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DETERMINATION OF TRACE ELEMENTS BY ATOMIC SPECTROMETRY

NATIONAL INSTITUTE OF HYDROLOGY
JAL VIGYAN BHAWAN
ROORKEE - 247 667
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CONTENTS

LIST OF FIGURES

ABSTRACT

The report describe some basic concepts, instrumentation and techniques of atomic spectrometry. In particular, attention is given to atomic absorption and atomic emission spectrometric techniques.

Although atomic absorption is a very sensitive technique, with detection limits in the ppm range, flame interference at extremely low concentrations has been the major source of problems. Recently, systems have been developed to overcome this problem by the introduction of nonflame atomizers, such as the graphite furnace. With flameless techniques, the detection limits are usually enhanced by a factor of 10^3. However, this technique does not replace the conventional flame method, but is regarded as a supplement for special studies. Being quicker and more precise, the conventional flame technique is given preference for routine analysis and automation.

The most promising development in the field of emission spectroscopy is the new source of excitation known as a plasma i.e., an electrically generated luminous gas containing a significant fraction of ionized atoms or molecules in inert gas. The inductively coupled plasma (ICP) derives its sustaining power by induction from high-frequency magnetic fields. It has been reported that the ICP has virtually ideal characteristics for simultaneous multi-element determinations.

The report has been divided into four chapters. Chapter 1 describe some fundamental concepts of atom and the atomic processes involved in various atomic spectrometric techniques. More detailed information about atomic absorption and atomic emission spectroscopy techniques have been presented in chapter 2 and 3 respectively. Important comparison criteria for selecting a particular technique for a particular analytical problem have been discussed in chapter 4. The report ends with some important references on the topic.

1.0 INTRODUCTION

The rapid development of sophisticated instrumentation coupled with concern over trace quantities of individual constituents has resulted in the application of analytical procedures using advanced instrumentation for the analysis of natural and wastewaters. Both the analyst and the scientist need to be aware of the availability of such advanced instrumentation and to have knowledge regarding its applicability to the analysis of trace elements.

The most commonly used techniques for trace element analysis in water and wastewaters are based on atomic spectrometry. As the name atomic spectrometry implies, these techniques involve electromagnetic radiation that is absorbed and/or emitted from atoms of a sample. By using atomic spectrometry techniques, meaningful quantitative and qualitative information about a sample can be obtained. In general, quantitative information is related to the amount of electromagnetic radiation that is emitted or absorbed while qualitative information is related to the wavelength at which the radiation is absorbed or emitted.

The science of atomic spectroscopy has provided three techniques for analytical use,

- atomic absorption spectroscopy
- atomic emission spectroscopy
- atomic fluorescence spectroscopy

Out of these three techniques the first two techniques i.e. atomic absorption spectroscopy and atomic emission spectroscopy are the most widely used techniques as far as water and wastewater laboratories are concerned. In order to understand the relationship of these techniques to each other, it is necessary to have an understanding of the atom itself and of the atomic process involved in each techniques.

The atom consists of a nucleus surrounded by electrons. Every element has a specific number of electrons which are associated with the atomic nucleus in an orbital structure which is unique to each element. The lowest energy, i.e., the most stable electronic configuration of an atom, is the normal orbital configuration of an atom, and is known as ground state configuration. If energy of the right magnitude is applied to an atom, the energy will be absorbed by the atom, and an outer electron will be promoted to a higher energy state or excited state. As this state is unstable, the atom will immediately and spontaneously return to its ground state configuration and radiant energy equivalent to the amount of energy initially absorbed in the excitation process will be emitted (Figure 1). The excitation process in step 1 is forced by supplying energy, however, decay process in step 2, involving the emission of light, occurs spontaneously.

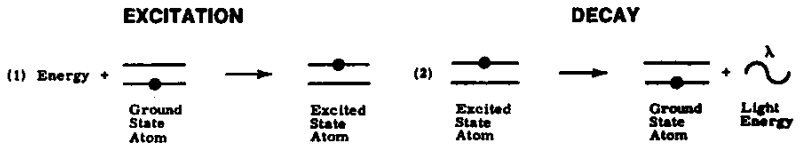

Figure 1: Excitation and Decay Processes

The wavelength of the emitted radiant energy is directly related to the electronic transition which has occurred. Since every element has a unique electronic structure, the wavelength of light emitted is unique property of each individual element. As the orbital configuration of a large atom may be complex, there may be many electronic transitions possible, each transition resulting in the emission of a characteristic wavelength of light, as shown in Figure 2.

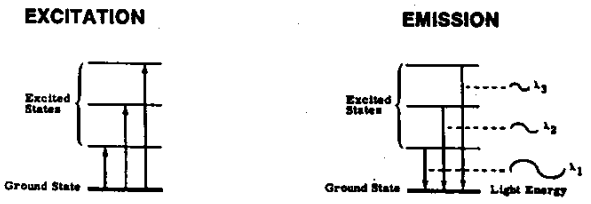

Figure 2: Energy Transitions

The process of excitation and decay to the ground state is involved in all the three fields of atomic spectroscopy, but either the energy absorbed in the excitation process or the energy emitted in the decay process is measured and used for analytical purposes.

In atomic absorption spectrometry (AAS), the quantity of interest is the amount of light which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed also increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element can be made.

In atomic emission spectrometry (AES), the intensity of light emitted at specific wavelengths is measured and used to

determine the concentrations of the elements of interest.

In atomic fluorescence spectrometry, ground state atoms created in a flame are, excited by focusing a beam of light into the atomic vapor. Instead of looking at the amount of light absorbed in the process, however, the emission resulting from the decay of the atoms excited by the source light is measured. The intensity of this fluorescence increases with increasing atom concentration, providing the basis for quantitative determination.

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 maximize lamp intensity with atomic fluorescence since sensitivity is directly related to the number of excited atoms which is a function of the intensity of the excited radiation.

An instrumental arrangement of the three techniques described above is shown in Figure 3.

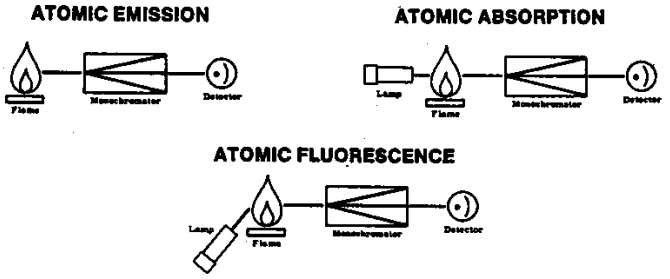

Figure 3: Atomic Spectroscopy Systems

This report describes some basic concepts, instrumentation and techniques about atomic spectrometry for the determination of trace elements.

2.0 ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption is a process that occurs when a ground state atom absorbs energy in the form of a light of a specific wavelength and is elevated to an excited state or higher energy state. The amount of light energy absorbed at this wavelength increases as the number of atoms of that particular element in the light path increases. This relationship between the amount of light absorbed and the concentration of analyte present in the standard is used to determine unknown concentration by measuring the amount of light absorbed. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

2.1 Flame Atomic Absorption

The basic instrumentation for atomic absorption requires a primary light source which emits the sharp atomic lines of the element to be determined, a sample cell which can generate atomic vapor in the light beam from the source, a monochromator to isolate the specific wavelength of light, a detector on which isolated wavelength of light is directed. This detector is a photomultiplier tube, which produces an electrical current dependent on the light intensity. The electrical current from the photomultiplier tube is then amplified and processed by the instrument electronics to produce a signal. This signal is further processed to produce an instrument readout directly in concentration units. The lay out of atomic absorption spectrometer is shown in Figure 4.

