
UNIT 10 ATOMIC EMISSION SPECTROMETRY

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10.1 INTRODUCTION

In Unit 9, you have learnt in detail about the underlying principles, instrumentation and applications of atomic absorption spectrophotometry (AAS). You would recall that in AAS the atomic vapours in the ground state absorb the characteristic radiation of the element and the absorbed radiation and its intensity form the basis for the qualitative and quantitative applications. In contrast to this, in the current unit we take up atomic emission spectrometry (AES) that concerns the emission of radiation by the suitably excited atomic vapours of the analyte. Here, the emitted radiation and its intensity form the basis for the qualitative and quantitative applications of the technique. AES is one of the oldest spectroscopic methods of analysis. It is a multi-element analytical technique that can be used for the analysis of materials in gaseous, liquid, powder or solid form. Its high detection power and wide variety of excitation sources makes it the most extensively used method for analysis. Of the various different atomic emission spectrometric methods we would deal with the one in which an inductively couple plasma (ICP) acts as an atomisation- excitation source; the technique being called ICP-AES. The number of elements that can be determined simultaneously is only limited by the availability of sufficiently sensitive interference free spectral lines.

We begin the unit with an explanation of the origin of atomic emission spectrum and learn about the principle behind atomic emission spectrometry being used as an important analytical technique. Then we will take up the instrumentation required for

the measurement of atomic emission spectrum. An account of the analytical methodology for qualitative and quantitative applications of AES will be followed by the possible interferences in atomic emission spectrometry. In the next unit you would learn about the applications of atomic absorption spectrophotometry and atomic emission spectrometry in diverse areas.

Objectives

After studying this unit, you will be able to:

- explain the principle of atomic emission spectrometry,
- enlist various excitation sources for atomic emission spectrometry,
- describe the different types of plasma sources and nebulisers used in ICP-AES,
- describe the methods of solution preparation for AES,
- draw a schematic diagram illustrating different components of an atomic emission spectrometer,
- compare and contrast the different types of instruments used for ICP-AES,
- illustrate the qualitative determination strategy of AES using suitable examples,
- outline the quantitative methodology of the atomic emission spectrometry using ICP as the source,
- discuss the interferences observed in atomic emission spectrometric determinations using ICP, and
- state some applications of atomic emission spectrometry based on ICP.

10.2 PRINCIPLE OF ATOMIC EMISSION SPECTROMETRY

In AES one invariably, starts with a sample, which may be in a solid, liquid, or gaseous form, and ends with analytical results, which may be qualitative, semi-quantitative, or quantitative.

In atomic emission spectrometry (AES) a reproducible and representative amount of the sample is introduced into an atomization-excitation source where it is converted into atomic vapours of the analyte in excited state. You would recall from Unit 7 on flame photometry that the analyte solution, when introduced into the flame, undergoes a number of processes to be atomised and then get excited. As the excited state is short lived, the excited atoms return back to the ground state after a very short lifetime (typically 10^{-6} to 10^{-9} s). This is accompanied by the emission of electromagnetic radiation, normally in the form of light in the UV-VIS region. This radiation is characteristic of the constituents of the sample. Due resolution of the emitted radiation generates an emission spectrum, whose detailed analysis can be exploited to obtain qualitative as well as quantitative details of the analyte. The versatility of AES is due to the availability of a wide range of atomisation-excitation sources. These extend from *dc* arc, *ac* spark and universal arc-spark, to *dc* plasmas, microwave plasmas, glow discharge lamps, lasers and inductively coupled plasma (ICP). Accordingly, there are many ways in which AES can be carried out, and each of these ways has many variations.

You have learnt about flame AES, or flame photometry as it is commonly called, in Unit 7. You would recall that it is a simple, rapid and inexpensive method for routine analysis of alkali and alkaline earth metals like, sodium, potassium, lithium, calcium and barium in environmental, clinical and biological samples especially in biological fluids and tissues. You know that in flame photometry natural gas and air flame is employed for atomisation and excitation of the analyte. As the temperature of the flame is not high enough to excite transition elements and non metals; the technique is quite restrictive. It can be efficiently employed for the detection of alkali and alkaline earth metals only.

The limitation of flame as an atomisation-excitation source led to the development of high temperature sources for atomic emission spectrometry. Historically, flame emission spectrometry (FES) was followed by emission spectrometry based on electric arc and electric spark as the atomisation-excitation source. These were better than FES as these allowed simultaneous determination of a number of elements. However, these were not suited to measurement of analytes in solution and provided very complex spectra. Today, high frequency inductively coupled plasma and microwave plasma sources are used for routine work in practically all large analytical laboratories. Consequently, the atomic emission spectrometry has emerged to be a successful technique for multielement analyses. The development of these high energy sources is matched by the developments in the spectrometer design. We would learn about the AES technique based on plasma sources.

10.2.1 Atomic Emission Spectrometry Based on Plasma Sources

Plasma is a high energy source which is an electrically neutral conducting gaseous mixture having a significant concentration of cations and electrons. As an electrical conductor it can be heated inductively by coupling with an oscillating magnetic field. The temperature of the plasma may be of the order of 5,000 to 8,000 K. You would learn about plasma sources in subsection 10.3.1. The plasma based AES in principle, is similar to the flame photometry; the only difference being that flame is replaced by much more energetic atomization-excitation processes using plasma. In emission work, the argon plasma is frequently employed.

The sun, lightning, and the aurora borealis are examples of plasmas found in nature.

The analyte sample is introduced into the centre of the plasma as an aerosol with the help of a nebuliser using argon flow. As in a flame, in plasma also the sample undergoes various transformations like desolvation, vaporisation, atomisation, ionisation and excitation. The excitation and ionisation occurs due to collisions of the analytical atoms with high energy electrons. The high temperature assures that most samples are completely atomised, however, some molecular species e.g., N_2 , N_2^+ , OH, C_2 , etc. do exist in the plasma and are measurable. As the energy of the plasma source is quite high it ensures the excitation of the atoms of all the elements present in the sample which then relax by emitting EM radiation of characteristic wavelengths of different elements. Thus, it is a multielement technique.

Depending on the composition of the analyte, the excited species consist of atoms, singly charged ions and sometimes the doubly charged ions. The emission lines observed are mainly from the excited atoms and singly charged ions; the emissions from the doubly charged ions however are relatively rare. The energies of the transitions are such that the emitted radiation falls in the ultraviolet and visible region of the spectrum i.e. between 160-900 nm. The emission lines from the atomic and ionic species are very narrow; the width being less than 5 pm.

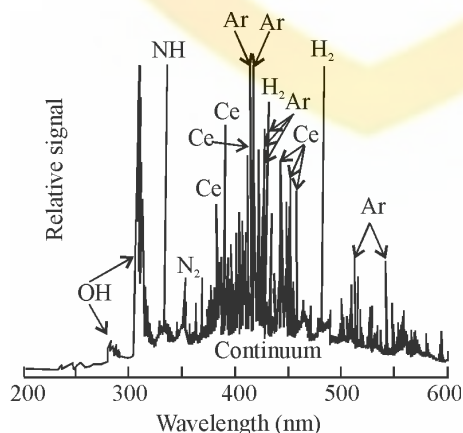


Fig. 10.1: ICP-AES spectrum of 100 pm cerium

A representative atomic emission spectrum based on plasma is given in Fig.10.1; it shows an ICP-AES spectrum of cerium having a concentration of 100 pico mol. You may note the presence of a number of lines from the analyte, the source gas (Ar), and the molecular species and other background radiation. This would give you an idea of what to expect for a multielement analyte.

Having learnt about the basic principles, let us learn about the instrumental aspects of atomic emission spectrometry based on plasma sources. However, why don't you solve the following SAQ before proceeding ahead?

SAQ 1

Enlist various atomisation-excitation sources used in atomic emission spectrometry.

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10.3 PLASMA AND ITS CHARACTERISTICS

You have so far learnt about three atomic spectroscopic methods in Unit 7 to Unit 9. On the basis of your understanding of different types of atomization-excitation sources or combinations about which you have learnt in these units, enlist some characteristics of an ideal atomization-excitation source in the space provided below.

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We are sure that you could pen down some of the characteristics expected of an ideal atomization-excitation source. You may compare your list with the following characteristics and complete your list if you missed on any characteristic.

An ideal atomization-excitation source should have the following characteristics.

1. It should completely separate the analyte from its **original matrix** so as to minimise interferences.
2. It should have appropriate energy to ensure complete atomisation but keep ionisation to a minimum.
3. It should provide an **inert environment**, so as to keep the undesirable molecular species formation to a minimum.
4. It should have none or negligible background radiation.
5. It should provide for the analysis of samples in all possible forms like, solids, liquids, gases or slurries.
6. Of course, it should be inexpensive, need minimal maintenance and be easy to operate.

