

Atomic Absorption Spectroscopy

13.1 Introduction

Since its introduction, by Alan Walsh in the mid-1950's, atomic absorption spectroscopy has proved itself to be the most powerful instrumental technique for the quantitative determination of trace metals in liquids. This method provides a total metal content of the sample and is almost independent of the molecular form of the metal in the liquid. For example, one can determine the sodium content of a water sample and in most of the cases it does not matter in what molecular form the sodium exists.

Since the work of Walsh, the growth of analytical atomic absorption spectroscopy has been phenomenal. The versatility of atomic absorption spectroscopy can be realized from the fact that 60-70 elements including most of the common rare earth metals, have been determined by this technique in concentrations that range from trace to macroquantities. Direct application of the technique is limited to metals, with the exceptions of B, Si, As, Se and Te. Several of the non-metals have been estimated by indirect methods.

By this technique, the determinations can be made in the presence of many other elements. It means that it becomes unnecessary to separate the test element from the other elements present in the sample and thus it saves a great deal of time and in the process eliminates several sources of error. Atomic absorption spectroscopy is not only restricted to solution but also to nonaqueous solutions.

As atomic absorption spectroscopy does not demand sample preparation, it is an ideal tool for non-chemist also, e.g., the engineer, biologist or clinician are interested only in the significance of the results.

Atomic absorption spectroscopy is a method of elemental analysis. It is particularly useful for determining trace metals in liquids and is almost independent of the molecular form of the metal in the sample. For example, we can determine the total cadmium content of a water sample—it does not matter whether the cadmium exists as a chloride, nitrate, sulfate, or other salt. The method is very sensitive and can detect different metals in concentrations as low as and frequently lower than 1 ppm. As an analytical technique, it has become increasingly important because of its high sensitivity and the comparative ease with which quantitative results can be obtained. A disadvantage of the method is that only one element can be determined at a time. A change in light source and a change of analytical wavelength are necessary to determine a second element. The method has limited use for qualitative analysis.

13.2 Principle

→ The absorption of energy by ground state atoms in the gaseous state forms the of atomic absorption spectroscopy. ✕

When a solution containing metallic species is introduced into a flame, the vapour of metallic species will be obtained. Some of the metal atoms may be raised to an energy level sufficiently high to emit the characteristic radiation of the metal—a phenomenon that is utilised in the familiar technique of emission flame photometry. But a large percentage of the metal atoms will remain in the non-emitting ground state. These ground state atoms of a particular element are receptive of light radiation of their own specific resonance wavelength (in general, the same wavelength as they would emit if excited). Thus, when a light of this wavelength is allowed to pass through a flame having atoms of the metallic species, part of the

light will be absorbed and the absorption will be proportional to the density of the atoms in the flame. Thus, in atomic absorption spectroscopy, one determines the amount of light absorbed. Once this value of absorption is known, the concentration of the metallic element can be known because the absorption is proportional to the density of the atoms in the flame. Mathematically, the total amount of light absorbed may be given by the expression as follows:

$$\text{At } \nu \text{ the total amount of light absorbed} = \frac{\pi e^2}{mc} N f \quad 13.1$$

where e is the charge on the electron of mass m , c the speed of light, N the total number of atoms that can absorb at frequency ν in the light path and f the oscillator strength or ability for each atom to absorb at frequency, ν . As π , e , m and c are constants, equation (13.1) can be simplified to the following expression:

$$\text{Total amount of light absorbed} = \text{constant} \times N \times f \quad 13.2$$

From expression (13.2), it follows that

- Firstly, there is no term involving the wavelength (or frequency) of absorption other than the indication of the actual absorption wavelength.
- Secondly, there is no term involving the temperature.

From above, it follows that absorption by atom is independent of the wavelength of absorption and the temperature of the atoms. These two features provide atomic absorption spectroscopy distinct advantages over flame emission spectroscopy.

It should be pointed out, however, that although the temperature does not affect the process of absorption by atoms, it does affect the efficiency with which atoms are produced from a sample and therefore indirectly affects the signal quite significantly. Furthermore, some atoms, particularly those of the alkali metals, easily ionize at high temperatures. Ions do not absorb at atomic absorption wavelengths. Atoms that become ionized are effectively removed from the absorbing population, resulting in a loss of signal.

13.3 Grotrian Diagrams

Quantum theory defines the electronic orbitals in an atom. For example, sodium is an atom with complete inner shells but one electron in the outer shell. Its configuration is therefore $1s^2, 2s^2, 2p^6, 3s^1$. This is frequently abbreviated to $3s$. In atomic absorption, UV radiation is absorbed that does not have sufficient energy to excite the inner shell electrons at the principal quantum numbers 1 and 2. Consequently, in sodium, only the $3s$ electron, sometimes called the *optical electron*, is involved. This is true of all elements: Only the optical electrons are involved in atomic absorption.

