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Inductively coupled plasma atomic emission spectroscopy



Outline of presentation

- Principles
- Instrumentation
- sample introduction techniques
- Alternative sample introduction technique
- Torches (emission production)
- Radio frequency generators (RF)
- Detection
- Microwave induced plasma optical emission

Principle

- ICP-AES is an emission spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state.
- The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its chemical character. Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength (or a very few) for a given element.
- The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantify the elemental composition of the given sample relative to a reference standard.

INDUCTIVELY COUPLED PLASMA (ICP)

- Plasma is a type of electrical discharge
- Plasma is any type of matter that contains an appreciable amount of less than 1% of electrons and +ve ions in equal numbers + atoms + neutral molecules

- **Plasma has 2 characteristics:**
 - i- can conduct electricity**
 - II- affected by magnetic fields**
- **Plasma is highly energetic ionized gases usually inert, recently reactive oxygen is used.**
- **ICP is the state-of-the-art plasma**
- **Other plasmas include direct current plasma (DCP) and microwave induced plasma (MIP)**

ADVANTAGES OF THE ICP

- **High degree of selectivity**
- **Ability to overcome depressive interference effects**
- **Capable of exciting several elements not excitable by ordinary flames**
- **Higher sensitive than Flame Photometry**
- **Simpler to operate than Arc Spark methods**
- **Higher degree of sensitivity than Arc Spark**
- **Lacks electrodes which gives freedom from contamination and extremely low background.**

GENERAL CHARACTERISTICS OF THE ICP

Up to 70 elements can be analyzed at concentrations below 1 ppm

(Fig 1)

ICP – AES Detection Limits ($\mu\text{g/L}$)

Li 2		Be 0.1												B 3	C 40	N n.a.			
Na 5		Mg 0.1												Al 5	Si 4	P 50	S 50	Cl n.a.	
K 70	Ca 0.1	Sc 0.3	V 3	Ti 0.5	Cr 3	Mn 0.4	Fe 3	Co 3	Ni 7	Cu 1	Zn 3	Ga 10	Ge 20	As 20	Se 50	Br n.a.			
Rb 100	Sr 0.06	Y 0.3	Nb 5	Zr 0.8	Mo 5		Ru 8	Rh 40	Pd 2	Ag 2	Cd 2	In 40	Sn 30	Sb 40	Te 50	I n.a.			
Cs 50000	Ba 0.1	La 1	Hf 15	Ta 20	W 20	Re 10	Os 0.4	Ir 20	Pt 30	Au 5	Hg 50	Tl 50	Pb 40	Bi 20					
Ce 10	Pr 40	Nd 50			Sm 40	Eu 3	Gd 20	Tb 20	Dy 10	Ho 6	Er 10	Tm 5	Yb 2	Lu 1					
Th 70		U 20																	

References:

L. Davidowski, R. Hergenreder, D. Hilligoss, A. Koch, E. Pruszkowski, and D. Yates, ICP Application Study No. 36, Sept. 1987, Perkin – Elmer Corp., Norwalk, CT

A. King and G. Wallace, ICP Bulletin No. ICPB – 5, Aug. 1983, Perkin – Elmer Corp., Norwalk, CT

R. Winge, V. Patterson, and V. Fassel, Appl. Spectrosc. 33, 206 (1979)

Figure 2-1. Periodic table with ICP-AES detection limits.

THE ICP DISCHARGE

(Fig 2)

☞ The argon gas is directed through a torch consists of 3 concentric tubes made of quartz

☞ A copper coil called the Load Coil surrounds the top end of the torch and connected to a Radio Frequency Generator (RF)

☞ When RF power (700 – 1500 Watts) is applied to the load coil, an alternating current moves back and forth within the coil or oscillates at a rate corresponding to the frequency of the generator (27 – 40 MHz). This RF oscillation causes the RF electric and magnetic fields to be set up in the area at the top of the torch.

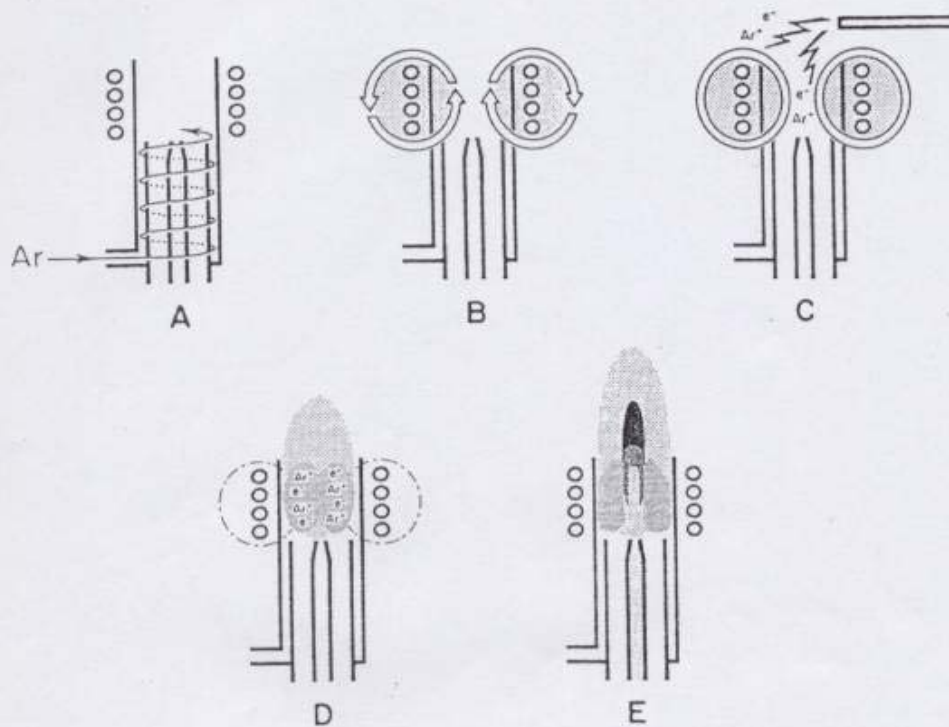


Figure 2-2. Cross section of an ICP torch and load coil depicting an ignition sequence. **A** - Argon gas is swirled through the torch. **B** - RF power is applied to the load coil. **C** - A spark produces some free electrons in the argon. **D** - The free electrons are accelerated by the RF fields, causing further ionization and forming a plasma. **E** - The sample aerosol-carrying nebulizer flow punches a hole in the plasma.

