

ATOMIC ABSORPTION SPECTROFOTOMETER  
*GENERAL REVIEW*



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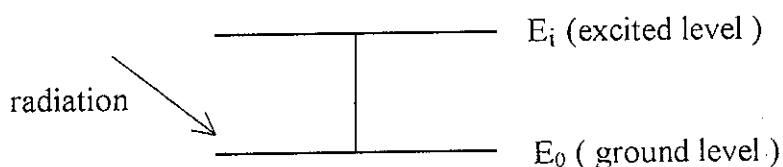
## I. INTRODUCTION

Atomic absorption spectroscopy (AAS) is a useful method for trace metal analysis in solution or readily soluble. “Ground state” metal atoms, which produced by aspirating the solution into a flame, absorb radiation of characteristic wavelengths from a radiation source. The attenuation of the radiation of a suitable spectral line can be measured and compared with the absorptions obtained by treating standard solutions of the metal in the same way. In that way, the concentration of the metal in the solution can be determined.

## II. Basic Principles

Bohr, who made the most important advance in the study of atomic spectra, postulated that any atom is allowed only certain discrete and characteristic energy values. Absorption or emission of radiation by an atom happens when it undergoes a transition between these energy levels.

If an atom which is in a “ground state” (refers to the lowest energy level of the atom) absorb an electromagnetic radiation, the outer electron will undergo a transition to one of the empty orbitals at a higher energy level. The atom now is in a new energy level called “excited” level. Figure 1 illustrates the transition between these energy levels.



**Fig. 1 Transition occurs in atomic absorption**

The frequency of the absorbed radiation depends on the difference between energy levels of the two states of the atom :

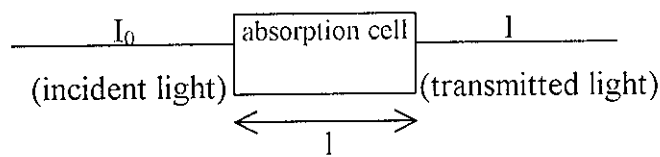
$$\Delta E = (E_i - E_0) = h \cdot \nu = h \cdot c / \lambda$$

where  $h$  is the Planck's constant,  $c$  is the velocity of light,  $\nu$  and  $\lambda$  is the frequency and the wavelength of the absorbed radiation.

In most atoms, a number of transitions are possible, each of them is related to the absorption of a specific spectral line in the radiation. However, the most

prominent absorption line is that related to the electron transition from the ground state to the lowest excited state. This is the most common spectral line (called resonance line) used in AAS practice. Other less intense absorption lines, which will result in transitions between other states of the atom, might be used if the analyte concentration is relatively high.

In atomic absorption, the intensity of a light beam subject to the absorption cell ( $I_0$ ) decreases after passing through the cell ( $I$ ). The quantification of atomic absorption can be describe by Lambert-Beer law, which similar with molecular absorption spectroscopy.



**Fig. 2 Attenuation in light intensity**

The transmitted light can be define:

$$I = I_0 \cdot e^{-k_\nu \cdot l}$$

$k_\nu$  = absorption coefficient at frequency  $\nu$ , which proportional to the analyte  
 . concentration

$l$  = the length of the absorption cell

In the form of the Lambert–Beer law :

$$A = \log \frac{I_0}{I} = \epsilon \cdot b \cdot c$$

$\epsilon$  = absorption constant

$b$  = the length of the absorption cell

$c$  = concentration of the analyte

### III. Technique

The principle of operating an atomic absorption spectroscopy is that a sharp line source (called hollow cathode lamp), consisting of a cathode containing the element(s) to be determined, is used as the resonance line source. In the lamp, the line characteristics of the element(s) are emitted and passed through the flame, where they are then absorbed by the atomic vapor.

Analyte atoms are produced thermally from the analyte solution through nebulisation and atomization process in the atom reservoir. In flames atoms are most commonly encountered in the ground state (Ebdon, 1982). The ground state atoms, which predominate under the experimental conditions, absorb the resonance radiation from the lamp, reducing the intensity of the incident beam.

