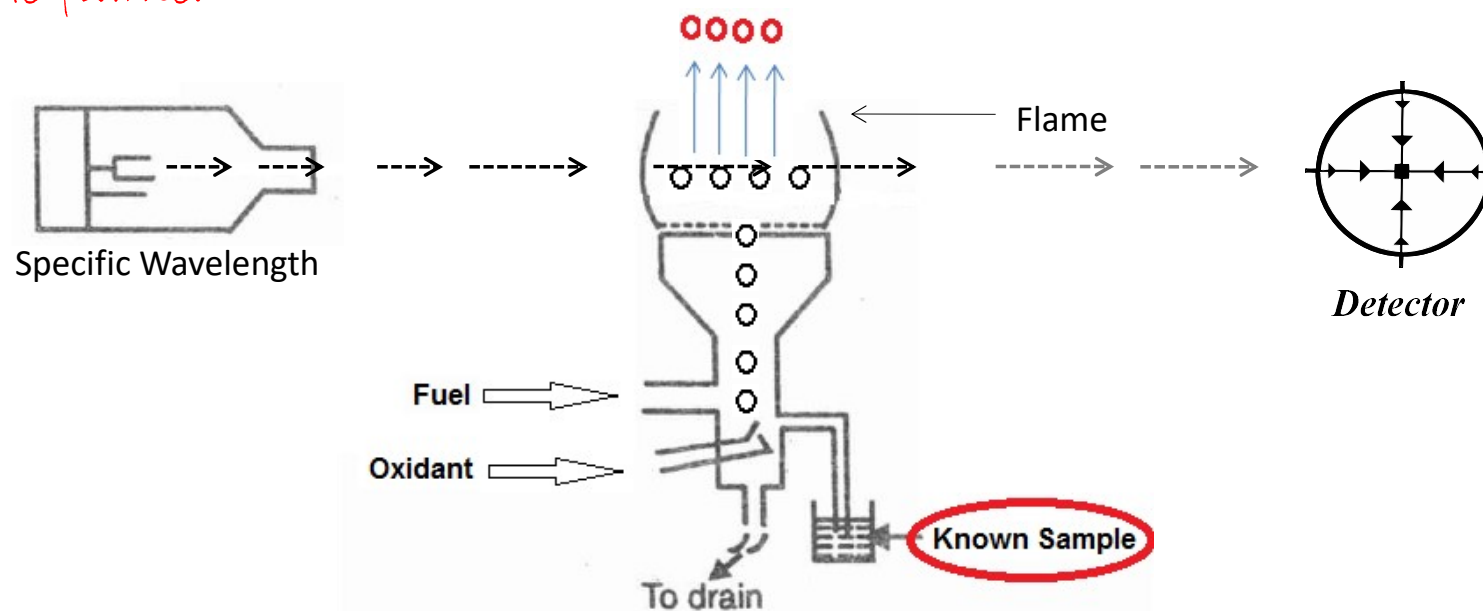


ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Atomic Absorption Spectroscopy

Principle

A sample solution containing **known** metal atoms, when introduced into the flame, is irradiated with light of their own specific wavelength will absorb light proportional to the density of atoms in the flame.



Thus, AAS measures Amount of Light Absorbed.

Principle



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Absorption \propto density of atoms in flame

Amount of light absorbed \propto concentration of metallic species

Total amount of light absorbed = $(\pi e^2/mc) N.f \rightarrow$

**Ability of atom to
absorb at freq. n**

**\downarrow
No. of atom to absorb at freq. ν**

Total amount of light absorbed = constant $\times N \times f$

Therefore, absorption is independent of temperature and wavelength

Better than FES

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															



Can be analyzed using AAS

Atomic Absorption Spectroscopy

- **Most powerful technique for the determination of trace metals in solution**
- **70-80 elements can be detected**
- **Determination can be made in the presence of many other elements**
- **No specific sample preparation is required**
- **Wide application**

Differences between AAS and FES

FES	AAS
Excitation of atoms – emission of photon and return to ground state. Emission intensity is measured	Signal is obtained in presence and absence of element and decrease in intensity of signal obtained. Absorption is measured
Emission intensity \propto No. of atoms in excited state	Absorption intensity \propto No. of atoms in ground state
Emission intensity depends on flame temperature	Absorption intensity does not depend on flame temperature
Beer's law is not obeyed over wide range of concentration	Beer's law is obeyed over a wide range