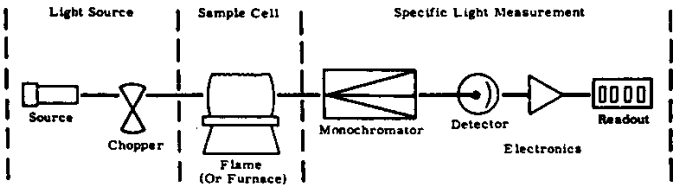

Figure 4: Lay out of Atomic Absorption Spectrometer

2.1.1 Light source

Light source normally used in atomic absorption are the hollow cathode lamp and the electrodeless discharge lamp. The hollow cathode lamp is an excellent, bright line source for most of the elements determinable by atomic absorption. Figure 5 shows the construction design of hollow cathode lamp. The cathode of

the lamp is a hollowed-out cylinder of the metal whose spectrum is to be produced. Anode and cathode are sealed in a glass cylinder normally filled with either neon or argon gas at low pressure and a window transparent to the emitted radiation is fused to the end of the cylinder.

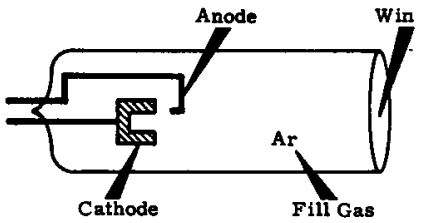

Figure 5: Hollow Cathode Lamp

When an electrical potential is applied between anode and cathode, some of the fill gas atoms are ionized. The positively charged fill gas ions accelerate through the electrical field to collide with the negatively charged cathode and dislodge individual metal atoms in a process called sputtering. Sputtered metal atoms are then excited to an emission state through a kinetic energy transfer by impact with fill gas ions.

For most elements, the hollow cathode lamp is a completely satisfactory source for atomic absorption with the exception of volatile elements where low intensity and short lamp life are a problem. The atomic absorption determination of these elements can often be dramatically improved with the use of brighter, more stable sources such as the electrodeless discharge lamp (Figure 6).

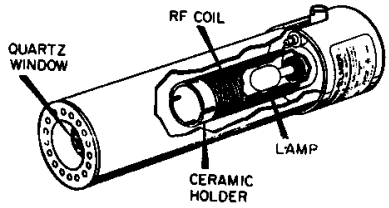

Figure 6: Electrodeless Discharge Lamp

In electrodeless discharge lamp a small amount of the metal or salt of the element for which the source is to be used

is sealed inside a quartz bulb. This bulb is placed inside a ceramic cylinder on which the antenna from a radio frequency generator is coiled. When an RF field of sufficient power is applied, the coupled energy will vaporize and excite the atoms inside the bulb, causing them to emit their characteristic spectrum.

2.1.2 Sample cell or atomizer

The sample cell, or atomizer, of the spectrometer must produce groundstate atoms (free atoms) necessary for atomic absorption to occur. This involves the application of thermal energy to break the bonds that holds atoms together as molecules. The most routine and widely applied sample atomizer is the flame. Here the source of energy for free atom production is heat, most commonly in the form of air-acetylene flame. The sample is aspirated through a nebulizer and sprayed as a fine aerosol into the mixing chamber. The sample aerosol is mixed with fuel and oxidant gases and finally carried to the burner head, where combustion and sample atomization takes place.

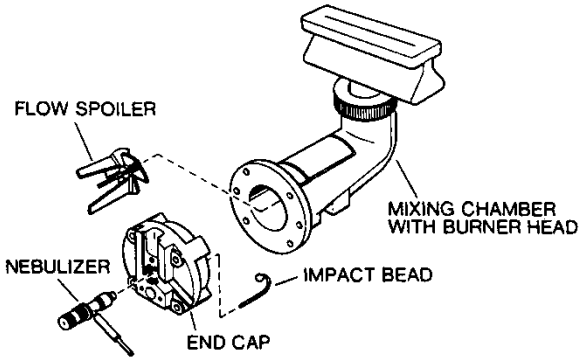

Figure 7: Atomic Absorption Burner System

2.1.3 Monochromator

Light from the source is focussed on the sample and directed to the monochromator, where the wavelengths of light are dispersed and the analytical line of interest is focussed onto the detector. Particular care must be taken in the monochromator to avoid excessive light loss. A typical monochromator design is shown in Figure 8. Light from the source enters the monochromator at the entrance slit and is directed to the grating where dispersion takes place. By adjusting the angle of grating, a selected emission line from the source can be allowed to pass through the exit slit and fall onto the detector.

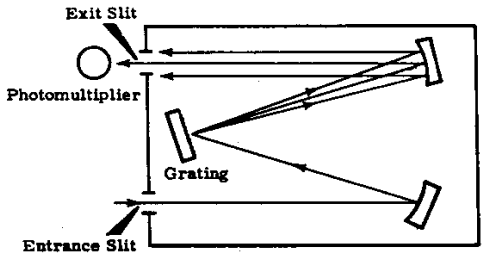

Figure 8: Monochromator

2.1.4 Limitations

The major limitation of atomic absorption using flame sampling is that the burner nebulizer system is a relatively inefficient sampling device. Only a small fraction of sample reaches the flame, and the atomized sample passes quickly through the light path. In order to atomize the whole sample and to retain the atomized sample in the light path for an extended period to enhance the sensitivity of the technique, the flame is replaced by an electrically heated graphite tube. Sample is introduced directly into the tube, which is then heated in a programmed series of steps to remove the solvent and major matrix components and then to atomize the remaining sample. In this way all of the analyte is atomized and atomized atoms are retained within the tube (and the light path, which passes through the tube) for an extended period. As a consequence of this sensitivity and detection limits are significantly improved.

Graphite furnace analysis times are longer than those for flame sampling, and fewer elements can be determined using GFAA. However, the enhanced sensitivity of GFAA and the ability of GFAA to analyse very small samples and directly analyse certain type of solid samples significantly expand the capabilities of GFAA.

2.2 Graphite Furnace Atomic Absorption (GFAA)

The most advanced and widely used high sensitivity sampling technique for atomic absorption is the graphite furnace. In this technique, a tube of graphite is located in the sample compartment of the spectrometer, with the light path passing through it. A small volume of sample is placed into the tube through a sample injection hole located in the center of the tube wall. The tube is then heated through a programmed temperature sequence until the analyte present in the sample is dissociated into atoms and atomic absorption occurs. As atoms are created and diffuse out of the tube, the absorption rises and falls in a peak shaped signal which is used as the analytical signal for quantification.

