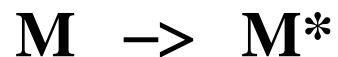


Chapter 9

Atomic emission and Atomic Fluorescence Spectrometry Emission spectrophotometric Techniques

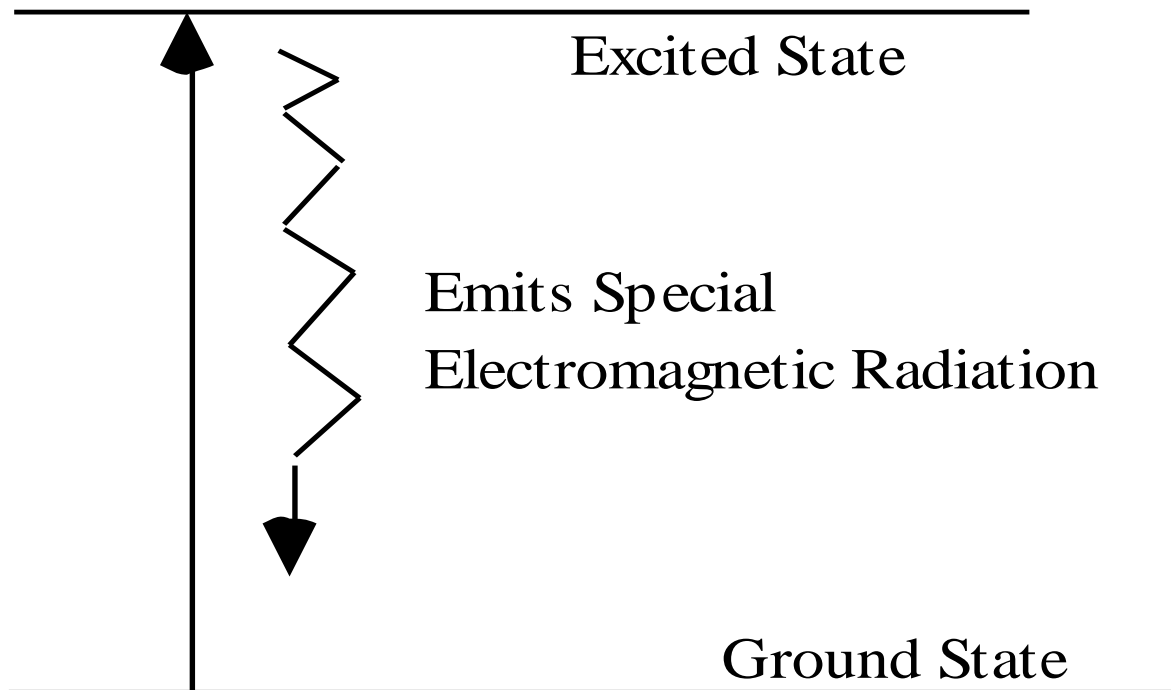
Emission Spectroscopy

- **Flame and Plasma Emission Spectroscopy are based upon those particles that are electronically excited in the medium.**
- **The Functions of Flame and Plasma**
 - 1. To convert the constituents of liquid sample into the vapor state.**
 - 2. To decompose the constituents into atoms or simple molecules:**
$$\text{M}^+ + \text{e}^- \text{ (from flame)} \rightarrow \text{M} + h\nu$$
 - 3. To electronically excite a fraction of the resulting atomic or molecular species**



Emission Spectroscopy

Measure the intensity of emitted radiation



Atomic emission

Qualitative analysis

Methods rely on the presence of specific emission lines.

Element	Major emission line, Å
Ag	3281
Cu	3248
Hg	2537
K	3447
Zn	3345

Emission Techniques

<u>Type</u>	<u>Method of Atomization</u>	<u>Radiation Source</u>
Arc	sample heated in an electric arc (4000-5000°C)	sample
Spark	sample excited in a high voltage spark	sample
Flame	sample solution aspirated into a flame (1700 – 3200 °C)	sample
Argon plasma	sample heated in an argon plasma (4000-6000°C)	sample

Why high energetic sources?

- **Flame techniques are limited to alkali (Li, Na, K, Cs, Rb) and some alkaline earth metals (Ca and Mg)**
- **More energetic sources are used for**
 - **more elements specially transition elements**
 - **simultaneous multielement analysis since spectra of dozen of elements can be recorded simultaneously**
 - **interelement interference is eliminated**
 - **liquids and solids**

Advantages and disadvantages of emission spectrometry

Advantages

- **Rapid**
- **Multielement (flame is limited for alkali and some alkaline earth metals) analysis is possible**
- **ICP-AES has become the technique of choice for metals analysis.**

Disadvantages

- **Flame is not suitable for elements other than alkali and alkaline earth metals.**
- **Initial cost of ICP instrumentation**
- **Continuing cost of operation (Ar required)**

Advantages of Plasma, Arc, and Spark Sources

- **Lower interelement interferences, due to higher temperatures.**
- **Spectra for most elements under single set of excitation conditions**
- **Spectra for dozens of elements simultaneously**
- **Determination of low concentrations of refractory compounds**
- **Wider dynamic range**