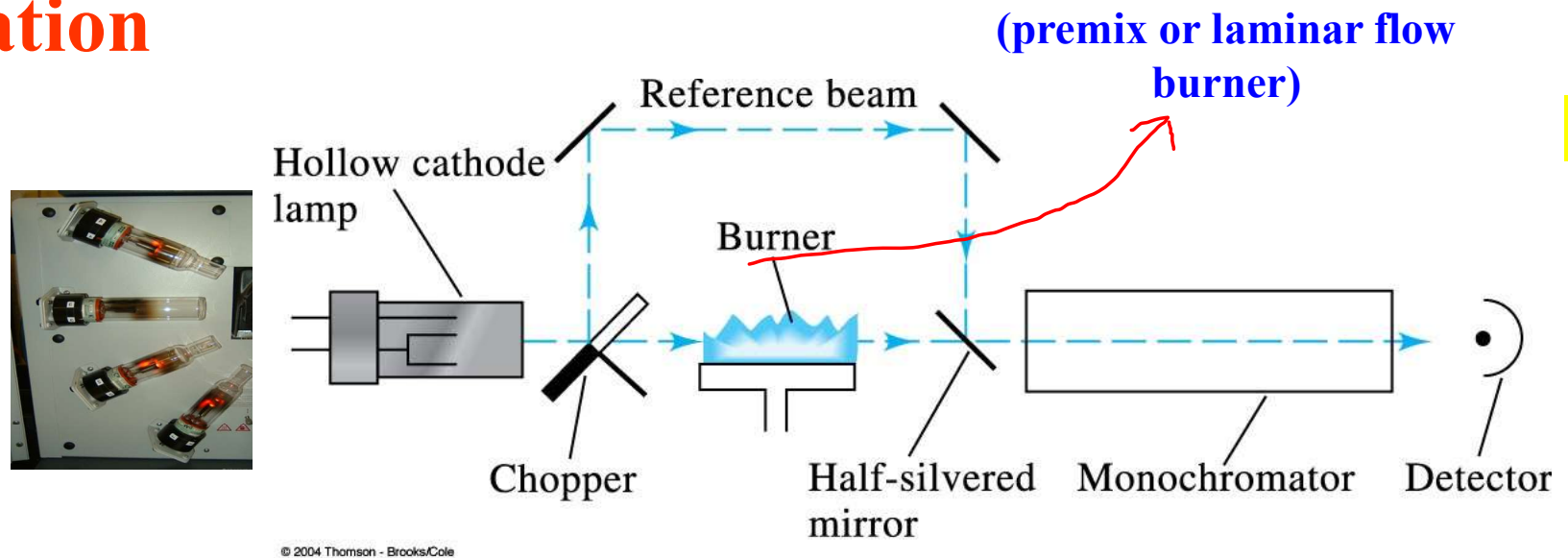
Advantages of AAS

- AAS - specific – Atom of a particular element can absorb radiation of their own wavelength – No spectral interference
- Much larger No. of atoms contribute in AAS signal so results are more authentic
- Variation in flame temperature has less effect
- Absorption intensity does not depends on flame temperature
- Detection limit of AAS and FES is quite similar
- 70-80 elements can detected

Disadvantages of AAS

- Different (HCL) lamp for each element is required
- Elements which form stable oxides eg. Al, Ti, W, Mo, do not give very good results

Instrumentation



INSTRUMENT FOR ATOMIC ABSORPTION :

- 1- Source of radiation (Hollow Cathode Lamp)
- 2- Chopper
- 3- Atomizer (Flame)
- 4- Monochromator (Prism)
- 5- Detector (Photo Cell)
- 6- Read out meter (Not in diagram)

Light separation and detection :

- AA spectrometers use monochromators and detectors for uv and visible light.
- The main purpose of the monochromator is to isolate the absorption line.
- Photo multiplier tubes are the most common detectors for AA spectroscopy

- Absorption is measured by the difference in intensity of transmitted signal in presence and absence of test element
- Production of atomic vapour- premix or laminar flow burner is used

Light separation and detection

- AA spectrometers use monochromators and detectors for uv and visible light
- The main purpose of the monochromator is to isolate the absorption line
- Photo multiplier tubes are the most common detectors for AA spectroscopy

Role of the Chopper

- Breaks steady light coming from the hollow cathode lamp into intermittent light
- It gives a pulsating current to photodetector
- Absorption is measured without any interference