As always, it is difficult to attain ideality, however, **plasma sources** are quite promising for the purpose of atomisation-excitation job in atomic emission spectrometry. You have learnt above that a plasma source is an electrically neutral, highly ionised gas that consists of ions and electrons. It is sustained by absorbing

energy from an electric or magnetic field. Three types of power sources have been employed in **argon plasma spectroscopy**. One is a powerful **radio frequency generator** that powers an induction coil, the magnetic field generated from it help in establishing the plasma. The second is a **dc electrical source** capable of maintaining a current of several amperes between electrodes immersed in the argon plasma and third one is a **microwave frequency generator** through which the argon flows. Accordingly, there are three types of plasma sources. These are as given below.

- Inductively coupled plasma (ICP)
- Direct current plasma (DCP)
- Microwave induced plasma (MIP)

Of the three, the radio-frequency, or inductively coupled plasma (ICP), source appears to offer the greatest advantage in terms of sensitivity and freedom from interference. On the other hand, the dc plasma source (DCP) has the virtues of simplicity and lower cost. Let us learn about the different types of plasmas.

10.3.1 Inductively Coupled Plasma

The inductively coupled plasma (ICP) is plasma induced by radiofrequency. The energy transfer is mediated by an induction in that produces a magnetic field which is helps in establishing and sustaining the plasma. The energy of a high frequency generator is transferred to a gas, generally argon, flowing at atmospheric pressure. A typical inductively coupled plasma source is called a **torch** (Fig.10.2). The most common ICP torch in use today has evolved over decades of development. It consists of a quartz tube whose upper part is surrounded by a radiofrequency work coil. The torch assembly is designed to deliver gases so that stable argon plasma is formed at the open end through which the sample aerosol can be injected. Let us learn about the different components of the ICP torch and their functions.

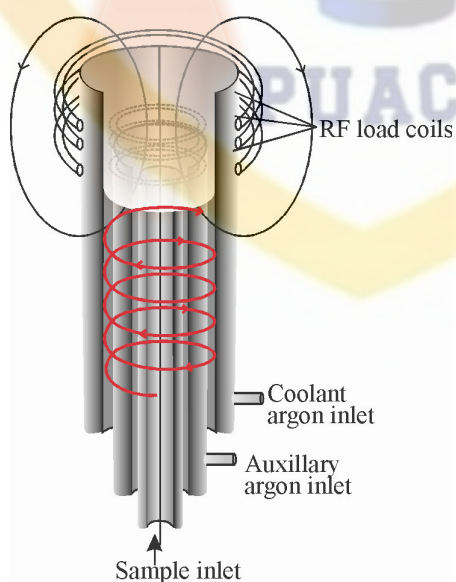


Fig. 10.2: A schematic section diagram of an ICP torch

Quartz tube: The body of the torch consists of three concentric quartz tubes; the diameter of the largest tube being about 2.5 cm. The tube has three separate gas inlets. The argon gas enters the plasma through the outer channel with a tangential flow pattern at a rate of 8 – 20 L min⁻¹. The gas traveling up the central channel is called **auxiliary gas** and also has a tangential flow pattern. The innermost third inlet is connected to the nebuliser from which the gas enters the plasma along with the sample in a laminar flow.

Radio Frequency Power Generators: The majority of radiofrequency (rf) power generators are crystal controlled radiofrequency generators. These are designed to operate within the industrial frequency bands of 27.12 or 40.68 MHz, although plasma generators have been described operating at between 5 to 100 MHz. The radio frequency at which the torch operates is an important parameter in sustaining plasma operation. At the lower frequency range it is necessary to deliver large power up to 30 kW to sustain the plasma. At a frequency of 27.12 MHz, the generators are normally designed with maximum power ratings of between 2 and 5 kW, and are often used routinely to deliver about 1 kW to the plasma. The radiofrequency power supply is so controlled that it ensures a constant power transfer to the induction coil.

Work coil: The work coil consists of a water-cooled induction coil that is powered by a radio frequency generator. The copper induction coil is wrapped two or three times around the ICP torch and has water flowing through it for cooling purposes. The lines of force, generated by the magnetic field, are directed along the axis of the solenoid inside the tube and take the form of an ellipse on the outside.

The cost of argon gas used is a major component of the routine plasma operation cost.

Argon gas supply: The conventional argon plasma torch uses **between 13 and 20 liters of argon per minute**, mainly to ensure that the outer quartz glass tubing adjacent to the plasma is adequately cooled. Such a high consumption of argon gas is met by installing a liquid argon supply Dewar flask rather than relying on conventional compressed gas cylinders.

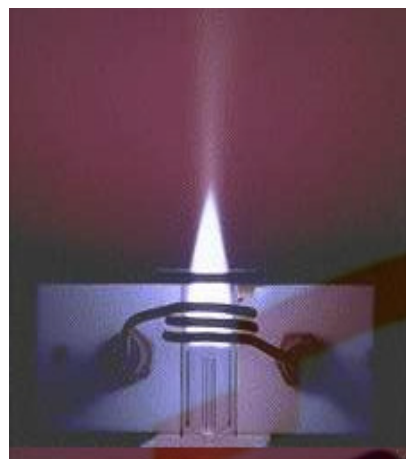
Mechanism of plasma formation

The ionisation of the argon gas flowing through the crystal tube inside the solenoid is initiated by a spark from a Tesla coil. The resulting ions and the electrons are subjected to the fluctuating magnetic field produced by the induction coil. This makes them flow in the closed annular paths within the coils. The induced or eddy currents are thus produced. These electrons rapidly acquire enough energy from the oscillatory field generated by the induction coil and sustain a high degree of ionisation. This leads to the formation of ring shaped **toroidal plasma**. The spacing between coil and torch, the distance between individual copper coils and the concentricity of both coil and torch are important parameters in the formation of stable plasma.

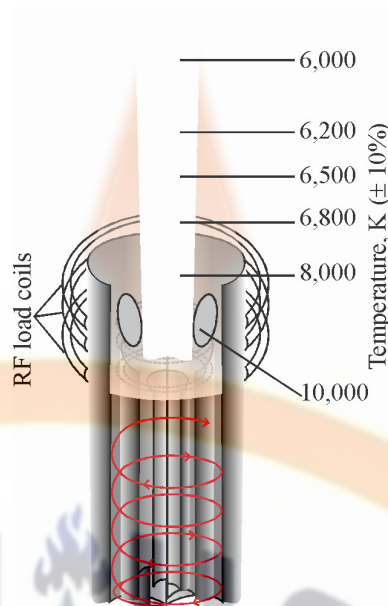
Appearance of ICP plasma

The typical plasma has a very intense, brilliant white, nontransparent core topped by a flame like tail as shown in Fig.10.3 (a). The analytical zone has a temperature of 5000-8000 K and is approximately 1 cm above the coils. It offers the best optical viewing area for maximum sensitivity. Fig.10.3 (b) shows the variation of temperature throughout the plasma. The plasma emits a continuum of background radiation that extends from the visible into the ultraviolet region. The radiation originates from electrons, Ar and Ar⁺ ions, as well as various atomic and molecular species in the matrix and their recombination products. In the region 10 to 30 mm above the core, the continuum fades, and the plasma is optically transparent. The spectral observations are generally made at a height of 15 to 20 mm above the induction coil. Here the background radiation is remarkably free of argon lines and is well suited for analysis.

The plasma is self maintaining and continuous.



(a)



(b)

Fig. 10.3: (a) An ICP torch (b) A schematic diagram showing the temperature profile of a typical ICP torch

10.3.2 Direct Current Plasma

In direct current plasma (DCP) the external source of energy is a *dc* electric source. The most recently developed DCP is the **three electrodes DCP** or inverted -Y shaped plasma, as it is generally called and shown in Fig. 10.4. It has two anodes set at an included angle of about 60° and a cathode. The anodes are made up of graphite and are surrounded by ceramic sleeves. The cathode block consists of a small tungsten electrode also surrounded by a ceramic sleeve. The argon gas is introduced through the sleeves around the anodes and transfers the discharge to the cathode block.