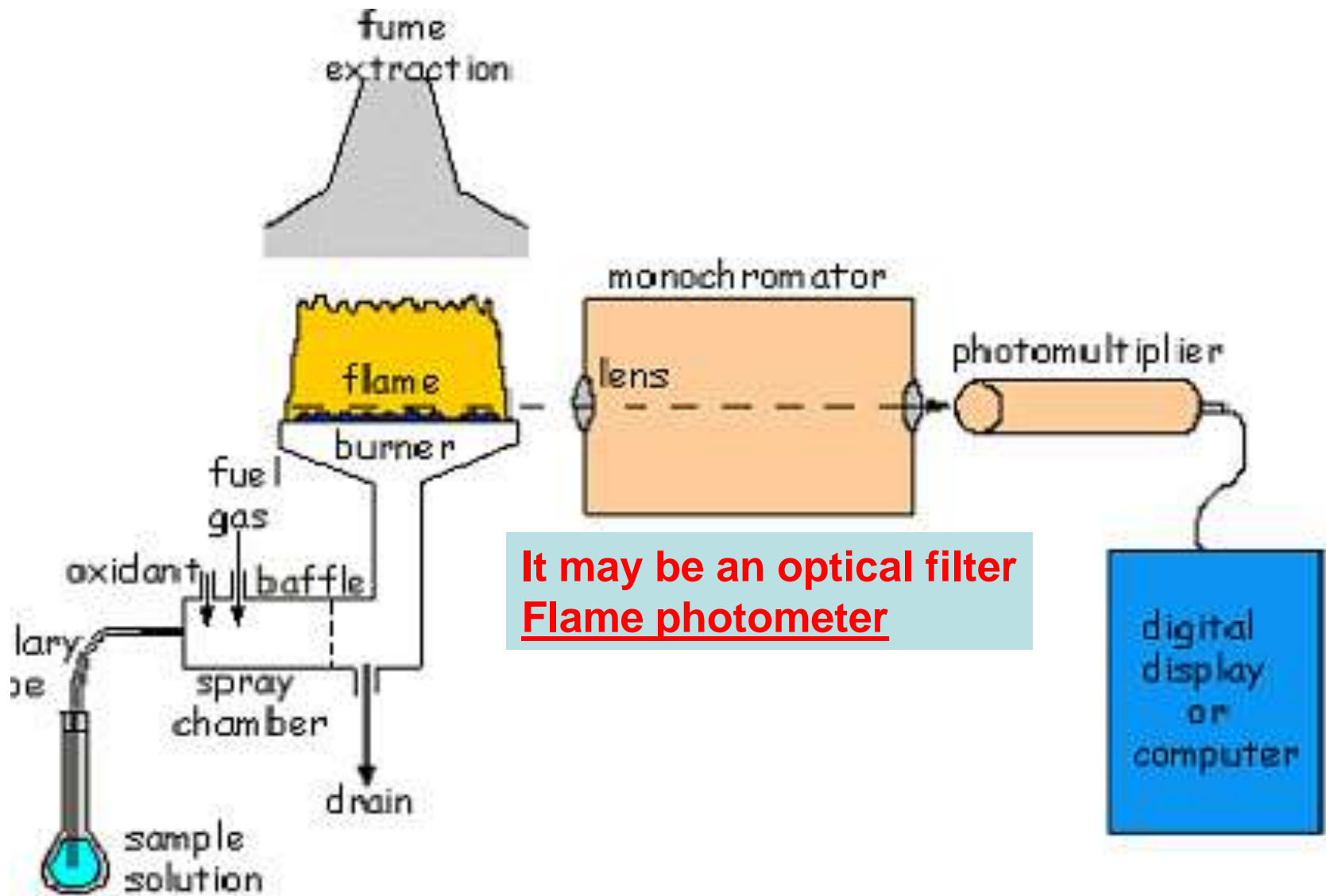
Advantages of Plasmas (over Arcs, Sparks)

- **Greater reproducibility of atomization conditions**
- **Factor of 10 improvement in precision**
- **Simpler, less expensive, more versatile equipment**

Advantages of Arcs and Sparks

More readily adapted to direct atomization of difficult samples, like refractory minerals, ores, glasses, and alloys

Flame Atomic Emission Spectrometer



Excitation Sources

Electrical

Relies on a pair of high purity carbon electrodes.

Arc - continuous electrical excitation.

Spark - short burst of excitation.

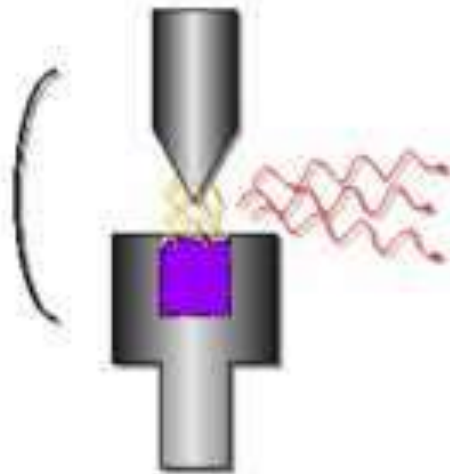
Temperature 4000 - 8000°C for a spark

Voltage 15,000 - 40,000 V

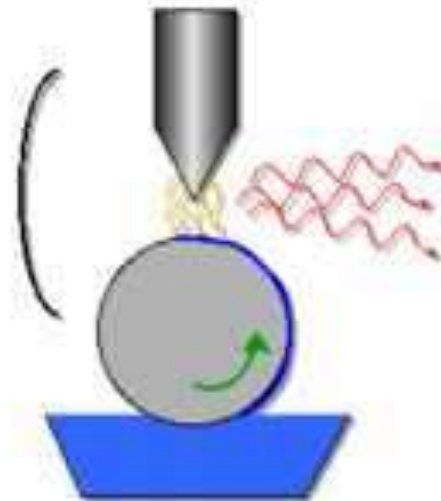
Excitation Sources

Electrical

The arrangement of the electrodes is based on the state of the sample.