2.2.1 Major Components

The graphite furnace is made up of following three major components:

- atomizer
- power supply
- programmer

The atomizer is located in the sampling compartment of the atomic absorption spectrometer, where sample atomization and light absorption takes place. The power supply controls power and gas flows to the atomizer under the direction of the programmer, which is usually built into the power supply or spectrometer. A description of each of these major components is as follows:

2.2.1.1 Atomizer

A basic graphite furnace atomizer is comprised of the following components:

- graphite tube
- electrical contacts
- enclosed water cooled housing
- inert purge gas controls

A graphite tube is normally the heating element of the graphite furnace. The cylindrical tube is aligned in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few microliter (usually 5-50) of sample is measured and dispensed through a hole in the center of the tube wall onto the inner tube wall or a graphite platform. The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential is applied to the contacts which causes current to flow through the tube resulting in the heating of the tube and the sample.

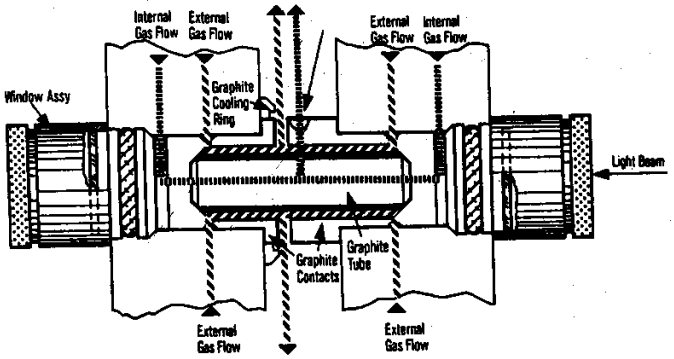

Figure 9: Graphite Furnace Atomizer

The entire assembly is mounted within an enclosed, water cooled housing. Quartz windows at each end of the housing allow light to pass through the tube. The heated graphite tube is protected from air oxidation by the end windows and two streams of argon. An external gas flow surrounds the outside of the tube, and a separately controllable internal gas flow purges the inside of the tube. The system should regulate the internal gas flow so that the internal gas flow is reduced or, preferably, completely interrupted during atomization. This helps to maximize sample residence time in the tube and increases the measurement signal.

2.2.1.2 Power supply and programmer

The power supply and programmer perform the following functions:

- electrical power control
- temperature program control
- gas flow control
- spectrometer function control

The power supply controls the electrical current applied to the graphite tube, which causes heating. The temperature of the tube is controlled by a user specified temperature program. Through the programmer the user can enter a sequence of selected temperatures and time to carefully dry, pyrolyze and finally atomize the sample. The program may also include setting for the internal inert gas flow rate and some spectrometer functions.

2.2.2 Graphite furnace analysis

A graphite furnace analysis consists of measuring and dispensing a known volume of sample into the furnace. The sample is then subjected to a multi-step temperature program. When the temperature is increased to the point where sample atomization occurs, the atomic absorption measurement is made. Variables under operator control include the volume of sample placed into the furnace and heating parameters for each step. These parameters include,

- temperature final temperature during step
- ramp time time for temperature increase
- hold time time for maintaining final temperature
- internal gas type and flow rate

The maximum volume of sample depends on the tube configuration. Where the graphite platform is not used, sample volume upto 100 ul can be used. With the platform in place, a sample volume of less than 50 ul is recommended. A convenient sample volume for most analysis is 20 ul. Where larger volumes are required, i.e., for improved detection limits, multiple injections can be used with appropriate drying and pretreatment steps between each injection to increase the effective sample

size.

The use of a autosampler is strongly recommended for dispensing samples into a graphite furnace. While skilled operators may obtain reasonable reproducibility by manual injection on a short term basis, auto samplers have been proven to provide superior results. With many graphite furnace systems, autosamplers can also generate working standards from a stock standard solution, add appropriate reagents and provide method of additions analysis or recovery measurements all automatically.

2.2.3 Temperature program

Normally the following five steps make up the typical graphite furnace temperature program as shown in Figure 10:

- drying
- pyrolysis
- cool down
- atomization
- clean out and cool down

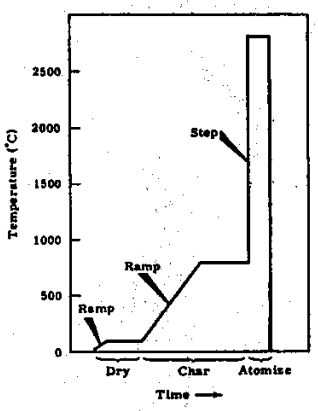

Figure 10: Graphite Furnace Temperature Program

2.2.3.1 Drying step

Once the sample is placed in the furnace, it must be dried at a sufficiently low temperature to avoid sample spattering, which would result in poor analytical precision. Temperature around 100-120°C are common for aqueous solution.

Use of a temperature ramp provides a variable time over which the temperature is increased. A longer ramp time provides a slower, more gentle increase in heating. When a platform versus the tube walls provides a natural ramping effect. Therefore ramp times of only 1 second are usually used when the sample is to be atomized from the tube wall.

After the temperature ramp, the furnace is held at the selected drying temperature until drying is complete. Since only a few microliter of sample is used, the drying hold time is usually less than a minute.

During the dry process, the internal gas flow normally is left at its default value (300 ml per minute) to purge the vaporized solvent from the tube.

2.2.3.2 Pyrolysis step

The purpose of the pyrolysis step (some times referred to as ashing, char or pretreatment step) is to volatilize inorganic and organic matrix components selectively from the sample, leaving the analyte element in a less complex matrix for analysis. During this step, the temperature is increased as high as possible to volatilize matrix components but below the temperature at which analyte loss would occur.

The internal gas flow is again left at default value i.e. 300 ml/minute in the pyrolysis step, to drive off volatilized matrix materials. For some sample types, it may be advantageous to charge the internal gas, e.g., to air, during the pyrolysis to aid in the sample decomposition.

2.2.3.3 Cool down step

For many furnace systems, the heating rate is a function of the temperature range to be covered. As the temperature range is increased, the rate of heating also increases. The use of a cool down step prior to atomization maximizes the heating rate and extends the isothermal zone within the tube immediately after heating. The extended isothermal zone has been shown to improve sensitivity and reduce peak tailing for a number of elements, including those which characteristically are difficult to atomize in the graphite furnace.

2.2.3.4 Atomization step

The purpose of the atomization step is to produce an atomic vapor of the analyte element, thereby allowing atomic absorption to be measured. The temperature in this step is increased to the point where dissociation of volatilized molecular species occurs. For atomization, it is desirable to increase the temperature as quickly as possible. Therefore, ramp times normally will be set to minimum values to provide the highest heating rate. It is also desirable to reduce or, preferably to totally interrupt the internal gas flow during atomization. This increases the residence time of the atomic vapor in the furnace, maximizing sensitivity and reducing some interference effects. At the beginning of this step, the spectrometer read function is triggered to begin the measurement of light absorption.

2.2.3.5 Clean out and cool down steps

After atomization, the graphite furnace is heated to still higher temperatures to burn off any sample residue which may remain in the furnace. An optional cool down step then allow the furnace to return to near ambient temperature prior to the introduction of the next sample.