A monochromator is then used to isolate the desired resonance line and allows this radiation to fall on a detector or a photomultiplier tube. In the detector, an electrical current whose magnitude depends on the light intensity is produced.

The electronics of the unit are designed to respond selectively to the pulsed radiation emanating from the radiation source, and measure the amount of light attenuation in the sample cell. By comparing the absorption of the sample with those of the standard solutions, the actual sample concentration can be obtained.

### IV. Instrumentation of AAS

The AAS basically consists of several important parts, which are light source, atom cell, monochromator, detector, and read out system.

#### a. Light source

Light or radiation source is a device to generate the radiation wave. There are two possible types of lamp can be used to generate the radiation light.

- continuum source

This kind of lamp is a common source that was used in the past. It is actually no more than a domestic filament bulb. This source emits a wide spectrum of radiation (300 nm - infrared), and it is difficult for the monochromator to make a good separation.

Monochromator capable of isolating spectral region narrower than 0.1 nm are excessively expensive, but typical atomic absorption lines may often narrower than 0.002 nm. The amount of radiation isolated by the conventional

monochromator (then viewed by the detector) is not significantly reduced by the very narrow atomic absorption signal, even with high concentrations of analyte. Thus, the amount of atomic absorption seen using a continuum source is negligible. This was the main reason of why analytical potential of AAS was not exploited until the middle of 1950s. (Ebdon, 1982).

- line radiation

The best sensitivity in this method is obtained when the source line is narrower than the absorption profile of the atoms in the flame. Spectral lines are not truly monochromatic or infinitely narrow. Spectral lines can be broadened by number of factors. In a flame, an absorption or emission line profile is governed almost entirely by the combined effects of natural broadening, Doppler broadening, and collisional broadening. Natural broadening is the result of the finite amount of time that atoms spend in the energy levels between which transitions take place. This broadening is relatively small than others. Doppler broadening is occurred due to the random thermal motions of the atoms relative to the detector, and the collisional broadening is due to interaction or collision of the absorbing or emitting atoms with other molecules or atoms, for examples, those of the flame gases. The spectral broadening of the absorption profile of analyte atoms in flames is generally considered to be governed by temperature and pressure (Ebdon, 1982). The higher temperature and pressure, the wider the bandwidth will be.

In 1955, Walsh (an Australian CSIRO's scientist) invented an atomic spectral source by using a relatively low temperature and pressure in the lamp compare to the conditions in the flame. This type of lamp is now known as hollow cathode lamp.

In this case, the monochromator only has to isolate the line of interest from other lines in the lamp (mainly lamp filler-gas lines). The atomic absorption signal exactly overlaps the atomic emission signal from the source and very large reductions in radiation then can be observed. This exact overlap is possible as the atomic emission line from the source has the same wavelength with the atomic absorption line.

The main feature of this lamp is the cathode that is made of the element or an alloy containing the element to be analyzed. For instance, a hollow cathode

lamp made of pure copper or brass should be used for copper analysis. The tube is filled with a low-pressure gas, usually neon. Anode is usually made of tungsten. If sufficient potential is applied across the electrodes to cause a current (1-50 mA) to flow, the filler gas will be positively charged and bombard the cathode and dislodge atoms of the cathode element. Collisional processes excite these atoms and therefore emission spectrum of the element at the cathode is produced.

b. Atom cell

Atom cell holds an important role in providing medium in which the solution is being atomized. The most common atom cell used in AAS is a flame. A solution undergoes several steps before it produces atoms.

i. nebulisation

The objective of nebulisation process is to distribute the liquid into very tiny droplets (5-10  $\mu\text{m}$ ). The sample solution is sucked up in a plastic capillary tube by the decreased pressure created by the expanding oxidant gas at the end of the capillary (ventury effect). The liquid is then drawn up into fine particles. Additionally, an impact bead, which usually placed near the nebuliser outlet, can be used to provide a secondary fragmentation of droplets by physical collision. The fine droplets are then mixed with the fuel gas and passes along the expansion chamber to the burner. Larger particles will drop and are flown out to the drain tube. About 90% of the sample go down the drain, thus only 10% that reach the flame. Nebulisation efficiency is defined as the ratio of sample reaching flame to sample entering nebuliser. The common efficiency of nebulisation is 10%, but it is still favored because only very small droplets reach the flame (Skoog, et al.,1988).

