

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 basis 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 that

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:

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

- (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.

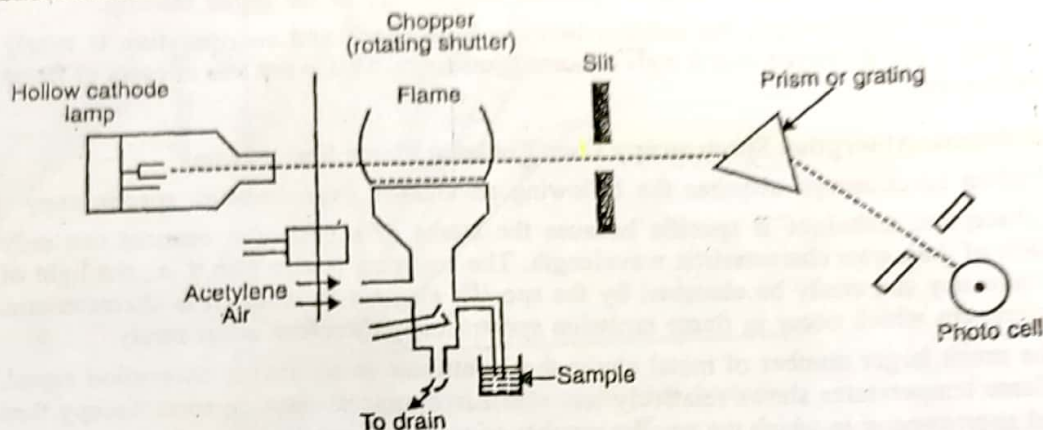


Fig. 13.2 : Arrangement for Atomic Absorption Spectroscopy.

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 evaporates 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 into 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 milliamperage 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 light (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.

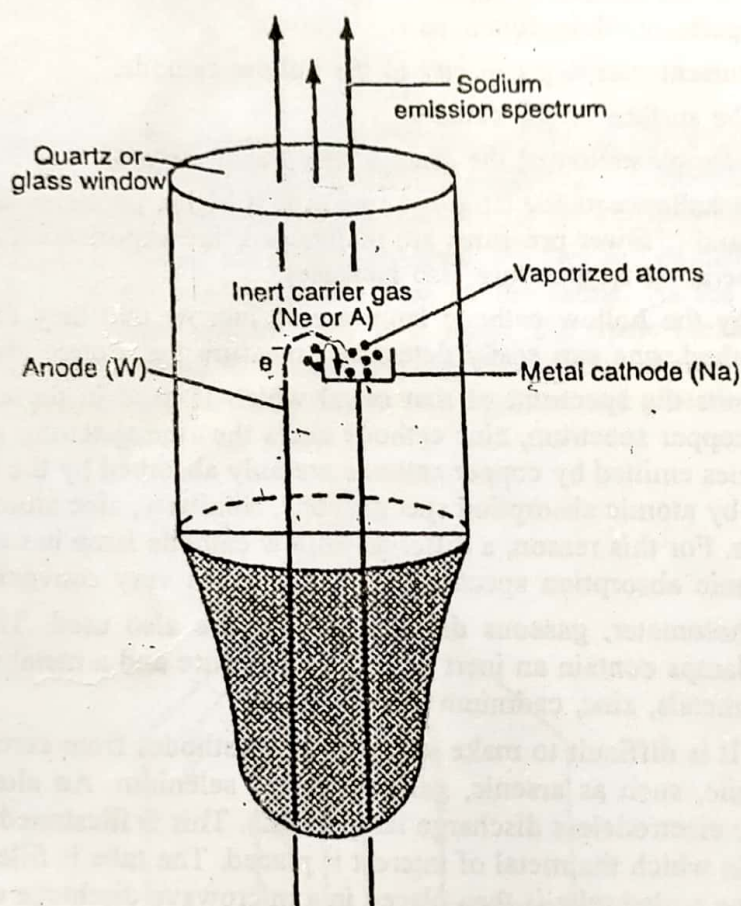


Fig. 13.3 : Schematic diagram of a hollow cathode source lamp for atomic absorption of sodium.

recorder is a potentiometer using a servomotor to move the recording pen. The displacement is directly proportional to the input voltage.

In some atomic absorption measurements, digital read-out devices are the used.

13.9 Operation of Atomic Absorption Spectrometer

In actual practice, a meter is adjusted to read zero absorbance or 100 per cent transmittance when a blank solution is sprayed into the flame, and the unobstructed light of the hollow cathode lamp passes on to the photomultiplier tube. When a solution containing the absorbing species is now introduced, a part of this light is absorbed, resulting in a decrease of light intensity falling on the photomultiplier and producing a deflection in the meter needle.

Standard solutions of the elements to be determined are used to make a calibration curve by which the contents in the test solutions can be measured. A typical calibration curve for copper at 3428\AA is shown in Fig. 13.16.

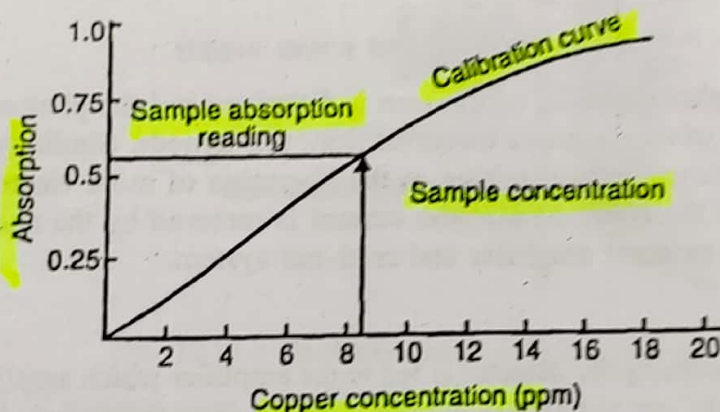


Fig. 13.16 : Calibration curve for copper at 3428\AA

From the calibration curve it is evident that the relationship between absorbance and concentration is linear over the range 2.0 to 10.0 ppm, but at higher concentrations the relationship is curved. When a quantitative analysis is to be performed, the sample is atomised and the absorbance is measured under exactly the same conditions when the calibration curve was prepared.