

## 5.4 ELEMENTAL ANALYSIS BY INDUCTIVELY COUPLED PLASMA

### 5.4.1 ELEMENTAL ANALYSIS

- Elemental analysis is a process where a sample of some material (e.g., soil, waste or drinking water, bodily fluids, minerals, chemical compounds) is analysed for its elemental and sometimes isotopic composition. Elemental analysis can be qualitative (determining what elements are present), and it can be quantitative (determining how much of each are present). Elemental analysis falls within the ambit of analytical chemistry, the set of instruments involved in deciphering the chemical nature of our world.

### 5.4.2 METHODS OF ELEMENTAL ANALYSIS

- ❖ CHNX analysis
- ❖ Quantitative analysis
- ❖ Qualitative analysis

**1. CHNX analysis** - The determination of the mass fractions of carbon, hydrogen, nitrogen and heteroatoms (X) (halogens, sulphur) of a sample.

- ❖ The various CHNX analysis are
- ❖ NMR (Nuclear Magnetic Resonance)
- ❖ Mass spectrometry chromatographic
- ❖ Combustion analysis

**2. Quantitative analysis** - Quantitative analysis is the determination of the mass of each element or compound present. The quantitative analysis are

- ❖ Gravimetry analysis
- ❖ Optical atomic spectroscopy (Flame atomic absorption, Graphite furnace atomic absorption, and inductively coupled plasma atomic emission spectroscopy)
- ❖ Neutron activation analysis

**3. Qualitative analysis** - To qualitatively determine which elements exist in a sample

- ❖ Mass spectrometric (atomic spectroscopy)
- ❖ Inductively coupled plasma mass spectrometry
- ❖ X-ray fluorescence
- ❖ Particle-induced X-ray emission
- ❖ X-ray photoelectron spectroscopy
- ❖ Auger electron spectroscopy
- ❖ Sodium fusion test

### 5.4.3 EXCITING SOURCE OF MASS AND EMISSION SPECTROMETRY

- ❖ The excitation source must desolvate, atomize, and excite the analyte atoms. A variety of excitation sources are flame, arc/spark and plasma.

#### 5.4.3.1 PLASMA

- ❖ Plasma is an electrical conducting gaseous mixture containing significant amounts of cations and electrons (net charge approaches zero).

### 1. ADVANTAGES OF PLASMA

- ❖ Increased atomization/excitation
- ❖ Wider range of elements
- ❖ Simultaneous multi element analysis
- ❖ Wide dynamic range