In the case of sodium and all other elements, the upper orbitals predicted by quantum theory are empty. Thus the $3p, 4s, 3d, 4p, 5s$, and so on, orbitals of an unexcited sodium atom are empty. These empty orbitals constitute the upper energy levels of the atom. The number of energy levels can be predicted from quantum theory. The actual energy differences of these levels has been deduced from studies of atomic spectra. These levels have been graphed in *Grotrian diagrams*. A partial Grotrian diagram for sodium is shown in Fig. 13.1.

The energy levels are split because the electron itself may spin one way or another, resulting in two similar energy levels and therefore two lines (a doublet) rather than a single line (a singlet). For the transition from the ground state to the first excited state of sodium, the electron moves from the $3s$ orbital to the empty $3p$ orbital. The latter is split into two levels $p^{1/2}$ and $p^{3/2}$ by the electron spin, so two transitions are possible. The differences in energy are $[E(3s) - E(3p^{1/2})] = h\nu_1$ and $[E(3s) - E(3p^{3/2})] = h\nu_2$. The wavelengths associated with these transitions are 589.5 and 589.0 nm, the well-known sodium D lines.

Suppose that the energy state of a given atom are $E_0, E_1, E_2, E_3, E_4, \dots$, where E_0 is a ground state and $E_1, E_2, E_3, E_4, \dots$ are excited states. The absorption frequency may correspond to the transition from the ground state to an excited state. The frequency may correspond to the transition from the ground state to an excited state. The frequency ν is given by $E_1 - E_0 = h\nu_1$ or $E_2 - E_0 = h\nu_2$ or $E_3 - E_0 = h\nu_3$, and so

on. If the transition were between two excited states, ν would be given by $E_2 - E_1 = h\nu_4$ or $E_3 - E_1 = h\nu_3$ and so on.

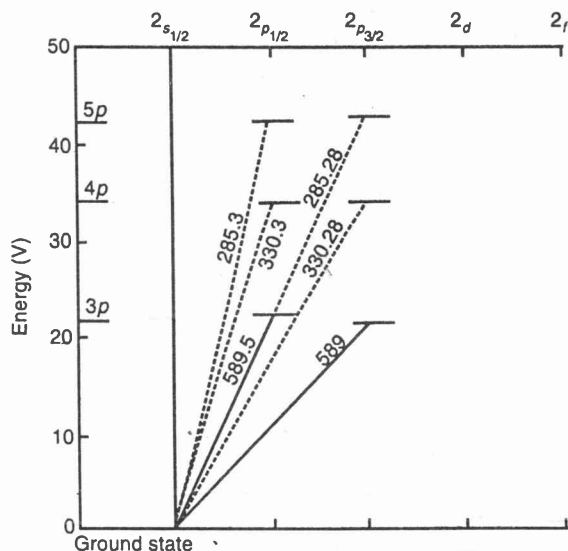


Fig. 13.1 : Partial Grotrian diagram for sodium.

Under normal conditions atoms exist in their lowest possible energy state, the ground state. Very few atoms are normally in the higher energy states. For example, it can be calculated from the Boltzmann distribution law that if zinc vapor with a resonance line at 213.8 nm is heated to 3000 K, there will be only one atom in the first excited state for every 10^{10} atoms in the ground state. Zinc atoms need a considerable amount of energy to become excited. On the other hand, sodium atoms are excited more easily than the atoms of most other elements. Nevertheless, at 3000 K only 1 sodium atom is excited for every 1000 atoms in the ground state. At room temperature the ratio the number of excited to unexcited atoms is greatly reduced. In a normal atom population, therefore, there are very few atoms in states E_1, E_2, E_3, \dots . The total amount of radiation absorbed depends, among other things, on how many atoms there are available to absorb. Consequently the total amount of radiation absorbed at frequencies ν_2, ν_3 , and so on, is exceedingly small and not useful analytically.

For practical purposes, all absorption is by atoms in the ground-state level. This greatly restricts the number of absorption lines that can be used in atomic absorption. Quite frequently only three or four useful lines are available in the UV spectral region for each element, and in some cases less than that. The wavelength of these absorption lines can be deduced from the Grotrian diagram of the element being determined.