Role of the Flame

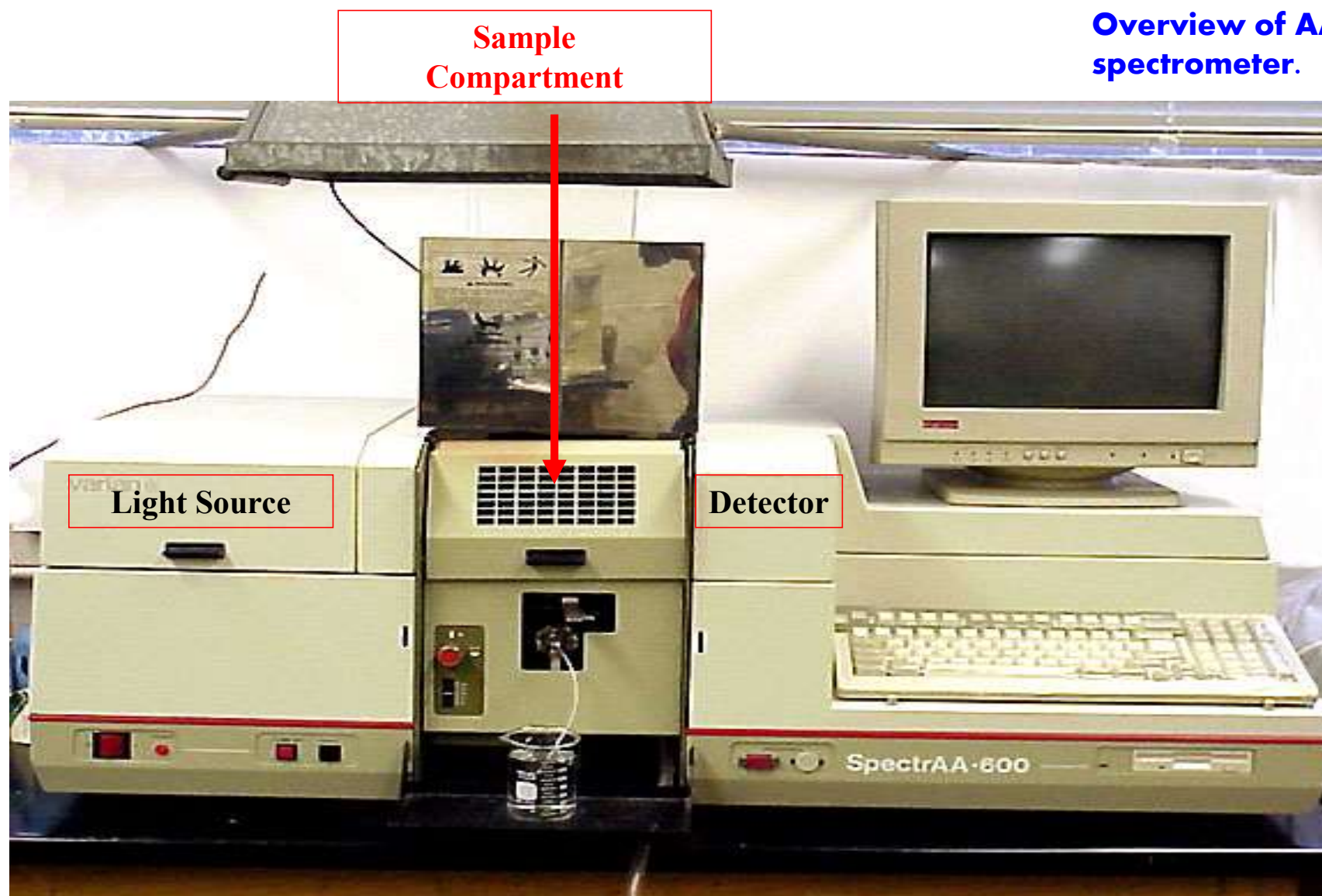
- Destroy any analyte ions and breakdown complexes
- Create atoms (the elemental form) of the element of interest
 Fe^0 , Cu^0 , Zn^0 , etc.

Role of the Monochromator

- Isolate analytical lines photons passing through the flame
- Remove scattered light of other wavelengths from the flame
- In doing this, only a narrow spectral line impinges on the Photo multiplier tube.