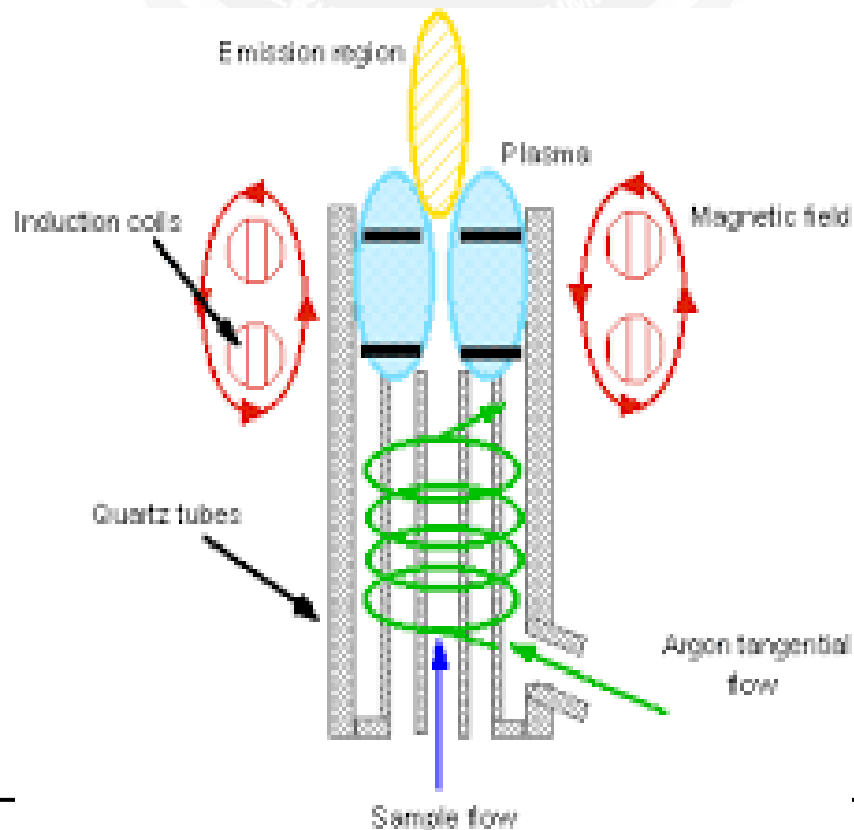
### 2. TYPES OF PLASMA

- ❖ **Direct-current plasma (DCP)** - In a DCP, a direct current passing between two electrodes heats the plasma gas, again typically argon, and produces a discharge. The most common version is the three- electrode system.
- ❖ **Microwave-induced plasma (MIP)** - A MIP is an electrode less discharge generated in a glass or quartz capillary discharge tube, often in a resonant cavity.
- ❖ **Capacitively Coupled Microwave Plasmas (CMP)** - A CMP formed using a magnetron to produce microwave energy at 2.45 GHz.
- ❖ **Inductively-coupled plasma (ICP)**

### 5.4.3.2 Inductively-Coupled Plasma (ICP)

- ❖ An inductively coupled plasma (ICP) or transformer coupled plasma (TCP) is a type of plasma source in which the energy is supplied by electric currents which are produced by electromagnetic induction, that is by time-varying magnetic fields.
- ❖ The most commonly used ion source for plasma spectrometry, the ICP, is produced by flowing an inert gas, typically argon, through a water-cooled induction coil which has a high-frequency field (typically 27 MHz) running through it.
- ❖ An inductively coupled plasma (ICP) is a very high temperature (7000-8000K) excitation source. ICP sources are used to excite atoms for atomic-emission spectroscopy and to ionize atoms for mass spectrometry.

#### 1. PRODUCTION OF PLASMA



### *Fig. 5.9. Production process of plasma*

- ❖ Inductively coupled discharge also uses RF power supply like capacitively coupled discharge.
- ❖ A radiofrequency (RF) generator (typically 1-5 kW @ 27 MHz) produces an oscillating current in an induction coil that wraps around the tubes.
- ❖ For a commonly used cylindrical plasma chamber shown below, antenna is usually wrapped around the electrically insulating chamber wall.
- ❖ RF generator drives high alternating current through coil antenna, which creates an alternating magnetic field within the plasma chamber.
- ❖ Oscillating magnetic field will generate an oscillating electric field in the plasma chamber.
- ❖ Eventually, the electric field will accelerate the electrons and generate plasma.
- ❖ The magnetic field in turn sets up an oscillating current in the ions and electrons of the support gas (argon). As the ions and electrons collide with other atoms in the support gas.
- ❖ Since the excitation force is delivered through magnetic field, inductively coupled discharge is also called "H-discharge". For some applications, it is described as "electrode less discharge" because there is no cathode or anode required for inductively coupled discharge.

