (e g viscosity, surface tension, vapor pressure , and density) .

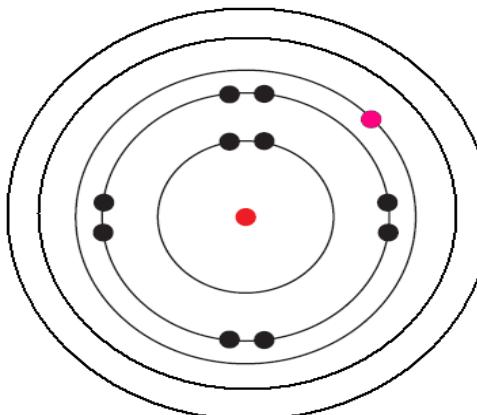
Atomic Emission Spectroscopy

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

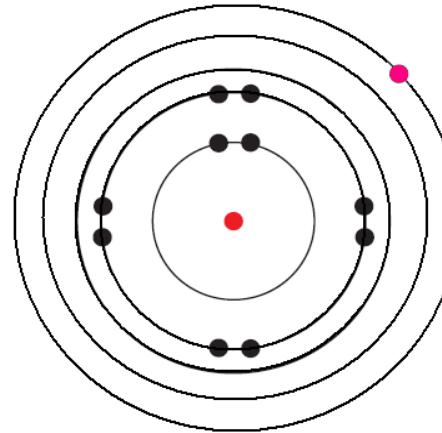
Excited atom

Ground state: sodium atom

Generally, atoms are in their ‘ground state’ but when an atom receives enough input of energy that their electrons require to be promoted to a higher energy level. They will then turn to their ‘excited state’.



Excited state: sodium atom



Since, an atom’s excited state is very **unstable** it rapidly ‘jump’ back down to its ground state. This ‘jump’ then causes the atom to release the energy it absorbed in the form of photons of light.



!Note: Take note that the electron can go back down to its ‘original’ place in more than one jump.

Atomic Emission Spectroscopy (AES)

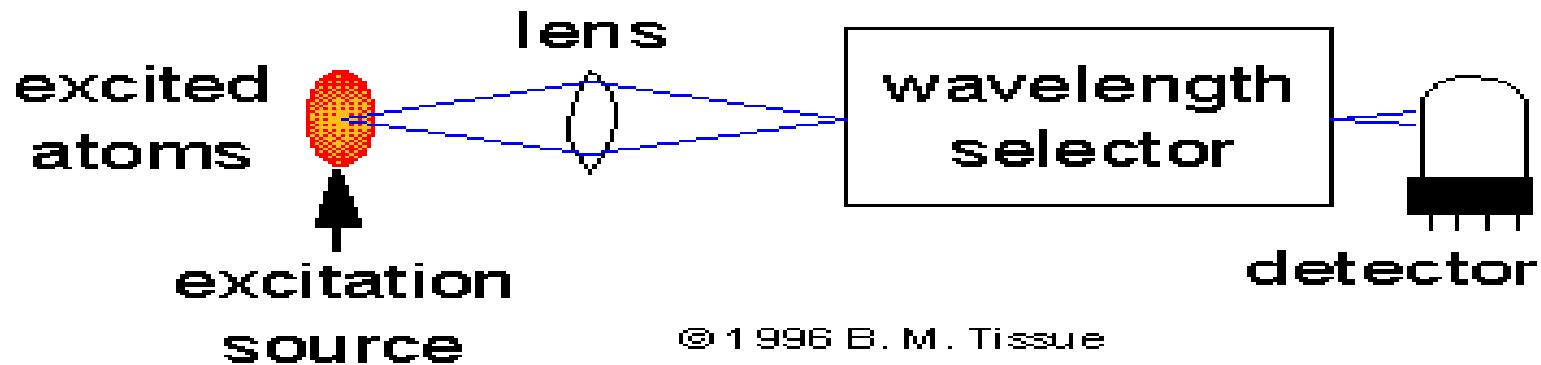
- ❖ No external radiation source is required ;the sample it self is the emitter
- The Atomizers not only **Atomize samples** also **excite** gaseous atoms to higher electronic states.

Thermal excitation ($\mathbf{M} \rightarrow \mathbf{M}^*$)

Radioactive decay to lower energy level $\mathbf{M}^* \rightarrow \mathbf{M} + h\nu$

