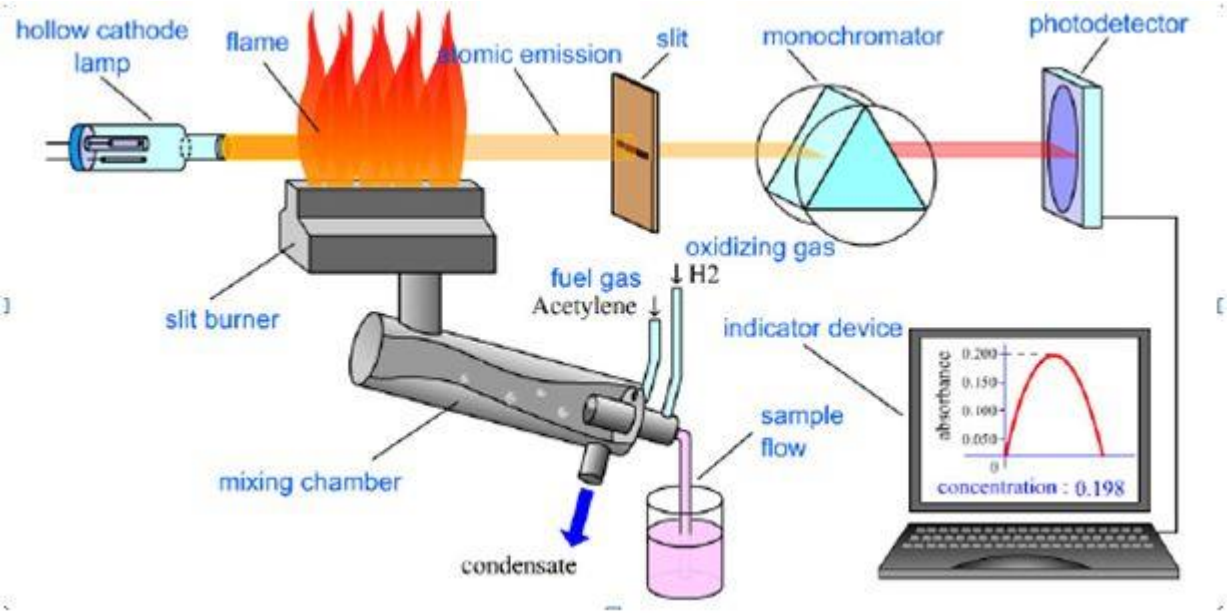
ATOMIC ABSORPTION SPECTROSCOPY



Atomic absorption spectroscopy is a quantitative technique that achieves accurate analysis of metal ions in solution and is extremely sensitive (concentrations as low as pictogram mL^{-1} may be determined by this method). In atomic absorption spectrophotometry the atomisation is performed by aspirating the sample solution into a flame where the analyte element is converted into gaseous phase atoms. Alternatively, the sample is fed into a graphite furnace where the atomisation is achieved electrothermally at relatively lower temperature, below 3000 K. As the temperature of atomisation is low; most of the atoms remain in the ground state which can absorb characteristic radiation from the radiation source made from the analyte element. The atomic vapours containing free atoms of an element in the ground state are illuminated by a radiation source emitting the characteristic radiation of the analyte. The radiation is absorbed by the analyte vapours and its intensity decreases. The degree of absorption is a quantitative measure of the concentration of ground state atoms in the vapours. The analysis is done by comparing the observed absorption with the one obtained by suitable standard samples of the analyte under similar experimental conditions, i.e. a calibration curve method is generally employed.

In AAS, the electrons of the atoms in the flame are promoted to higher orbitals for an instant by absorbing a set quantity of energy (a quantum). This amount of energy is specific to a particular electron transition in a particular element. As the quantity of energy put into the flame is known, the quantity remaining at the other side (at the detector) can be measured, and thus get a signal that is proportional to the concentration of the element being measured.

