UNIT 8 ATOMIC FLUORESCENCE SPECTROMETRY

Structure

8.1 INTRODUCTION

In the previous unit on flame photometry you have learnt about an analytical method based on the emission of radiation by the atomic species that have been excited with the help of the thermal energy of flame. In this unit you would learn about another atomic spectrometric technique; however, in this technique the excitation is caused by an electromagnetic radiation. It is called atomic fluorescence spectrometry (AFS) as we monitor the fluorescence emission from the excited state. It is the most recently developed of the basic atomic spectroscopic analytical tools for the determination of concentration levels of different elements in diverse range of samples.

In AFS, the gaseous atoms obtained by flame or electrothermal atomisation are excited to higher energy levels by absorption of the electromagnetic radiation and the fluorescence emission from these excited atoms is measured. This technique incorporates aspects of both absorption and emission.

The main advantage of fluorescence technique as compared to absorption measurements is the greater sensitivity achievable because of very low background and the interference in the fluorescence signal. AFS is useful in studying the electronic structure of atoms and in quantitative elemental analysis. It is used mostly in the analysis of metals in biological, agricultural, industrial and environmental samples.

We begin the unit with an understanding of the origin of atomic fluorescence and learn about different mechanisms of the same. Then we will take up the principle of atomic fluorescence spectrometry which is followed by the instrumental aspects. In the end we will take up some qualitative and quantitative applications of atomic fluorescence spectrometry. In the next block you would learn about atomic absorption and atomic emission spectrometric methods and their applications in diverse areas.

Objectives

After studying this unit, you will be able to:

- explain the origin of atomic fluorescence and its different mechanisms,
- explain the principle of atomic fluorescence spectrometry,
- draw a schematic diagram illustrating different components of an atomic fluorescence spectrometer,
- discuss the factors affecting atomic fluorescence spectrometric determinations,
- enlist the applications of atomic fluorescence spectrometry, and
- state the merits and limitations of the atomic fluorimetric technique.

8.2 ORIGIN OF ATOMIC FLUORESCENCE

The development of atomic fluorescence spectrometry as an analytical technique is credited to **Wineforder** and **West** who did the pioneering work in this direction. The technique finds applications in diverse fields. However, it is not used extensively as it generally does not offer a distinct advantage over other established atomic spectroscopic methods like atomic absorption spectrometry and atomic emission spectroscopy (to be discussed in the next block). Yet, this technique offers some advantages over other techniques for some specific elements. Let us learn about the origin of the atomic fluorescence spectrum.

8.2.1 Atomic Fluorescence Spectrum

You know that an atom contains a set of quantised energy levels that can be occupied by the electrons depending on the energy. The atoms obtained by the process of atomisation in a low temperature flame are primarily in the ground state. When exposed to an intense radiation source consisting of radiation that can be absorbed by the atoms, these get excited. The source can be a **continuous source** like xenon lamp or a **line source** like a hollow cathode lamp, electrodeless discharge lamp or a tuned laser. The radiationally excited atoms relax back to the ground state accompanied by a radiation. This phenomenon is called **atomic fluorescence emission**. The radiative excitation and de-excitation processes for analytical AFS measurements are in the UV-VIS range. The intensity of emitted light is measured with the help of a detector which is placed in a direction perpendicular to that of incident radiation and absorption cell. A plot of the measured radiation intensity as a function of the wavelength constitutes **atomic fluorescence spectrum** and forms the basis of analytical fluorescence spectrometric technique.

In place of the flame, a graphite furnace can be employed for conversion of the analyte into gaseous atoms in the ground state. The graphite furnace atom cell combined with a laser radiation source can provide the detection limits in the range of femtogram (10^{-15}) to attogram (10^{-18}) which is quite promising.

8.2.2 Types of Atomic Fluorescence Transitions

The fluorescence emission can occur through different pathways as we have different types of atomic fluorescence transitions. The most common types of atomic fluorescence transitions are as given below.

- Resonance fluorescence
- Stokes direct line fluorescence
- Stepwise line fluorescence
- Two step excitation or double resonance

- Thermal fluorescence
- Sensitised fluorescence

Let us learn about the different types of fluorescence transitions in terms of the energy level diagrams.

Resonance Fluorescence

Resonance fluorescence occurs when the excited states emit a spectral line having the same wavelength as that used for excitation. Fig. 8.1 (a) gives the origin of resonance fluorescence line in terms of a schematic energy level diagram.

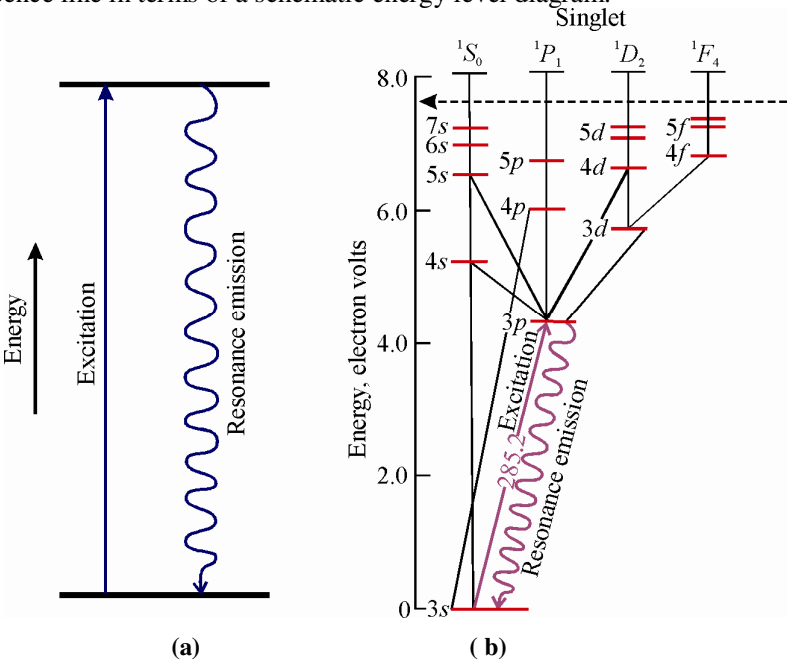

Fig. 8.1: Schematic representation of (a) Energy transitions involved in resonance fluorescence spectral line and (b) Grotrian diagram of magnesium atom showing the origin of resonance fluorescence line