➡ **With Argon gas being swirled through the torch, a spark is applied to the gas causing some electrons to strip out from their Argon atoms**

➡ **These electrons are then caught up in the magnetic field and accelerated by them.**

➡ **Adding energy to the electrons by the use of the coil in this manner is called “Inductively Coupling”**

➡ **These high-energy electrons in turn collide with other Argon atoms, stripping off still more electrons**

☞ This collisional ionization of Argon continues in a chain reaction thus breaking down the gas into a Plasma consisting of Argon atoms, electrons, and Argon ions know as “ICP” discharge

☞ This ICP discharge is sustained

☞ This ICP discharge appears as intense, brilliant, white and tear-drop shaped (Fig 3)

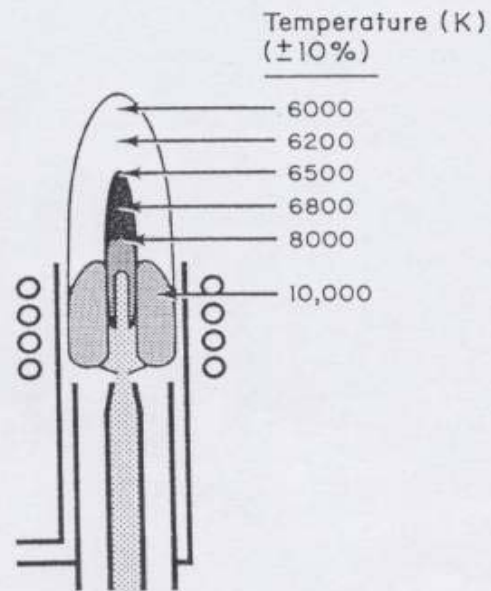


Figure 2-5. Temperature regions of a typical ICP discharge.

➤ (Fig 4)

Explains what happens to aerosol samples introduced into the plasma

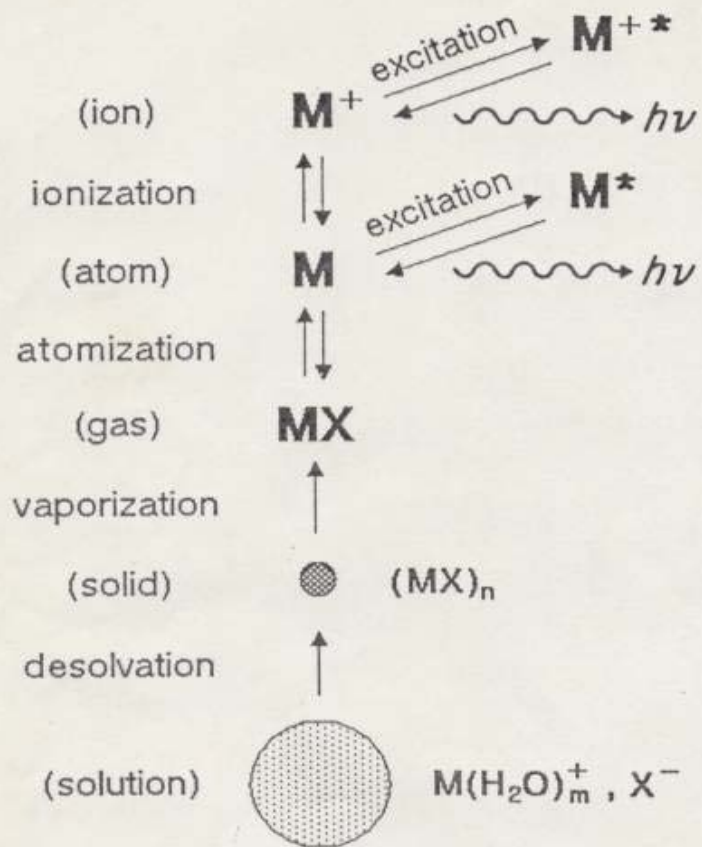


Figure 2-4. Process that takes place when a sample droplet is introduced into an ICP discharge.

(Fig 5)

Explains advantage of the plasma with respect to stability, high temperature surrounding the sample for long time (2 milliseconds) thus resulting into lack of matrix interferences.