From Beer Lambert's Law, $\log(P_0/P) = A = \varepsilon bc$ where P_0 = radiant power of incident light, P = radiant power of transmitted light, b = thickness of the absorbing medium, ε = absorption coefficient, and c = concentration of absorbing analyte atoms. Thus, absorbance of the sample is directly proportional to the concentration of the analyte. Therefore, a calibration plot of concentration of analyte element versus absorbance is drawn from the standard solutions and the concentration of element in unknown solution is read directly from the graph. However, such a linear relationship between the absorption and the concentration can be observed only if all radiation passing through the sample is absorbed to the same extent by the analyte atoms. However, the experimental concentration versus intensity calibration curve is observed to be deviating from the linearity as a result of the presence of non-absorbed radiation and other interferences. Therefore, suitable measures need to be taken so as to minimise the interferences and obtain the linearity in the calibration curves.

A calibration plot is drawn by aspirating standard solutions of known concentration into the flame and measuring absorbance for each solution. The concentration of the unknown solution is then determined from the calibration plot. Despite the fact that Beer's law is followed in AAS, in practice the departures from linearity are encountered. The non-linearity is due to the transmission of unabsorbed light from the radiation source. In addition, a number of uncontrolled variables in atomisation and absorbance measurements may also affect the measurements. Therefore, we need to find the concentration range in which the Beer Lambert's law holds i.e. we get a straight line.

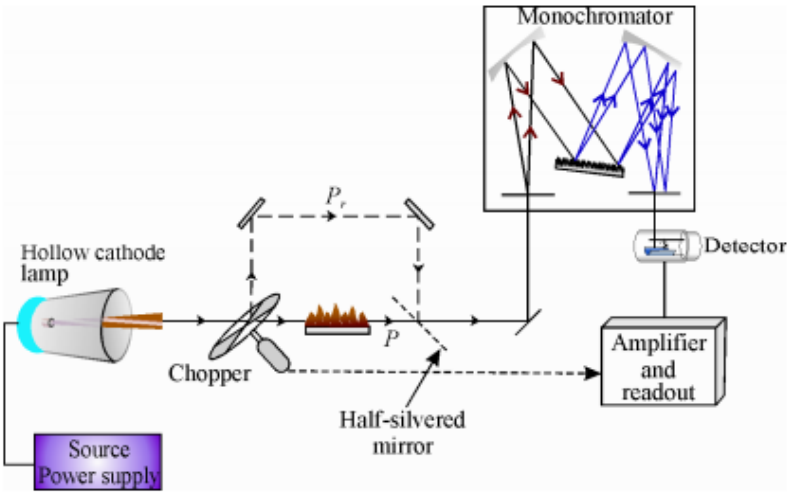
A typical atomic absorption spectrophotometer consists of the following components: radiation source, flame/furnace, monochromator, detector and readout device.

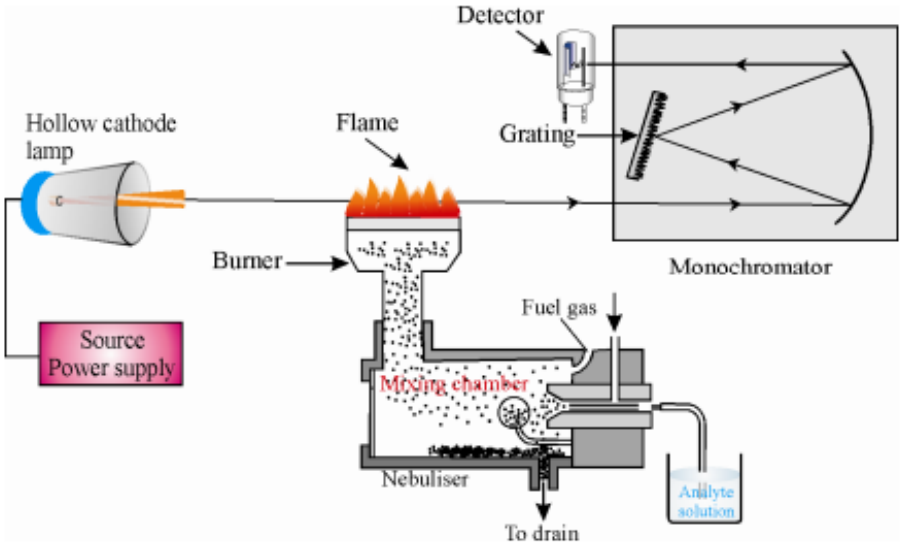
The radiation source, a hollow cathode lamp, is made specifically of the element under investigation which allows analysis of one metal. When a large voltage is applied across the anode and cathode, excitation of the element occurs producing a certain emission spectra characteristic of the element under investigation. When this is passed through the sample, it has the exact energy required to cause electron transitions within the element in the sample while not exciting other atoms in the sample.