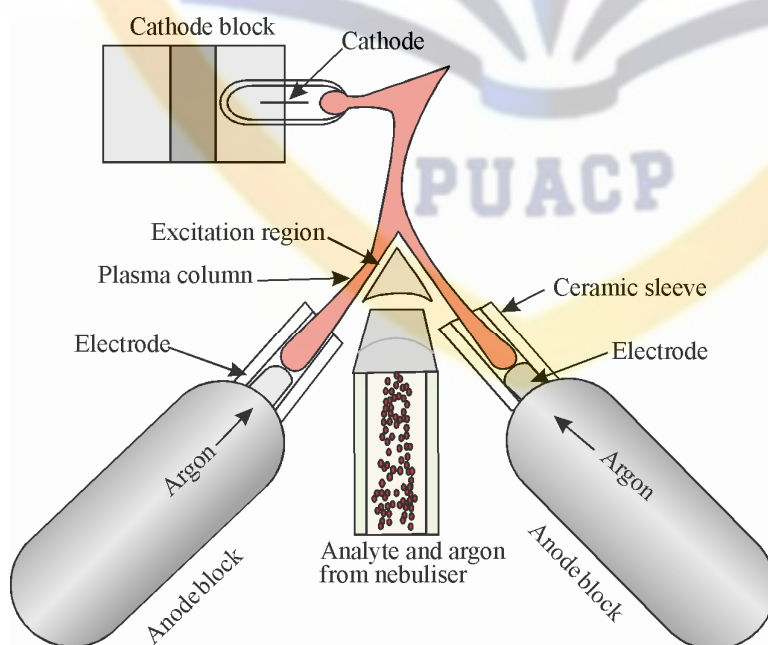


Fig. 10.4: A schematic diagram showing the positioning of the electrodes and the sample insertion in a typical DCP

The sample in the form of an aerosol is introduced at a rate of about $2 \text{ cm}^3 / \text{min}$ below the intersection of the two anodic columns. The spectral observation region is just below this intersection. The background radiation is relatively low. However, the excitation region is relatively small, and good spatial stability is essential to prevent drifts in observed intensities. The DCP is subject to some matrix effects and fairly severe ionisation interferences, i.e. enhancement or depression in intensities due to the presence of an easily ionisable element. It has been reported that the detection limits for DCP-AES are inferior to those obtainable by ICP-AES.

10.3.3 Microwave Induced Plasma

In a microwave induced plasma (MIP) source frequencies in the microwave region are used as external energy source. A microwave radiation of a frequency of 2450 MHz is commonly used. A microwave induced plasma is obtained when the ultrahigh frequency *ac* power is capacitatively coupled into a stream of noble gas (helium or argon) or nitrogen at about $3 \text{ dm}^3 / \text{min}$. in a resonant cavity.

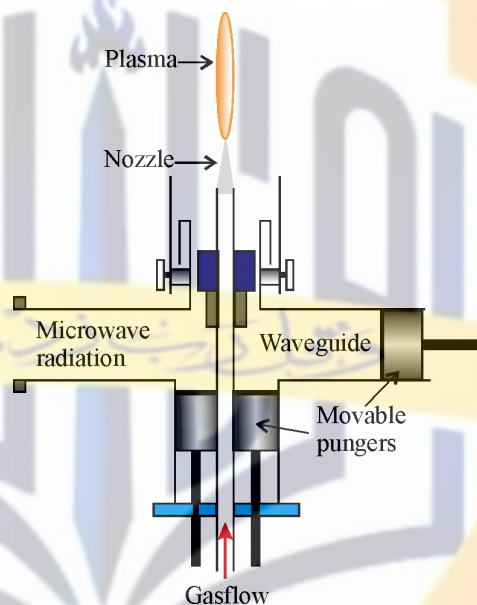


Fig.10.5: A schematic diagram showing the generation of a microwave induced plasma

Low power MIP (50 to 100W) cannot accept solution aerosols without prior desolvation, high power MIP (800W) are more robust and can vaporise and atomise aerosols without desolvation. The MIP is also useful for the excitation of volatile hydride forming elements after stripping the hydrides from the excess of hydrogen. With different trapping techniques, detection limits down to the sub-ng level can easily be obtained.

In one of the microwave plasma torches the microwave power generated by a 2 kW magnetron is guided to the tip of the torch using waveguides. A conical hollow nozzle acts as the tip of the torch through which the plasma gas argon flows. As there is only one flow channel, the sample is also injected through the same. The small size of microwave sources is an advantage over the ICP because it makes it more flexible and less expensive. However, the MIP is found to be inferior to the ICP in respect of detection limits, sensitivity, reproducibility, ionization interference etc. The MIP needs close matching of the calibration and samples solution and very frequent re-calibration is generally required to compensate for large drifts in sensitivity of the MIP. The sample preparation procedures in MIP-AES are also quite tedious and make it an inconvenient analytical method.

Although the MIP cannot compete in popularity with the DCP or the ICP, it has found acceptance for a variety of trace determinations.

10.3.4 Choice of Argon as Plasma Gas

You may be wondering that in all the three types of plasma sources discussed why is it that argon only is used as the plasma gas? Let us see the rationale behind the choice of argon. Some of the reasons for this choice are as given below.

- Argon being an inert gas, does not form stable compounds with analyte elements, therefore there would be lesser chemical interference in the event of atomisation in the plasma.
- As its emission spectrum is relatively simple and it is optically transparent in the UV-visible region of the spectrum it does not offer spectral interference in emission spectrometry.
- Argon has a moderately low thermal conductivity, so the heat is retained within the plasma fireball sustaining stable operation at moderate power inputs.
- As the abundance of argon is reasonable (1% in air), it is economical as compared to other noble gases.
- As the first ionisation energy of argon is quite high (15.75) eV, it has the capacity to atomise, ionise and excite most of the elements of the periodic table which in turn permits the determination of almost all elements that can be excited to emit lines in the UV-visible region.

Nitrogen has been used as plasma gas, either alone or mixed with argon. However, as excited nitrogen emits a complex band spectrum that can cause undesirable spectral interference, it has not been widely adopted. Some investigations have been carried out using helium plasmas. However, due to the high thermal conductivity of the gas and consequent higher power inputs make this also NOT a favourable choice.

Table 10.1: Physical properties of plasma gases

Gas	Electrical resistivity at 25°C $10^{-2} \Omega \text{ cm}$	Thermal conductivity at 25°C $10^{-6} \text{ cal / S cm}^2 \text{ } ^\circ\text{C}$	Specific heat at 25 °C cal/g
Helium	5	340	1.25
Argon	2	39	0.13
Nitrogen	10	57	0.25

There are only three other gases that have higher ionisation energies as compared to argon and would therefore be suitable for exciting difficult elements such as F, Cl, Br or S. These are fluorine (17.4 eV), neon (21.6 eV) and helium (24.6 eV). In addition, nitrogen has been proposed as a cheap alternative plasma gas. The relevant physical properties of He, Ar and N₂ are summarised in Table 10.1.

SAQ 2

Enlist different components of ICP torch and give their function in one line each.

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10.4 INSTRUMENTATION FOR ICP-AES

The essential components of a plasma based atomic emission spectrometer are as given below.

- **Plasma source:** an atomisation-excitation device
- **Nebuliser :** a sample introduction device
- **Monochromator:** a dispersion device
- **Detector:** a radiation detection device
- **Processing and readout device**

A schematic layout of an ICP-AES spectrometer is given in Fig. 10.6. The sample in the solution form is nebulised and injected into the plasma source with the help of a suitable nebuliser. The emitted radiation is passed through monochromator and after dispersion it is detected by a photodetector and sent to the processing unit for the processing and generating suitable output.

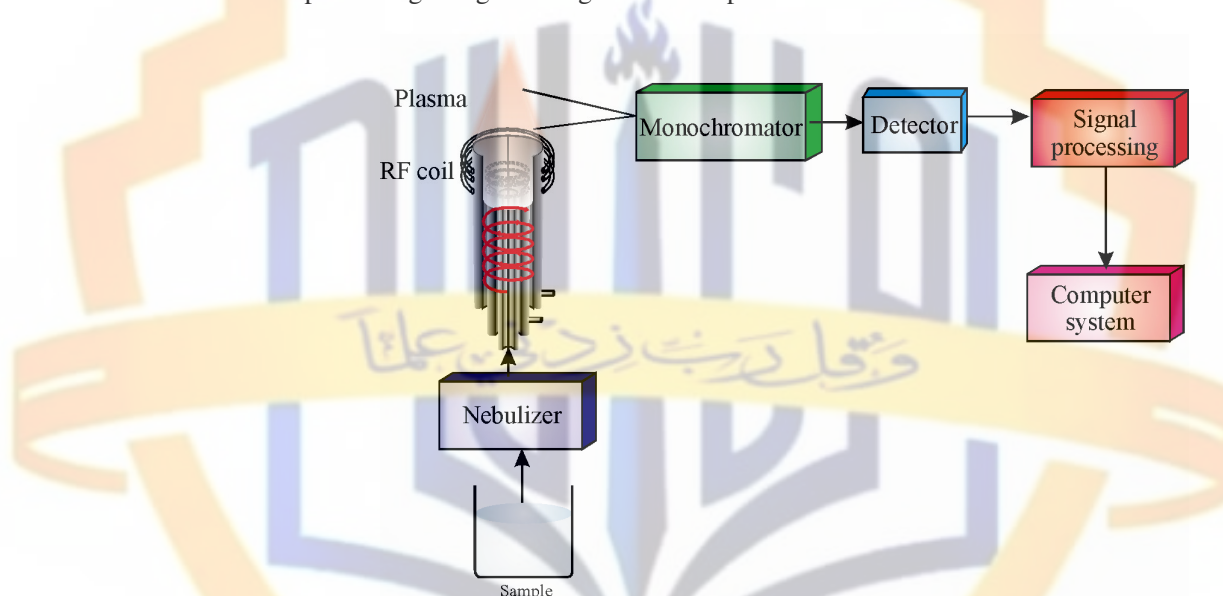


Fig. 10.6: A schematic layout of different components of an ICP-AES spectrometer

You have learnt about the formation and characteristics of different types of plasma source in the previous section. As we are discussing about the instrumentation for ICP-AES, the inductively coupled plasma acts as a source.