ii. atomization

The result of the nebulisation step is merely fine mist, no atoms have been formed at this stage. In the flame AAS, atomization takes place in the flame, which is formed by the combination of a fuel gas with an oxidant. The function of the flame is not only to vaporize the solvent and atomize the analyte, but also to breakdown any refractory compounds that might react with the analyte.

Atomization efficiency (ratio of the number of atoms to the total number of analyte species, atoms, ions, and molecules in the flame) for most element is

approximately 1 (Ebdon, 1982).

The following table illustrates the sequence that is undergone by solution in atomization process.

**Table 1. Summary of the nebulisation and atomization process**

Place:	Process:	Form of analyte:
<i>Nebuliser</i>	<ul style="list-style-type: none"> <li>• Nebulisation of solution MX into fine particles</li> </ul>	Primary aerosol
<i>Spray chamber</i>	<ul style="list-style-type: none"> <li>• Removal of large droplets</li> <li>• Mixing of gases</li> </ul>	Secondary aerosol
<i>Flame</i>	<ul style="list-style-type: none"> <li>• Desolvation</li> <li>• Vaporisation</li> <li>• Atomisation (by thermal and chemical dissociation)</li> <li>• Ionisation</li> </ul> <p>Excitation</p> <p>Compound formation</p>	<ul style="list-style-type: none"> <li>• Dry aerosol</li> <li>• Molecular gases</li> <li>• Free atom M</li> <li>• <math>M^+</math></li> <li>• <math>M^*</math></li> <li>• MH ; MO ; etc</li> </ul>

c. Monochromator

Monochromator is an instrument that can isolate a narrow range of wavelengths (0.01-1 nm ) anywhere in a comparatively wide spectral range (for AAS typically 190~900 nm). The wavelength to be isolated is the resonance absorption line from other lines emitted by the source of radiation.

d. Detector

Photomultiplier tubes are now widely used as detectors of spectral radiation. It consists of a photosensitive cathode and a series of dynodes at successively more positive potentials, culminating in an anode. The whole device, enclosed in a vacuum, has a window to allow the radiation into the tube. When photon strike the cathode, electrons are ejected which are then accelerated down the dynode chain. Each electron impacting upon the first dynode causes a number of secondary electrons to be ejected which are focused on to the next dynode, and the process repeats itself. In this way, an anode current will be produced of the order

of 1 mA. Usually a semi conductive material containing an alkali metal is used as the photosensitive material.

e. Read out system

A variety of read out system are in use. These include analogue meters, often with the capability of reading linearly in absorbance, chart recorders, paper print-out, digital display, and several microprocessor-controlled displays. With the latter, calibrations may be performed automatically, and data on concentration, standard deviation, etc. presented on a visual display unit.

## V. Flame

Atomization process takes place in the flame, which is formed from the combination of a fuel gas with an oxidant. There are several oxidant-fuel mixtures that can be used to generate the flame. The following mixtures are the most common:

a. Air-propane.

This mixture has a very limited use and produce a relatively low temperature flame ( $\pm 2,200$  K). This flame is good for analyzing temperature-sensitive metals, such as alkali metals which are easily ionized in high temperature:



The production of ions of the analyte will give interference effects since the ions can not absorb radiation.

b. Air-Hydrogen

The temperature of the flame produced by this mixture is slightly higher than air-propane mixture that is about 2,300 K. This mixture is superior when working at short wavelengths, such as determination of low concentration of tin.

c. Air-acetylene

It is the most widely used mixture in AAS analysis. This flame ( $\pm 2,500$ K) is stable and simple to operate and gives sufficient atomization to get a good sensitivity.

d. Nitrous oxide-acetylene

Some metals such as tin, molybdenum, and some alkaline earth metals are only slightly or even can not atomized at all under air-acetylene flame. Increasing the oxygen content of the flame to more than 20% normally present in air can raise the flame temperature, but it will decrease atomization as more refractory oxides may



be produced. Nitrous oxide-acetylene mixture gives a hot ( $\pm 3,150$  K) and reducing flame. The oxidant contains less oxygen, thus reduces the oxygen pressure and makes a fuel rich mixture. This flame produce highly reducing species such as CH-, free carbon and CO. The high temperature and the formation of these reducing radicals can result in a better atomization in this flame.