solids



liquids

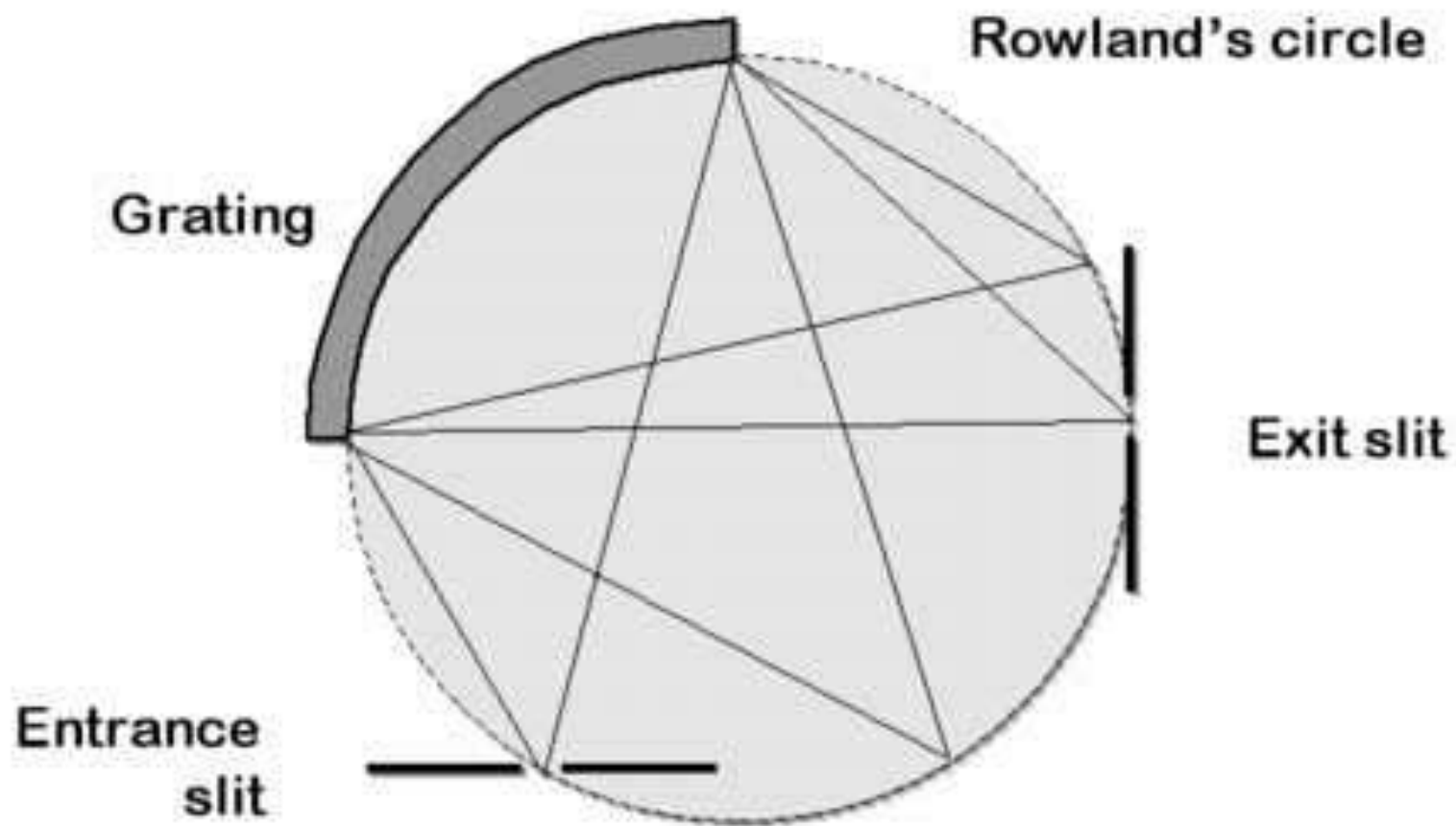
Monochromator system

Because emission lines are very narrow ($< .01 \text{ nm}$), high resolution grating are required.

One common approach is to use a curved grating.

This approach disperses the lines with focal points based on the curvature of the grating - **Rowland's circle.**

Monochromator system

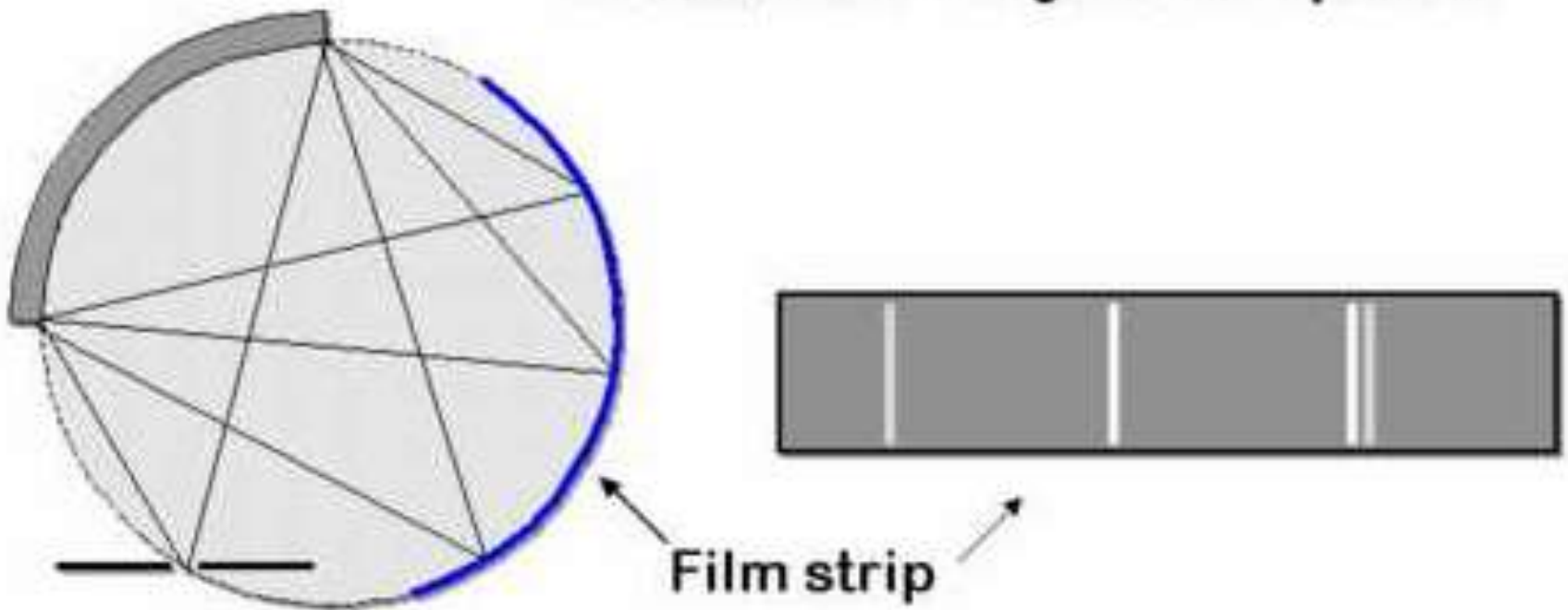


Film Detection

Film can be used as a detector

Qualitative - position of lines

Quantitative - degree of exposure



Detection by a photomultiplier tube

A PM tube provides a means of obtaining quantitative data.

Typically, it is easier to move the tube.

Moving the grating will alter the position of the Rowland's circle.