When magnesium atoms are exposed to an ultraviolet source, a radiation of 285.2 nm is absorbed leading to the excitation of 3*s* electrons to 3*p* level, this then emits a resonance fluorescence radiation at the same wavelength which can be used for analysis. The origin of resonance fluorescence in case of magnesium atom is given in terms of a **Grotrian diagram** in Fig. 8.1 (b). This type of fluorescence is generally used for most analytical determinations.

Grotrian diagram gives the allowed transitions between different energy levels of the atom.

However, scattering of incident radiation by the particles in the flame poses a serious drawback in this method. This is so because the scattered radiation has the same wavelength as that of fluorescence emission; therefore false high values are observed.

Stokes Direct Line Fluorescence

Stokes direct line fluorescence is observed when an atom excited to higher energy state by absorption of radiation, goes to lower intermediate level by emission of radiation. From this intermediate level, it returns to ground state by a radiationless process. A schematic energy level diagram is shown in Fig. 8.2(a).

Thus, direct line fluorescence will always occur at a higher wavelength than that of the resonance line which excites it. It is also called as **Stokes fluorescence.** The advantage of using direct line fluorescence is that it eliminates interference due to scattered radiation which is encountered in resonance fluorescence.

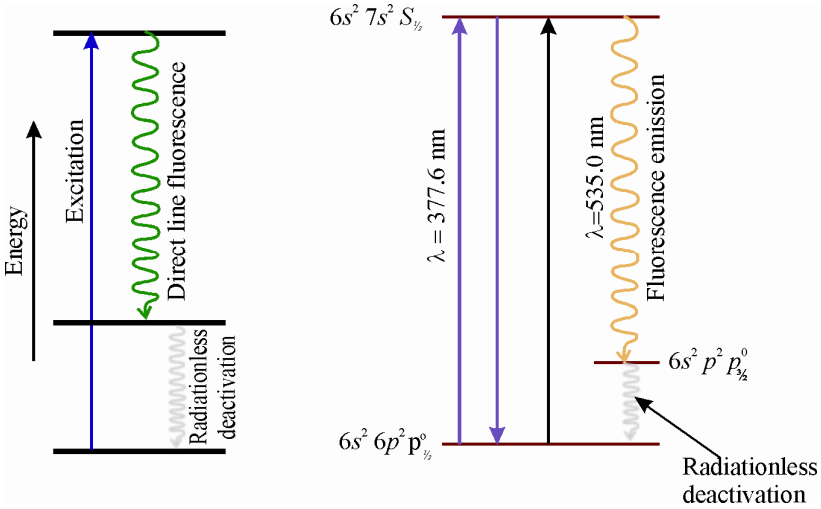

Fig. 8.2: Schematic representation of (a) Energy transitions involved in direct line fluorescence spectral line and (b) Grotrian diagram of thallium atom showing the origin of direct line fluorescence

Thallium atom is an example of an atom showing direct line fluorescence. Consider the energy level diagram of thallium atom shown in Fig. 8.2 (b). You can observe that when excited by a radiation having a wavelength of 377.6 nm, the thallium atom returns to the ground state in two steps producing a fluorescence emission line at 535.0 nm followed by radiationless deactivation.

Stepwise Line Fluorescence

In this type of fluorescence an atom initially excited to a higher energy state by absorption of radiation, undergoes deactivation by a radiationless process to a lower excited state, from which it emits radiation to return to the ground state. It is also a type of Stokes fluorescence. The schematic energy level diagram showing the origin of stepwise like fluorescence is given in Fig. 8.3 (a).

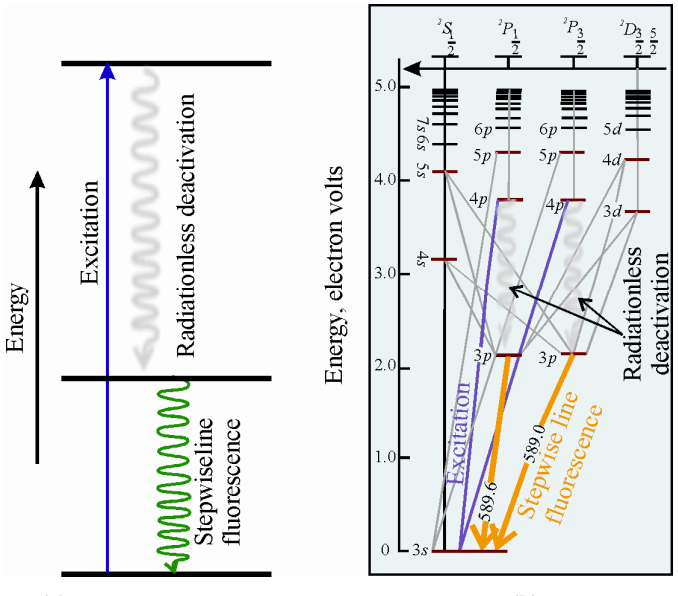

Fig. 8.3: Schematic representation of (a) Energy transitions involved in stepwise line fluorescence and (b) Grotrian diagram of sodium atom showing the origin of stepwise fluorescence line

The fluorescence emission by sodium atom is an example of stepwise line fluorescence, as shown in Fig. 8.3 (b). In sodium atom a 3*s* electron is excited to 4*p* level by a 330.2 nm radiation. This electron then relaxes down to an intermediate level (3*p*) in a radiationless process. It is the fluorescence emission at 589.0 nm. The further relaxation from this level is nonradiative in nature.