## **2. CHARACTERISTICS OF OPTICALLY COUPLED PLASMA**

- ❖ High temperature (7000-8000 K)
- ❖ High electron density ( $10^{14}$ - $10^{16}$ cm<sup>-3</sup>)
- ❖ Appreciable degree of ionization for many elements
- ❖ Simultaneous multielement capability (over 70 elements including P and S)
- ❖ Low background emission and relatively low chemical interference
- ❖ High stability leading to excellent accuracy and precision
- ❖ Excellent detection limits for most elements (0.1-100 ng mL<sup>-1</sup>);
- ❖ Wide linear dynamic range (LDR) (four to six orders of magnitude).
- ❖ Applicable to the refractory elements cost-effective analyses

#### 5.4.4 OPTICAL EMISSION SPECTROSCOPY

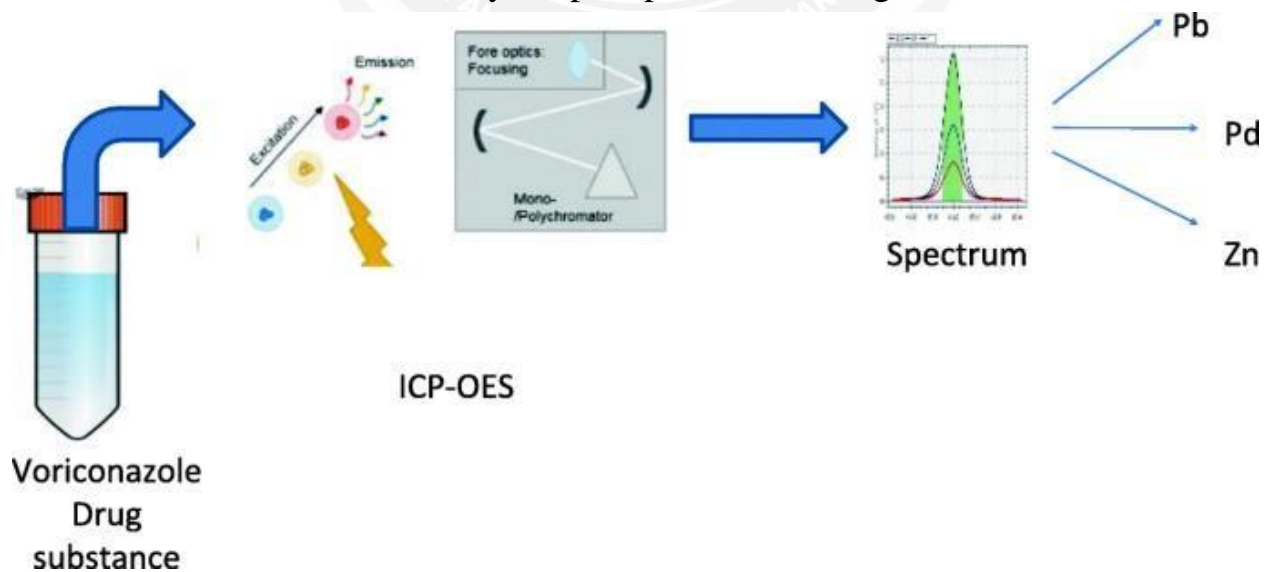
- ❖ Optical Emission Spectroscopy, or OES analysis, is a rapid method for determining the elemental composition of a variety of metals and alloys.

Based on excitation source Optical Emission Spectroscopy is classified as,

- ❖ Inductively Coupled Optical Emission Spectroscopy
- ❖ Glow Discharge Optical Emission Spectrometry (GD-OES) or Glow Discharge MS (GD-MS)
- ❖ Arc spark Optical Emission Spectroscopy
- ❖ Flame emission spectroscopy

#### 5.4.5 INDUCTIVELY COUPLED PLASMA OPTICAL EMISSIONSPECTROMETRY

5.4.5.1 The Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) analysis method uses high-frequency inductively coupled plasma as the light source, and is ideal for



