Atomic Absorption Spectrophotometer

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Atomic absorption spectrophotometer is used to determine the concentration of elements present in a sample by the measurement of absorption of the characteristic radiation by the atomic vapour of the element. It is based on the principle that when radiation characteristic of a particular element passes through an atomic vapour of the same element, absorption of radiation occurs in proportion to concentration of atoms in the light path. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others. The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals.

Atomic Absorption Process

The atom in an element is made up of a nucleus surrounded by electrons. Every element has a specific number of electrons characteristic of that element which rotate around the atomic nucleus in an orbital structure. The electrons occupy orbital positions in an orderly and predictable way. The lowest energy, most stable electronic configuration of an atom, known as the “ground state”, is the normal orbital configuration for an atom. If light of right wavelength impinges on a free, ground state atom, the atom may absorb the light as it enters an excited state in a process known as atomic absorption. The important factor in atomic absorption measurements is the amount of light at the resonant wavelength, which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way (Fig 1). The capability of an atom to absorb very specific wavelengths of light is utilized in atomic absorption spectrophotometry. The light used to excite the atom is produced by a hollow cathode lamp, the cathode being made of the element desired to be estimated. The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. Aspirating a solution of the sample into a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state and are capable of absorbing light at the

![Fig. 1. The atomic absorption process](image-url)
analytical wavelength from a source lamp.

Quantitative Analysis by Atomic Absorption

The quantitative analysis by atomic absorption spectrophotometry is illustrated in Fig. 2. Light at the resonant wavelength of initial intensity, Io, is focused on the flame cell containing ground state atoms. The initial light intensity is decreased by an amount determined by the atom concentration in the flame cell. The light is then directed onto the detector where the reduced intensity, I, is measured. The amount of light absorbed is determined by comparing I to Io.

Absorbance is the most convenient term for characterizing light absorption in absorption spectrophotometry, as this quantity follows a linear relationship with concentration

\[ A = \log \left( \frac{I_0}{I} \right) \]

Beer's Law defines this relationship:

\[ A = abc \]

where “A” is the absorbance; “a” is the absorption coefficient, a constant which is characteristic of the absorbing species at a specific wavelength; “b” is the length of the light path intercepted by the absorption species in the absorption cell; and “c” is the concentration of the absorbing species. This equation simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions. This direct proportionality between absorbance and concentration is observed in atomic absorption. When the absorbance of standard solutions containing known concentrations of analyte are measured and the absorbance data are plotted against concentration, a calibration relationship similar to that in Fig. 3 is established.

Over the region where the Beer's Law relationship is observed, the calibration yields a straight line. As the concentration and absorbance increase, nonideal behavior in the absorption process can cause a deviation from linearity, as shown.

After such a calibration is established, the absorbance of solutions of unknown concentrations may be measured and the concentration is determined from the calibration curve. In modern instrumentation, the calibration can be made within the instrument to provide a direct readout of unknown concentrations. Since the advent of microcomputers, accurate calibration, even in the nonlinear region, is possible.
Parts of Atomic Absorption Spectrophotometer

The atomic absorption spectrophotometer consists of a light source, an atomization unit and a means of specific light measurement.

Light Source

The two most common light sources used in atomic absorption are the hollow cathode lamp and the electrode less discharge lamp.

Hollow cathode lamp

Most of the elements can be determined by using hollow cathode lamp (Fig 4). It consists of a glass or quartz envelope containing two electrodes. The cathode is cup shaped and made up of the specified element. The lamp is filled with a low-pressure noble gas, usually neon or argon. Application of 100 to 200 volts will produce a slow discharge with most of the emission coming from the cathode. Positive ions from the inert gas bombard the cathode, removing metal atoms by a process known as sputtering. These atoms can then accept energy of excitation and emit their characteristic radiation. The emission consists of discrete lines of the metal plus those of fill gas. The gas is selected to give the least spectral interference with the metal concerned. The loss of metal from the cathode at normal operating currents usually does not affect lamp performance. Fill gas atoms can be trapped during the metal deposition process, which does affect lamp life.