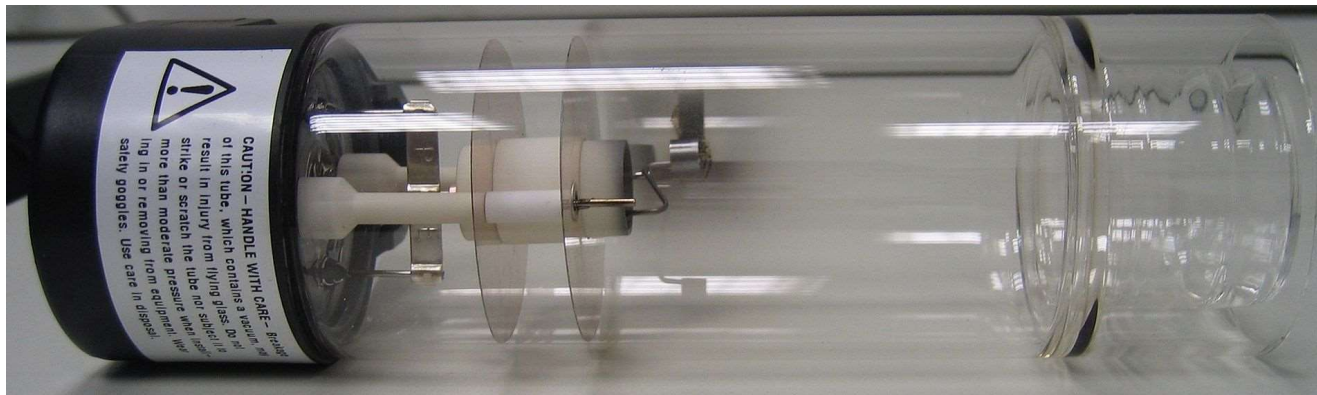
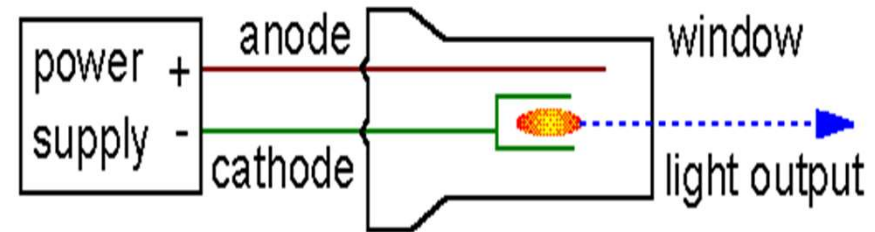
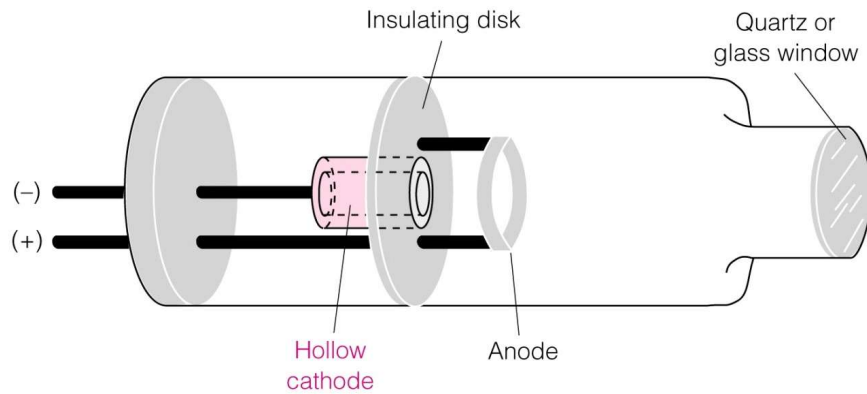
Overview of AA spectrometer.



Job of the Hollow Cathode Lamp (Radiation source)



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Sequence of events in hollow-cathode lamp

- ▶ **Ionization of rare gas atoms** $\text{Ar} + \text{e}^- \rightarrow \text{Ar}^+ + 2\text{e}^-$
- ▶ **Sputtering of cathode atoms:** $\text{M(s)} + \text{Ar}^+ \rightarrow \text{M(g)} + \text{Ar}$
- ▶ **Excitation of metal atoms:** $\text{M(g)} + \text{Ar}^+ \rightarrow \text{M}^*(\text{g}) + \text{Ar}$
- ▶ **Light emission:** $\text{M}^*(\text{g}) \rightarrow \text{M(g)} + h\nu$
- ▶ The cathode contains the element that is analysed.
- ▶ Light emitted by hollow-cathode lamp has the same wave length as the light absorbed by the analyte element
- ▶ Different lamp required for each element