Multielemental work requires several PM tubes or recalibration after tube movement.

INDUCTIVELY COUPLED PLASMA

- **Main components of the instrument**
- **Performance of ICP**
- **ICP-mass spectrometry**
- **interferences**

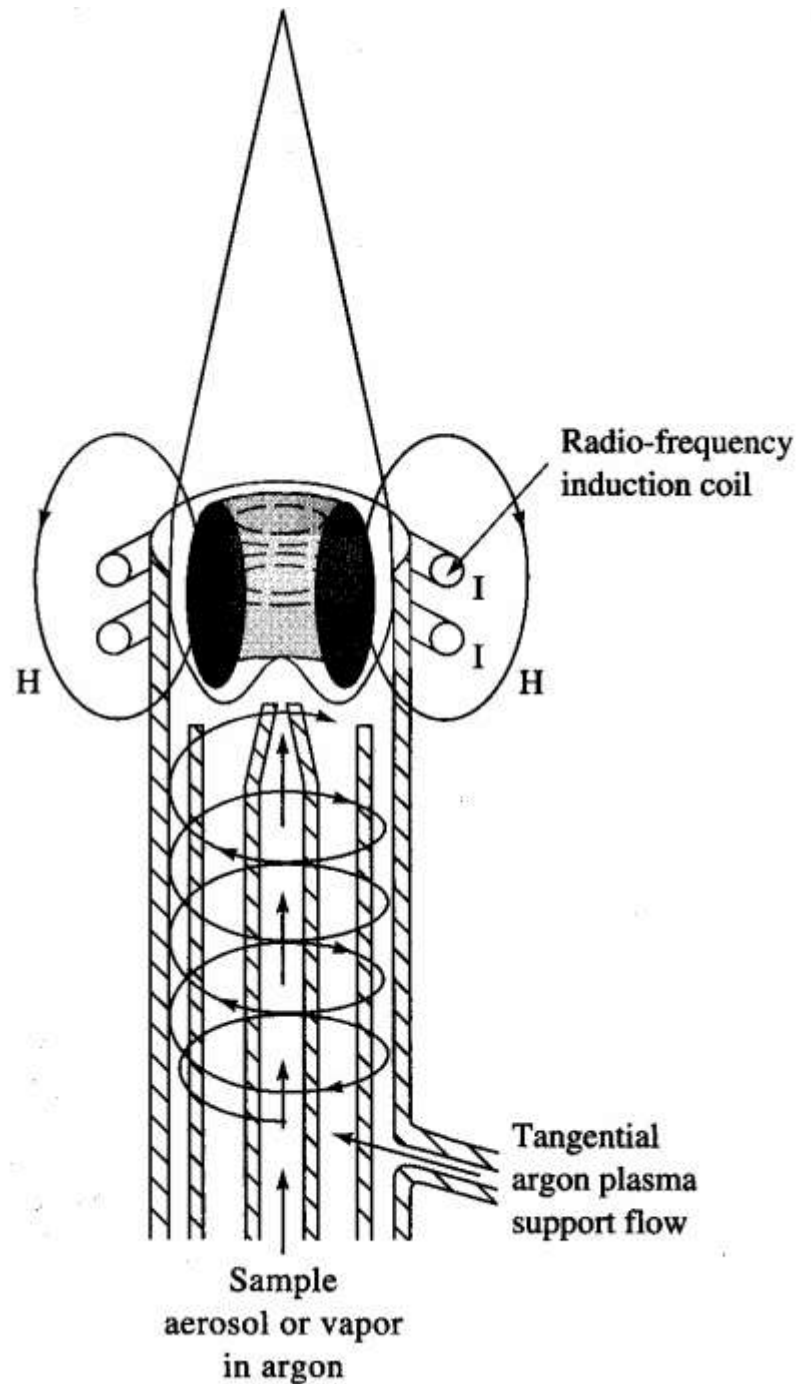
Introduction

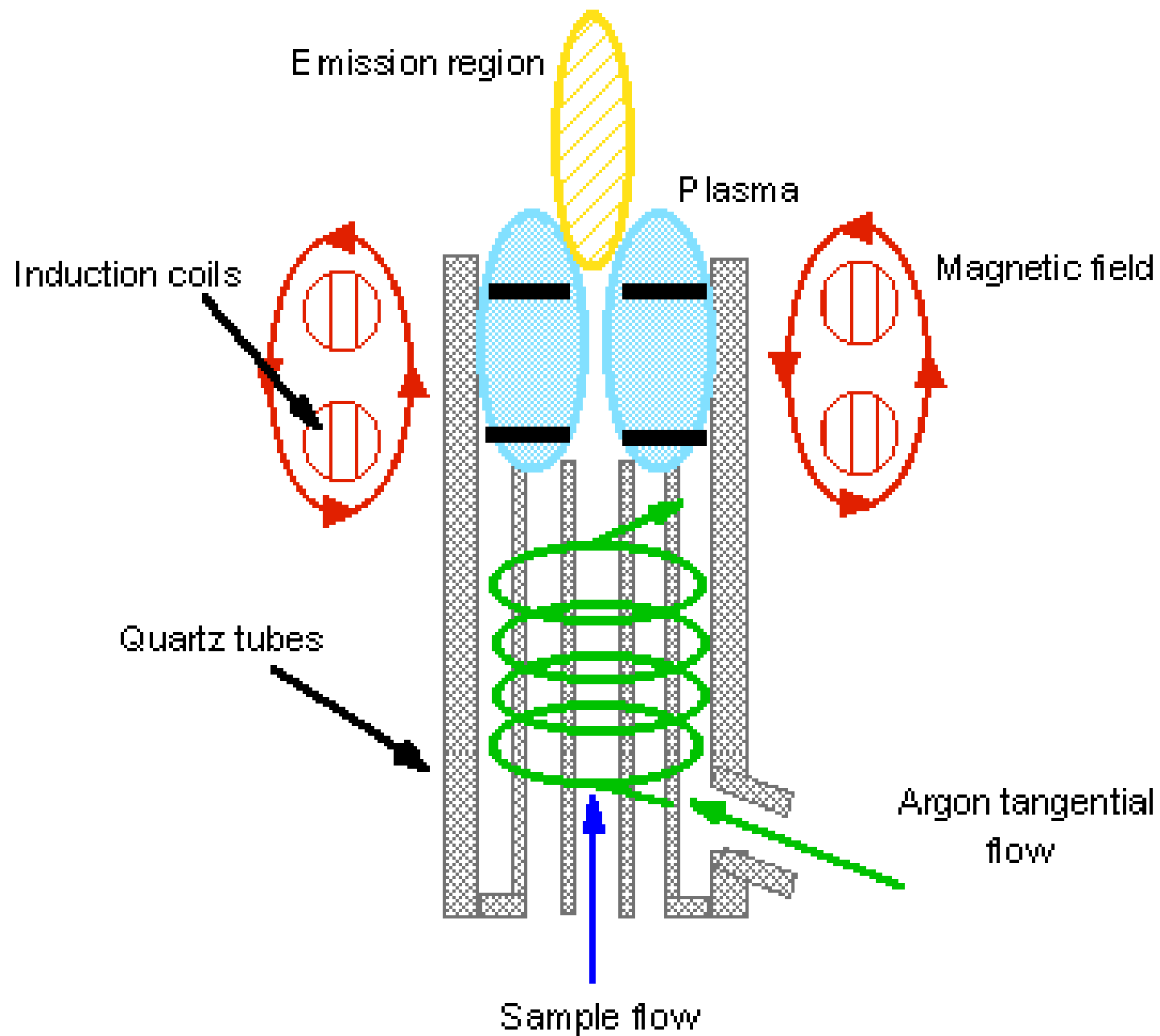
- The device which produces the ICP is commonly referred to as the ICP torch.
- It consists of two to four argon flows depending on the manufacturer:
 - Nebulizer gas (inner Argon flow), at about 1 L/min, carries the analyte aerosol
 - Sheath gas for producing a laminar flow to improve low excitation energy elements e.g., group I & II elements
 - Auxiliary gas (if present), lifts the plasma above the injector tube, used when measuring organics
 - Plasma gas, at about 12-16 L/min, sets the plasma conditions, e.g., excitation temperature