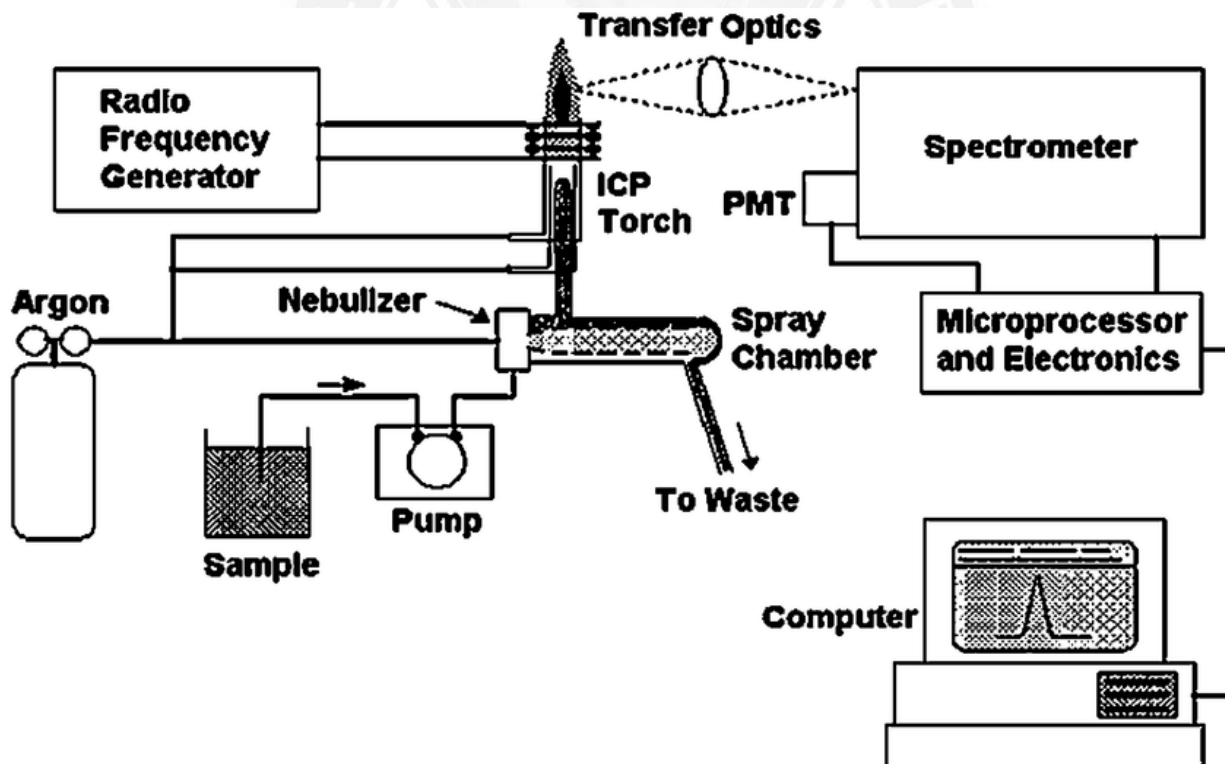
the element analysis of sample solutions.

*Fig. 5.10. Flow diagram of ICP-OES*

## 1. PRINCIPLE

- When plasma energy is given to an analysis sample from outside, the component elements (atoms) is excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured.

## 2. COMPONENTS



*Fig. 5.11. A representation of the layout of a typical ICP-OES instrument.*

## 3. CONSTRUCTION

- ❖ Sample introduction
- ❖ Production of emission
- ❖ Collection and detection of emission

- ❖ Signal processing and instrument control

## **(a) SAMPLE INTRODUCTION**

### **1.Nebulizer**

- ❖ With a nebulizer, the sample liquid is converted into an aerosol and transported to the plasma.



## **2. Pumpe**

- ❖ It require for the solution to be pumped into the nebulizer, the Peristaltic pumps are almost exclusively the choice for ICP-OES applications. These pumps utilize a series of rollers that push the sample solution through the tubing using a process known as peristalsis.

## **3.Spray chambers**

- ❖ A spray chamber is placed between the nebulizer and the torch. Only. very small droplets in the aerosol are suitable for injection into the plasma, it can be injected into the plasma by spray chamber.

## **4. Drains**

- ❖ The drain carries excess sample from the spray Chamber to a waste container can have an impact on the performance of the ICP instrument.