13.4 Detection of Non-metals by Atomic Absorption Spectroscopy

Grotrian diagrams correctly predict that the energy required to reach even the first excited state of nonmetals is so great that they cannot be excited by ultraviolet radiation. Their resonance lines are in the vacuum UV. Consequently, atomic absorption cannot be used for the direct determination of nonmetals, although with the use of a capillary discharge lamp, iodine has been measured directly. However, nonmetals have been determined by indirect methods. For example, chlorides can be precipitated as silver chloride from the subsequent determination of silver, the chloride can be calculated.

13.5 Differences Between Atomic Absorption Spectroscopy and Flame Emission Spectroscopy

The main differences between atomic absorption spectroscopy and flame emission spectroscopy are as follows :

- In flame emission spectroscopy, the atoms when put in a flame, become excited. The excited atom, which is unstable, quickly emits a photon of light and returns to a lower energy state, eventually

reaching the unexcited state. The measurement of this emitted radiation forms the basis of flame emission spectroscopy. Analytical signal in flame emission is the sum of all energies emitted as excited atoms drop to the ground state. The signal comes entirely from the emitting atoms.

In atomic absorption spectroscopy, the signal is obtained from the difference between the intensity of the source in the absence of metallic elements present in the liquid and the decreased intensity obtained when metallic elements are present in the optical path. ✱

- (b) In flame emission spectroscopy, the emission intensity is dependent upon the number of exciting atoms and is, therefore, greatly influenced by temperature variations. ✱

In atomic absorption spectroscopy, atomic absorption depends upon the number of unexcited atoms and the absorption intensity does not depend upon the temperature of the flame directly.

- (c) In atomic absorption spectroscopy, the relation between absorbance and concentration is nearly linear, that is, Beer's law is obeyed over a wide concentration range. This is not true in cases of flame emission spectroscopy. ✱

13.6 Advantages of Atomic Absorption Spectroscopy Over Emission Flame Spectroscopy

Atomic absorption spectroscopy acquires the following advantages over emission spectroscopy.

- (a) The atomic absorption technique is specific because the atoms of a particular element can only absorb radiation of their own characteristic wavelength. The converse is also true, i. e., the light of a particular frequency can easily be absorbed by the specific element to which it is characteristic. Spectral interferences which occur in flame emission spectroscopy therefore occur rarely. ✱
- (b) Because of the much larger number of metal atoms that contribute to an atomic absorption signal, variation in flame temperatures shows relatively less effect in atomic absorption spectroscopy than flame emission spectroscopy in which the smaller number of atoms are producing an emission signal. In short, it means that atomic absorption spectroscopy is independent of flame temperature.
- (c) In terms of detection limits atomic absorption and flame emission are quite similar, i.e., some elements possess lower detection limits by flame emission and others by atomic absorption. Table 13.1 gives the list of elements in three categories which are as follows :
 - (i) those more sensitive by flame emission,
 - (ii) those of about equal sensitivity by emission and absorption, and
 - (iii) those more sensitive by atomic absorption.

Table 13.1 : Comparison of Sensitivity of Flame Emission and Atomic Absorption

More sensitive by flame emission	About equally sensitive	More sensitive by atomic absorption
Al	Cr	Ag
Ba	Cu	As
Ca	Mn	Au
Eu	Mo	B
Ho	Pd	Bi
In	Rh	Cd
K	Ni	Co
La	V	Fe

13.7 Disadvantages of Atomic Absorption Spectroscopy

Some disadvantages of atomic absorption spectroscopy are as follows :

- (a) A separate lamp for each element to be determined is required. An attempt is being made these days to overcome this difficulty by using a continuous source with a very high resolution monochromator or alternatively to produce a line source by introducing a flame.

- (b) This technique cannot be used very successfully for estimation of elements like Al, Ti, W, Mo, Si etc., because these elements give rise to oxides in the flame. However, the estimations can be carried out under modified conditions.
- (c) In aqueous solutions, the predominant anion affects the signal to a negotiable degree.

13.8 Instrumentation

A schematic diagram of the atomic absorption spectrophotometer is shown in Fig. 13.2. The principle of the instrumentation is similar to other spectroscopic absorption methods.