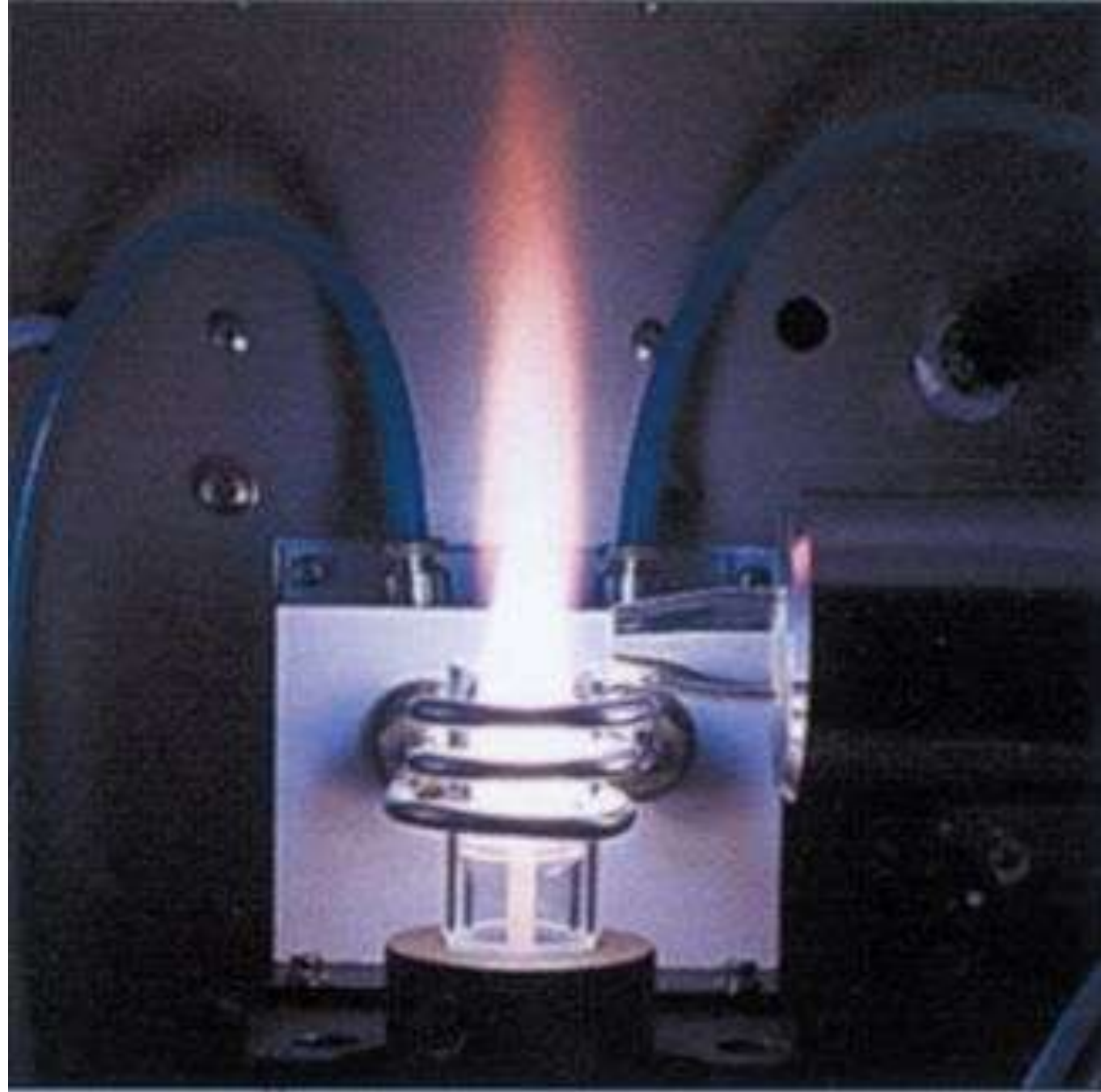
Sample Introduction

- **An ICP-AES instrument consists of a sample delivery system, an ICP to generate the signal, one or more optical spectrometers to measure the signal, and a computer for controlling the analysis.**
- **The most common sample delivery system consists of a peristaltic pump and capillary tube to deliver a constant flow of analyte liquid into a nebulizer.**