Two Step Excitation or Double Resonance

The double resonance fluorescence involves a two step excitation process using two dye lasers. The first laser excites the analyte from ground state to an excited state from where it further gets excited to another higher excited state with the help of a second laser. The de-excitation of this higher excited state to a lower energy state is accompanied by fluorescence emission. This is called as **double resonance fluorescence**. The excitation and de-excitation transitions responsible for double resonance fluorescence are shown schematically in Fig. 8.4 (a).

Thermally Assisted Fluorescence

In thermally assisted fluorescence, the electron excited to a given level by absorption of radiation gets further excited with the help of thermal energy in a radiation less process. The fluorescence emission occurs from both the excited energy levels. In this case part of the emitted radiation has shorter wavelength (higher energy) as compared to the exciting radiation. It is also called as **anti-Stokes fluorescence**. The origin of this type of fluorescence in terms of the energy level diagram is given in Fig. 8.4 (b).

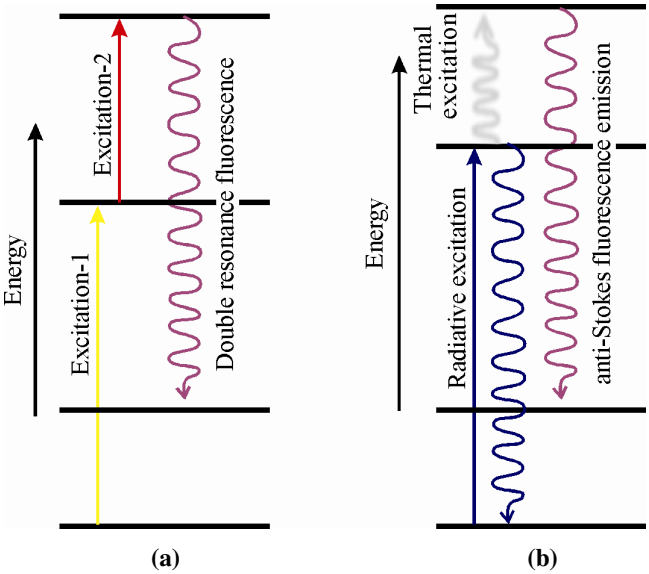

Fig. 8.4: Schematic energy level diagram showing the excitation and de-excitation processes involved in origin of (a) double resonance fluorescence and (b) thermally assisted fluorescence

Sensitised Fluorescence

In sensitised fluorescence, the energy of the excited atom is transferred to another atom which gets excited and relaxes back accompanied by fluorescence emission. The process of sensitised fluorescence emission can be represented as follows.

$$S^{\#} + A \longrightarrow S + A^{\#}$$

$$A^{\#} \longrightarrow A + h\nu\,(\text{Fluorescence})$$

However, the thermally assisted fluorescence and sensitised fluorescence generally are not employed for analytical purposes.

SAQ 1

In what way the measurement based on direct line fluorescence are better than that based on resonance fluorescence?

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8.3 PRINCIPLE OF ATOMIC FLUORESCENCE SPECTROMETRY

Atomic fluorescence spectrometry is the analytical method based on optical emission from gas-phase atoms that have been excited to higher energy levels by absorption of radiation. It incorporates aspects of both absorption and emission of radiation. In atomic fluorescence spectrometry the analyte is brought into an atom reservoir which could be a flame, plasma, glow discharge, or a furnace and is excited by focusing a beam of monochromatic electromagnetic radiation emitted by a suitable primary source. The radiation source can be of a continuous type like xenon lamp or a line source. Hollow cathode lamp (HCL), electrodeless discharge lamp (EDL) or a tuned laser are the commonly employed line sources.

Instead of looking at the amount of light absorbed in the process, we focus our attention to the fluorescence emission resulting from the relaxation of the excited atoms. Similar to the molecular fluorescence, about which you have learnt in Unit 5, the atomic fluorescence is also measured in a direction perpendicular to the direction of exciting radiation. The fluorescence radiation emitted from the excited species is measured with or without being spectrally resolved.

As you have learnt above, the fluorescence emission may be of the same wavelength i.e., resonance fluorescence or of a different wavelength due to other fluorescence mechanisms. Again, each element has own characteristic atomic fluorescence spectrum. The location of the fluorescence emission signal indicates the identity of the analyte whereas the intensity is a measure of its concentration. The intensity of the 'fluorescence' increases with increasing atom concentration in the flame, providing the basis for its quantitative determination.

It is found that the atomic fluorescence intensity is related to the exciting light source and the radiating intensity, besides the concentration of some of the elements in the sample to be determined. Let us work out a relationship between the intensity of fluorescence emission and analyte concentration in the following subsections.

8.3.1 Fluorescence Intensity and Analyte Concentration

As you have learnt so far, there are two main processes involved in fluorescence emissions which are given below.

i) Absorption of radiation to generate excited atoms

ii) De-excitation of excited atoms by emission of radiation

You know that according to Beer's law, when a radiation of intensity P_0 is passed through an analyte of concentration c mol dm^{-3} taken in a cell of thickness b cm, the intensity of transmitted radiation (P) by an analyte is given by **Lambert-Beer's** law, viz.,

$$P = P_0\, e^{-\varepsilon cb}$$

Amount of light absorbed, $P_{abs} = P_0 - P = P_0(1 - e^{-\varepsilon cb})$

The intensity of fluorescence, P_f, is proportional to the quantity of radiation energy absorbed.

$$P_f \propto P_{abs} = P_{abs}\, \phi$$

$$P_f = P_0(1 - e^{-\varepsilon cb})\, \phi$$

where, P_f = Intensity of fluorescence (total),

P_{abs} = quantity of radiant energy absorbed,

ϕ = fraction of excited atoms that undergo fluorescence when εcb is small.

$$P_f = P_0\, 2.303 \varepsilon cb \times \phi$$

In instruments using graphite furnace as atom cell and laser as a radiation source, the linearity may extend upto 7 orders of magnitude.