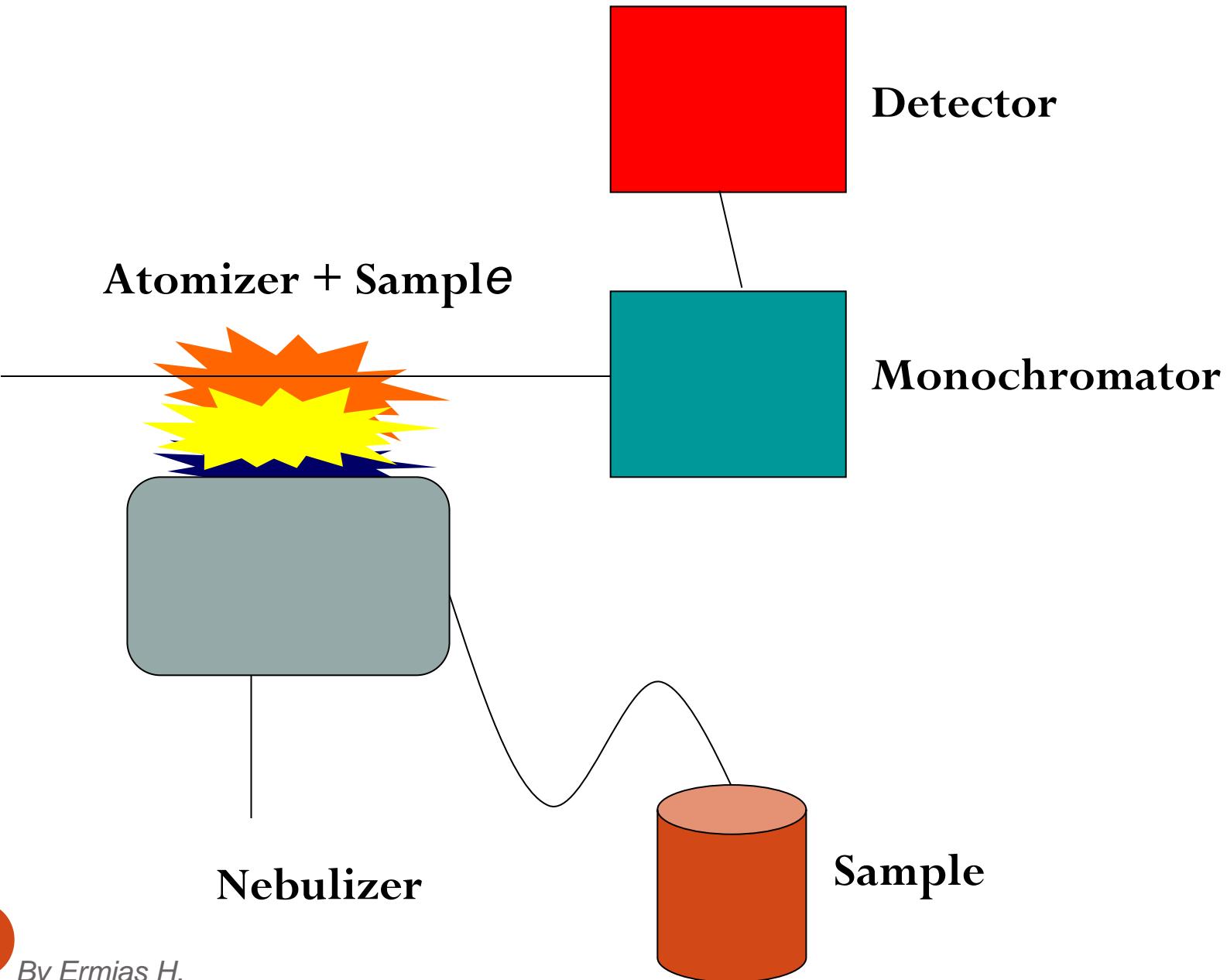
- Emission signal directly proportional to concentration
- The analyte atoms are promoted to a higher energy level by the sufficient energy that is provided by the high temperature of the atomization sources .
- The excited atoms decay back to lower levels by emitting light.
- Emissions are passed through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

- The instrumentation of atomic emission spectroscopy is the same as that of AA 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.



- The source of energy in Atomic Emission could be a flame like the one used in AA or an inductively coupled plasma(ICP).
- The flame (1700 – 3150 °C) is most useful for elements with relatively low excitation energies like Na, K and Ca .
- The ICP (6000 – 8000 °C) has a very high temp & is useful for elements of high excitation energies .

AE Spectrometer



Background

Sources of Background: scattering or molecular emission

Background Correction:

- With blank sample

$$A_c = A_t - A_{\text{blank}}$$

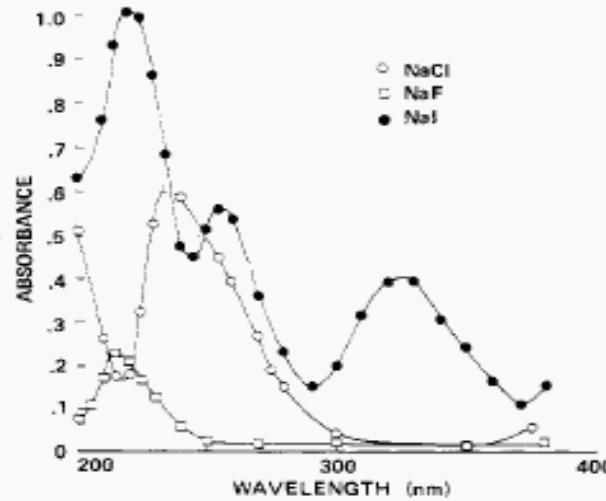


Figure 1. Molecular spectra of NaCl, NaF, and NaI using 5 μ l of 0.1% (w/v) solutions