Inductively Coupled Plasma Torch



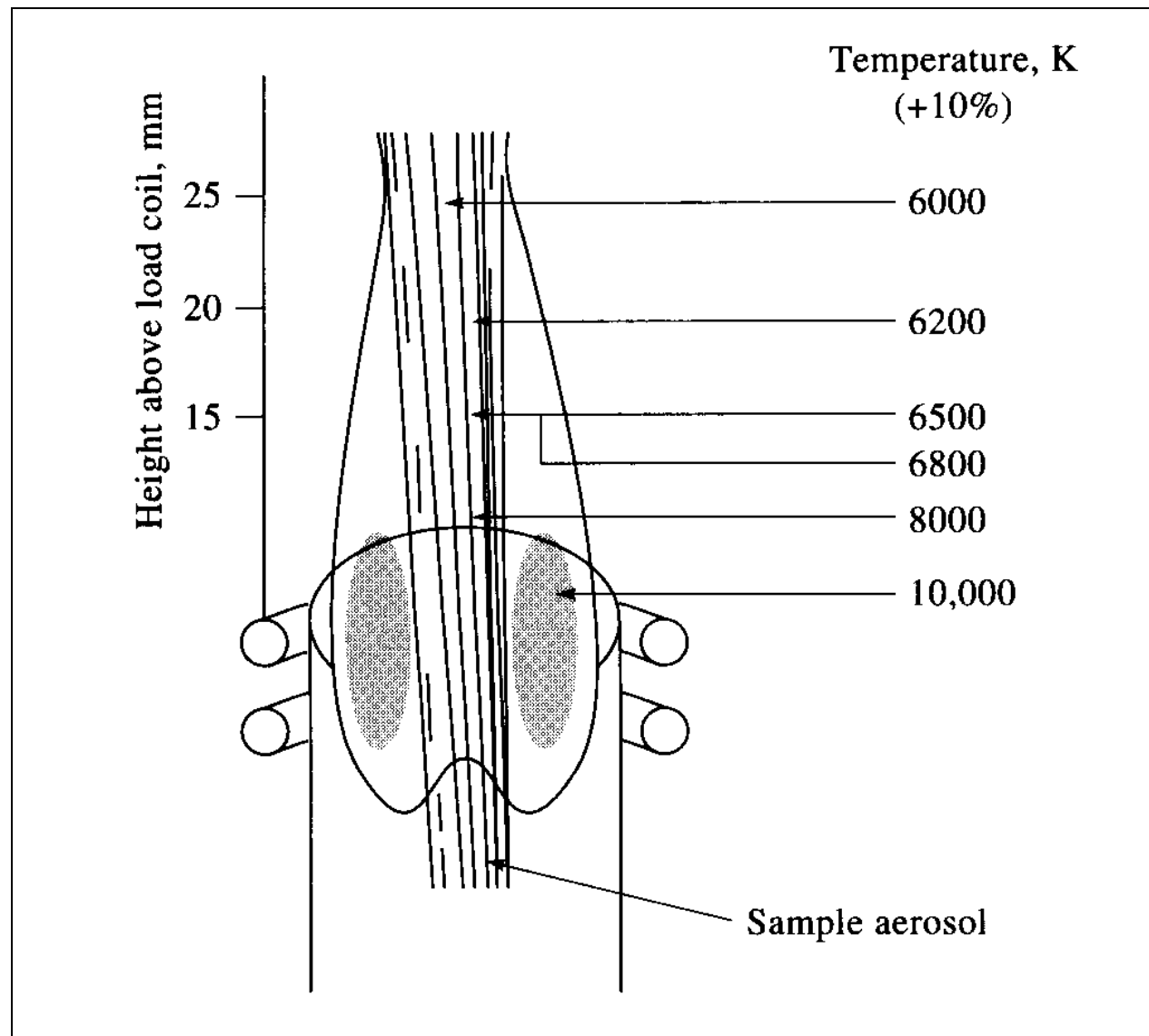




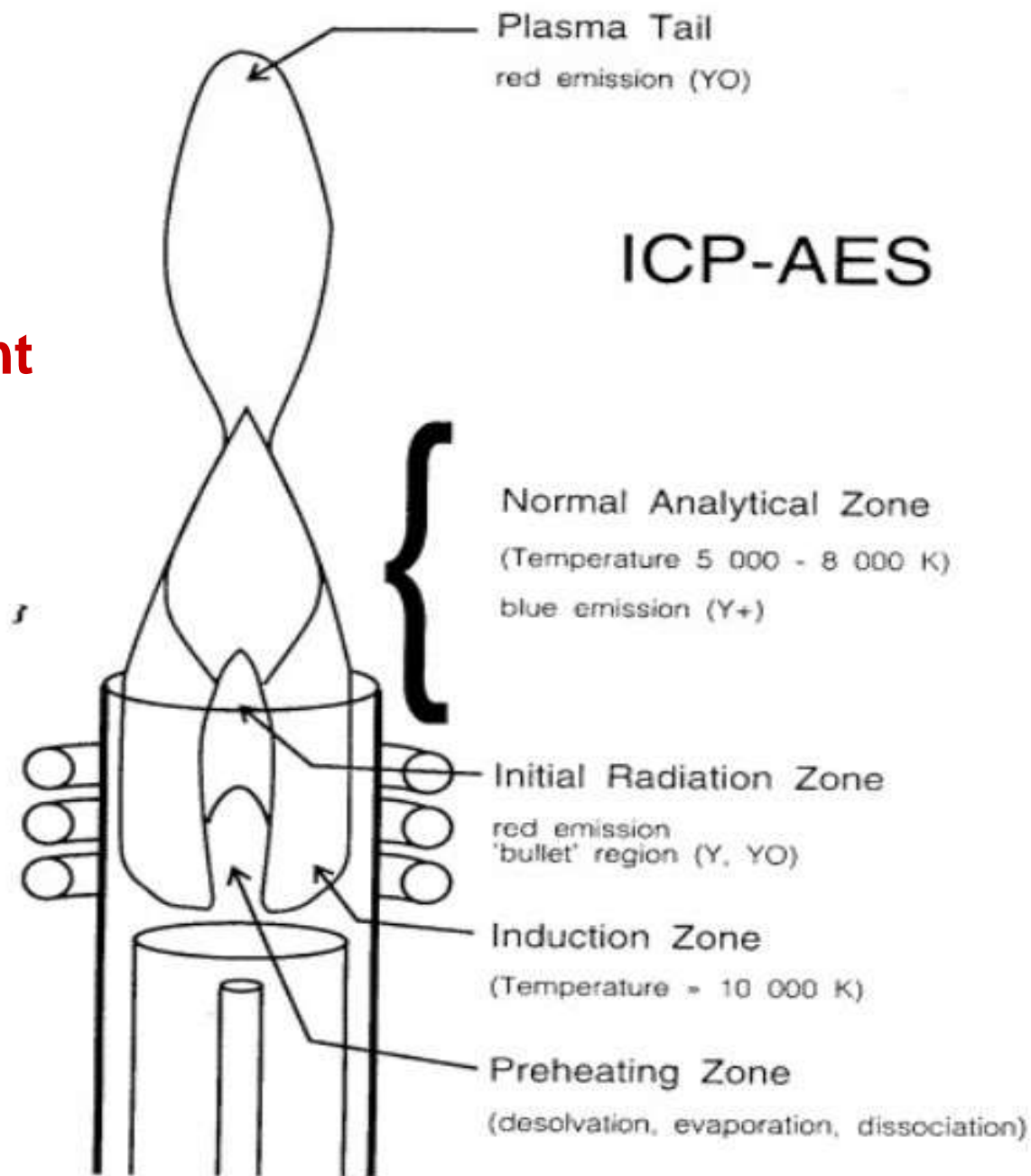
How does plasma generate?