2.2.4 Measuring the graphite furnace signals

In flame atomic absorption, the absorption signal is steady state. That is, as long as solution is aspirated into the flame, a constant absorbance is observed. For graphite furnace analysis, however, the signal is transient. As atomization begins, analyte atoms are formed and the signal increases, reflecting the increasing atom population in the furnace. The signal will continue to increase until the rate of atom generation becomes less than the rate of atom diffusion out of the furnace. At that point, the falling atom population results in a signal which decreases until all atoms are lost and the signal has fallen to zero. To determine the analyte content of the sample, the resulting peak-shaped signal must be quantitated.

2.2.4.1 Peak height measurement

Peak height is a measure of maximum atom population which occurred in the furnace during atomization. If matrix components in the sample affect the rate of atom formation, the maximum atom population and the peak height are also affected, as shown in Figure 11 for the determination of lead in blood.

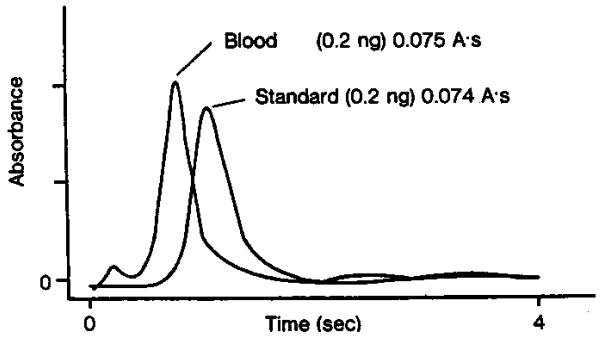

Figure 11: Effect of Matrix on Peak Height and Area

This susceptibility to matrix effects makes graphite furnace AA vulnerable to interferences when peak height measurement is used for quantitation. Therefore, peak height measurement are seldom used with modern graphite furnace AA systems.

2.2.4.2 Peak area measurement

Modern instrumentation provides the capability to integrate absorbance during the entire atomization period, yielding a signal equal to the integrated peak area, that is, the area under the peak signal. If the temperature in the furnace is constant during the measurement process, the peak area will represent a count of all atoms present in the sample, regardless of whether the atoms were generated early or late in the atomization process. Integrated peak area measurements are independent of the atomization rate, and are therefore much less subject to matrix effects. As a result, peak area is preferred for graphite furnace analysis.

2.2.5 L'vov platform

B.V.L'vov, one of the pioneers in graphite furnace atomic absorption, developed the use of a small platform made from a flat piece of solid pyrolytic graphite which is placed in the bottom of the graphite tube (Figure 12). Sample is pipetted into a shallow depression in the platform from the top of the graphite tube. The presence of L'vov platform helps to eliminate non-spectral interferences.

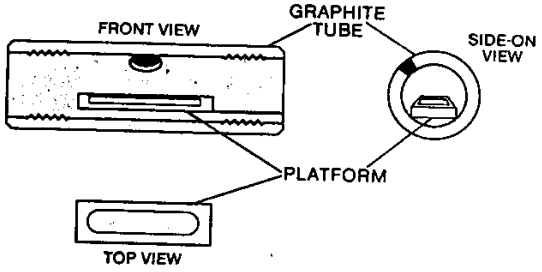

Figure 12: L'vov Platform

The platform is constructed entirely of solid pyrolytic graphite, and therefore resists any tendency for solution to soak into the surface prior to or during drying. The platform also tolerates high acid concentrations.

To understand the concept of the L'vov platform, let us first consider what happens when analyte is atomized directly from the graphite tube wall when no platform is used. At the beginning of the atomization step, the temperature of the tube wall increases rapidly. The sample, which is in direct contact with the tube wall, will immediately experience the increase in wall temperature at which analyte atoms are produced and therefore, atoms are released from the hot tube surface into an inert gas atmosphere, the temperature of which lags behind that

of the tube wall and which is cool relative to the surface. This sudden cooling inhibits atomization of the vaporized molecular species, and nonspectral interference results.

By contrast, when sample is placed on a L'vov platform, the sample experiences the temperature of the platform, and not the temperature of the tube wall. Since the flat platform is by design in poor contact with the round tube surface, the platform is heated primarily by radiant energy rather than convective energy. This means that the platform will heat more slowly than the graphite tube. During the rapid heating which occurs at atomization, when the platform does finally reaches the atomization temperature for the analyte, atoms are released into the furnace environment the temperature of which is similar to that of the platform and therefore atomization takes place.
Figure 10 shows the atomization signals of a sample volatilized from the tube wall and from a L'vov platform versus the tube temperature.

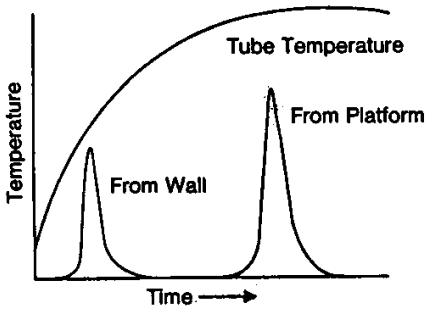

Figure 13: Tube Wall and platform Temperature profiles

When the wall of the furnace tube reaches a temperature at which the analyte will vaporize, the metal is driven from the surface into the gas phase. Both the temperature at which the analyte first starts to volatilize and the rate at which it volatilizes will depend on the quantity and the specific nature of the matrix constituents.

Since the platform is heated by radiation from the walls of the tube, the temperature of the sample on the platform is delayed relative to the wall of the tube and, therefore, to the vapor within the tube. Instead of volatilizing the analyte as the temperature is changing, appropriate conditions can be found to volatilize the analyte after the tube wall and the gas phase reached a more stable or steady state condition.

3.0 ATOMIC EMISSION SPECTROSCOPY

Atomic emission is a process in which the light emitted by excited atoms or ions is measured. The emission occurs when sufficient thermal or electrical energy is available to excite a free atom or ion to an unstable energy state. Light is emitted when the atom or ion returns to a more stable configuration or the ground state. The wavelengths of light emitted are specific to the elements which are present in the sample.

The basic instrument used for atomic emission is very similar to that used for atomic absorption with the difference that no primary light source is used for atomic emission. One of the more critical components for atomic emission instrument is the atomization source because it provides sufficient energy to excite the atoms as well as to atomize them. Most commonly atomization source used in emission instrument is ICP discharge.

3.1 ICP Discharge

The ICP is an argon plasma maintained by the interaction of an RF field and ionized argon gas. The ICP is reported to reach temperatures as high as 10,000 K, with the sample experiencing useful temperature between 5500 K and 8000 K. These temperatures allow complete atomization of elements, minimizing chemical interference effects.

The plasma is formed by a tangential stream of argon gas flowing between two quartz tubes, as shown in Figure 14. A copper coil, called the load cell, surrounds the top end of the torch and is connected to a radio frequency (RF) generator.