Let us learn about the other components of the ICP-AES spectrometer in details.

10.4.1 Sample Introduction

Inductively coupled plasma emission spectroscopy is used primarily for the qualitative and quantitative analysis of samples that are dissolved or suspended in aqueous or organic liquids. The sample is brought as a fine aerosol into the plasma, which generally is achieved by pneumatic nebulisation. These are carried into the torch by argon gas flowing at a rate of 0.3 to 1.5 dm³/min through the central quartz tube. The aerosol enters the hot plasma zones with a low injection velocity so as to have a residence times of the order of ms that is required for an efficient atomisation and excitation. Thus, there are two steps in the sample introduction. These are as follows.

- a) Sample preparation
- b) Nebulisation

Let us learn about these.

a) Sample preparation

The solution preparation for the analysis using ICP-AES depends on the nature of the sample and the concentration of elements to be determined. There are two main types of sample preparation methods used for ICP analysis. These are explained below.

i) Acid digestion method

You have learnt about the acid digestion method of sample preparation in Unit 9, sub section 9.7.1. In the acid digestion method, the acids use their oxidising or reducing properties for the dissolution of the analyte. You would recall that acid digestion generally produces a clear solution of the analyte without loss of any of the elements to be determined. However, one must take care of the possible loss of volatile elements. For example, in the acid digestion using HCl, there is a possibility of the loss of As, Se, Sn as their volatile chlorides. Similarly, in case of sulphuric acid, the formation of precipitates of Ca, Ba, Pb is also a potential source of error.

Another aspect that needs attention of the analyst is that the quantity of acid or flux in the solution must be as low as possible so that there is minimum perturbation of the plasma. Some of the acids perturb the plasma more than the others. Accordingly, there is an order of preference of the acid to be used for sample preparation. The decreasing order of their preference is as follows.



ii) Dry attack method

In dry attack method, the sample preparation involves an alkaline fusion as well as high temperature calcination (450 - 600 °C) followed by acid recovery of ashes. However in this method the losses due to volatilisation and insolubilisation are not negligible. More so there is a possibility of contamination of the solution due to the reagents.

b) Nebulisation

The analyte samples in all three states (solid, liquid, gas) have been successfully introduced into an ICP. For solutions, a nebuliser is used to convert the liquid stream into an aerosol consisting of particles that are 1–10 mm in diameter. Direct injection of liquids into the plasma would either extinguish the plasma or cause the atoms to be improperly desolvated, making excitation and emission less efficient. You have learnt about nebulisation and different types of nebulisers in Units 7, 8 and 9. Let us learn about different types of nebulisers employed in ICP-AES.

Atomic Emission

In the direct analysis of solids the sample preparation procedures include electrothermal vaporisation, laser and spark ablation, and glow discharge.

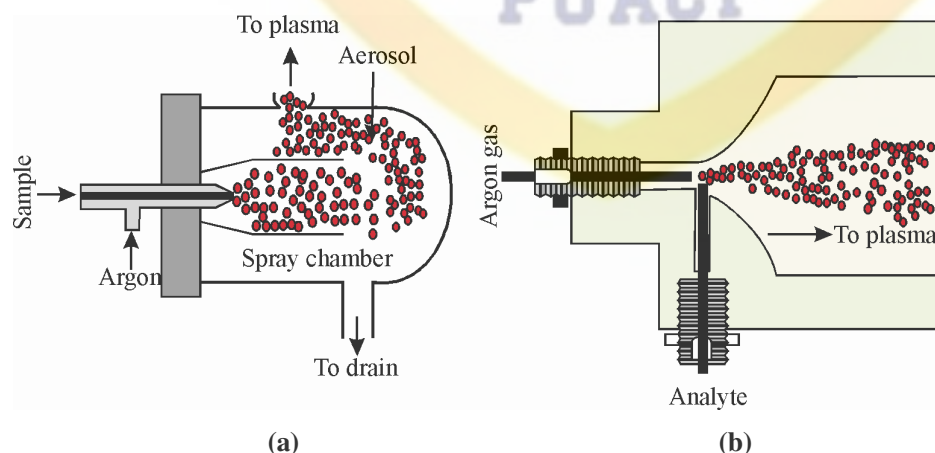


Fig. 10.7: Pneumatic nebulisers used in ICP-AES, (a) Concentric tube type and (b) cross flow type

Nebulisers for ICP-AES

As you have learnt in earlier units, **nebuliser is a device that converts a solution of the analyte into finely divided droplets that are carried into the atomiser.** You would recall that in concentric type pneumatic nebulisers the sample solution is aspirated through a capillary by the flow of a nebulising gas using **Bernoulli's principle** and is converted into a fine aerosol by the gas jet. In a cross flow nebuliser, another type of pneumatic nebuliser, the aspirated sample is nebulised by a stream of argon, and the resulting finely divided droplets are carried into the plasma. A schematic diagram of the two types of pneumatic nebulisers used in ICP-AES is given in Fig.10.7.

In a frit nebuliser as shown in Fig 10.8 (a), **the sample solution is pumped to a glass frit membrane, consisting of a porous coral like synthetic material.** The argon gas passes through the membrane and converts the sample into an aerosol spray. This is then directed into the plasma. You would recall from Unit 9 that in **ultrasonic nebuliser**, the sample is pumped on to a **piezoelectric crystal** vibrating at ultrasonic frequencies (50 kHz to 4 MHz). **The vibrations of the crystal break the droplets into smaller particles which are transported to the plasma.** Larger aerosol drops are drained out. A schematic diagram of the ultrasonic nebuliser used in ICP-AES is given in Fig.10.8 (b).

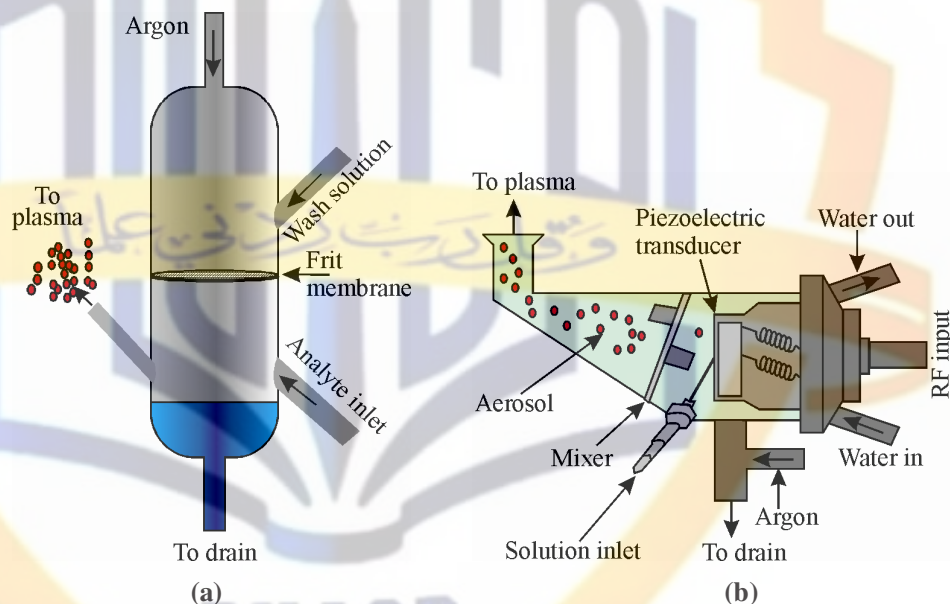


Fig. 10.8: (a) **Frit nebuliser** and (b) **ultrasonic nebuliser** used in ICP-AES

You have also learnt about the **electrothermal vaporisation and the hydride generation** as the methods of introducing the sample in the atomiser. In electrothermal vaporisation method the sample is vapourised on a conductor like carbon rod or a heated metal and is carried by argon to the plasma. On the other hand in hydride generation method, some elements are converted into volatile hydrides which are then directed into the plasma. The schematic diagram of electrothermal nebuliser used in ICP-AES is given in Fig.10.9.

Electrothermal vaporisation coupled with a plasma torch offers the microsampling capabilities and low detection limits of electrothermal furnaces while maintaining the wide linear working range, the freedom from interference, and the multielement capabilities of ICP.