## **(b) Production of Emission**

### **1. Torches**

- ❖ It contains a ring-shaped toroidal plasma is formed, where the sample aerosol passes centrally through the hot plasma.
- ❖ The burner consists of three concentric quartz tubes. The aerosol is led with its carrier gas through the central tube.
- ❖ Between the outer and the intermediate tube a gas flow is introduced tangentially. It takes up the high-frequency energy and also prevents. the torch from melting.

### **2. Radio Frequency Generators**

- ❖ The radio frequency (RF) Generator is the device that provides the power for the generation and sustainment of the plasma discharge.
- ❖ The plasma with the energy of a high-frequency generator (in the frequency range of around 6-100 MHz) is transferred to a gas flow at atmospheric pressure (mostly argon) in a quartz tube system with the aid of a working coil.



- ❖ The electrons take up energy and collide with atoms, by which a plasma with a temperature of up to 6000 K is formed.

### **(c) Collection and Detection of Emission**

#### **1. Transfer Optics**

- ❖ The emission radiation from the region of the plasma known as the normal analytical zone (NAZ) is sampled for the spectrometric measurement.

#### **2. Wavelength Dispersive Devices**

- ❖ The next step in ICP-OES is the differentiation the emission radiation from one element from the radiation emitted by other elements and molecules. The physical dispersion of the different wavelengths is done by
  - ❖ Diffraction gratings
  - ❖ Prisms
  - ❖ Filters
- ❖ To separate polychromatic light the grating is incorporated in an optical instrument called a spectrometer. The spectrometer receives white light or polychromatic radiation and disperses it into monochromatic radiation. One or more exit slits on the exit plane or circle are then used to allow certain wavelengths to other Wavelengths. pass to the detector while blocking out
- ❖ The monochromatic radiation which is diffracted from the grating is composed primarily of wavelengths representative of the light emitted by a particular elemental or molecular species in the ICP.

#### **3. Detectors**

- ❖ Once the proper emission line has been isolated by the Spectrometer, the detector and its associated electronics are used to measure the intensity of the emission line. The most common detector is photomultiplier tube.
- ❖ A photomultiplier tube (PMT) consists of a photosensitive cathode, several dynodes and a collection anode. The dynodes are responsible for the increase in signal by electron multiplication.

## **(d) Signal Processing and Instrument Control**

### **1. Signal Processing**

- ❖ The electrical current measured at the anode of the PMT is converted into information that can be used by a computer.

### **2. Computers and Processors**

- ❖ The computer to control the spectrometer and to collect, manipulate, and report analytical data, the amount of computer control over other functions of the instrument varies widely from model to model.

### **3. Software**

- ❖ ICP-OES instrument would be that it could prepare the standards and samples, develop the analytical method, analyse the samples, report the results, and make decisions based on those results all from a single keystroke.

## **4. WORKING OF ICP-OES**

- ❖ The first step in an analysis is to prepare the samples and Standards for introduction to the ICP. This step depends on the physical and chemical characteristics of the samples and from simple dilution to a complex series of chemical reactions and other preparation steps.
- ❖ The next step in the analysis concerns the sample introduction method and hardware to be used. For most ICP-OES analyses, the standard sample introduction system provided with the instrument will be sufficient.
- ❖ In inductively coupled plasma-optical emission spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, 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 desolated, 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 information for the analyst.
- ❖ The next step in the development of an analysis methodology is to program the instrument, using the computer software provided with the instrument, to perform the data collection and processing steps.
- ❖ To do this, decisions must be made concerning the operating conditions, wavelength selection, instrument calibration, emission measurement, and the actual sample analysis.