- RF induction coil powered by RF generator will generate a fluctuating magnetic field around the coil
- Ionization of Ar is initiated by a spark
- Ar^+ and e^- will interact with the magnetic field thus they will be forced to move in annular paths
- Ohmic heating is the result of their resistance to the forced movement in limited area

Temperature profiles of inductively coupled plasma emission source



**Schematic diagram
showing the different
regions in the IC
Plasma**



- **RF**

- The function of the plasma generation system is to deliver high energy RF current through the induction coil. The alternating current through the induction coil provides the magnetic fields required to produce and sustain a plasma as an excitation source
- Plasma generation systems for commercially available ICP-ES instruments are generally PC controlled. The software allows the operator of the instrument to select the level of RF power required by the type of analysis of interest
- Plasma generation systems consist of an RF system and control circuitry

RF

- There are two frequencies currently commercially available
 - 27 MHz
 - 40 MHz
- 40 MHz RF systems are seen to have reduced background and provide greater plasma stability, particularly for organic analysis
- ICP-ES RF systems are required to produce uniform power levels under the varying conditions of sample loading
- Two main requirements have to be met to reduce these effects:
 - Impedance matching
 - level control

RF-Generator

- ICP's generally require an RF power of 1-2 kW maximum output to maintain the plasma.
- **High efficiency required - especially for organics (not less than 1.5 Kw)**

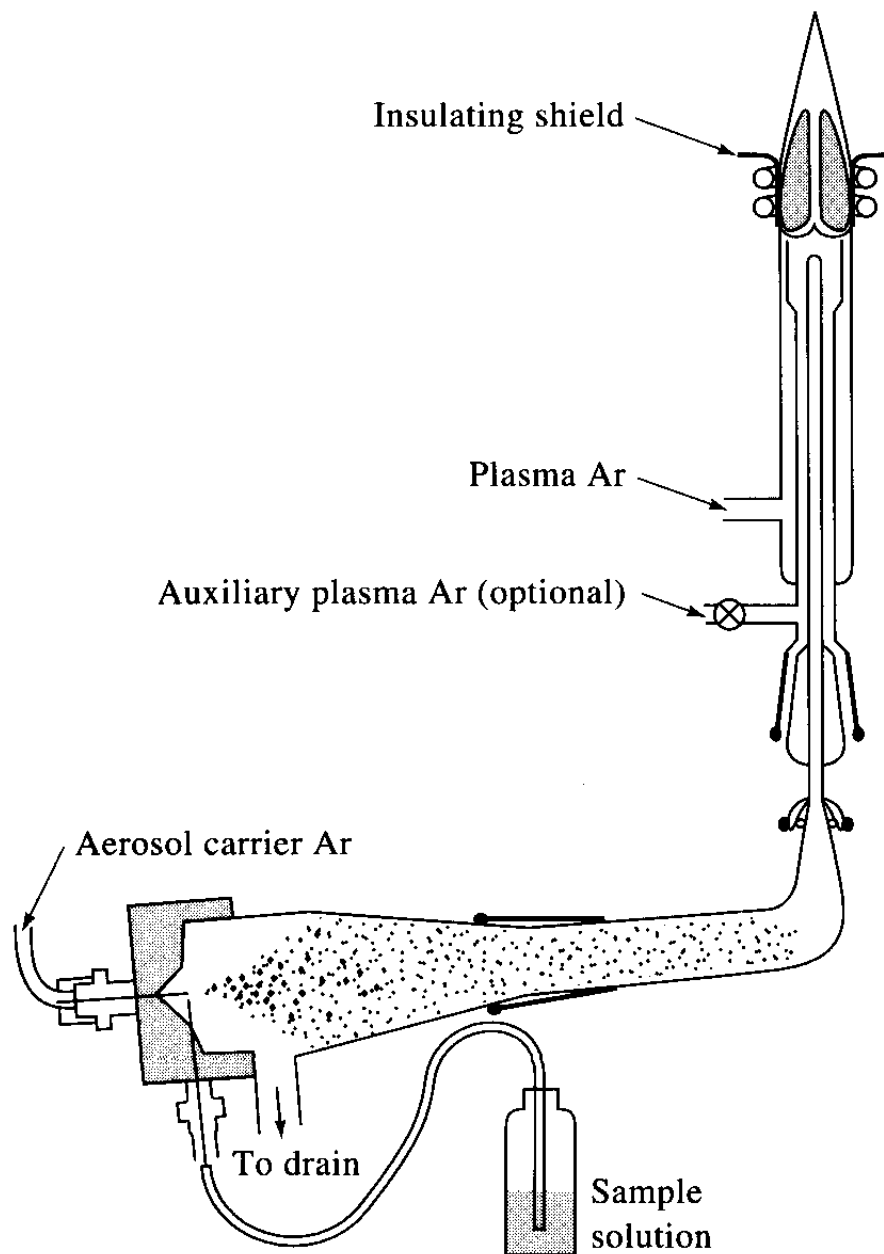
Frequency

- Fixed versus Free Running
 - Fixed: Crystal controlled, eg at 40 MHz
 - Free running: floats eg at 40 MHz \pm 2 MHz
- 40 MHz versus 27 MHz
 - Because of the skin-effect in RF plasmas, higher frequency gives a thinner plasma with a wider dynamic range (less self-absorption), with lower backgrounds and fewer interferences.