Function of hollow cathode lamp

- Provide the analytical light line for the element of interest
- Provide a constant yet intense beam of that analytical line

Hollow cathode lamp (Radiation source)

- **It should emit stable intense radiation of the element to be determined, resonance line of the element**
- **DC voltage is applied across anode and cathode**
- **Atom of the filler gas ionized at the anode and attracted by the cathode**
- **Inert gas ions strike the cathode and displace the surface metal atoms in the inert gas**
- **Further collision of vaporized metal atoms with energetic inert gas ions result in excited metal atoms emit the characteristic spectrum of the metal used to construct the cathode**
- **Each HCL emits the spectrum of the metal used in the cathode**
- **Spectral lines emitted by the copper HCL can only be absorbed by the copper atom present in the flame**

Hollow cathode lamp (Radiation source)

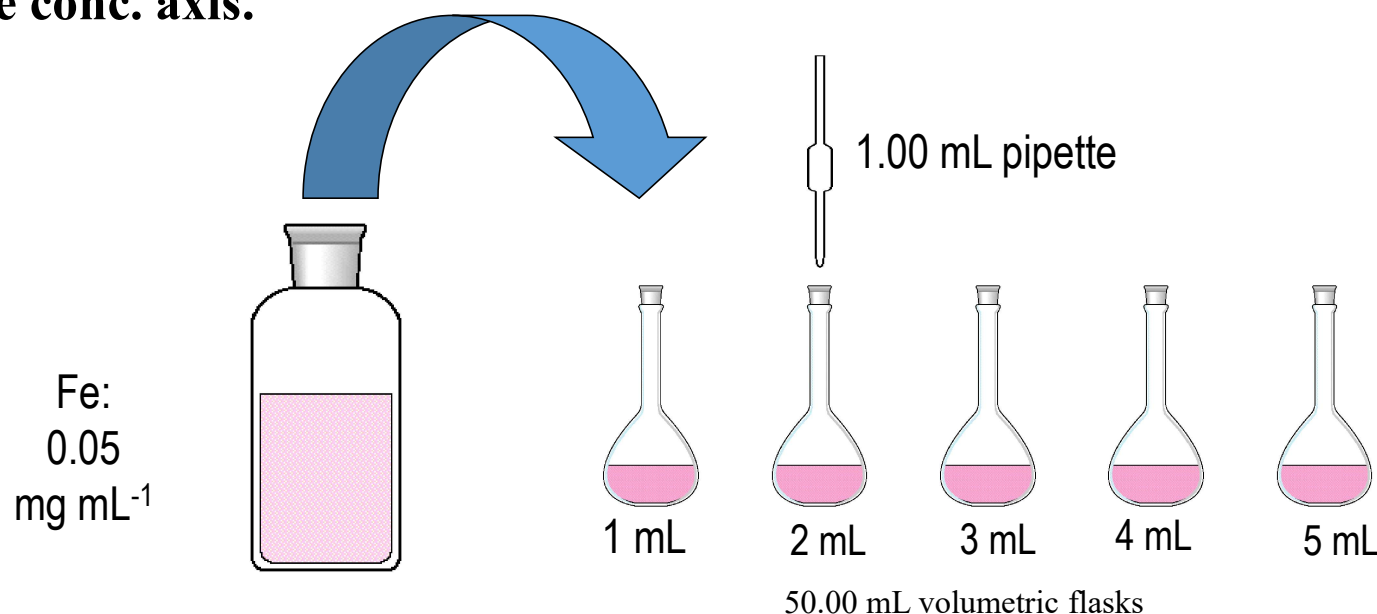
- **Hollow-cathode lamps are a type of discharge lamp that produce narrow emission from atomic species. They get their name from the cup-shaped cathode, which is made from the element of interest.**
- **The electric discharge ionizes rare gas atoms, which are accelerated into the cathode and sputter metal atoms into the gas phase.**
- **Collisions with gas atoms or electrons excite the metal atoms to higher energy levels, which decay to lower levels by emitting light.**

- **Atomic-absorption (AA) spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame.**
- **The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels.**