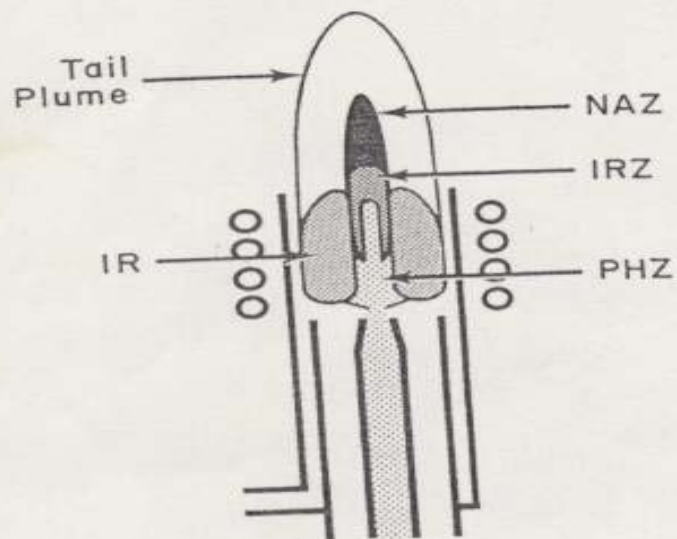


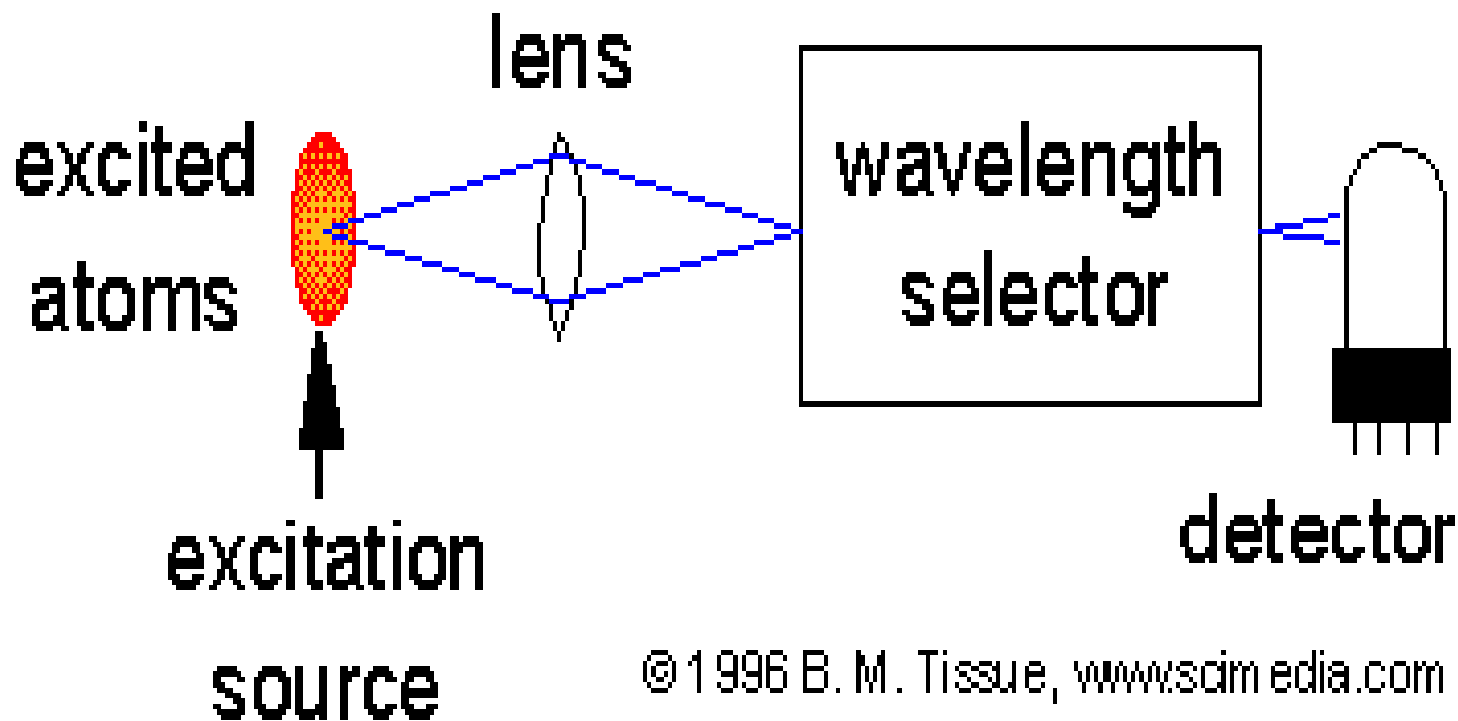
Figure 2-3. Zones of the ICP. IR - Induction Region, PHZ - Preheating Zone, IRZ - Initial Radiation Zone, NAZ - Normal Analytical Zone.

General Information

- ➡ **Used for Qualitative Analysis**
- ➡ **Used for Quantitative Analysis**
- ➡ **Detection limit is in ppb range**
- ➡ **Not possible to determine: H, N, O, C or Ar in trace levels as they are used in solvents and plasma**
- ➡ **Not possible to determine F, Cl and noble gases at trace levels as they require high excitation energy**
- ➡ **Not used for determining radioactive elements**

- ➡ **Upper limit for linear calibration is 10000 – 1000000 times the detection limits for a particular emission line**
- ➡ **Only 2 standard solutions are required for the calibration plot as linearity is infinite**
- ➡ **ICP has a multi-elemental capability for analysis**

INSTRUMENTATION



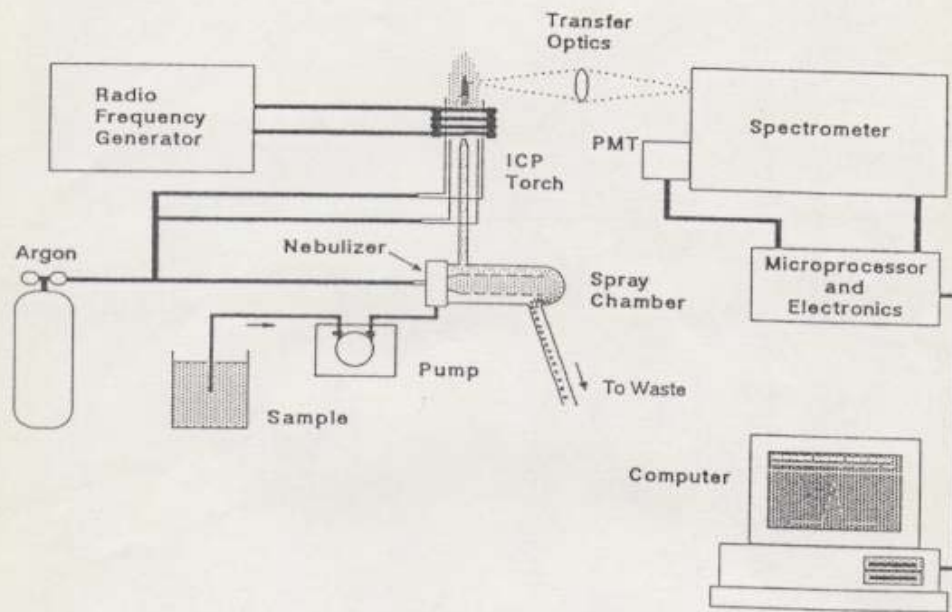


Figure 3-1. Major components and layout of a typical ICP-AES instrument.