Thus, the fluorescence intensity is directly proportional to its concentration. In quantitative AFS, the instrument is generally standardised by a calibration curve. The graph is drawn between the logarithm of the intensity of atomic fluorescence signal versus the logarithm of analyte concentration (Fig. 8.5). As you can see, the linear relationship between the concentration and the fluorescence intensity extends over 3 to 5 orders of magnitudes.

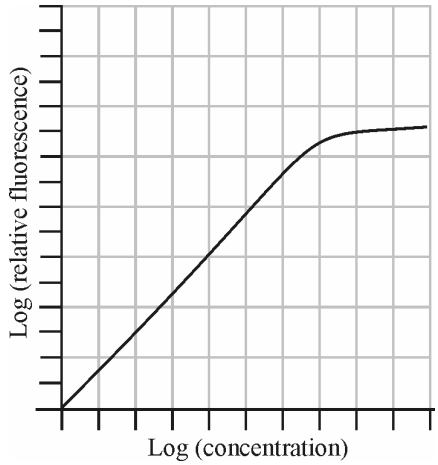

Fig. 8.5: Typical calibration curve for atomic fluorescence spectrometric determination

However, it is valid only at the low concentration of the element. At higher concentration, when fluorescence emission is high, part of emitted light will be absorbed by the atoms in ground state. This is called **self absorption**. It will lower the intensity of the emitted radiation and the proportionality is lost. Further, the efficiency of the fluorescence emission (ϕ) is lowered if the atoms in the excited states lose their energy by a radiationless path e.g, by collisions with other atoms, where the energy of excited state is transferred to the vibrational levels of these atoms. You know from Unit 5 that such a mechanism of deactivation of an excited state is called **quenching**. The proportion of deactivation by quenching mechanism can be decreased by surrounding the atomisation flames by a noble gas like argon or by using nonflame methods to convert the sample into atoms.

The atomic fluorescence spectrometric method offers advantage over the atomic absorption method as the fluorescence radiation, in principle, is measured against a zero background.

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The atomic fluorescence measurements are dependable for low concentrations only. Comment.

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8.4 INSTRUMENTATION FOR ATOMIC FLUORESCENCE SPECTROMETRY

Atomisation is by far the most critical step in the atomic spectroscopy.

You have learnt so far that the atomic fluorescence spectrometry concerns the measurement of fluorescence emission of the atomic species that have been excited with the help of a suitable electromagnetic radiation. This in turn requires that vapourised atoms of the analyte should be in ground state. Thus, in the atomic fluorescence analysis of samples the analyte atoms need to be desolvated, vapourised, and atomised at a relatively low temperature. This can be achieved with the help of a heat pipe, flame, or graphite furnace. Once the vapourised atoms are generated a hollow cathode lamp or a tuned laser usually provides the monochromatic radiation for resonant excitation to promote the atoms to higher energy levels.

There are very few commercial atomic fluorescence instruments available and nearly all work has been done with research equipments.

Thus, in atomic fluorescence spectrometry the analyte is brought into an atom reservoir (flame, furnace, etc.) and excited by absorbing monochromatic radiation emitted by a primary source. The atomic fluorescence radiation emitted by the excited atoms is then suitably dispersed and detected by monochromators and photomultiplier tubes, as in case of atomic emission spectroscopy instrumentation and sent to appropriate readout device. The atomic fluorescence spectrometer consists of the following essential components.

- radiation source
- atom reservoir
- monochromator
- detection system
- readout device

The equipment used is similar to that used with in atomic absorption experiment, except that the detector is put in a position perpendicular to that of the incident radiation. A block diagram showing different components and their relative arrangement is given in Fig. 8.6 (a) whereas a schematic representation of the spectrometer is given in Fig. 8.6 (b).

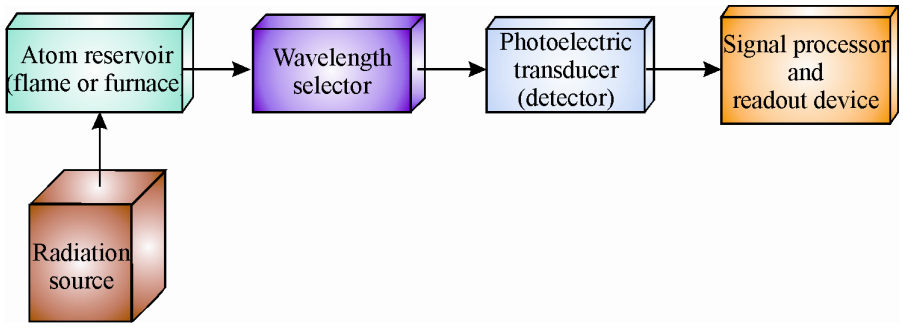

Fig. 8.6 (a): Block diagram showing the essential components of atomic fluorescence spectrometer

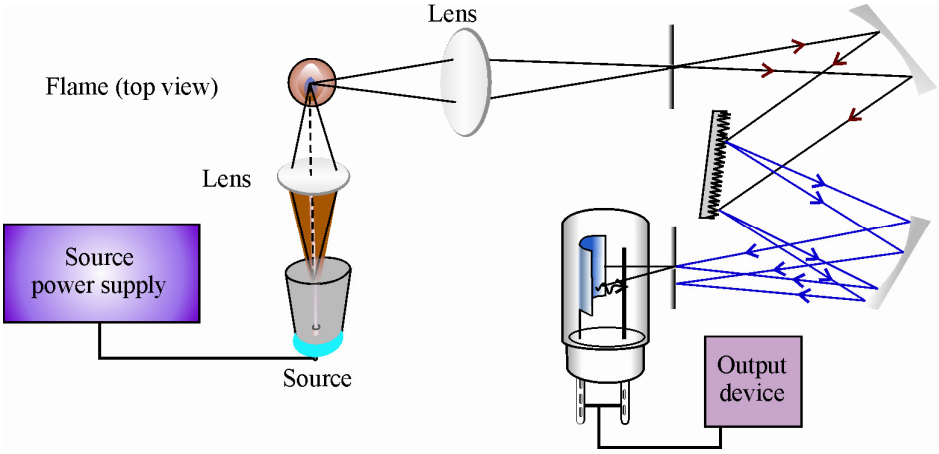

Fig. 8.6 (b): A schematic representation of an atomic fluorescence spectrometer

Let us learn about different components used in the atomic fluorescence spectrometer in the following subsection.