The purpose of atomiser is to provide a representative portion of the analyte in the optical path and convert it into free neutral ground state atoms. The most widely used flame is the air/acetylene flame which produces a temperature of about 2300^{o}C and allows for the analysis of about 30 elements.

The monochromator are designed to selectively provide radiation of a desired wavelength out of the range of wavelengths emitted by the source or emitted by analyte sample. In AAS, the monochromators select a given emission line and isolate it from other lines due to molecular band emissions and all non-absorbed lines. As the wavelengths of resonance lines fall in UV region, the most commonly used detector in atomic absorption spectrophotometry is photomultiplier (PM) tube whose output is fed to a readout system.

The readout systems include meters, chart recorders and digital display meters. In addition, it is necessary to eliminate interferences caused by emission of radiation by the atoms in the flame itself. This is solved by causing the intensity of the source to fluctuate at a constant frequency (called modulation). The detector then receives two types of signals, an alternating one from the source and a continuous one from the flame. These signals are converted to the corresponding types of electrical responses and the detector only responds to the alternating current and amplifies this ignoring the unmodulated DC signal. This modulation can be achieved by interposing a circular disk (chopper) in the beam between the source and the flame. Alternate quadrants of this disk are removed to permit passage of light. Rotation of the disk at constant speed provides a beam that is "chopped" to the desired frequency. Hence the machine focuses entirely upon the light generated by the lamp and eliminates the effects of light produced in the flame.





We normally dilute the sample when using AAS. This is because at higher concentrations, there are more absorbing particles in AAS and thus a greater reduction in the transmittance beam. If there are too many absorbing particles, the intensity of the transmitted beam cannot be measured and so cannot be compared to the incident beam's intensity for the absorbance to be determined. We select the wavelength of highest absorbance because at the wavelength of strongest absorbance (lambda-max), absorbance is most sensitive to concentration. Also, there is usually a broadening of peak within a certain interval of wavelength near lambda-max and thus there is no appreciable change in the value of absorbance which is quite advantageous due to instrumental error (selecting wrong wavelength). A blank solution is also commonly used to reduce the effect of other absorbing species. The reference solution should be the same as the solution to be analysed except that it has zero concentration of the absorbing species. It is used because the solvent and other compounds in the solution (excluding species under investigation) may absorb the same wavelengths of the species under investigation. The reference solution takes into account absorbance of the solvent and other molecules that interfere with the analyte, allowing the detector to only take into account the absorbance of the species under investigation. It also takes into account background effects.

Using solutions of known concentration of the analyte under investigation and passing light of the desired wavelength through them establishes a relationship between absorption and concentration, thus allowing a construction of a calibration curve in which the concentration of the analyte in the sample can be read off. Calibration curves enable the concentration of the species under investigation to be calculated.

The interferences to AAS include spectral, chemical and physical. Most probable spectral interferences are the ones of the molecular emissions from oxides of other elements in the sample. In case of AAS, such interferences occur if a DC instrument is used and can be eliminated by employing an AC instrument. Chemical interferences are due to ionisation, formation of low volatility compounds, dissociation etc. During atomisation in the flame, several reactions occur resulting in the formation of analyte compounds which decrease atomic population in the cell. Such interferences can be avoided by increasing the flame temperature whence these interfering compounds are decomposed. Physical interferences can include the viscosity of the solution, changes in flame temperature etc. which can be corrected through the use of internal standards.

**Note: VCE tends to use Absorbance (A) = $\log_{10}(1/T)$, $A \propto$ concentration