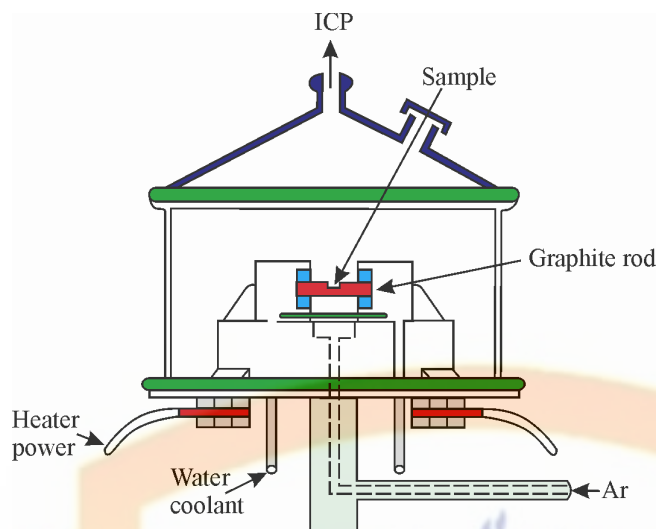


Fig. 10.9: Schematic diagram of an electrothermal nebuliser for ICP-AES

10.4.2 Monochromators

Emission from plasma is usually polychromatic in nature which implies that it consists of a large number of radiation of different wavelengths. More so, the bandwidths of optical emission lines from the plasma are typically of the order of 0.001 nm. These need to be suitably dispersed to analyse for the possible elements in the analyte. Resolution is important because of the complexity of ICP emission spectra, in terms of very large number of individual emission lines observed from samples. If not resolved, it would cause extensive spectral interference. You have learnt in Unit 2 that there are three common devices used for the separation or dispersion of light. These are gratings, prisms and Michelson interferometers. In ICP-AES spectrometers, the resolution of the complex spectra is achieved by using ruled grating monochromators having a large number of grooves on the grating. Some instruments on the other hand employ holographic gratings.

10.4.3 Detectors

As you have learnt in Block 1 on molecular spectroscopic methods, there are three basic types of detector systems. These are photomultiplier tubes (PMTs), photodiode arrays (PDAs), and charge coupled devices (CCDs). Most of the instruments use photoelectric means of detection in the form of photomultiplier tubes (PMTs), or with photodiode arrays. You have learnt about these devices in Unit 2 and Unit 4 respectively. In addition to this, in some cases photoplates are also used for detection purposes in AES. A number of modern instruments have now switched to solid state array detectors that use charge coupled devices (CCDs) or charge injection devices (CIDs).

10.4.4 Processing and Readout Device

Whether the detection of the analyte signal is done sequentially or simultaneously, a large amount of data needs to be handled in terms of the positions of the spectral lines and their intensities. Therefore the processing of the data needs good computers along with multichannel analog to digital converter to acquire and save the detected signals for further processing. The results of the determinations are printed out by a dedicated printer.

The dispersion and detection devices are typically combined with other essential components in different configurations to create different types of instruments. Let us learn about these after you have tried answering the following SAQ.

SAQ 3

What precautions should be observed while preparing samples for ICP-AES using acid digestion method?

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10.5 TYPES OF INSTRUMENTS FOR ICP-AES

Two general arrangements of instrumentation are widely used in ICP-AES. The basic principle or the set up is similar for these. However, these differ on the type of dispersion method or the monochromator assembly used to disperse or resolve the large number of emission lines emerging out of the plasma and the detector device. The two types of spectrometers for ICP-AES are as given below.

- Sequential spectrometers
- Simultaneous spectrometers

The sequential and simultaneous spectrometers are extensively used in the analytical laboratories. Of these, the sequential spectrometers are less expensive and more flexible but usually require a higher degree of operator skill and experience. On the other hand, the simultaneous spectrometers are more precise and accurate and are obviously more expensive. The simultaneous spectrometers employing solid state array detectors are of recent origin and are also capital intensive. However, these are quite sensitive, precise and accurate. Let us learn about these spectrometers in some details.

10.5.1 Sequential Spectrometers

These instruments use a moveable grating monochromator to select wavelengths in sequential order and use a single photomultiplier tube to detect them. The grating of the monochromator is of holographic type having a large number of grooves. The monochromator is programmed to make measurements in turn or sequentially at a pre-programmed series of peaks and background wavelengths to cover the elements of interest.

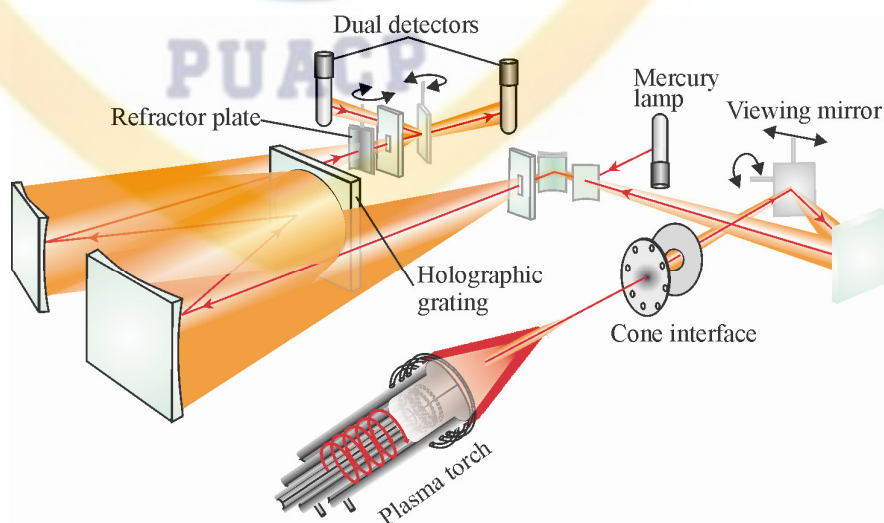


Fig. 10.10: A schematic diagram showing the optical diagram of a sequential ICP optical emission spectrometer

For this purpose, the grating of the monochromator is rotated in a controlled manner so as to sequentially focus a predetermined wavelength on the exit slit. Alternatively, the grating is kept fixed and the slit and the photomultiplier detector are moved to detect the desired wavelengths. As only a few components are used these instruments are economical.

A schematic diagram of a sequential spectrometer is shown in Fig. 10.10. However, longer analysis times, poorer accuracy and precision are the major disadvantages of sequential instruments. In addition to these, the reproducibility of wavelength selection is another area of concern. To partly overcome the problem of longer analysis times **slew scan instruments** have been developed. In these instruments the monochromator or the detector and slit combination are moved in such a way that they quickly reach on to a wavelength of interest for a given analyte and then slowly scan around it in small steps. Needless to say, this can be achieved only with the help of an electronic control by a suitable computer.

10.5.2 Simultaneous Spectrometers

These instruments are designed to simultaneously measure the response at different wavelengths so as to overcome the drawbacks of the sequential spectrometers. There are two types of spectrometers belonging to this category. These are given below.

a) **Polychromators**

b) **Solid state array based spectrometers**

The polychromators use multiple photodetectors whereas the solid state array based spectrometers depend on charge coupled or charge injection based devices as detectors. You have learnt in Unit 4 that the charge coupled devices are capable of simultaneous measurement. Let us learn about the two types of spectrometers.

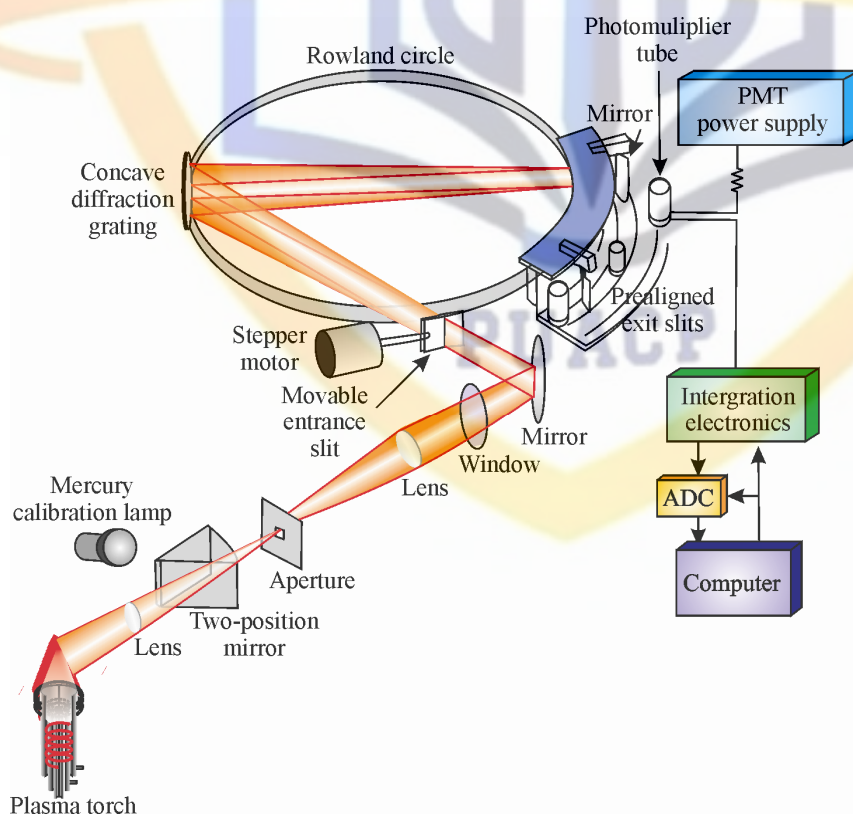


Fig. 10.11: A schematic diagram showing the layout and optical diagram of a ICP polychromator

The matrix-dependent interferences can be taken care of by installing multiple detectors for an element.

a) Polychromators

These simultaneous spectrometers are designed with a fixed diffraction grating monochromator and multiple 'exit slits' and associated photomultipliers. It means that these spectrometers have a number of photomultiplier tubes. Each of the photomultiplier is optimised to detect a specified wavelength corresponding to an element of interest. Typically, about 60 photomultiplier tubes or detectors are installed in a polychromator. Therefore, the simultaneous measurement of a prespecified range of elements becomes very rapid. A schematic diagram showing the setup of a polychromator is given in Fig.10.11.