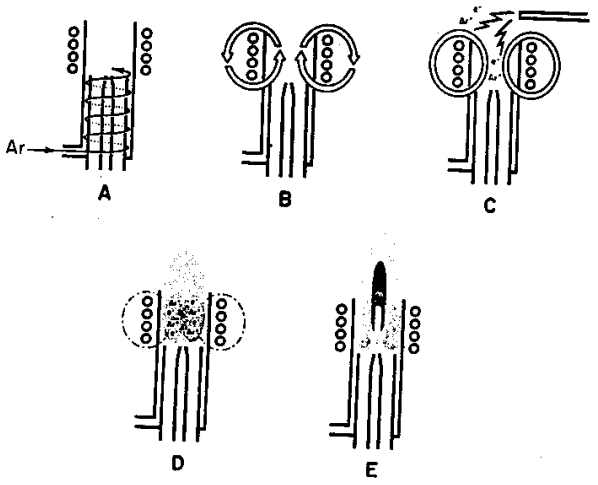

Figure 14: Cross Section of an ICP Torch and Load Coil

When RF power (typically 700-1500 watts) is applied to the load cell, an alternating current moves back and forth within the coil, or oscillates, at a rate corresponding to the frequency of the generator. In most ICP instruments this frequency is either 27 or 40 megahertz (MHz). This RF oscillation of the current in the coil causes RF electric and magnetic fields to be set up in the area at the top of the torch. The plasma is created when the argon is made conductive by exposing it to an electrical discharge which creates seed electrons and ions. These electrons are then caught up in the magnetic field and accelerated by them. Adding energy to the electrons by the use of a coil in this manner is known as inductive coupling. These high energy electrons in turn collide with other argon atoms, stripping off still more electrons. This collisional ionization of the argon gas continues in a chain reaction, breaking down the gas into a plasma consisting of argon atoms, electrons and argon ions, forming what is known as inductively coupled plasma (ICP) discharge. The ICP discharge is then sustained within the torch and load coil as RF energy is continuously transferred to it through the inductive coupling process.

Figure 15 shows a cross-sectional view of the discharge along with the nomenclature for different regions of the plasma.

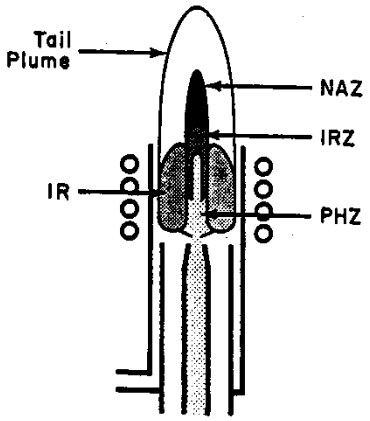

Figure 15: Zones of the ICP: IR-Induction Region; PHZ-Preheating Zone; IRZ-Initial Radiation Zone; NAZ-Normal Analytical Zone

As viewed from the top, the plasma has a circular doughnut shape. The sample is injected as an aerosol through the center of the doughnut. The body of the doughnut is called the induction region (IR) because this is the region in which the inductive energy transfer from the load coil to the plasma takes

place. This is also the area from which most of the white light, called the argon continuum, is emitted. This characteristic of the ICP confines the sample to a narrow region and provides an optically thin emission source and a chemically inert atmosphere. This results in a wide dynamic range and minimal chemical interactions in an analysis.

Most samples begin as liquids that are nebulized into an aerosol, a very fine mist of sample droplets, in order to be introduced into the ICP. The sample aerosol is then carried into the center of the plasma by the nebulizer argon flow. Figure 16 depicts the processes that take place when a sample droplet is introduced into an ICP discharge.

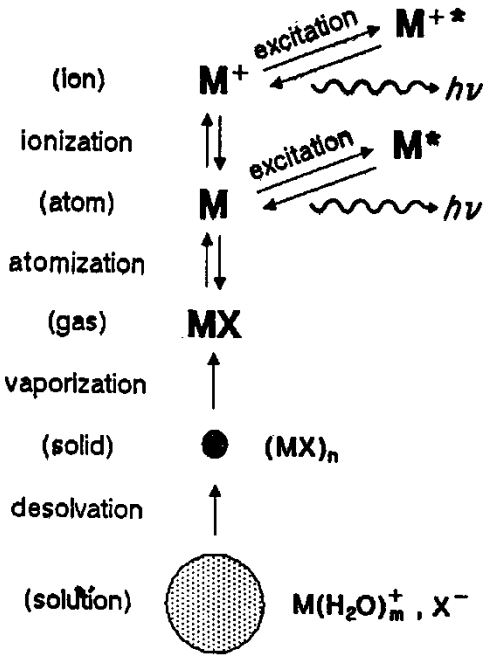

Figure 16: Processes Taking Place in an ICP Discharge

The first function of the high temperature plasma is to remove the solvent from, or desolate, the aerosol, usually leaving the sample as microscopic salt particles. The next steps

involve decomposing the salt particles into a gas of individual molecules (vaporization) that are then dissociated into atoms (atomization). These processes, which occur predominantly in the preheating zone (PHZ) are the same processes that take place in flames and furnaces used for atomic absorption spectrometry.

Once the sample aerosol has been desolvated, vaporized, and atomized, the plasma has one, or possible two, functions to perform. These functions are excitation and ionization. In order for an atom or ion to emit its characteristic radiation, one of its electrons must be promoted to a higher energy level through an excitation process. Since many elements have their strongest emission lines emitted from the ICP by excited ions, the ionization process may also be necessary for some elements. The excitation and ionization processes occur predominantly in the initial radiation zone (IRZ) and the normal analytical zone (NAZ). The NAZ is the region of the plasma from where analyte emission is typically measured.

It is generally believed that most of the excitation and ionization in the ICP takes place as a result of collisions of analyte atoms with energetic electrons.
There is also some speculation about the role of argon ions in these processes. In any case, the chief analytical advantages of the ICP over other emission sources are derived from the ICP's ability to vaporize, atomize, excite, and ionize efficiently and reproducibly a wide range of elements.

One of the important reasons for the superiority of the ICP over flames and furnaces is in the high temperature within the plasma. Figure 17 shows approximate temperatures for different regions of the ICP.

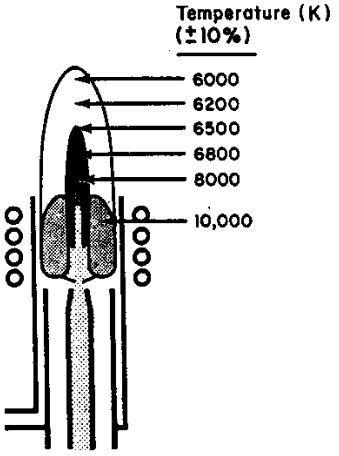

Figure 17: Temperature Regions of ICP Discharge

While flames and furnaces have upper temperature ranges of the order of 3000°C, the gas temperature in the center of the ICP is about 6000°C. Besides improving excitation and ionization efficiencies, the higher temperature of the ICP also reduces or eliminates many of the chemical interferences found in flames and furnaces.

3.2 Instrumentation

In ICP-AES, the sample is first injected into the instrument as a stream of liquid sample through a peristaltic pump where the liquid is converted into an aerosol through a process known as nebulization. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized, and excited and/or ionized by the plasma. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration units. The layout of a typical ICP-AES instrument is shown in Figure 18.