8.4.1 Radiation Sources

In atomic fluorescence, the excitation can be performed both with continuous as well as with monochromatic sources, which consequently affects the fluorescence intensities obtainable and the freedom from stray radiation. When a continuous source such as a **tungsten halide** or a **deuterium lamp** is used as primary source, it has the advantage that the multielement determinations can be taken up. However, due to their low radiant densities, detection power is not fully exploited. Alternatively, when line sources such as hollow cathode lamps and electrodeless discharge lamps, are used, these provide much higher radiance but we cannot do multielement analysis. Lasers are being used as the radiation source in modern AFS instruments with the advantage of high radiant power. Let us learn about these radiation sources.

Hollow cathode lamp (HCL) : It consists of a sealed cylindrical glass tube with a quartz window at one end and a hollowed cylindrical cathode together with an anode wire made of tungsten. The cathode is fabricated from the analyte element and the lamp is filled with an inert gas such as argon or neon under vacuum (100-200 Pa). A schematic diagram of a hollow-cathode lamp is shown in Fig. 8.7. When a voltage of ~300 V corresponding to 5-50 m A current is applied between the two electrodes, a low pressure glow discharge confined to the inside of the cathode material is produced.

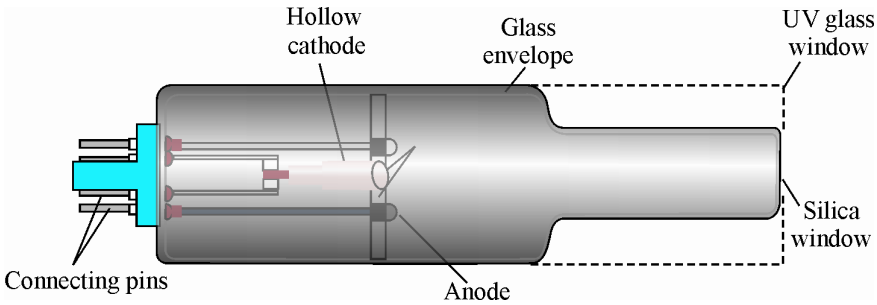

Fig. 8.7: Schematic diagram of hollow cathode lamp illustrating different components

Basic function of the gas in the tube is to bombard the cathode and vapourise the atoms from the cathode surface. For this the gaseous cations are accelerated towards the cathode. The collision energy is sufficient to cause some atoms of the cathode to be transformed into gaseous atoms in a process called **sputtering**. These metal atoms

are then excited by collisions with electrons and ions thus emitting characteristic emission lines.

The emission spectrum of the cathode material includes a number of intense, sharp lines due to transitions between excited states and the ground state, often called **resonance lines**. Intensity of resonance lines from an HCL increases with increasing current. As of now, HCL for over 60 elements are available. However, these days multielement cathode lamps are more in use for routine determinations, though their performance is not very reliable. In this case, cathode is made up from alloys of metals having similar melting point such as Ca-Mg, Ag-Au, Cu-Fe, Zn-Cd, etc. When elements having different melting points are used, more volatile element is lost first resulting in gradual weakening of its spectrum and degeneration into one element lamp.

Electrodeless discharge lamp (EDL): It contains a few milligram amount of a volatile element or a volatile compound such as halide, together with neon or argon, under vacuum in a quartz tube. On the application of voltage, discharge is produced and the gaseous atoms are excited by application of microwave field or radio frequency of typical frequency. As the excited atoms decay to the ground state or to other low energy levels, characteristic radiation of the atom is emitted. The radiations emitted by EDLs are about 10-100 times more intense than for the corresponding HCL.

The source lamp for atomic fluorescence is mounted at an angle to the rest of the optical system, so that the light detector sees only the fluorescence in the flame and not the light from the lamp itself. It is advantageous to maximise lamp intensity since sensitivity is directly related to the number of excited atoms which in turn is a function of the intensity of the exciting radiation.

The stray radiations are particularly low with monochromatic primary sources and while using nonresonance fluorescence lines with wavelengths differing from that of the exciting radiation. Thus, in the case of atomic fluorescence the selectivity is already partly realised by the radiation source delivering the primary radiation.

The electrodeless discharge lamps are available for a number of elements. However, their performance is not as reliable as of the halogen cathode lamps.

8.4.2 Atom Reservoirs

As mentioned earlier in AFS the analyte sample is to be converted into atom vapour in gfound state before being excited by suitable radiation. The container or cell having these vaporised atoms is called **atom reservoir** or **atom cell.** Let us learn about different types of atom reservoir employed in AFS.

In flame atomic fluorescence spectrometry the flame acts as the atom reservoir. It is also called as **flame atom cell**. The majority of the atomic fluorescence work is generally done in the **hydrogen diffusion flame** as this has an extremely low background level. The hottest parts of this flame are only around 1000°C while the bulk of the flame is at about 350 - 400°C. This permits excellent detection limits to be obtained because of the very low background. However, analysis in these flames seriously suffers from matrix effects. Such flames are only really useful when relatively pure solution is used. This can be achieved with the help of separation/isolation/ preconcentration operations on the sample.