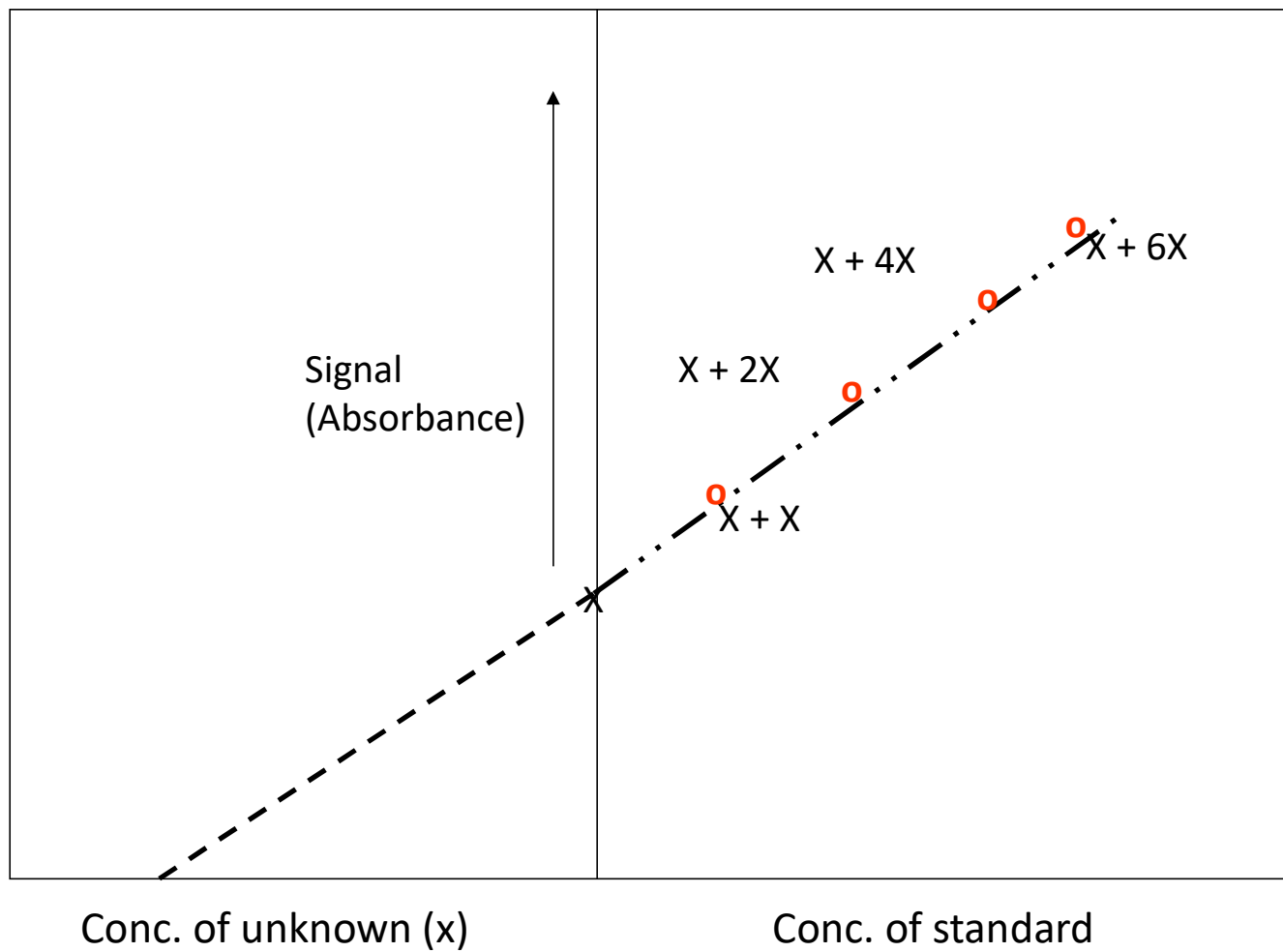
- **The analyte concentration is determined from the amount of absorption.**
- **Applying the Beer-Lambert law directly in AA spectroscopy is difficult due to variations in the atomization efficiency from the sample matrix.**
- **Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.**

Calibration curve- Standard addition method

- **Signal intensity of unknown sample X is taken**
- **Series of solutions having standard sample of X are prepared and signal is obtained by aspirating them in flame**
- **Plot is drawn between the signal intensity vs conc. of unknown X + Conc. of standard X**
- **From the plot, the conc. of unknown can be determined from the intersection of the curve with the conc. axis.**