In **Echelle spectrometers** a special configuration of diffraction grating is used that displays the entire spectrum as a two-dimensional array, each line in the array representing a particular multiple order of diffraction. A schematic diagram of this spectrometer based on Echelle grating is shown in Fig. 10.12.

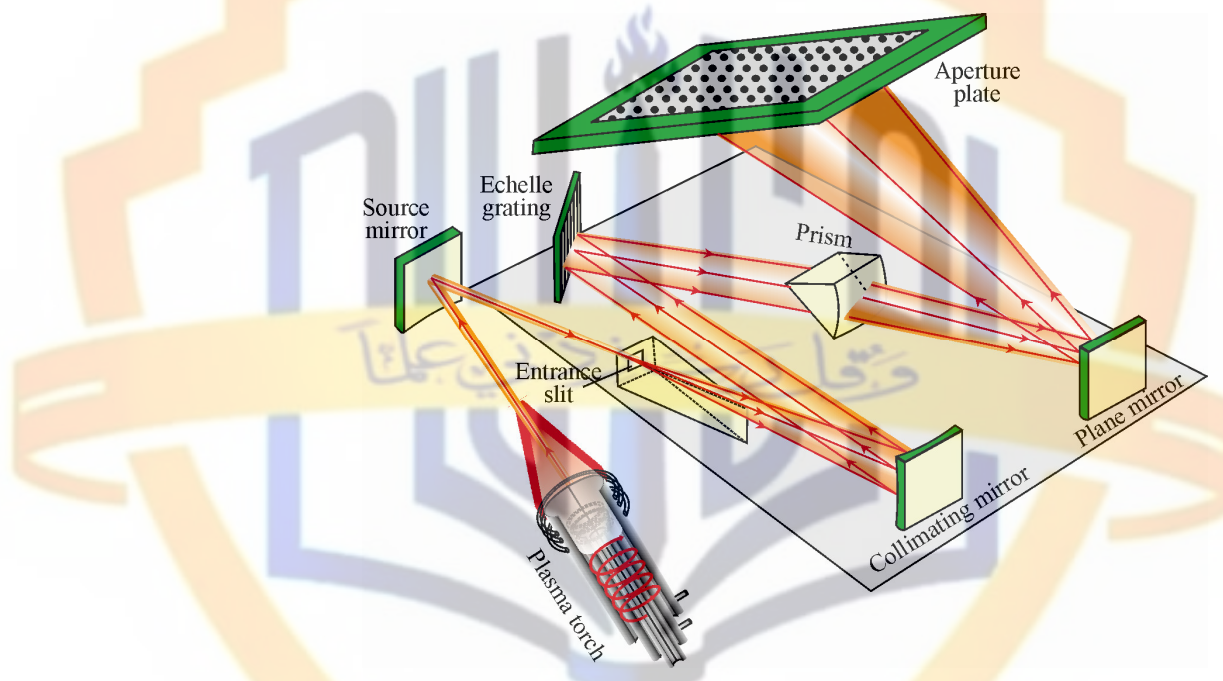


Fig. 10.12: A schematic diagram showing the layout and optical diagram of a spectrometer based on Echelle grating

The monochromators used here are very compact and offer particular advantages in simultaneous detection. These spectrometers are faster, more precise and accurate for a given combination of analytes and interferants.

The major drawback of the simultaneous spectrometers or direct readers as these are generally called is related to the lack of flexibility. One has to make a detector available for each analyte of interest which makes it very expensive. Further, if a newer analyte sample is to be analysed one needs to procure new detectors for the same and augment the battery of the detectors present in the instrument. Further, if a new matrix is encountered, one or more of the analytical lines may have severe spectral interferences or background shifts. This may compromise with the precision and accuracy of the system.

b) Solid State Array Detector Spectrometers

These spectrometers are of recent origin and as the name suggests these make use of solid state detectors. These have allowed the analysts to get over the problems of

conventional sequential and simultaneous spectrometers. Recent commercial instruments have started using two dimensional detectors. These incorporate charge injection devices (CIDs) or charge coupled devices (CCDs). These devices may allow the simultaneous measurement of more than 250,000 lines and 5000 lines respectively. Fig. 10.13 depicts a schematic representation of the solid state array detector based spectrometers.

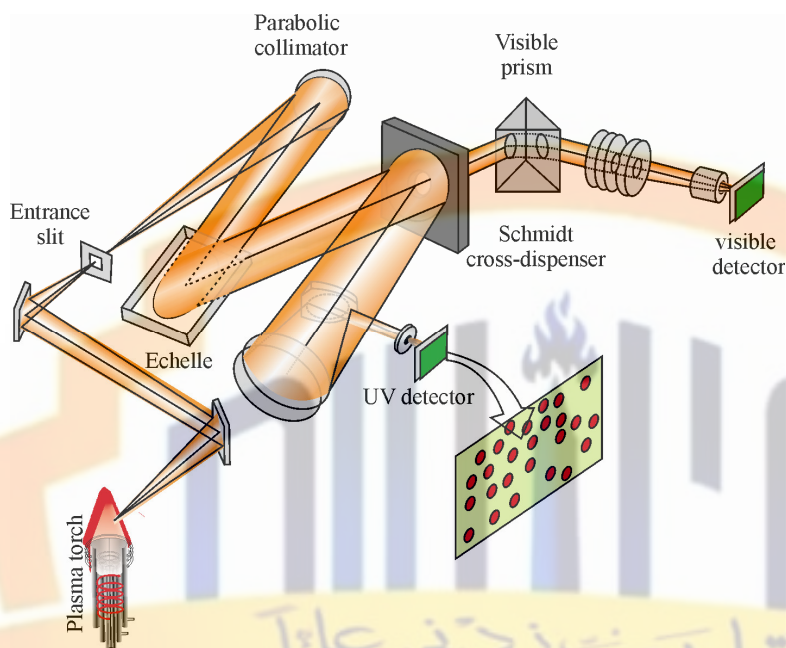


Fig. 10.13: A schematic diagram showing the layout and optical diagram of spectrometer based on solid state detector

In the **CCD based spectrometers** the whole analytically usable part of the spectrum is measured on a series of CCDs placed in the **Rowland circle** of a spectrometer. The important aspect of these instruments is that these give the resolution and sensitivity virtually identical to sequential or direct reading polychromators using photomultiplier tubes. The **CID based instruments** on the other hand are Echelle spectrometers that incorporate the CIDs as the detectors.

These instruments are expected to replace photomultiplier based direct reading ICP emission spectrophotometers in the next few years.

SAQ 4

What are slew scan instruments? What is their importance?

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10.6 ANALYTICAL METHODOLOGY IN ICP-AES

The analytical determination of different elements on the basis of characteristic emission spectrum has developed a lot from the times of Bunsen and Kirchhoff. These developments have been made possible by the availability of better atomisation-excitation sources, dispersion and detection devices, etc. The atomic emission spectra for some elements such as Na and K are simple, consisting of only a few wavelengths, while in others, such as Fe and U, thousands of distinct reproducible wavelengths are

present. Today with plasma based sources and state of the art monochromators coupled with solid state detection devices the potential of the technique in terms of the range, accuracy and the detection limits has become excellent.

In principle, all metallic elements can be determined by plasma emission spectrometry and these can be measured simultaneously in a given analyte. However, for the determination of the nonmetals such as boron, phosphorus, nitrogen, sulfur, and carbon, a vacuum spectrometer is necessary. This is so because the emission lines for these elements lie at wavelengths below 180 nm where the atmospheric gases absorb strongly. In practice, the plasma emission spectroscopy is generally limited to the determination of about 60 elements.