- Deuterium lamp (arc in deuterium atmosphere; continuum 200-380 nm
 - absorption of deuterium lamp represents $A_{\text{background}}$
 - absorption of HCL radiation represents A_t

Advantage over blank sample: observe fluctuations in flame

Method of Standard Additions

- In order to quantitate the element of interest in a sample, it is necessary to calibrate with the method of standard additions.
- The analytical signal for the sample, S_x , is obtained (after measuring the blank signal).
- A small vol V_s , of concentrated standard so/n of known conc c_s , is added to a relatively large vol, V_x of the analytical sample.
- The analytical signal for the standard addition solution, S_{x+s} , is obtained.

$$c_x = (S_x V_s c_s) / [S_{x+s} (V_x + V_s) - S_x V_x]$$

$$c_x = (S_x V_s c_s) / [(S_{x+s} - S_x) V_x]$$

if $V_s \ll V_x$

Problem:- determination of Pb in a brass sample is done with AAS. The 50mL original sample was introduced into the instrument & an A of 0.42 was obtained. To the original so/n, 20mL of a 10mg/mL Pb standard was then added. The absorbance of this so/n was 0.580. Find the conc of Pb in the original sample.

AAS: Figures of Merit

- **Detection limits:**
 - * Generally lower LOD for very volatile elements
 - * Higher LOD for carbide-forming elements (e.g. Ba, B, Ca, Mo, W, V, Zr)
 - * Conc in GF up to 1000 times higher than in flame; much lower LOD for GF.
 - * Lower LOD for GF-AAS than ICP-AES unless atomization requires high temperature
 - * Generally similar LOD for flame-AAS and ICP-AES
 - * Improve LOD by adding ethanol or methanol to decrease droplet surface tension during nebulization
 - **Chemical interferences:**
 - * HCl often avoided as acid in GF-AAS because metal chlorides are more volatile than sulfates or phosphates.
 - * Addition of Cs salt to sample suppresses ionization.
 - * La precipitates phosphate, facilitating Ca analysis.
 - * Proteins may clog burners and are precipitated with trichloroacetic acid.

TABLE 10-3

Typical detection limits and characteristic concentrations for flame and electrothermal AAS

Element	Wavelength (nm)	Flame			Electrothermal ^a			DL (ng mL ⁻¹)
		m_A (ng mL ⁻¹)	DL (ng mL ⁻¹)	m_A (pg)	m_A (ng mL ⁻¹)	DL (pg)		
Ag	328.1	30	3	2	0.1	0.2	0.01	
Al	309.3	340	30	10	0.5	2	0.1	
As	193.7	500	200	20	1	10	0.5	
Au	242.8	80	20	10	0.5	10	0.5	
B	249.8	7000	2000	1000	50	—	—	
Ba	553.6	160	20	20	1	5	0.25	
Be	234.9	20	2	1	0.05	0.6	0.03	
Bi	223.1	160	30	12	0.6	2	0.1	
Ca	422.7	20	1	1	0.05	0.5	0.25	
Cd	228.8	9	1	0.5	0.025	0.2	0.01	
Co	240.7	40	4	10	0.5	6	0.3	
Cr	357.9	40	4	6	0.3	0.6	0.03	
Cs	852.1	100	20	6	0.3	—	—	
Cu	324.8	25	2	3	0.15	1	0.05	
Eu	459.4	300	40	16	0.8	2	0.1	
Fe	248.3	50	6	10	0.5	5	0.25	
Ga	287.4	1100	50	40	2	20	1	
Ge	265.2	1500	200	100	5	50	2.5	
Hg	253.6	4000	500	200	10	100	5	
K	766.5	20	2	5	0.25	1	0.05	
Li	670.8	20	1	10	0.5	5	0.25	
Mg	285.2	3	0.2	0.4	0.02	0.04	0.002	
Mn	278.5	20	2	1	0.05	0.2	0.01	
Mo	313.3	20	5	20	1	5	0.5	
Na	589.0	5	0.2	1	0.05	0.4	0.02	
Ni	232.0	50	3	20	1	10	0.5	
Pb	217.0	60	8	5	0.25	2	0.1	
Pd	244.8	100	20	20	1	20	1	
Pt	266.0	1000	50	100	5	50	2.5	
Rb	780.0	40	5	15	0.8	10	0.5	
Sb	217.6	260	20	30	1.5	10	0.5	
Se	196.0	260	200	40	2	10	0.5	
Si	251.6	1500	20	80	4	20	1	
Sn	235.5	720	15	40	2	100	5	
Sr	460.7	50	4	20	1	10	0.5	
Ti	276.8	350	20	100	5	20	1	
V	318.4	500	25	100	5	20	1	
Zn	213.9	10	1	0.2	0.02	0.1	0.005	

^aSample size for electrothermal AA is 20 μ L.