A combination of **acetylene/nitrous oxide** and **hydrogen/oxygen/argon** using a rectangular flame with a premix laminar flow burner is also used extensively. The higher temperatures of premixed hydrogen and hydrocarbon flames gives much better atomisation of many species, but still with considerably higher backgrounds.

In some instruments atom reservoirs made of graphite are used. These are called **non-flame cells** and are in the shape of a bowl, in which the solid sample can be vapourised by a high current pulse. The atomisation is achieved by electrothermal methods. In these cells argon gas is used to surround the sample so as to reduce fluorescence quenching. You would learn about graphite furnace in Unit 9. The electrothermal method of atomisation has an advantage that a very small volume of the sample is required and the sensitivity is quite high.

Cold vapour cells are used for the determination of mercury and involve the conversion of dissolved mercury into elemental mercury by reacting it with $SnCl_2$. The elemental mercury so obtained is then transported into a quartz cell with the help of gas flow .This quartz cell acts as the atom cell or reservoir. The simple design, low cost and high sensitivity are some of the advantages of these cells.

Hydride generation technique is commonly used for the determination of the elements that form hydride, for example, antimony, arsenic, selenium and tellurium. In this technique the analyte sample is treated with sodium borohydride and hydrochloric acid to generate a volatile hydride of the analyte. This is then carried to the atom cell with the help of an inert gas. The hydride generation technique provides better sensitivity for these elements as compared to other flame atomic spectrometric techniques.

8.4.3 Monochromators

The fluorescence emission from the excited atomic species is generally dispersed by monochromators. As you know, the monochromators are devices that select a given emission line and isolate it from other lines due to molecular band emissions and all nonabsorbed lines. Most commercial instruments use diffraction gratings for the purpose. These grating instruments can maintain a high resolution over a range of wavelengths. In laser induced ionisation spectrometry no spectral isolation is required at all. In some cases, the detection can be performed without the need for spectral dispersion, e.g., by using only filters.

8.4.4 Detectors

The emission radiation dispersed by monochromators or filters is sent to a detector. Here, the signal is detected by photomultiplier tubes; same as in case of flame photometry or atomic emission spectrometry. You have learnt about the photomultiplier tubes in Unit 2 on UV-VIS spectrometry.

8.4.5 Readout Devices

The output from the detector is suitably amplified and displayed on a readout device like a meter or digital display. The sensitivity of the amplifier can be changed so as to be able to analyse samples of varying concentrations. Nowadays the instruments have microprocessor controlled electronics that provides outputs compatible with the printers and computers whereby minimising the possibility of operator error in transferring data.

Nondispersive instruments

As an electrodeless discharge lamp or hollow cathode lamp are employed as sources in atomic fluorescence spectrometers, in principle there is no need for a monochromator. This is so because the radiation emitted by the source is of a single element and would therefore excite only the atoms of that element. Therefore nondispersive instruments can be assembled using a source, an atomiser and a detector. Such instruments have an advantage of simplicity, low cost, adaptability to multielement analysis and high sensitivity, etc. However, these instruments can prove useful only if the possible interferences (discussed later) are taken care of.

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In what way is electrodeless discharge lamp better than hollow cathode lamp?

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8.5 APPLICATIONS OF ATOMIC FLUORESCENCE SPECTROMETRY

The atomic fluorescence spectrometry has been used in the analysis of more than about sixty different elements present in diverse variety of samples. The general use of AFS is to determine the concentration of elements in samples i.e., elemental analysis. In favourable conditions for some elements (e.g. Cd, Pb, Tl), detection limits in the range of attogram (10^{-18} g) have been obtained. The quantitative analysis using AFS can be carried out by employing standard calibration plot method or standard addition method as in the case of other spectrometric methods. These methods have been explained in Unit 7. The linear calibration curves extend from 4 to 7 orders of magnitude.

In a typical quantitative determination using a high intensity hollow cathode lamp of the element to be determined as the radiation source, a series of solutions of the metal ions of varying concentration are prepared and aspirated into the flame and the corresponding fluorescence intensity is measured. A plot of fluorescence intensity versus concentration of the metal ion is plotted. This curve is linear at low concentration of metal ions, but is convex at higher concentration. The fluorescence intensity for the solution containing the analyte in unknown concentration is measured and the concentration of the metal ion is determined from the standard curve.

Table 8.1 gives the emission wavelengths and the corresponding detection limits for some commonly determined elements. Some of the applications of atomic fluorescence spectrometry in diverse areas given below indicate the importance of this analytical method.

Clinical: Analysis of Pb, Hg, As, Sb, Bi, Ge, Se, in blood, urine, tissue, nail, hair; Cu, Zn and Pb in blood serum and urine samples.

Environmental: Determination of Hg at 1 ng/L levels; As, Se, Sb, and Te with detection limits between 10 and 50 ng/L; in environmental samples. Mercury in air can be determined at levels as low as 10 pg. Determination of femtogram (10^{-15} g) quantities of elements in samples by graphite furnace laser-excited AFS is also done.

Agricultural: Analysis of dairy, wine, feed, meat, cigarettes, and other products for As, Hg, Pb, Sb, Se.

Geological and Metallurgical: Analysis of ore, rock, mineral, metals for Ge, Hg, Se, As in Sb, Se, Te in Cu.

Pharmaceutical: Determination of Hg, Pb, As, Se in active ingredients and fillers.

Petrochemical: Quantitative determination of Pb, Hg, Cd, As, Sn, Zn in fuels, lubricant, crude oil.

Alloys: Some of the example of elements determined in alloys are, Cu, Fe, Mg, Mn, Ni, and Zn.

When combined with chromatography, AFS can provide qualitative and quantitative information on chemical form of elements i.e. **metal speciation** in a sample.