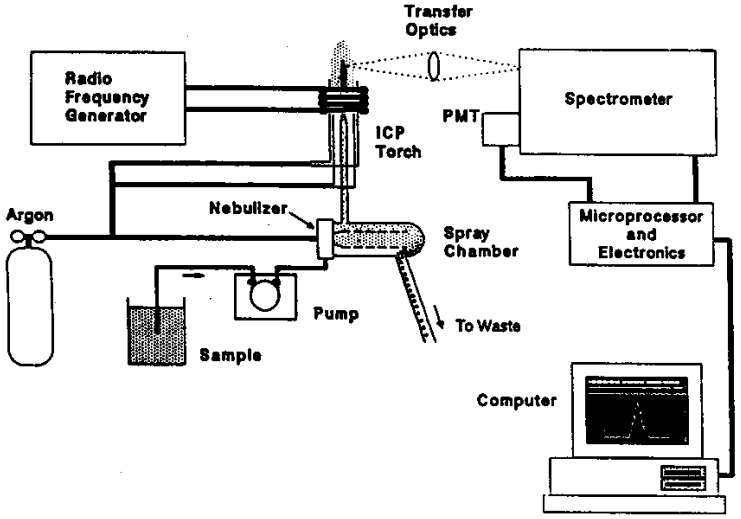

Figure 18: Layout of a Typical ICP-AES Instrument

3.2.1 Sample introduction

3.2.1.1 Nebulizers

Nebulizers are devices that convert a liquid into an aerosol that can be transported to the plasma. The nebulization process is one of the critical steps in ICP-AES. Because only

small droplets are useful in the ICP, the ability to produce small droplets for a wide variety of samples largely determines the utility of a nebulizer for ICP-AES. The forces commonly used to break up a liquid into an aerosol are pneumatic forces and ultrasonic mechanical forces. Most commercial ICP nebulizers are of the pneumatic type. These nebulizer use high-speed gas flow to create an aerosol.

One of the first nebulizers to be used for ICP-AES is the concentric nebulizer shown in Figure 19. In this nebulizer, the solution is introduced through a capillary tube to a low-pressure region created by a gas flowing rapidly past the end of the capillary. The low pressure and high speed gas combine to break up the solution into an aerosol.

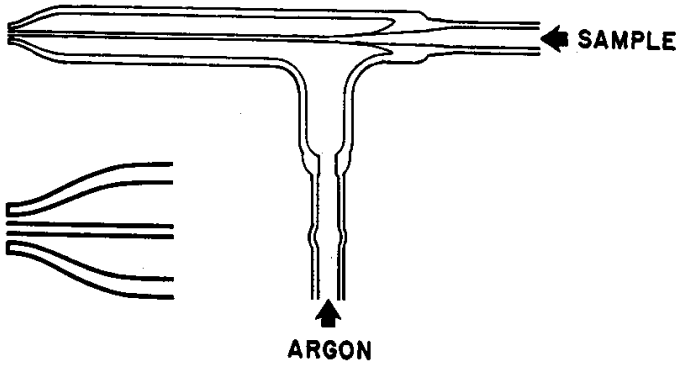

Figure 19: Concentric Nebulizer

A second type of pneumatic nebulizer is the cross-flow nebulizer shown in Figure 20.

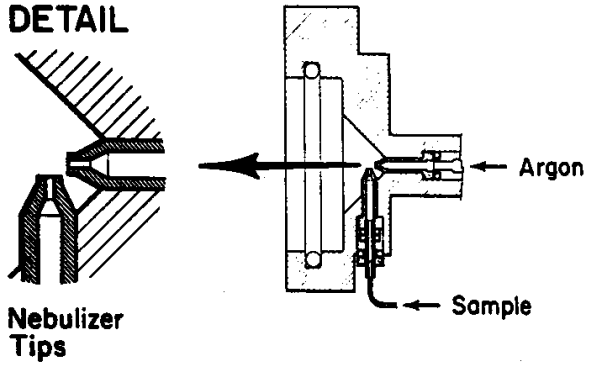

Figure 20: Cross-Flow Nebulizer

In this nebulizer a high speed stream of Argon gas is directed perpendicular to the tip of a capillary tube (in contrast to the concentric nebulizer where the high-speed gas is parallel to the capillary). The solution is either drawn up through the capillary tube by the low-pressure region created by the high-speed gas or forced up the tube with a pump. In either case, contact between the high speed gas and the liquid stream causes the liquid to break into an aerosol. Cross flow nebulizers are generally not as efficient as concentric nebulizers in creating the small droplets needed for ICP analysis. However, the larger diameter liquid capillary and longer distance between liquid and gas injectors minimize clogging problems.

The third type of pneumatic nebulizer used for ICP-AES is the Babington nebulizer shown in Figure 21. In this case the liquid is allowed to flow over a smooth surface with a small hole in it. High speed argon gas emanating from the hole shears the sheet of liquid into small drops. This nebulizer is the least susceptible to clogging and can nebulize very viscous liquids.

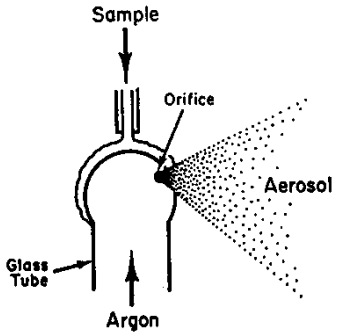

Figure 21: Babington Nebulizer

A variation of the Babington nebulizer is the V-groove nebulizer shown in Figure 22.

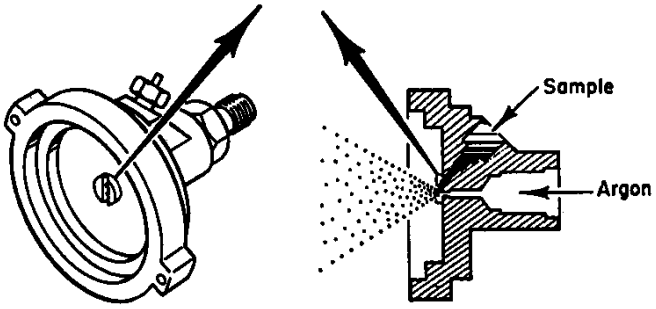

Figure 22: V-groove Nebulizer

In the V-groove nebulizer, the sample flows down a groove which has a small hole in the center for the nebulizing gas. This nebulizer is being used increasingly for nebulization of solutions containing high salt and particulate concentrations.

3.2.1.2 Spray chambers

Since only very small droplets in the aerosol are suitable for injection into the plasma, a spray chamber is placed between the nebulizer and the torch. The primary function of the spray chamber is to remove large droplets from the aerosol. A secondary purpose of the spray chamber is to smooth out pulses that occur during nebulization, often due to pumping of the solution. Some typical ICP spray chamber designs are shown in Figure 23.

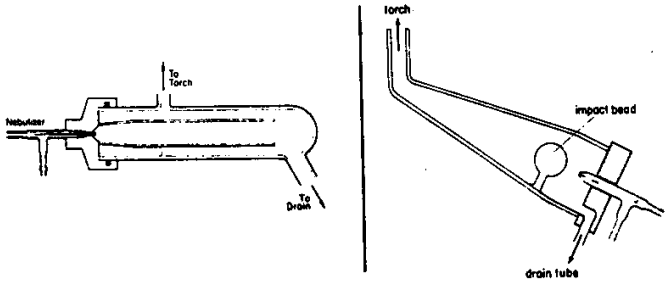

Figure 23: Spray Chambers : A - Scott Double Pass Type;
B - Conical Single Pass Type with Impact Bead

In general, spray chambers are designed to allow droplets with diameters of about 10 µm or smaller to pass to the plasma. With typical nebulizers, this droplet range constitute about 1-5% of the sample that is introduced to the nebulizer. The remaining 95-99% of the sample is drained into a waste container.