Nebulization

- Nebulization: This is the introduction of liquid analyte sample into the instrument
- This converts liquids to the aerosol and transports them to the plasma
- Only small droplets are needed
- (Fig. 1)

- Two sources have been used to break a liquid to an aerosol
- (a) Pneumatic forces
- Ultrasonic mechanical force
- Pneumatic nebulizers are high speed gas flow of 1 liter/min.
- ICP pneumatic nebulizer is the concentric nebulizer type (Fig. 2)

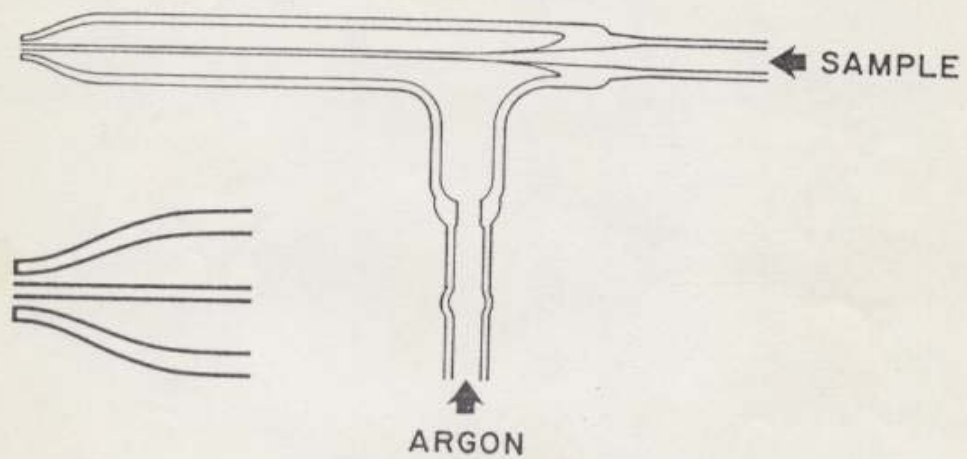


Figure 3-2. Concentric nebulizer used for ICP-AES.

- ICP pneumatic nebulizer is the concentric nebulizer type
- **Cross Flow Nebulizer:** A high speed argon directed perpendicular to the tip of the capillary tube (concentric is parallel)
- Concentric causes clogging problems
- Cross flow nebulizer is more rugged and corrosion resistant
- (Fig. 3)

- **Babington Nebulizer:** (Fig.4)
- **for** nebulizing foil oil for industrial burners. It can nebulize very viscous liquids.
- It works by allowing the liquid to flow over a smooth surface with a small hole in it. High speed Argon gas emanating from the hole shears the liquids into small drops.
- Another type of Babington nebulizer is V-groove (Fig. 5)

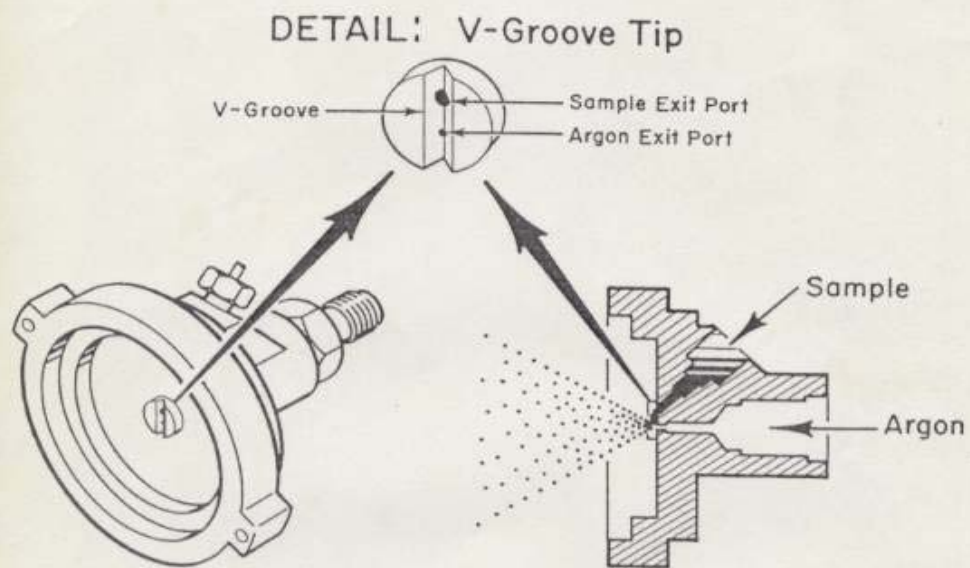
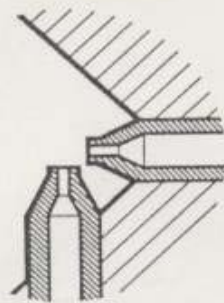


Figure 3-5. V-groove nebulizer, a variation of the Babington nebulizer.

DETAIL



Nebulizer
Tips

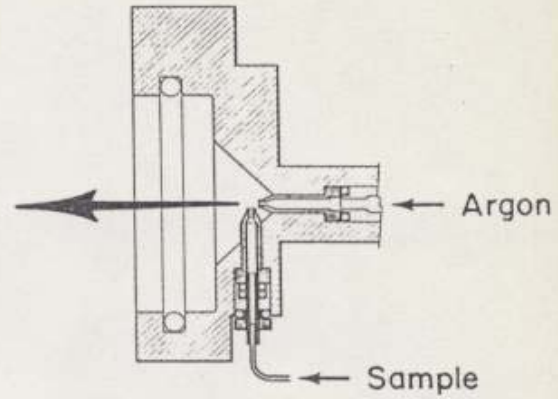


Figure 3-3. Cross-flow nebulizer.