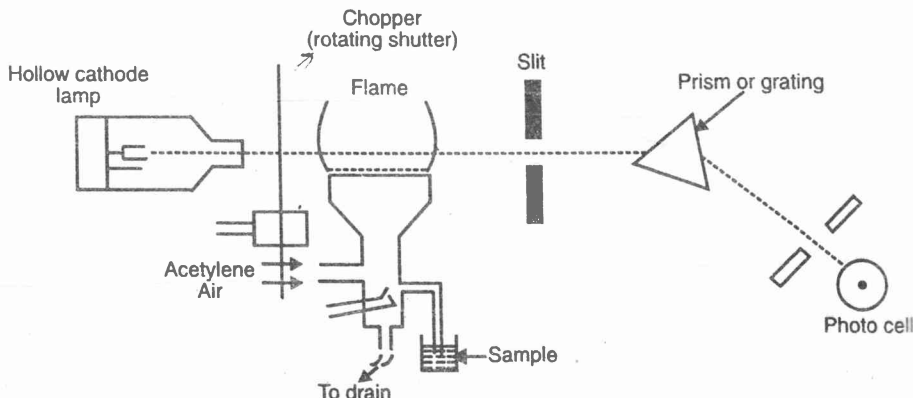


Fig. 13.2 : Arrangement for Atomic Absorption Spectroscopy.

Light of a certain wavelength (produced by a special kind of lamp), which is able to emit the spectral lines corresponding to the energy required for an electronic transition from the ground state to an excited state, is allowed to pass through the flame. Meanwhile the sample solution is aspirated into the flame. Before it enters the flame, the solution gets dispersed into a mist of very small droplets which evaporate in the flame to give the dry salt, and then the vapour of the salt. At least a part of this vapour will be dissociated into atoms of the element to be measured. Thus, the flame possesses free unexcited atoms which are capable of absorbing radiation, from an external source when the radiation corresponds exactly to the energy required for a transition element from the ground electronic state to an upper excited level. Then the unabsorbed radiation from the flame is allowed to pass through a monochromator which isolates the exciting spectral lines of light source. From the monochromator the unabsorbed radiation is led to the detector which is then registered by a photodetector, the output of which is amplified and measured on a recorder. Absorption is measured by the difference in transmitted signal in the presence and absence of test element.

For all types of atomic absorption spectrometer, the following components are required :

1. **Radiation Source.** The radiation source for atomic absorption spectrophotometer should emit stable, intense radiation of the element to be determined, usually a resonance line of the element. Preferably, the resonance spectral lines should be narrow as compared with the width of the absorption lines to be measured. These lines should not be interfered from other spectral lines which are not resolved by spectrophotometer. There should be no general background or other extraneous lines emitting within the band pass of the monochromator. The problem of using such narrow spectral lines has been solved by adopting a hollow cathode lamp as the radiation source.

- (a) **Hollow Cathode Lamp.** Hollow cathode lamp is shown in Fig. 13.3. The cathode consists of a hollow cup. In the cup is the element which is to be determined, in this case sodium. The anode is a tungsten wire. The two electrodes are housed in a tube containing an inert gas. The lamp window is constructed of either quartz, silica, or glass. The exact material depends upon the wavelength which is to be transmitted. When a potential is applied between the two electrodes, a current in the milliamperes range arises, the inert gas is charged at the anode, and the charged gas is attracted at high velocity to the

cathode. The impact with the cathode vaporizes some of the sodium atoms. These are excited and upon returning to the ground state give rise to the sodium emission spectrum.

The manufacturer's recommended current for the lamp should not be exceeded or the lifetime of the lamp may be considerably shortened. Excess current may also give rise to a self-absorption process wherein the sputtered ground-state atoms absorb some of the emitted energy, resulting in a lessening of intensity of the emitted the (see Figure 13.4). On the other hand, if the source lamp is run below the recommended current, a loss of intensity and a corresponding loss of sensitivity will result.

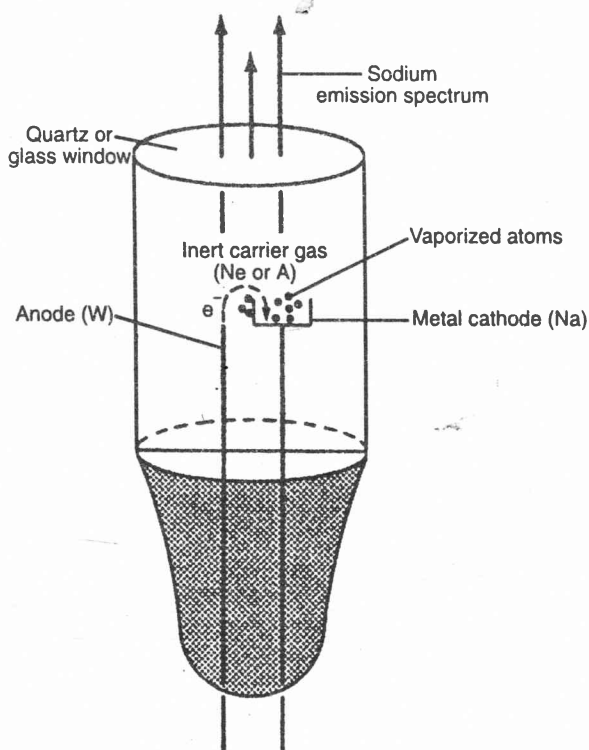


Fig. 13.3 : Schematic diagram of a hollow cathode source lamp for atomic absorption of sodium.