## **5. Advantages**

- ❖ Extremely high sensitivity
- ❖ Almost full elemental coverage needs for specific excitation sources
- ❖ Linear range of several orders of magnitude
- ❖ Very accurate quantification at low concentrations
- ❖ By using bulk samples, a true bulk analysis is obtained (this is often difficult or impossible for many other methods)
- ❖ The ability to analyze most any sample type even with limited availability (most commonly samples are about 0.1-1 g but can be as small as a few milligrams)
- ❖ Even gases may be analyzed when introduced into the torch using methods such as gas chromatography.
- ❖ High sample throughput enabling the efficient analysis of large batches
- ❖ Simultaneous determination of multiple elements in each sample
- ❖ Complementary analysis to techniques like XRF
- ❖ Large dynamic linear range
- ❖ Low chemical and matrix interference effects

## **6. DISADVANTAGES**

- ❖ Cumbersome sample preparation
- ❖ The need to generate calibration curves from samples as similar in all respects as the samples under investigation
- ❖ Initial progress is often time consuming and tedious

- ❖ In the case of failure analyses method development will often be necessary each time a new sample type is encountered
- ❖ Relatively long analysis times
- ❖ The method is inherently destructive

## **7. APPLICATIONS**

- ❖ Trace analysis of environmental soil and water samples
- ❖ Assessment of metal ores for mass balances and process control
- ❖ Trace metal analysis of any material that can be digested into an aqueous matrix
- ❖ Boron and Lithia in glasses
- ❖ Forensic analysis
- ❖ Trace analysis of food and drink samples such as; metals in wine; and elements bound to proteins
- ❖ Metal release testing of tableware.
- ❖ Determination of toxic, trace and major constituents in coal and slags
- ❖ Analysis of low alloy steels for As, B, Bi, Ce, La, P, Sn and Ta; High-precision determination of Si in steels.
- ❖ Determination of contaminants in high-purity Al.
- ❖ Analysis of superconducting materials for trace.

### **5.4.6 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**

- ❖ Inductively coupled plasma mass spectrometry (ICP-MS) is an instrumental analytical technique based on the use of a high temperature ionisation source (ICP) coupled to a mass spectrometer.
- ❖ It is an elemental analysis technology capable of detecting most of the periodic table of elements at milligram to Nano gram levels per liter.
- ❖ It is used in a variety of industries including, but not limited to, environmental monitoring, geochemical analysis, metallurgy, pharmaceutical analysis, and clinical research.

## 1. PRINCIPLE

- ❖ It is a type of mass spectrometry that uses an inductively coupled plasma to ionize the sample. It atomizes the sample and creates atomic and small polyatomic ions, which are then detected.
- ❖ It is known and used for its ability to detect metals and several non-metals in liquid samples at very low concentrations. It can detect different isotopes of the same element, which makes it a versatile tool in isotopic labelling.

## 2. SAMPLE PREPARATION

- ❖ This internal standard consists primarily of deionized water, with nitric or hydrochloric acid, and Indium and/or Gallium. Depending on the sample type, usually 5 mL of the internal standard is added to a test tube along with 10-500 microliters of sample.