Let us learn about the methodologies adopted in using the technique for qualitative and quantitative determinations.

10.6.1 Qualitative Analysis using ICP-AES

In principle it is possible to obtain qualitative information from ICP emission spectrometry by using sequential spectrometers. However, this technique has not been exploited for the purpose. This is so because the amount of sample and instrument time required are prohibitive. Similarly, as it is almost impossible to install individual photomultipliers to monitor multiple lines for each possible element of interest the direct reading spectrometers or polychromators are also not used for qualitative analysis. Yet the method has the potential and is used to some extent for qualitative purposes.

The persistent lines and line groupings that are characteristic for the element are used to identify the presence of an element.

The qualitative analysis is based on the principle that each element has a characteristic spectrum consisting of the most persistent lines and the characteristic lines. These are used to identify the presence of an element in the analyte. The most **persistent** or **RU** (*raies ultimes*) lines are the ones that persist even when the concentrations of the respective elements are progressively reduced to zero. The RU lines are not necessarily the most intense lines. For example, in manganese spectrum, a triplet at 279.8 nm is more intense at normal concentrations than the 403.3 nm triplet, but the latter are the three most persistent lines for manganese. Further each element has a set of **characteristic line groupings** such as doublets, triplets, groups of doublets, etc. However, for an element the characteristic line groupings do not necessarily consist of the most persistent lines. For example, the most persistent line for magnesium is the single line at 285.213 nm, while the characteristic magnesium emission occurs at 277.62782 nm.

The atomic spectral lines are very narrow with respect to the whole spectral range, yet there is a possibility of encountering **line coincidences**. It is important to note that more than 200 000 lines in the spectral range of 200-400 nm have been tabulated and assigned to different elements of the periodic table. In addition there are a large number of lines in other regions also. Therefore, high-resolution spectrometers have to be used for the qualitative evaluation of the spectra. The unambiguous detection and identification of a single noninterfered atomic spectral line of an element is sufficient to indicate its presence in the analyte sample. However, use of more than one line is necessary to conclude the presence or absence of an element.

Qualitative emission spectral analysis is quite easy when the spectra are recorded on a photographic plate or with a scanning monochromator. A number of atlases are available for the photographically recorded spectra; spectra are reproduced and the most sensitive lines are indicated in these atlases. The spectrum of an analyte can then be compared with the collated spectra in the atlases to identify it. Also books with spectral scans around the analysis lines with superimposed spectra from possible

interferants have been published, e.g. for the case of ICP-AES. These are also useful for the practising analytical chemist.

In order to facilitate quantitative determinations, **spectral line tables**, in which the wavelengths of the spectral lines together with their excitation energy and a number indicating their relative intensity for a certain radiation source are tabulated. These are available for different sources, such as arc and spark sources, but also in a much less complete form for newer radiation sources such as inductively coupled plasmas.

10.6.2 Quantitative Analysis using ICP-AES

The strength of ICP-AES lies in quantitative analysis. The intensity of an elemental atomic or ion line is used as the analytical signal in quantitative atomic emission spectrometry. In fact the spectral intensities are unequivocally related to the elemental concentration in the analyte. However, in practice, AES is a relative method and a calibration has to be performed. Once the analyte matrix is understood and the background and spectral overlap correction details have been worked out the calibration of the instrument becomes rapid and straightforward. The analyst however does not need to bother about making the calibration standards as high purity multielement plasma calibration solutions are commercially available. The calibration curves most often consist of a plot of the output current or voltage of a transducer as a function of analyte concentration. For large concentration ranges log-log plots are employed. Fig. 10.14 shows typical calibration curves for the trace elements analysis by AAS.

In ICP-AES analytical determinations the analyte spectral line intensities are compared with that of one or more well-characterized standard reference materials.

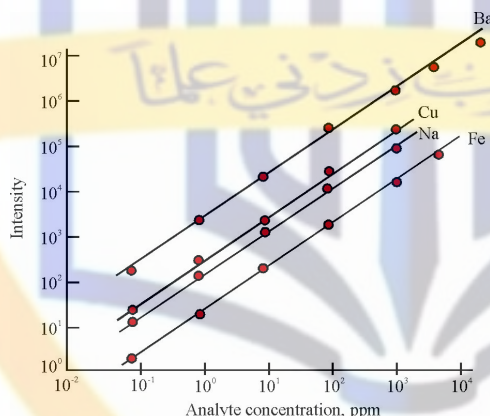


Fig. 10.14: Typical calibration curves obtained for trace elemental analysis by AAS

In one of the quantitative determination strategies the sample is spiked with several elements that are not present in the sample. That is we add a kind of internal standard to the sample. The emission spectrum of the **spiked sample** is then monitored in terms of the relative emission intensities of several lines of the spiking elements to the magnitude of other elements present in the analyte. In this case the vertical axis of the calibration curve is the ratio or the log ratio of the detector signal for the analyte to the detector signal for the spiked element or the internal standard. This can then be used to obtain a reasonably precise and accurate determination of the concentrations of the elements present in the sample.

High sensitivity and large linear range are the strengths of ICP emission spectrometry. The sensitivity in the UV region of the spectrum can be attributed to the high temperature of the plasma which makes it an efficient excitation source and to the fact that in the ultraviolet region, the plasma background is very low. As most of the elements have one or more useful emission lines in the ultraviolet region, these can be easily determined as **the signal-to-background ratios** are very good.

SAQ 5

Define the following terms in the context of qualitative applications of atomic emission spectrometry.

- i) Persistent lines
- ii) Characteristic lines

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10.7 INTERFERENCES IN ICP-AES

You have learnt earlier in the context of other atomic spectrometric methods that any chemical, physical or spectral process that adversely affects the measurement of the radiation of interest can be classified as interference. In case of ICP-AES the interferences may occur in any stage of the operation; starting from the sample preparation stage to the plasma operating conditions. Let us learn about different types of interferences in ICP-AES.

10.7.1 Spectral Interferences

Spectral interferences in ICP-AES are caused by the following.

- overlap of a spectral line from another element
- unresolved overlap of molecular band spectra
- recombination phenomena
- background emission from the source
- stray light from the line emission of high concentration elements,

A common interference involves the overlap of the spectral lines of two or more elements in the matrix emitting radiation at the same wavelength. For example, Cu emission at 515.323 nm is likely to show an overlapping with the emission from Ar at 515.139 nm. These spectral interferences can be minimised either by using a high resolution dispersion system or by using more than one analytical line for the detection of a single element. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference.

Another common spectral interference involves the formation of undesired species (e.g., ions, metal oxides). Some metals are extremely sensitive to small plasma fluctuations. This results in the changes in the relative amounts of neutral atom and the corresponding ions. You may note that the emission spectrum of an atom of a specific element (e.g., Fe) is quite different from that of its ions (e.g., Fe^+ , Fe^{+2} , etc.). Similarly, the formation of metal oxides or metal carbides, are also potential source of interference and need to be evaluated on an individual basis.

Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak.

10.7.2 Physical Interferences

These interferences are associated with the processes of sample nebulisation and transport. The differences in the physical properties of the sample and calibration solutions lead to variations in the aerosol droplet size. This may influence the efficiency of the nebuliser and the sample introduction. The changes in viscosity and surface tension of the solutions can also cause significant inaccuracies. These become especially important in samples containing high amounts of dissolved solids or high acid concentrations. The physical interferences can be reduced by diluting the sample. The use of an internal standard also proves to be useful.

10.7.3 Chemical Interferences

The chemical interferences include molecular compound formation, ionisation effects, and solute vaporisation effects. Some of these have already been discussed under spectral and physical interferences. These effects are generally not very significant in ICP-AES. If present, these can be minimised by carefully controlling the operating conditions such as incident power, observation position, matrix matching, etc. Memory effects resulting from the presence of the analytes in a previous sample and contributing to the signals measured in a new sample are also an area of concern. These can be minimised by purging the system with a blank in between samples. The purging or the rinsing times necessary for a particular element must be suitably estimated before undertaking the analysis.

10.8 APPLICATIONS OF ICP-AES

The ICP-AES technique is a versatile tool in the hands of analytical chemists. As many as 60 elements can be determined by it in a wide range of analyte samples such as rocks, minerals, soil, air, water, agriculture, forestry ecology, food analysis, etc. Therefore it has become an indispensable technique. Some of the important analytical applications in different areas are given below, you would learn about the applications in detail in the next unit.

Agricultural science	Analysis of agricultural products and foods besides soil analysis.
Health sciences	Determination of Al in blood, Cu in brain tissue, Se in liver, Na in breast milk. Direct determination of Ca, Fe, Cu, Mg, Na and K in serum samples.
Geological sciences	Presence of lanthanides and other elements in rock samples.
Forensic Sciences	Crime scene soil analysis.
Metallurgy	Analysis of trace elements in stainless steel.
Environmental science	Waste water analysis, determination of pollutant metals in variety of matrices.
Industry	Presence of metals like Cu, Fe, Ni, and Si in lubricating oils or gasoline at tracer concentration. Traces of metals like Ca, Cu, Fe, Mn, Mg, P, K and Zn in beer or wine; determination of trace elements in polymers, evaluation of catalysts, and so on.