3.2.2 Production of emission

3.2.2.1 Torches

The torch contain three concentric tubes for organ flow and aerosol injection as shown in Figure 24. The spacing between the two outer tubes is kept narrow so that the gas introduced between them emerges at high velocity. The outside chamber is also designed to make the gas spiral tangentially around the

chamber as it proceeds upward. One of the functions of this gas is to keep the quartz walls of the torch cool and thus this gas flow was originally called the coolant flow. However, since this is the only gas flow needed to sustain a plasma, it is now more often referred to as the plasma flow. For argon ICP's, the plasma gas flow is usually about 7-15 liters per minute.

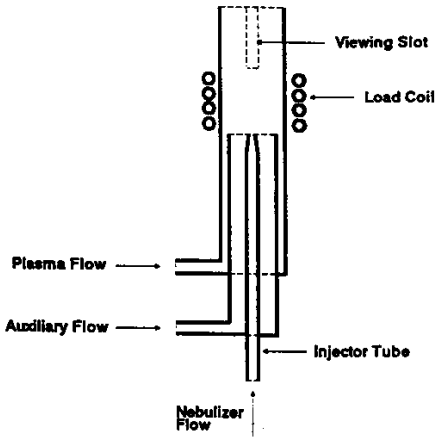

Figure 24: Torch Used for ICP-AES

The chamber between the plasma (or coolant) flow and the sample flow sends gas directly under the plasma toroid. This flow keeps the plasma discharge away from the intermediate and injector tubes and makes sample aerosol introduction into the plasma easier. In normal operation of the torch, this flow is usually about 1 liter/min. This flow is called auxiliary flow.

The gas flow that carries the sample aerosol is injected into the plasma through the central tube, or injector. Due to the small diameter at the end of the injector, the gas velocity is such that even the 1 liter/min of argon used for nebulization can punch a hole through the plasma. Since this flow carries the sample to the plasma, it is often called the sample flow. However, since it is also used as the nebulization gas, it is also referred to as nebulizer flow.

The classic ICP torch design is the one-piece torch shown in Figure 25. This torch consists of three concentric quartz tubes sealed together. This torch generally provide good plasma stability and is easy to use. The disadvantages of the one-piece torch are i) they are not resistant to corrosion by hydrofluoric acid, and ii) if the torch is damaged, usually the entire torch need to be replaced.

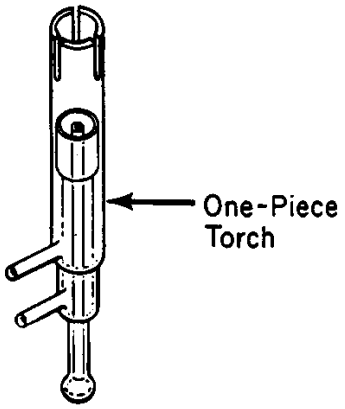

Figure 25: One Piece Torch

3.2.2.2 Radio frequency generator

The radio frequency (RF) generator is the device that provides the power for the generation and sustainment of the plasma discharge. This power, typically ranging from 600 to 1800 watts, is transferred to the plasma gas through a load coil surrounding the top of the torch. The load coil, which acts as an antenna to transfer the RF power to the plasma, is usually made from copper tubing and is cooled by water or gas during operation. Most RF generator used for ICP-AES operate at a frequency between 27 and 56 MHz.

3.2.3 Collection of emission

The radiation is usually collected by a focussing optic through a condensing lens which is then focusses the image of the plasma plume onto the entrance slit of the wavelength dispersing device. The dispersion of the different wavelength is done by a diffraction grating. When light strikes such as grating, the light is diffracted at an angle that is dependent on the wavelength of light and the line density of the grating. In general, the longer the wavelength and the higher the line density, the higher the angle of diffraction will be. Figure - shows schematically the paths that rays of two different wavelength would take when diffracted from a grating.

To separate polychromatic light predictably, the grating is incorporated in a optical instrument called a spectrometer. The function of a spectrometer is to form a light

into a well defined beam, disperse it according to wavelength with a grating, and focus the dispersed light onto a exit plane or circle. One or more exit slits on the exit plane or circle are then used to allow certain wavelengths to pass to the detector while blocking out other wavelengths.

Multielemental analysis of several elements is accomplished by using polychromator where several exit slits and detector are used in the same spectrometer. Each exit slit in a polychromator is aligned to an atomic or ionic emission line for a specific element to allow simultaneous multielement analyses. A monochromator, on the other hand, normally uses only one exit slit and detector. Monochromators are used in multielement analyses by scanning rapidly, or slewing, from one emission line to another. This is done either by changing the angle of the diffraction grating by rotating it or by moving the detector in the exit plane of the monochromator while leaving the grating in a fixed position. When the monochromator slews between lines with sufficient speed, rapid sequential multielement analysis are possible.

The most popular polychromator design consists of an entrance slit, a concave grating and multiple exit slits, all on the periphery of what is known as Rowland circle (Figure 26). For monochromator, the Czerny-Turner and Ebert mounts (Figure 27) are being used widely. These compact spectrometers have an entrance slit, a plane grating, either one (Ebert) or two (Czerny-Turner) mirrors for collimating and focussing the light, and a single exit slit.

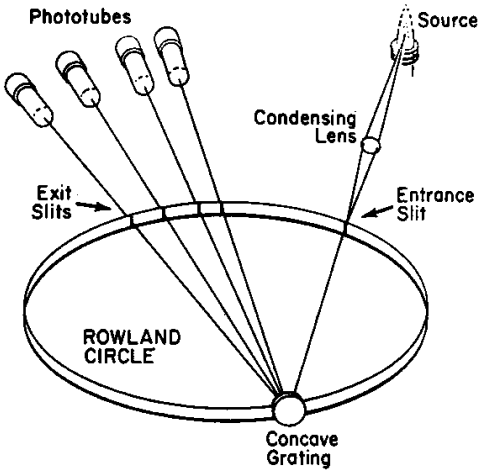

Figure 26: Paschen-Runge Mount Used in a Rowland Circle Polychromator

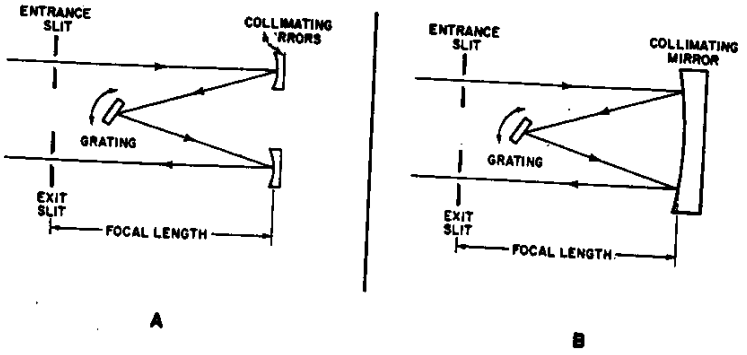

Figure 27: A - Czerny-Turner Monochromator Mount
B - Ebert Monochromator Mount

3.2.4 Detection of emission

The most widely used detector for ICP-AES is the photomultiplier tube (PMT). The PMT is a vacuum tube that contains a photosensitive material, called the photocathode, that eject electrons when it is struck by light. These ejected electrons are accelerated towards a dynode, which ejects two to five secondary electrons for every one electron which strikes its surface. The secondary electrons strike another dynode, ejecting more electrons which strike yet another dynode causing a multiplicative effect along the way. Figure 28 shows how a PMT amplifies the signal produced by a photon striking a photocathode.