Electrode less Discharge Lamp (EDL)

For most elements, the hollow cathode lamp is a satisfactory source for atomic absorption. In a few cases, however, the quality of the analysis is impaired by limitations of the hollow cathode lamp. The primary cases involve the more volatile elements where low intensity and short lamp life are the problems. The determination of these elements can be improved with the use of brighter, more stable sources such as the electrode less discharge lamp. A small amount of the metal or salt of the element for which the source is to be used is sealed inside a quartz bulb. This bulb is placed inside a small, self-contained RF generator or Driver. When power is applied to the driver, an RF field is created. The coupled energy will vaporize and excite the atoms inside the bulb, causing them to emit their characteristic spectrum. Electrode less discharge lamp (EDL) are typically much more intense and in some cases, more sensitive than hollow cathode lamps. They offer better precision and lower detection limits. The lifetime of an EDL is typically much greater than hollow cathode lamp for the same element. However, the optical image for the EDL is considerably larger than that in hollow cathode lamp. As a result, the performance benefits of the EDL can only be observed in instruments with optical systems designed to be compatible with larger image.

Atomization

Three modes of atomization is possible in AAS namely flame atomization, graphite
furnace atomization and volatile hydrides.

**Flame atomization**

In flame atomization, fuel and oxidants are fed into a mixing chamber, where they proceed through a series of baffles to ensure complete mixing, to the burner head. The flame orifice is in the form of a long narrow slot so that ribbon flame is produced. The sample is aspirated into the mixing chamber by a small air jet.

**Graphite furnace atomization**

In this case, electrical heating is employed for atomization. The temperature of the graphite atomizer is generally programmed in three steps. First the temperature is raised to 300°C, held there for a minute to evaporate the solvent, organic matter is next removed by charring at 1700°C for another minute and after this the temperature is raised to 3000°C to dissociate inorganic compounds into atoms.

**Volatile hydrides**

Another sample handling device is available for those metals, which form volatile hydrides eg. Bi, As, Sb etc. The hydrides are produced by reaction of the salts of these elements with alkaline sodium borohydride. The effluent (Hydride) can then be swept out from the solution with a stream of air, directly into the atomization device of the atomic absorption spectrophotometer.

In a similar manner Hg can be reduced to the elemental state and swept out in an air current into a quartz tube, which need not be heated (cold vapour atomic Absorption spectroscopy).

**Optics and the monochromator system**

The portion of an atomic absorption spectrometers optical system, which transmits the light from the source to the monochromator is referred to as the photometer. Three types of photometers are typically used in atomic absorption instruments namely single beam, double beam and compensated single-beam or pseudo double-beam. An important factor in determining the baseline noise in atomic absorption instrument is the amount of light energy reaching photomultiplier tube (PMT). Lamp intensity is optimized to be as bright as possible. Light from the source must be focused on the sample cell and directed to the monochromator, where the wavelengths of light are dispersed and the analytical line of interest is focused onto the detector.

**Sample preparation**

The sample is digested in a automatic microwave digester or using acid digestion method as per the standard protocol.

**Operation of AAS**

The nebuliser with the aid of stream of air /N₂ draws the sample which is converted to a mist and mixed with fuel gas (acetylene) in the empty chamber (Fig 5). It is then fed to the burner designed to give a laminar flame. The specific radiation produced by the hollow cathode lamp is focused along the axis of the flame. The burner while
burning the sample produces gaseous atoms of the element in the sample, which will absorb a part of radiation proportional to the concentration of the analyte element. The unabsorbed radiation falls on a monochromator. The monochromator is manipulated suitably to select the specific wavelength characteristic of the analyte element, which in turn is sent to the photomultiplier tube. The current developed by the photomultiplier is amplified calibrated to read in terms of transmittance. Using a blank the transmittance can be adjusted to read 100 and sample concentration can be determined by comparison with a standard. The instrument can be calibrated to read absorbance or concentration.

**Background correction**

Background signal arises in part from the radiation emitted by the hot sample itself. This source of background is unique to AA, resulting from the inevitable electronic excitation of the analyte atoms that spontaneously emit photons at the same wavelength being studied in absorption. This can be eliminated by chopping the radiation from the hollow cathode lamp leaving the radiation originating in the sample untouched. The electronic amplifier can be synchronized with chopper so that, the component of the signal, which is generated by emission from the sample, is subtracted from the total signal. The background may also contain contribution due to absorption by other components of the sample. This can be minimized by the use of a continuous source of $H_2$ or $D_2$ lamp simultaneously with the line source. Radiation from the auxiliary lamp passes through the sample along with resonance radiation from the hollow cathode lamp. The electronic system sort out the signals from the two sources and takes their ratio.

**Application**

AAS is useful in quantitative determination of large number of metals, especially at trace levels. It is widely used in number of fields such as analysis of water, food, pharmaceuticals, environmental and metallurgical samples.