Some reference books suggest these following elements are best analyzed by using indicated fuel-oxidant mixture (Pungor, 1995):

**Table 2. Suggested flame for AAS analysis**

Propane-air	Acetylene-air	Acetylene-nitrous oxide
Li , Na , K, Rb , Cs.	Mg . Ca , Sr . Ba. Ni. Cu. Zn. Ga . Rh, As. Se. Te. Ir. Pt. Au. Hg. Ti. Pb, Bi.	Ti, V, B, Al, Si, Ge, Y, Zr, Nb, Mo, Sn, La, Ta, W, Re, Os.

## VI. Interferences and Errors

Basically there are two type of errors that are possible encountered in preparing a sample for AAS analysis, which are :

a. Sample pretreatment error :

- contamination in dissolution; can be overcome by using analytical grade reagents
- losses during treatment; can be avoided by applying appropriate method of dissolution, acids, and conditions
- adsorption of metals on to glassware; can be minimized by keeping acid concentration high or using plastic laboratory ware.

b. Operator error :

- poor standard preparation, i.e. the standards are wrongly made by the analyst
- decomposition/aging of standards, because usually trace metal standards are unstable.

There are four types of interferences are commonly found in AAS applications. But they can be satisfactory reduced by applying right treatments/procedures. The interferences are:

a. Spectral interferences

Spectral-line interference occurs when two atomic lines overlap or are unresolved. This interference is more likely encountered in atomic emission, and

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### a. Spectral interferences

Spectral-line interference occurs when two atomic lines overlap or are unresolved. This interference is more likely encountered in atomic emission, and

very rarely in atomic absorption. The reason of this is that in atomic absorption, the line that is being measured is the resonance line from the source, which has a very narrow bandwidth of 0.001 nm and ensures effective resolution.

A common type of spectral interference in absorption measurements arises from the occurrence of band absorption spectra due to molecular species in the flame or light scattering due to solid particles that is inherent in the flame or produced during atomization process. Molecular spectral interferences and light scattering interferences can be overcome by using a continuum lamp to measure the non-atomic absorption and then subtracting this value from the total absorbance. This technique is known as 'background correction' technique.

b. Chemical interferences

Chemical interference is the most important interference in flame AAS. The common interference of this type is the formation of refractory (less-volatile) compounds with the test element, usually by an anion in the aspirated solution, and thus suppresses the signal. A classic example of this interference is the production of pyrophosphate in the flame from the reaction between phosphate and alkaline earth metal ions. This kind of interference can generally be minimized by adding an appropriate releasing agent, which action is to either compete for the interfering substance or displace it from the test element or protective agents, which prevent the formation of the refractory compounds. Another way to minimize this interference is to use higher flame temperature (nitrous oxide-acetylene flame).

c. Ionization interferences

Ionization interferences are usually encountered in the alkali and some of the alkaline earth metals analysis, due to their high potential to be ionized in higher temperature. Ionization interference can be overcome by adding a large amount (200-1000 ppm) of an easily ionized element (ionization suppressor) such as potassium to both sample and standard solutions. This will effectively suppress ionization of the test element to a small and constant value and then will increase the sensitivity of the analysis.

d. Physical interferences

Physical interferences are caused by differences in some physical property (such as viscosity, surface tension, vapor pressure, or temperature) of the sample and standard solutions. This will cause a change in aspiration, nebulisation, or

atomization rate and efficiency. The problem is usually overcome by matching standards and sample solutions.

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