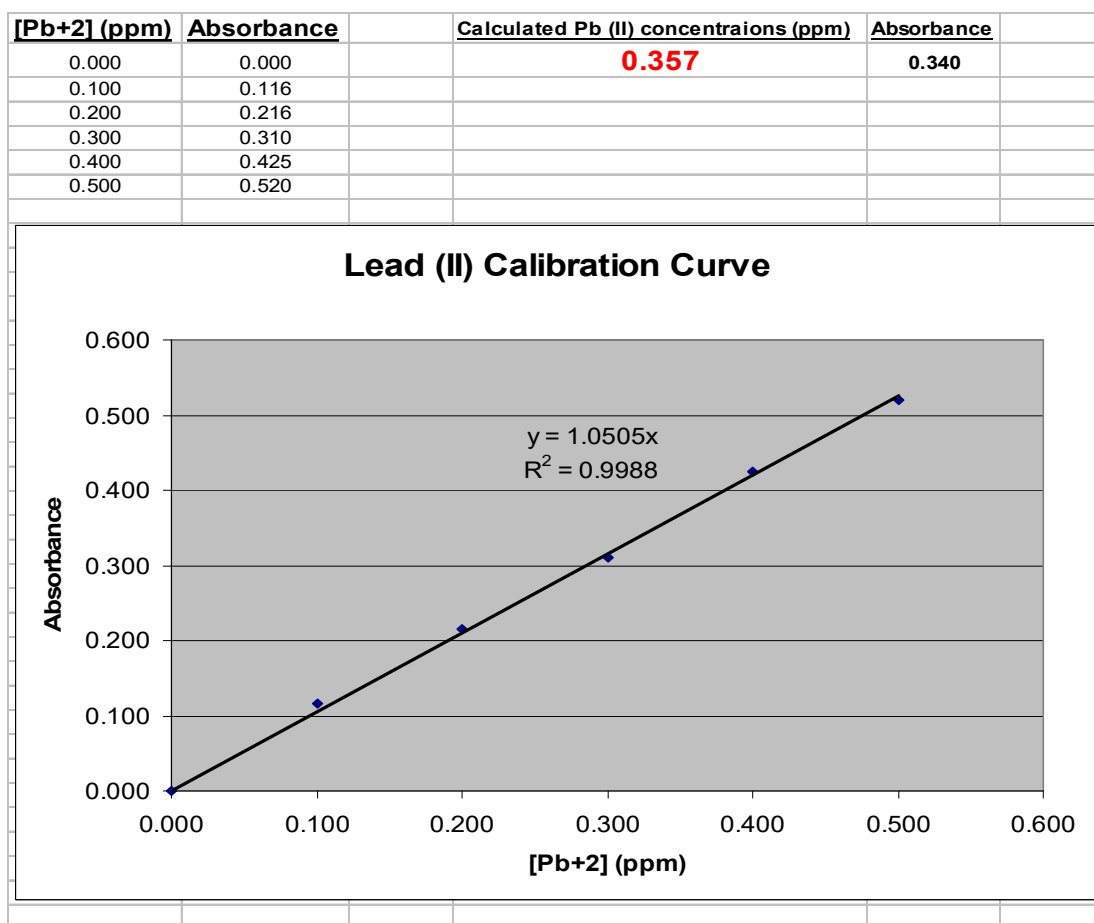
Standard Addition Curve



Calibration curve- Standard addition method

- **Signal intensity of unknown X is taken by aspirating sample solution to flame**
- **Series of solutions having unknown X + varying amounts of standard X are prepared and signal is obtained by aspirating them in flame**
- **Plot is drawn between the signal intensity against Conc. Of unknown X + Conc. Of standard X**
- **From the plot, the conc. of unknown can be determined from the intersection of the curve with the concentration axis.**
- **AAS compensates for any unexpected interfering material present in the sample solution**