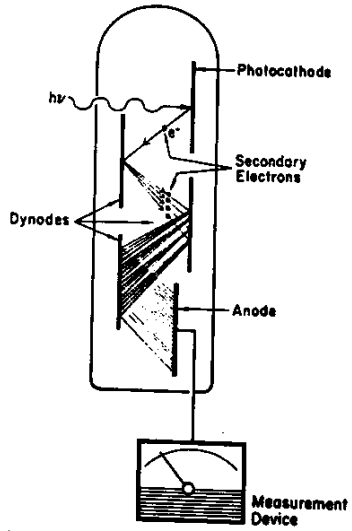

Figure 28: Layout of Photomultiplier Tube

Typical PMT's contain 9 to 16 dynode stages. The final step is the collection of the secondary electrons from the last dynode by the anode. As many as 10^8 secondary electrons may be collected as a result of a single photon striking the photocathode of a nine dynode PMT. The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT.

3.2.5 Processing of signals

The electrical current measured at the anode, which represents emission intensity, of the PMT is converted into voltage signal. Since virtually all commercial ICP-AES instruments utilize digital signal processing, the voltage signal is then converted into digital information. This digital information is then used for further processing by a computer to represent either relative emission intensity or concentration.

4.0 COMPARISON

Important criteria for selecting an analytical technique include detection limits, analytical working range, sample throughput, cost, interferences, ease of use and the availability of proven technology. These criteria are discussed in this chapter for flame AA, graphite furnace AA (GFAA), ICP emission and ICP-mass spectrometry (ICP-MS).

4.1 Detection Limit

The detection limits achievable for individual elements represent a significant criteria of the usefulness of an analytical technique for a given analytical problem. Without adequate detection limit capability, lengthy analyte concentration procedures may be required prior to analysis. Typical detection limit ranges for major atomic spectroscopy techniques are shown in Figure 29.

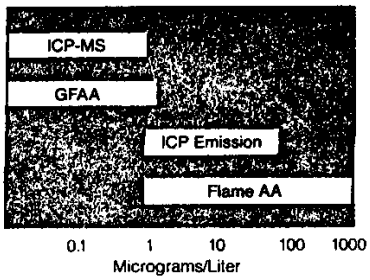

Figure 29: Detection Limit Ranges for Some Atomic Spectroscopy Techniques

Generally best detection limits are attained using ICP-MS or graphite furnace AA. Samples containing ppb level can be analysed by ICP while samples containing ppm level can be analysed by AAS.

4.2 Analytical Working Range

Analytical working range can be defined as the concentration range over which quantitative results can be obtained without having to recalibrate the system. Selecting a technique with an analytical working range and detection limits based on the expected analyte concentrations minimizes analysis times by allowing samples with varying analyte concentrations to be analysed together. A wide analytical working range also reduces sample handling requirement and minimize potential errors. Figure 30 shows typical analytical working ranges for some atomic spectroscopy techniques.

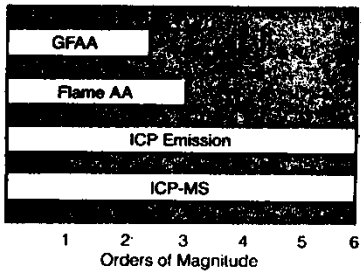

Figure 30: Analytical Working Ranges for Some Atomic Spectroscopy Techniques

4.3 Sample Throughput

Sample throughput is the number of samples which can be analysed or elements which can be determined per unit time. Flame AA provides exceptional sample throughput when analyzing a large number of samples for a limited number of elements. A typical determination of a single element requires only 5-10 seconds. However, flame AA requires specific light sources and optical parameters for each element to be determined and may require different flame gases for different elements. therefore, it is generally considered to be a single element technique.

Graphite furnace AA has a relatively low sample throughput because of the need to thermally program the system to remove solvent and matrix components prior to atomization. A typical graphite furnace determination normally requires 2-3 minutes. It is basically a single element technique.

ICP emission is a multielement technique with exceptional sample throughput. ICP emission systems can determine 10-40 elements per minute in individual samples. However, where only a few elements are to be determined, ICP is limited by the time required for equilibrium of the plasma with each new sample, typically about 15-30 seconds.

ICP-MS is also a multielement technique with same advantages and limitations of ICP emission. The sample throughput for ICP-MS is slightly less than that of ICP emission.

4.4 Cost

Instruments for single element atomic spectroscopy (Flame AA and GFAA) is generally less costly than that for multielement technique (ICP and ICP-MS). There is also considerable variation in cost among instrumentation for the same technique. Instruments offering only basic features are less

expensive than more versatile systems, which frequently offer a greater degree of automation. Figure 31 shows a comparison of cost ranges for the major atomic spectroscopy techniques.

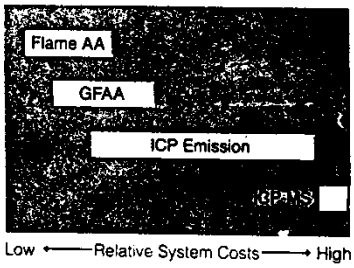

Figure 31: Relative Costs for Major Atomic Spectroscopy Systems

4.5 Comparison Summary

Flame AA is very easy to use and extensive applications information is available. It is preferred for the determination of major constituents and higher concentration analytes. GFAA has exceptional detection limit capabilities but with a limited analytical working range. Sample throughput is less than that of other atomic spectroscopy techniques. ICP emission is the overall multielement atomic spectroscopy technique, with excellent sample throughput and wide analytical range. ICP-MS is a relatively new technique with exceptional multielement capabilities at trace and ultratrace concentration levels and the ability to perform isotopic analysis. The main selection criteria for atomic spectroscopy techniques, concentration range and analytical throughput, are summarized in Figure 32. Where selection is based on analyte concentrations, flame AA and ICP are favored for moderate to high levels while graphite furnace AA and ICP-MS are favored for lower levels. ICP emission and ICP-MS are multielement techniques and are favored where large number of samples are to be analysed.

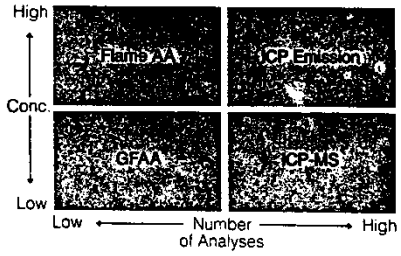

Figure 32: General Selection Guide for Major Atomic Spectroscopy Instrumentation

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DIRECTOR	SATISH CHANDRA
STUDY GROUP	C K JAIN N C GHOSH