Table 8.1: Atomic fluorescence analysis of some common elements

S. No.	Element	Emission wavelength (λ)	Detection limit (ng / mL)
1.	Al	309.2	5
2.	As	193.2	100
3.	Ca	422	0.01
4.	Cd	228	0.01
5.	Cr	357	4.0
6.	Cu	324	1.0
7.	Fe	373.5	8
8.	Hg	185.0	20
9.	Mg	285.0	1.0
10.	Mn	279	2
11.	Mo	313	60
12.	Na	589	-
13.	Ni	232	3.0

You have learnt in Unit 7 that the success of atomic spectrometric methods depends on how effectively the possible interferences are managed. Let us learn the causes of interferences in AFS in the following subsection.

8.5.1 Interferences

The interferences are produced by sample matrix i.e., the non-analyte components of the sample. The interferences could be chemical arising out of molecular species containing analyte which in turn reduce the percentage of gaseous analyte atoms or spectral due to radiation other than the atomic fluorescence. Scattering is another area of concern and appropriate measures need to be taken up to minimise them. The possible interferences which can influence the results of analysis by AFS are as follows.

Spectral interference: In analysis of samples, it may be necessary to correct for spurious, spectral interference. These arise when the matrix emission overlaps or lies too close to the emission of the sample and result in the decrease in resolution of the spectrum, for example, (As/Cd), (Co/In), (Co/Hg), (Fe/Mn) and (Ni/Sn) show fluorescence at similar wavelengths. In AFS the spectral interferences consists of the scattered light, non analyte fluorescence, molecular fluorescence and the light emission by the atom cell. Of these, the scattered light and the atoms cell emission are more crucial while the other two are not very common. However, this type of matrix effect is rare when hollow cathode lamps are used as primary sources since the intensity is low.

Chemical interference: The chemical reactions between the analyte and other components of the sample that may reduce the number of free atoms produced, give rise to chemical interference. For example, the oxide formation can affect the result of the determination. This is because oxides exhibit broad band absorptions and can scatter radiation thus interfering with signal detection. Further, when the sample

contains organic solvents, scattering can occur due to the carbonaceous particles left from the organic matrix.

In the analysis of mercury by AFS, the presence of species that may inhibit the formation of elemental mercury in the vapour generation process are potential chemical interferences. On the other hand in the hydride generation method, a number of transition metal ions are found to suppress the formation of volatile hydrides and thereby act as chemical interferences.

SAQ 4

Name the methods of quantitative analysis used in AFS?

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8.5.2 Merits and Limitations

The atomic fluorescence spectrometric method like all other spectrometric methods of analysis has associated merits and limitations. These are briefly outlined here. These prove to be useful in the process of selecting a suitable method for the determination of an analyte.

Merits

- The main advantage of fluorescence detection compared to absorption measurements is the greater sensitivity achievable because the fluorescence signal has a much lower background as compared to the one observed in atomic absorption method. Further, the interferences are also less. It exhibits its greatest sensitivity for elements having higher excitation energies.
- AFS offers distinct advantages for some metals and metalloids like Pb, Cd, Tl, Hg, As, Sb, Se, Te, etc.
- The detection limits are similar to those for AAS and AES but vary for different elements. Better sensitivities and much lower detection limits are obtained for favourable elements like Hg, As, Sb, Se etc.
- Linear calibration curves often extend over a wide range. These may be valid over as high as 4 to 7 orders of magnitude.
- The samples in solid, liquid and gaseous state can be analysed, although most samples are converted to liquids before analysis.
- When combined with separation techniques such as chromatography, the method can provide information about the chemical form of the analyte, i.e, speciation studies can be carried out in environmental samples.

Limitations

Though AFS offers a number of advantages in the analysis of some metals and metalloids, it suffers from some limitations too. Some of these are given below.

- AFS requires combination with chromatography to provide information regarding chemical form of the analyte during chemical separation.
- Sample preparation especially for the solids, is often very tedious and time-consuming process.

- The analysis may involve chemical interference due to the chemical reactions between the analyte and other components of the sample (matrix) that may reduce the number of free atoms produced.
- In analysis of many samples, it may be necessary to correct for the spectral interferences especially when continuous sources are used.
- The technique is limited primarily to the determination of metals and metalloids.

SAQ 5

Why has AFS not found widespread acceptance as an analytical technique?

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8.6 SUMMARY

In atomic fluorescence spectrometry, the gaseous atoms obtained by flame or electrothermal atomisation are excited to higher energy levels by absorption of the electromagnetic radiation and the fluorescence emission from these excited atoms is measured. The fluorescence emission can occur through different pathways. Accordingly, we have different types of atomic fluorescence transitions. The common types of atomic fluorescence transitions are termed as resonance fluorescence, Stokes direct line fluorescence, stepwise line fluorescence, two step excitation or double resonance fluorescence, thermal fluorescence and sensitized fluorescence. Of these, the thermally assisted fluorescence and sensitized fluorescence generally are not employed for analytical purposes.

The intensity of the fluorescence radiation is measured at right angles to the direction of incident radiation and is correlated to the concentration of the element present, forming the basis of quantitative analysis. In quantitative atomic fluorescence spectrometric determinations the instrument is generally standardised by a calibration curve. The graph is drawn between the logarithms of the intensity of atomic fluorescence signal versus the log of analyte concentration. The linearity of such curves extends over 3 to 5 orders of magnitudes. However, at higher concentration, the linearity is lost due to self absorption.

The instrument used for AFS consists of atom reservoir which may be a flame or a furnace etc., a primary source emitting the characteristic absorption radiation of the element being determined, a monochromator, detector, signal processor and readout device. The primary source is usually a hollow cathode lamp or a tuned laser.

Atomic fluorescence spectrometry is useful in study of electronic structure of atoms and in quantitative elemental analysis. Applications include determination of Pb, Hg, Cd, As(III), As(V) Sb(III), Sb(V), Se(IV,VI), etc in clinical, environmental, geological and metallurgical, pharmaceutical and petrochemical samples. The main advantage of fluorescence measurements as compared to absorption measurements is the greater sensitivity as the signal has very low background and lesser interferences. It does suffer form the interference from matrix emission, oxide formation and scattering due to organic solvents but not as severely as the other atomic spectrometric methods.