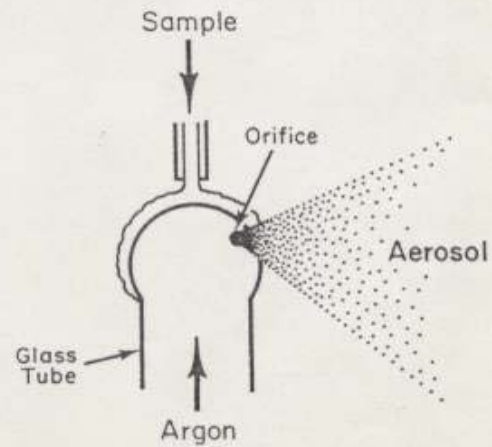


Figure 3-4. Babington nebulizer.

- **Ultrasonic Nebulizer:** (Fig. 6)
- High speed frequency mechanical waves are used to generate an aerosol.
- It produces very small droplets efficiently.
- Desolvation unit is added to sample introduction.
- Turning radiofrequency source is the major drawback of it being used routinely.

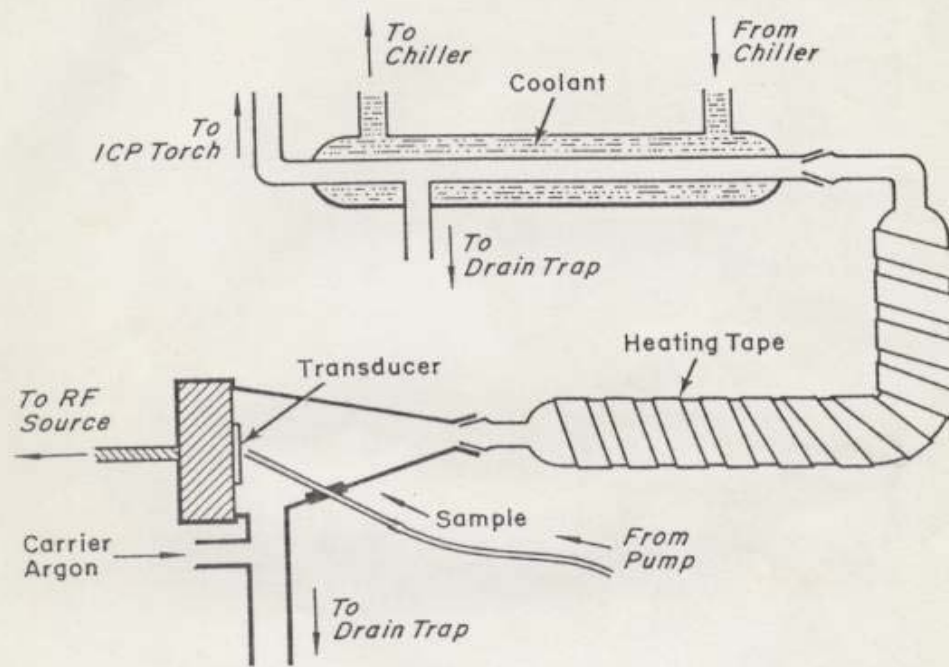


Figure 3-6. Ultrasonic nebulizer with desolvation unit.

- **Pumps:** (Fig. 7)
- **required** to pump solution into nebulizer
- Useful to control flow rate due to variation of viscosity and surface tension.
- **Peristaltic pumps:** They utilize a series of rollers to push solution through tubing by a process known as peristalsis.
- Tubing should be compatible with sample such as acid or organics.

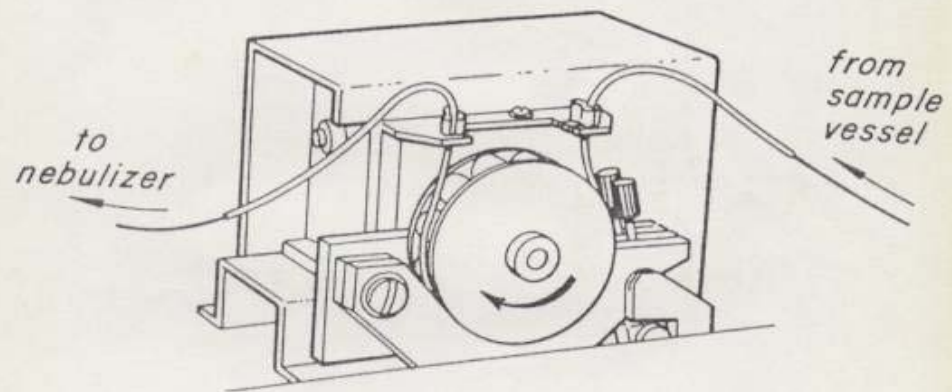


Figure 3-7. Peristaltic pump used for ICP-AES.

- Sample aerosol transported to torch and injected into the plasma. A spray chamber is placed between nebulizer and torch. This is to remove large droplets from aerosols or smooth out pulses.