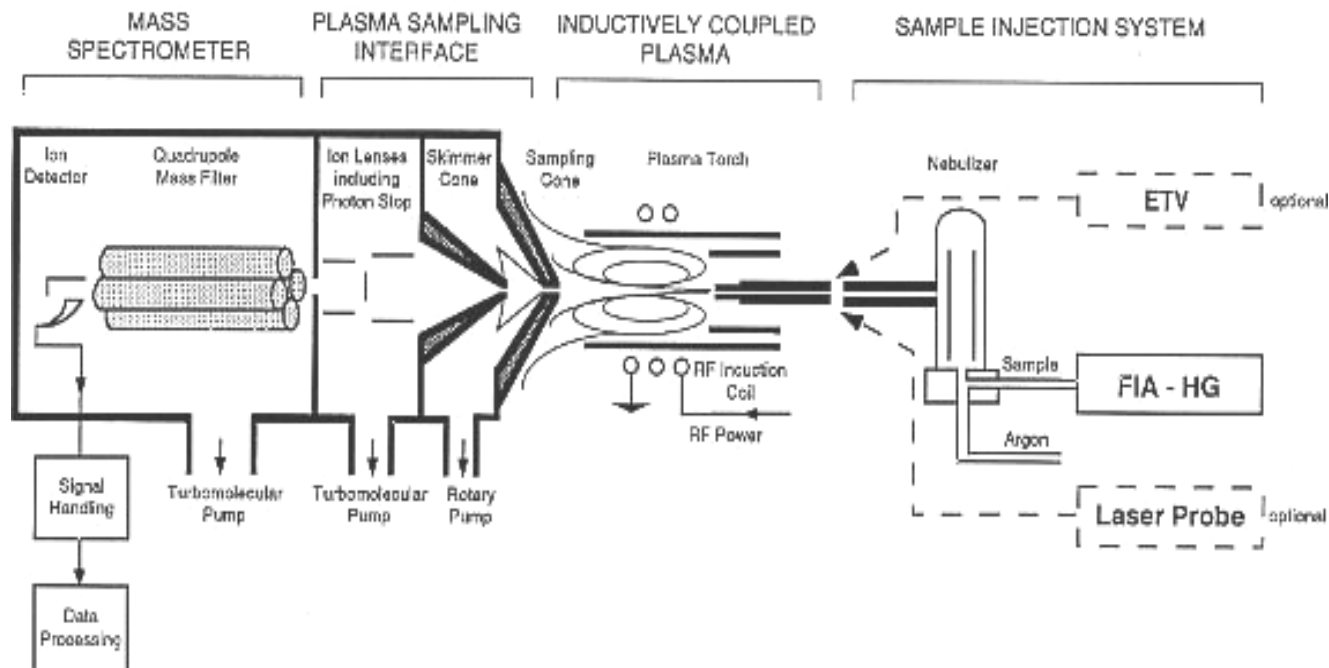
## 3. COMPONENTS

- ❖ **Peristaltic Pump** - Ensures constant flow of liquid irrespective of differences in viscosity between samples, standards and blanks. Sample pumped at 1ml/min.
- ❖ **Nebulizer and spray chamber** - It uses supersonic expansion of gas to turn the liquid into a fine mist, and the spray chamber then removes any droplets that are too large to be processed in the plasma. This occurs at the sample interface of the instrument.
- ❖ **Torch** - The plasma torch consists of three concentric quartz tubes through which streams of argon flow. The nebulizer gas which carries the analyte into the plasma flows in the central tube. The auxiliary gas flows around the central tube and adjusts the position of the plasma relative to the torch. The coolant gas streams tangentially through the outer tube, serving to cool the inside walls and centre of the torch, and stabilizes the plasma.
- ❖ **Plasma Ionization Source** - Inductively coupled plasmas are formed by coupling energy produced by a Radio Frequency generator to the plasma support gas with an electromagnetic field. The field is produced by applying an RF power (typically 700-1500 W) to a load coil.

- ❖ **Interface Region (Skimmer cone & Sampler cone)** - A section that connects the ionizing section at ambient pressure to the mass spectrometer at high vacuum. Function is to export the ions produced in argon plasma and transport them to the mass spectrometer.
- ❖ **Ion Focusing Region** - One or more electrostatically controlled lens component made up of series of metallic plates or cylinders having a voltage placed on them Ions are separated from Photons & Neutrals
- ❖ **Mass Analyzer (Mass spectroscopy)** - Quadrupole is a sequential mass filter, which separates ions based on their  $m/z$ . Measurement of the  $m/z$  of the ion allows qualitative identification of the isotope or molecule. Magnitude of the ion current is used to provide quantitation of the amount of the analyze in the original sample.
- ❖ **Spectral Interferences** - Polyatomic or molecular Spectral Interferences severely compromise detection capability of certain elements by ICP -MS using the Quadrupole mass analyser technology. Generated by combination of Plasma/nebulizer Gas, solvent and matrix derived ions.
- ❖ **Collision Reaction Cell (CRC)** - The CRC devices in commercial instruments have been designed to remove polyatomic species.
- ❖ **Ion Detectors** - Detector is an Electron Multiplier Device which can generate a measurable signal pulse from the impact of a single ion. Each electron which strikes a dynode releases several electrons from that surface and hence the device is called "electron multiplier".