Merits of the technique include very low detection limits for favourable elements and the possibility of handling solid, liquid or gaseous samples, although most samples are

converted into liquid before analysis. On the other hand, time-consuming sample preparation, need to combine with chromatography for speciation information, chemical and spectral interference, etc. are the limitations of the method. Except for some favourable metals and metalloids like Pb, Cd, Tl, Se, Te, As, Sb, etc. there is no special advantage over more established AAS. Hence, it is not very popular.

8.7 TERMINAL QUESTIONS

1. Explain the principle of atomic fluorescence spectrometry.

2. What are the major components of instrumentation involved in atomic fluorescence spectrometry? Give the block diagram of the components of an atomic fluorescence spectrometer.

3. Elaborate on the different types of interferences encountered in analysis by atomic fluorescence spectrometry.

4. State some important applications of atomic fluorescence spectrometry.

5. Describe the merits of atomic fluorescence spectrometry technique.

6. Outline the limitations of atomic fluorescence spectrometry method.

8.8 ANSWERS

Self Assessment Questions

1. Direct line fluorescence refers to the fluorescence emission observed when an atom excited to higher energy state by absorption of radiation, goes to lower intermediate level by emission of radiation and returns to ground state by a radiationless process. The advantage of using direct line fluorescence is that it eliminates interference due to scattered radiation encountered in resonance fluorescence.

2. The fluorescence intensity is directly proportional to its concentration only at low concentration of the element. At higher concentration this linearity is lost due to self absorption.

3. The radiations emitted by electrodeless discharge lamp are about 10-100 times more intense than for the corresponding hollow cathode lamp.

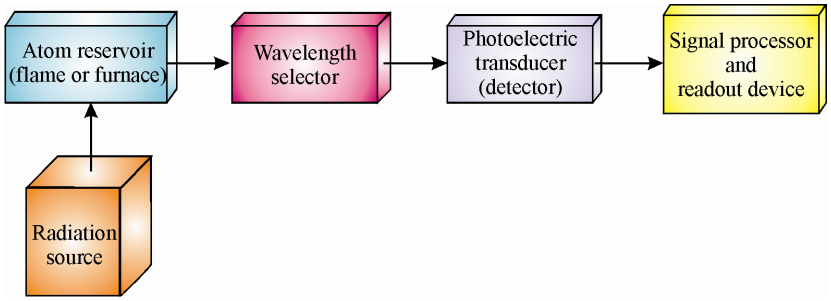
4. The quantitative analysis in AFS can be carried out by using one of the standard methods like calibration curve method or standard addition method.

5. AFS has not found wide spread success because there does not seem to be a distinct advantage over established methods like AES.

Terminal Questions

1. In AFS, the analyte is converted into gaseous atoms in the ground state using a suitable atomization technique. These are then excited by characteristic monochromatic radiation from a primary source like a xenon lamp or a hollow cathode lamp, electrodeless discharge lamp or a tuned laser. The fluorescence radiation emitted by the decaying atom is then measured in the direction perpendicular to that of the incident radiation. The position and intensity of the emitted radiation forms the basis of qualitative and quantitative analysis by atomic fluorescence spectrometry.

2. The instrumentation for AFS consists of atom reservoir which may be a flame or a furnace etc., a primary source emitting the characteristic absorption radiation of the element being determined, a monochromator (or filter), detector, signal processor and readout device. The primary source is usually a hollow cathode lamp or a tuned laser. The block diagram of the equipment required for AFS is shown below:



3. In an atomic spectrometric method, interferences are produced by the non-analyte components of the sample. The possible interferences which can influence the results of analysis by AFS are as follows.

   - The chemical interferences arising out off molecular species containing analyte which in turn reduce the percentage of gaseous analyte atoms or spectral due to radiation other than the atomic fluorescence.
   - The spectral interferences arise due to the overlapping of the matrix emissions with the emission of the sample and result in the decrease in resolution of the spectrum. The spectral interferences consist of the scattered light, non analyte fluorescence, molecular fluorescence and the light emission by the atom cell.
   - Scattering is another area of concern and appropriate measures need to be taken up to minimise them.

4. In general AFS is used to determine the concentration levels of elements in samples (elemental analysis). For favourable elements (e.g. Cd, Pb, Tl), detection limits in the attogram (10^{-18} g) range have been obtained. When combined as hyphenate technique with chromatography, AFS can provide qualitative and quantitative information on chemical form of elements (metal speciation) in a sample.

   Determination of Hg at low ppt levels (1 ng/L), and determination of As, Se, Sb, and Te with detection limits between 10 and 50 ng/L in environmental samples using commercial instrumentation. The determination of metals and metalloids like Pb, Hg, As, Sb, Bi, Ge, Se, Te, etc. in clinical, geological and metallurgical, agricultural, pharmaceutical and petrochemical samples are some common applications of AFS.

5. The merit of the AFS technique lies in the greater sensitivity achievable due to low background and interference. It exhibits its greatest sensitivity for elements having higher excitation energies and offers advantages for some metals and metalloids like Pb, Cd, Tl, Hg, As, Sb, Se, Te, etc.

   The linear calibration curves often extend 4 to 7 orders of magnitude and samples in solid, liquid and gaseous state can be analysed, although most samples are converted to liquids before analysis. When combined with techniques such as chromatography, the method can give information about the chemical form of the analyte.

6. In AFS the sample preparation, particularly for solids, is often time-consuming step and the method has associated chemical and spectral interferences. Further, the technique is limited to determination of metals and metalloids and in most analytical determinations it does not offer distinct advantages over the established methods like AAS and AES.

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