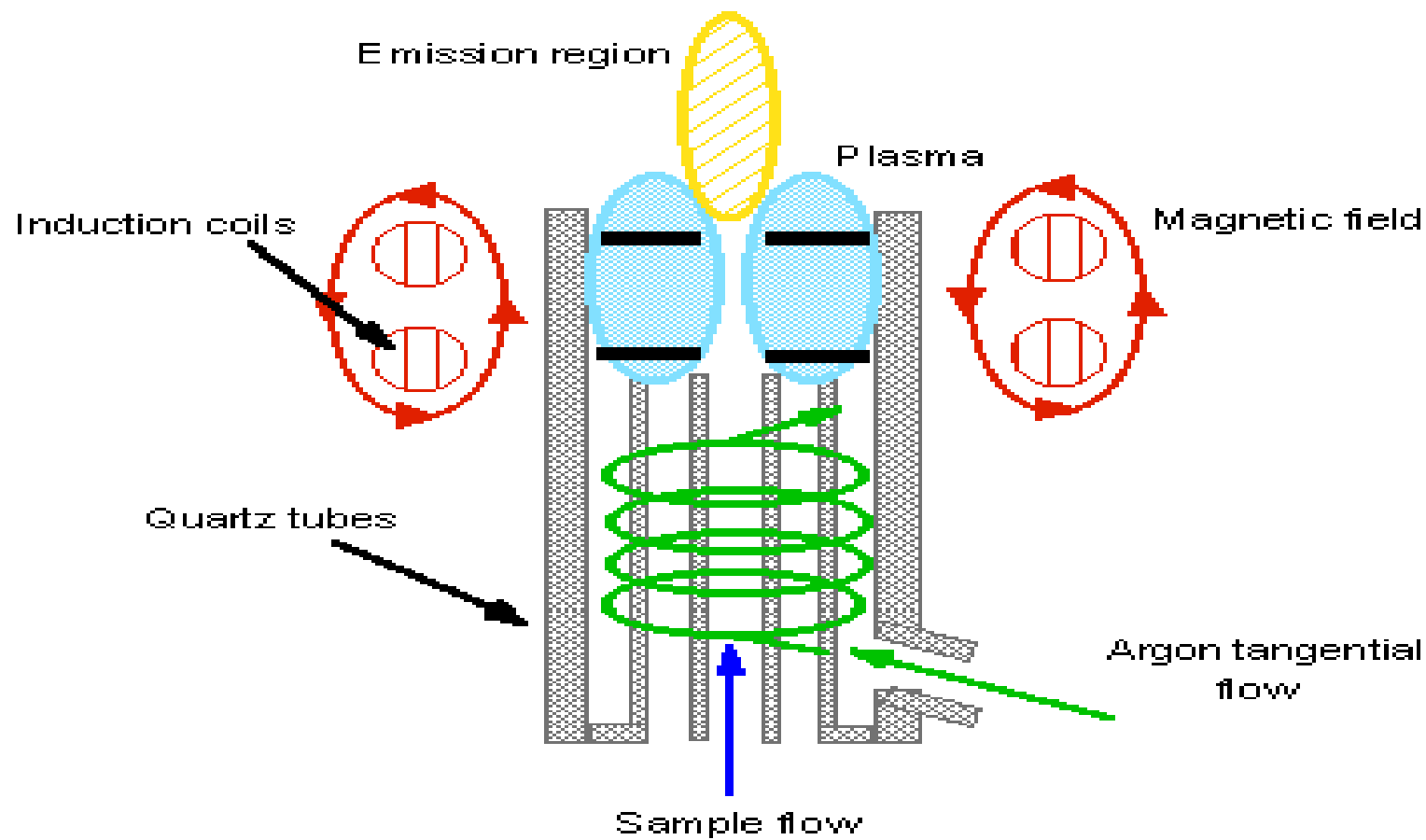
Alternative sample introduction

- **Hydride Generation** : (Fig. 9)
- Sample + HCl + sodium borohydride (reductant) are used to generate the volatile hydride of these metals Sn, Te, Se, Pb, Ge, Bi, As, Sb, .
- These are transported to the plasma where they are excited .
- Introduction rate is 10 times that of pneumatic nebulizers.

- Efficiency of nebulization is high
- Other methods are
- **Graphite furnace**
- **Direct Injection**

Production of emission

- **Torches:** (Fig. 13)
- This contains 3 concentric tubes for Argon and aerosol injection.
- Spacing between the outer tubing is kept narrow so that the gas is introduced between emerges at high velocity. This outside chamber is also designed to make the gas spiral around as it proceeds upwards.



- One function of the gas is keeping quartz walls of the torch cool known as coolant flow.
- Since this is the only gas flow needed to sustain a plasma, it is now known as plasma flow which is 7-15liter/min.
- Sample is carried with the gas flow into the plasma high central tube or injector.

- **Classic one piece ICP torch** (Fig. 14)
- This consist of 3 concentric tubes (quartz) sealed together
- It is easy to use
- Its not resistant to corrosion by HF
- It should be replaced when damaged.

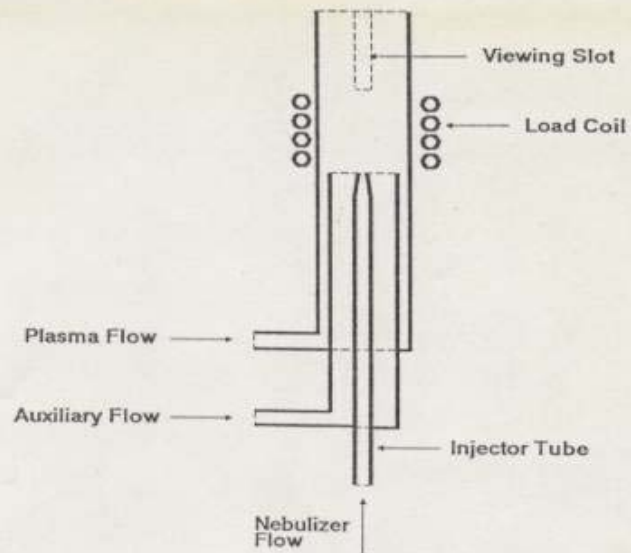


Figure 3-13. Schematic of a torch used for ICP-AES.

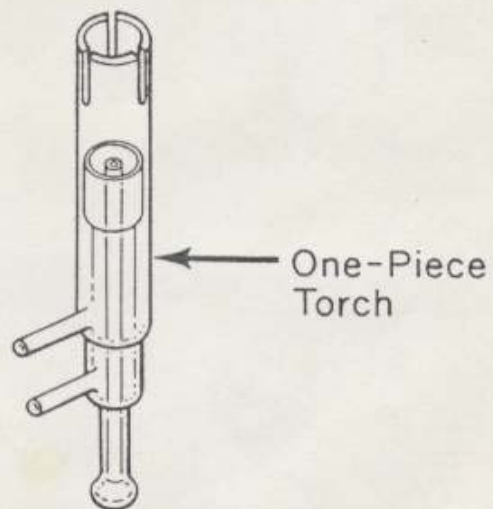


Figure 3-14. One-piece ICP torch.