The detection limits of some commonly determined elements by ICP-AES are given in Table 10.2.

Table 10.2: The detection limits of some commonly determined elements by ICP-AES

Elements	Detection limit ICP-AES (ng/ cm ³)	Elements	Detection limit ICP-AES (ng/cm ³)
Ag	7	Li	80
Al	20	Mg	0.1
Au	20	Mn	1
B	5	Ni	10
Cd	3	Pb	40
Ce	50	Se	70
CO	6	Te	40
Cr	6	Th	60
Fe	5	Ti	4
Ge	50	U	250
Hg	20	W	30
La	10	Zn	2

The wide applicability of ICP-AES in the quantitative analysis of various materials can be attributed to the following advantages offered by the technique.

- Rapid and simultaneous multi-element analysis.
- Lack of chemical interferences.
- High temperature of the excitation source : 5000 to 10000K.
- Low sample requirements.
- Absence of self absorption, the cause of non-linear calibration plots in FES.
- Validity of calibration curves over 4 to 6 orders of magnitude.
- Low detection limits: 1 to 100 ng/g or µg/l (part per billion).
- Good accuracy and precision: relative standard deviation of about 1 per cent.
- Applicability to elements that are difficult to be determined by AAS: B, C, Ce, La, Nb, Pr, S, P, Ti, Ta, V and Zr can also be measured.

Let us summarise what have we learnt about atomic emission spectrometry based on ICP.

10.9 SUMMARY

In atomic emission spectrometry (AES), a reproducible and representative amount of the sample is introduced into an atomization-excitation source where it is converted into atomic vapours of the analyte in excited state. In the atomisation-excitation source

the analyte undergoes a number of processes to be atomised and then get excited. As the excited state is short lived, the excited atoms return back to the ground state accompanied by the emission of electromagnetic radiation that is characteristic of the constituents of the sample. The AES is a versatile method due to the availability of a wide range of atomisation-excitation sources.

Plasma is a high energy source which is an electrically neutral conducting gaseous mixture having a significant concentration of cations and electrons. As an electrical conductor it can be heated inductively by coupling with an oscillating magnetic field. The temperature of the plasma may be of the order of 5,000 to 8,000 K.

In the ICP-AES the analyte sample is introduced into the centre of the plasma as an aerosol with the help of a nebuliser using argon flow. As the energy of the plasma source is quite high it ensures the excitation of the atoms of all the elements present in the sample which then relax by emitting EM radiation of characteristic wavelengths of different elements. Thus, it is a multi element technique.

Three types of power sources have been employed in argon plasma spectroscopy accordingly; there are three different types of plasmas. These are the inductively coupled plasma (ICP), the direct current plasma (DCP) and the microwave induced plasma (MIP). These plasmas use radiofrequency, direct current and microwave radiation respectively as the power sources.

Argon gas is used as plasma gas in most of the plasma instruments. This is due to its inertness, whereby it does not form stable compounds with analyte elements, its simple emission spectrum that makes it optically transparent in the UV-visible region of the spectrum, moderately low thermal conductivity, and good natural abundance.

The essential components of a plasma based atomic emission spectrometer are plasma source, a nebuliser, a monochromator, a detector and a processing and readout device. In a typical AES determination the sample is prepared by using acid dissolution method or dry attack method and is inserted into the plasma source with the help of a suitable nebuliser. The spectral emission is suitably resolved, detected, processed and utilised for qualitative and quantitative determinations.

The two types of spectrometers for ICP-AES are: sequential spectrometers and simultaneous spectrometers. These have the capabilities of measuring the different elements present in the analyte in a sequential manner or simultaneously. Of these, the sequential spectrometers are less expensive and more flexible but usually require a higher degree of operator skill and experience. On the other hand, the simultaneous spectrometers are more precise and accurate and are obviously more expensive.

The qualitative analytical determination of different elements on the basis of characteristic emission spectrum has developed a lot. The qualitative analysis is based on the principle that each element has a characteristic spectrum consisting of the most persistent lines and the characteristic lines. On the other hand the intensity of an elemental atomic or ion line is used as the analytical signal in quantitative atomic emission spectrometry. In fact the spectral intensities are unequivocally related to the elemental concentration in the analyte. However, in practice, AES is a relative method and a calibration has to be performed.

The ICP- AES spectrum is influenced by spectral, physical and chemical interferences and suitable procedures are to be followed to undertake analytical determinations using ICP-AES.

10.10 TERMINAL QUESTIONS

1. State the principle of atomic emission spectrometry based on induced coupled plasma.
2. Enlist different types of plasma sources used for atomic emission spectrometry and state the sources of their energies.
3. Explain the working of a Frit nebuliser.
4. What property of helium makes it a potential gas to be used in a plasma source?
5. Why nitrogen gas is generally not used as a plasma gas in plasma based atomic emission spectrometry?
6. Briefly describe the working of a polychromator.
7. Enlist the advantages of ICP-AES method that makes it widely applicable for quantitative analysis.

10.11 ANSWERS

Self Assessment Questions

1. The following atomisation-excitation sources are used in atomic emission spectrometry
 - dc arc,
 - ac spark,
 - universal arc-spark,
 - rotating electrodes,
 - lasers
 - dc plasmas,
 - microwave plasmas,
 - inductively coupled plasma (ICP)
2. The different components of ICP torch and their functions are as follows.
Quartz tube: Inlet for the plasma gas and the nebulised sample.
Radio frequency power generators: Generate radiofrequencies to power the plasma.
Work coil: Generates magnetic field which provides a mechanism of energy transfer to the plasma.
3. While preparing samples for ICP-AES using acid digestion method the following precautions should be observed:
 - i) The possible loss of volatile elements and volatile compounds of elements should be avoided.
 - ii) The quantity of acid or flux in the solution must be as low as possible so as not to cause perturbation of the plasma.

- The slew scan instruments are sequential spectrometers used for AES. In these instruments the monochromator or the detector and slit combination are moved in such a way that they quickly reach on to a wavelength of interest for a given analyte and then slowly scan around it in small steps.

These help in reducing the analysis times and improve the accuracy and precision of the measurement.

- Persistent lines:** These are the emission spectral lines that persist even when the concentrations of the respective elements are progressively reduced to zero.

Characteristic lines: These are the characteristic groupings such as doublets, triplets, groups of doublets, etc. in the atomic emission spectrum of an element.

Terminal Questions

- The analyte sample is introduced into the centre of the plasma as an aerosol with the help of a nebuliser using argon flow. In the plasma the sample undergoes various transformations like desolvation, vaporization, atomisation, ionisation and excitation. As the energy of the plasma source is quite high it ensures the excitation of the atoms of all the elements present in the sample which then relax by emitting EM radiation of characteristic wavelengths of different elements. The emitted radiation are then utilised for the qualitative and quantitative determinations of the analyte.
- The three types of plasma sources and the sources for their power are as given below.

Plasma Source	Source of power
The inductively coupled plasma (ICP)	Radiofrequency
The direct current plasma (DCP)	Direct current
The microwave induced plasma (MIP)	Microwaves

- In a frit nebulizer the sample solution is pumped to a glass frit membrane, consisting of a porous coral like synthetic material. The argon gas passes through the membrane and converts the sample into an aerosol spray. This is then directed into the plasma.
- The high ionisation energy of helium (24.6 eV) makes it a potential gas to be used in plasma source.
- The nitrogen gas is generally not used as a plasma gas in plasma based atomic emission spectrometry because the excited nitrogen emits a complex band spectrum that can cause undesirable spectral interference.
- Polychromator is a type of simultaneous spectrometer. It has a fixed diffraction grating monochromator and multiple 'exit slits' with associated photomultipliers. Each of the photomultiplier is optimized to detect a specified wavelength corresponding to an element of interest. The emission radiation from the source is dispersed by the grating and sent through different exit slits to be detected by appropriate photomultiplier tube.

7. The wide applicability of ICP-AES in the quantitative analysis of various materials can be attributed to the following advantages.
- Rapid and simultaneous multi-element analysis.
 - Lack of chemical interferences.
 - High temperature of the excitation source : 5000 to 10000K.
 - Low sample requirements.
 - Absence of self absorption, the cause of non-linear calibration plots in FES.
 - Validity of calibration curves over 4 to 6 orders of magnitude.
 - Low detection limits: 1 to 100 ng/g or $\mu\text{g/l}$ (part per billion).
 - Good accuracy and precision: relative standard deviation of about 1 per cent.
 - Applicability to elements that are difficult to be determined by AAS: B, C, Ce, La, Nb, Pr, S, P, Ti, Ta, V and Zr can also be measured.