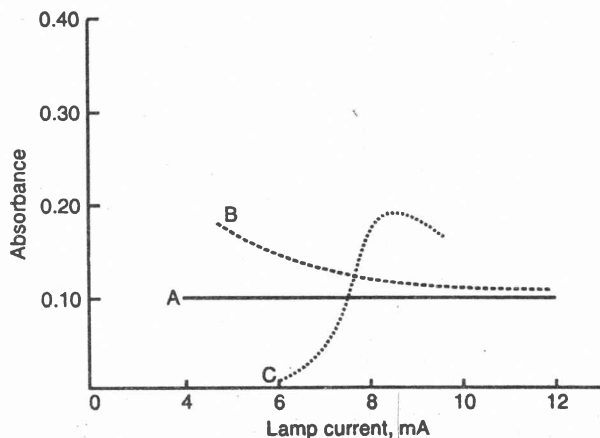


Fig. 13.4 : Typical absorbance vs. lamp current curves for hollow cathode lamps. Note that the lamp which gives curve C would have an optimum current at 8.6 mA.

When a dc voltage of 300–500 V is put across the anode and the cathode, the atoms of the filler gas undergo ionisation at the anode and are rapidly attracted by the cathode. Then, the fast moving ions strike the surface of the cathode and physically displace the surface metal atoms of the cathode into neon (or argon) gas. Further collisions of the vaporised metal atoms from the cathode with energetic filled gas ions result in excited metal atoms which emit the characteristic spectrum of the metal used to construct the cathode. Thus, the emission spectrum produced by a hollow cathode lamp is a sharp line spectrum of the cathode material and the filled gas. The neon or helium gas filled in the hollow cathode lamp performs three functions :

- (i) It is the main source of current-carrying capacity in the hollow cathode.
- (ii) It dislodges atoms from the surface of the cathode.
- (iii) It is primarily responsible for excitation of the ground state metal atoms.

The pressure maintained in the hollow cathode lamp is 1 to 5 torr. If higher pressures are maintained, the discharge tends to be unstable and if lower pressures are maintained, the vaporisation of the hollow cathode metal increases and the operating temperature also increases.

The spectral lines produced by the hollow cathode lamp are so narrow that they are completely absorbed by the atoms. By this method, one can easily detect and measure the atomic absorption.

Each hollow cathode lamp emits the spectrum of that metal which is used in the cathode. For example, copper cathode emits the copper spectrum, zinc cathode emits the zinc spectrum and so on. At the same time, the narrow spectral lines emitted by copper cathode are only absorbed by the copper atoms present in the sample to be analysed by atomic absorption spectroscopy. Similarly, zinc atoms will absorb spectral lines emitted by zinc cathode. For this reason, a different hollow cathode lamp has to be used for each element to be analysed by atomic absorption spectroscopy. This is not very convenient.

In atomic absorption spectrophotometer, gaseous discharge lamps are also used. These are also called arc lamps. Gaseous discharge lamps contain an inert gas at low pressure and a metal or metal salt. These lamps are useful for the alkali metals, zinc, cadmium and mercury.

(b) Electrodeless Discharge Lamp. It is difficult to make stable hollow cathodes from certain elements, particularly those that are volatile, such as arsenic, germanium, or selenium. An alternative light source has been developed in the electrodeless discharge lamp (EDL). This is illustrated in Fig. 13.5. It consists of an evacuated tube in which the metal of interest is placed. The tube is filled with argon at low pressure and sealed off. The sealed tube is then placed in a microwave discharge cavity. Under these conditions the argon becomes a plasma and causes excitation of the metal sealed inside the tube. The emission from the metal is that of its spectrum, including the resonance line. The intensity of these lamps is very high, and they have been made quite stable in recent years.

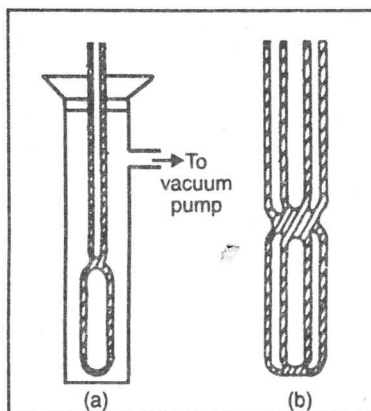


Fig. 13.5 : Electrodeless discharge lamps with vacuum jackets: (a) Dismountable and (b) permanent.