- **Demountable ICP Torch:** (Fig. 15)
- **This** can be taken apart so that tubes can be modified or replaced without replacing entire torch.
- Advantages
- Lower torch replacement cost
- Ability to come in a variety of injector tubes, including corrosion-resistant ceramic injectors

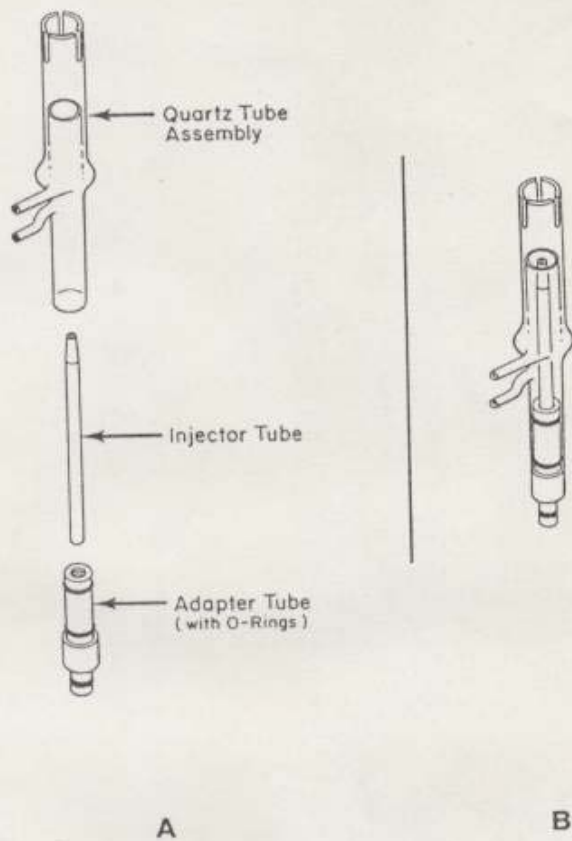


Figure 3-15. Demountable ICP torch. A- expanded view, B - assembled view.

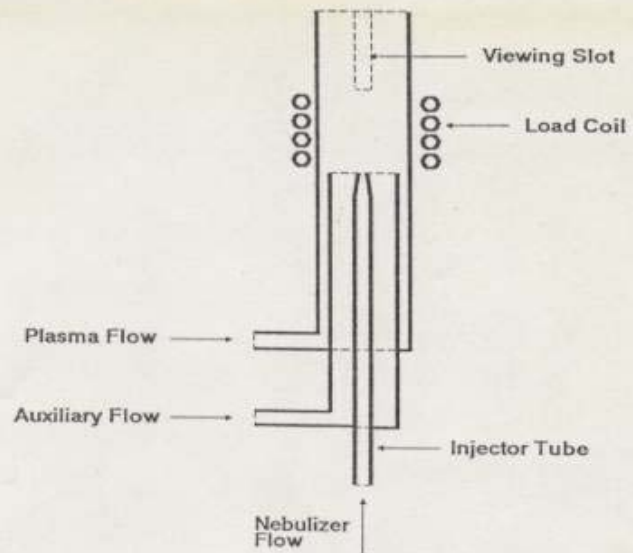


Figure 3-13. Schematic of a torch used for ICP-AES.

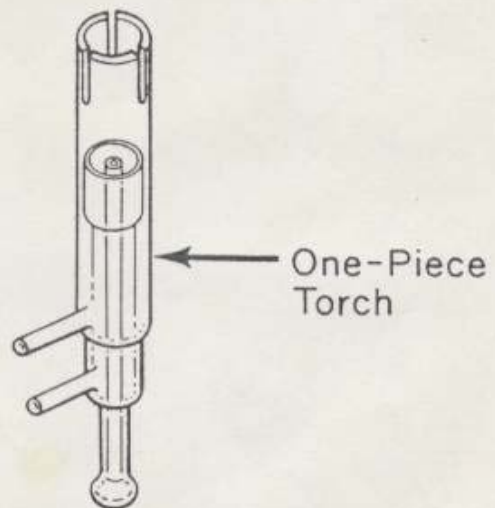


Figure 3-14. One-piece ICP torch.

- Narrow bore injectors for organics and wide bore injectors for samples with high dissolved solids.

Radiofrequency Generators

- It is the device that provides the power for generation and sustainment of plasma discharges.
- The power generated ranges from 600-1800 watts and is transferred to plasma gas through a load coil surrounding the top of torch, which is made of copper and cooled by water or gas during operation.

- It operates at frequency of 27-65MHz
- The two types of RF used are
- (a) **Crystal controlled generators:** they use a piezoelectric quartz crystal to produce an RF oscillating signal that is amplified by the generator before applied to load coil.
- (b) **Free running Generators:** operate at an oscillation frequency dependent on conditions within plasma discharge.

- Operates automatically to compensate for any changes in plasma.

Detection

- Emission radiation from the region of plasma normal analytical zone (NAZ) is sampled for spectrometric measurement.
- Radiation is collected by focussing optics such as convex or concave mirrors.
- This optic focuses image of plasma onto entrance slit or wavelength dispersing service, such as :diffraction grating incorporated with a spectrometer.

- **Multielement analysis** :Accomplished by dispersive devices in 2 ways.(1) using a polychromator with several exit slits.
- (2) Using a monochromator by scanning rapidly or slewing from one emission line to another.