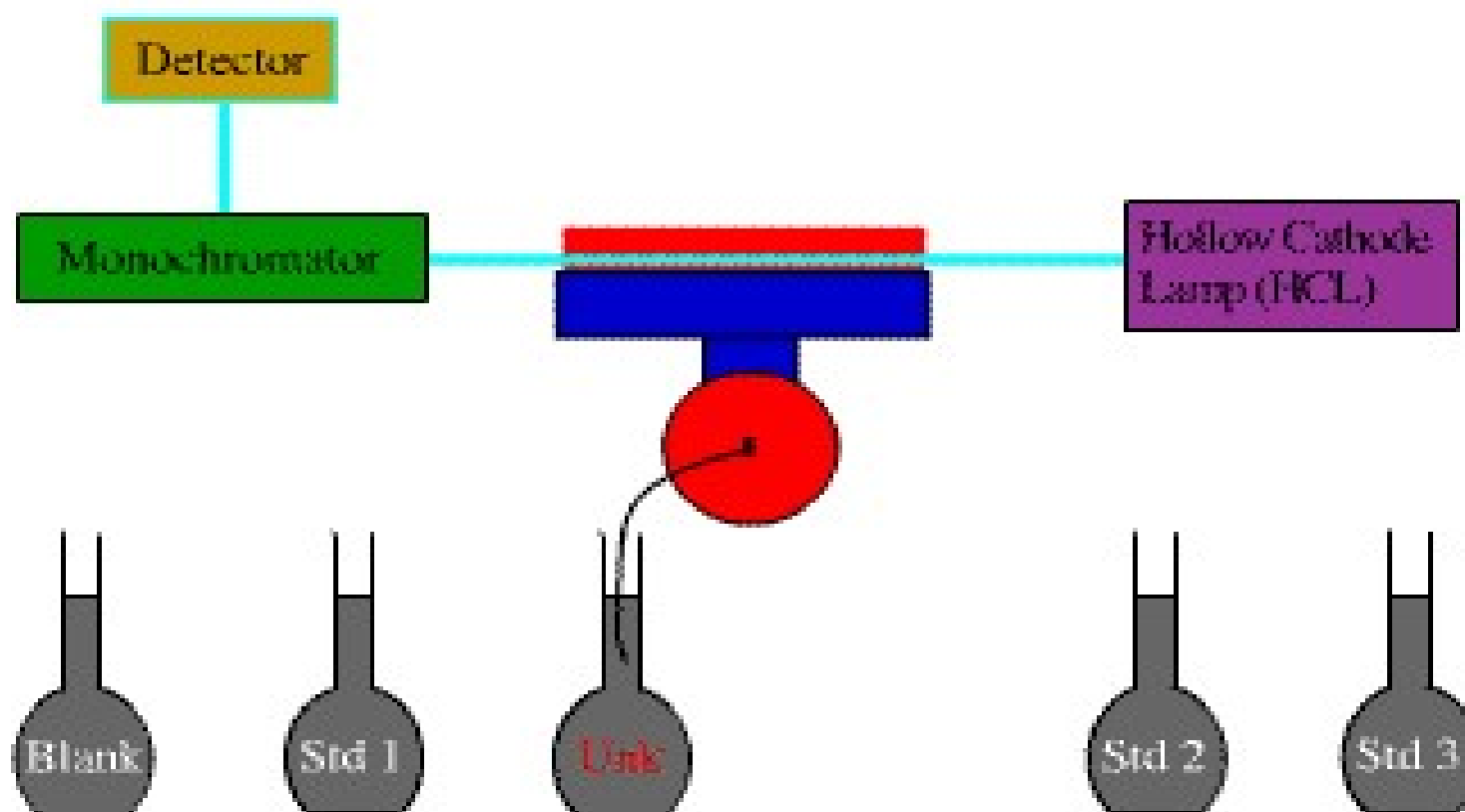
Lead is extracted from a sample of blood and analyzed at 283 nm and gave an absorbance of 0.340 in an AA spectrometer. Using the data provided, graph a calibration curve and find the concentration of lead ions in the blood sample.



- The data provided in the problem appears in the upper left hand corner of this MS EXCEL worksheet.
- The graph is used to calculate the best fit line.
- The equation is then used to calculate the concentration of Pb (II) ions with an absorbance of 0.340.
- The result, **0.357 ppm**, is displayed above the graph.

Advantages

AAS compensates for any unexpected interfering material present in the sample solution



SPECTROSCOPY

Atomic Spectroscopy: Introduction to atomic spectroscopy, atomic absorption spectrophotometry and flame photometry.

Molecular Spectroscopy: Beer-Lambert's Law, molecular spectroscopy, principle, instrumentation and applications of UV-Vis and IR spectroscopy.

Learning Outcomes: The students will be able to reflect on atomic and molecular spectroscopy fundamentals like Beer's law, flame photometry, atomic absorption spectrophotometry, UV-Vis and IR.