#### 4. WORKING OF ICP-MS

- ❖ The sample solution is introduced into the device by means of a peristaltic pump.
- ❖ There it becomes nebulized in a spray chamber.
- ❖ The resulting aerosol is injected into an argon-plasma that has a temperature of 6000-8000 K.
- ❖ Inside the plasma torch, solution is removed from the sample and also atomization and ionization occur.



**Fig. 5.12. Working flow of ICP-MS carrier gas**

- ❖ To be processed efficiently in the plasma, samples must be in either gas or vapor (aerosol) form. So, while gases can be analyzed directly by the plasma (e.g., when separated by gas chromatography), solids and liquids have to be converted to aerosol form using either a nebulizer (for liquids) or an ablation device (for solids).
- ❖ Only a small amount part of the ions produced in the plasma further penetrate to the mass-spectrometer part.
- ❖ After mass separation, ions must be detected and amplified in order to determine their intensities,
- ❖ Electron multipliers (also known as secondary electron multiplier, or SEM, detectors) can detect extremely small ion currents, including even single ions, coming from the mass analyzer. They operate on the principle of secondary electron emission, in which charged particles with sufficient energy incident on a 'dynode' stimulate the emission of electrons from the surface,

## 5. MAINTENANCE OF ICP-MS

- ❖ Pump tubing has the tendency to stretch, which changes the amount of sample being delivered to the nebulizer

- ❖ Tip of the nebulizer should not get blocked.
- ❖ Microscopic particles can build up on the tip of the nebulizer without the operator noticing, which, over time, can cause a loss of sensitivity, imprecision, and poor long-term stability.
- ❖ Drain of spray chamber must function properly. Malfunctioning or leaking drain can produce changes in the spray chamber backpressure, producing fluctuations in the analyte signal, resulting in erratic and imprecise data
- ❖ Staining and discoloration of the outer tube of the quartz torch because of heat and the corrosiveness of the liquid sample can cause electrical arcing
- ❖ The most common types of problems associated with the interface are blocking or corrosion of the sampler cone & skimmer cone

## 6. ADVANTAGES

- ❖ Quantitative analysis is the fundamental tool used to determine analyte concentrations in unknown samples.
- ❖ Increased sensitivity and wide dynamic range
- ❖ Extremely low detection limits
- ❖ A large linear range
- ❖ Possibilities to detect isotope composition of elements
- ❖ Wide Elemental Coverage
- ❖ Extremely Low Detection Limits (ppt/ppm) or (ng/L to mg/L)
- ❖ Fast Analysis times (all elements at once)
- ❖ Simple Spectra Isotopic Information
- ❖ High Throughput & Productivity

## 7. APPLICATION

- ❖ Simple metal analysis during metal-based drug development
- ❖ Impurity limit tests
- ❖ Metals present in Active Pharmaceutical Ingredients
- ❖ Quality Control Tests of natural products for toxic impurities testing
- ❖ Monitoring metabolites of an administered drug
- ❖ Detection of metal impurities from leachable packaging material



- ❖ For elemental speciation
- ❖ Pharmaceutical Waste Water monitoring

## **8. DISADVANTAGE**

- ❖ The high capital cost of the instrumentation.
- ❖ Lower precision compared with atomic absorption spectrometry (AAS)
- ❖ The total dissolved salts should be less than 1000 ppm
- ❖ Severe matrix effects
- ❖ Heavier elements, such as lead, are well-suited for ICP-MS analysis, whereas lighter elements are prone to more interference.