Detectors

- This measures the intensity of emission.
- **Photomultiplier Tubes** : It is a vacuum tube containing photosensitive material called a photocathode which ejects electrons when struck by light. These electrons are accelerated towards a dynode which ejects 2-5 secondary electrons from one electron.

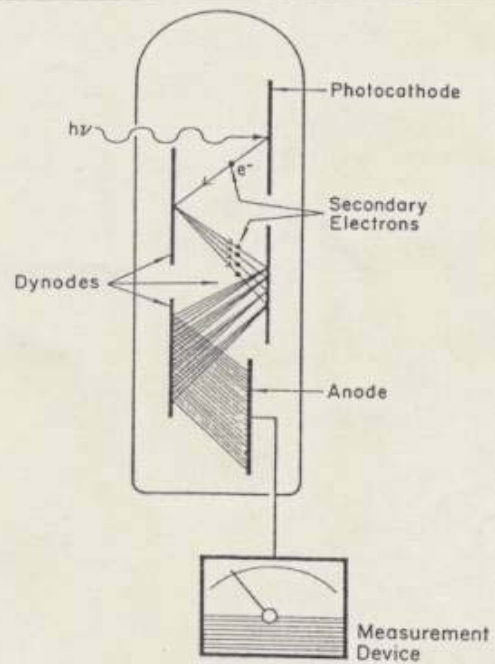
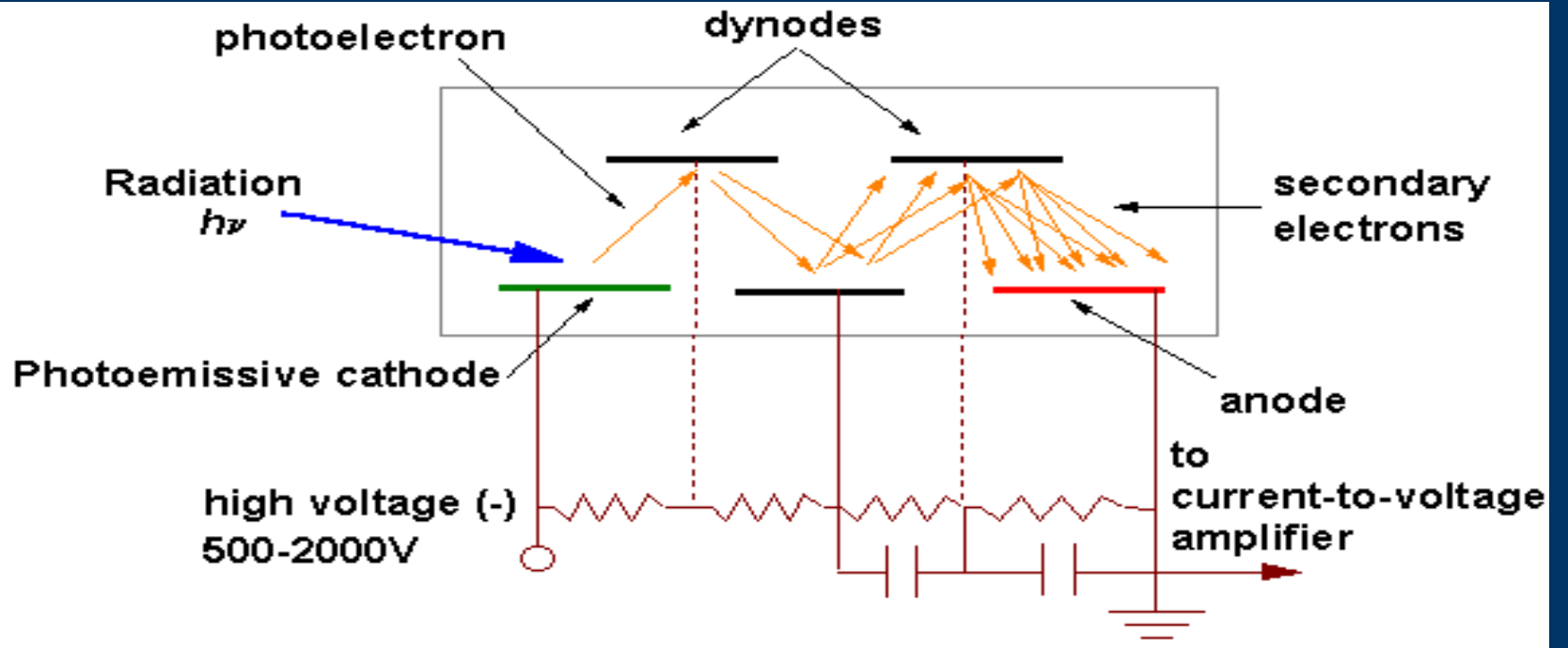


Figure 3-19. Photocathode, dynode, and anode layout of a photomultiplier tube.



- Secondary electrons strikes another dynode thus causing multiplication effect.
- At the end the anode collects secondary electrons from last dynode
- Electrical current measured is proportional to intensity.

■ **Advantage**

- It measures light over a relatively wide wavelength range.
- It can amplify weak emission levels.

Microwave induced Plasma Optical Emission Spectroscopy

- Microwave frequency generator is used
- Quartz or aluminum tubes used
- Argon, Helium, nitrogen, air or mixture.
- To determine chloride, bromine (halide), sulphur in aqueous solution.
- Samples introduced by electrothermal chemical vaporization technique.

- Photomultiplier tubes is used.
- Different wavelength are obtained when N₂ He or Argon.
- Optimized for the following:
 - Microwave forward and reflected powers
 - Plasma gas flow rate and nature of gas
 - Selection of emission lines or bands
 - 4 Optical arrangement, signal detection

- Sample introduction system

■ Applications

- Agriculture, food, clinical, geological, environmental, water, metal and organics, pesticide, pharmaceuticals, petroleum.
- Biologically used for determination of Se in liver, Al in blood.
- Silicates in lithium metaborates for fusion

- For organic use high RF Power than in aqueous solution, special pump tubings are used (acid/flex)

Thank You