Level control

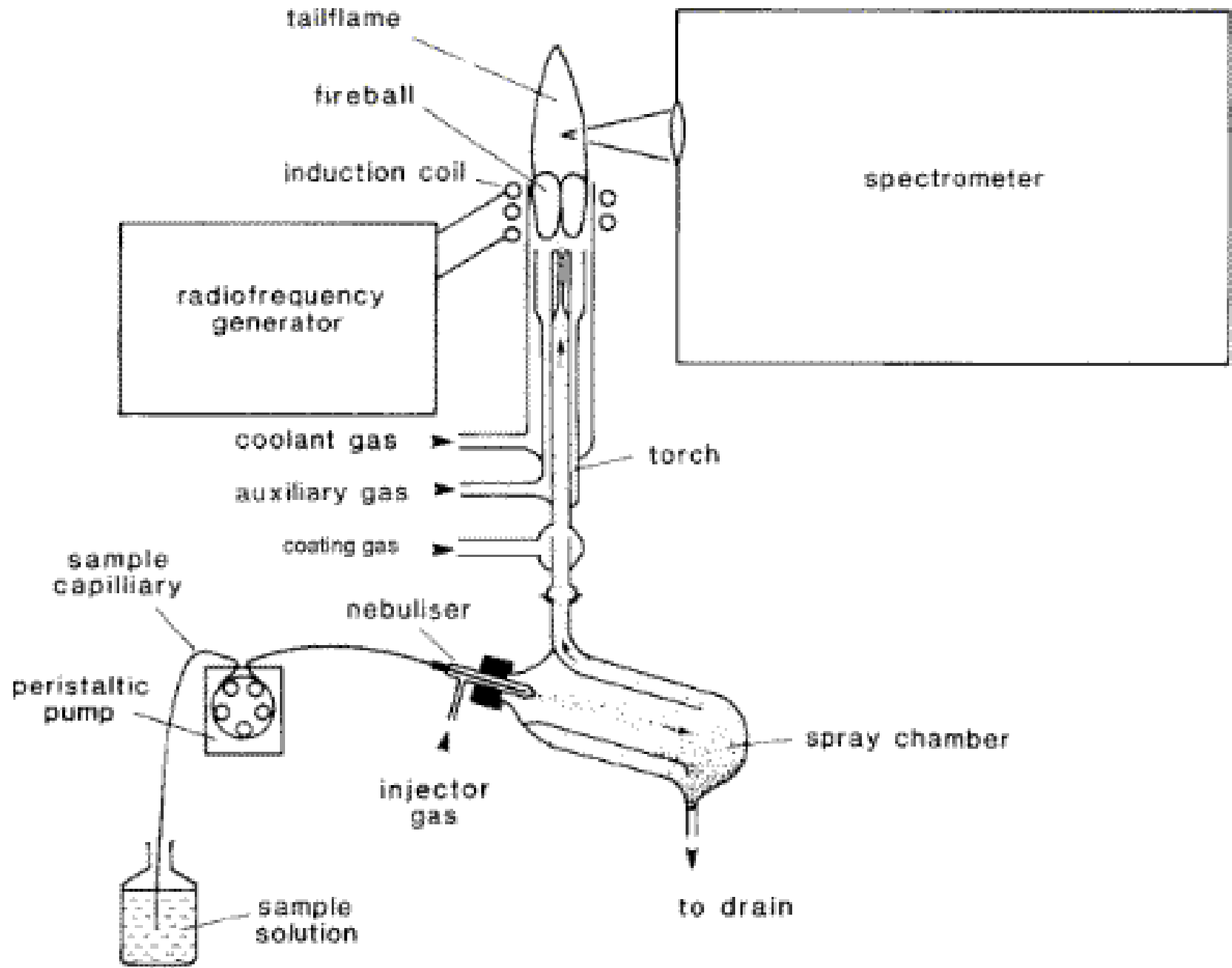
- In order to control the amount of RF power supplied to the plasma a sample of the RF energy must be made**
- The level of alternating current passing through the induction coil or the amplitude of the RF signal being transferred to the coil provide an indication of the amount of RF energy available to the plasma**
- This level must then be compared with the operator selected power level**
- The difference of the desired value to the known value then results in the control circuitry increasing or decreasing the amount of energy applied to the RF system**

Inductively Coupled Plasma Emission Source and Supply



- **An ICP torch can be used to atomize and ionize materials for quantitative trace and ultratrace elemental analysis**
- **The compounds in the samples are broken down into their elemental form and some fraction of each elemental species is simultaneously ionized**
- **The monocationic (+1) form is preferred for the assay, and conditions are set to enhance production of that form**
- **The torch is normally operated at a temperature of ~3000K**

Schematic diagram of a typical ICP-OES instrument



Processes that take place in the plasma

- **Aerosol vapor is transported to the plasma**
- **Vapor desolvates**
- **Atomization occurs within the plasma**
- **Atoms get excited to atomic and ionic states**
- **Rich spectra produced because of presence of both atomic and ionic lines**

Typical detection limits in ICP-OES

Typical detection limits

< 1 ppb

 $< 10 \text{ ppb}$

< 5 ppb

> 10 ppb

The periodic table is color-coded by concentration ranges. The ranges are:

- < 1 ppb (orange)
- < 5 ppb (green)
- > 10 ppb (blue)
- > 100 ppb (pink)

The table includes elements from Hydrogen (H) to Oganesson (Og). The color-coding is as follows:

- < 1 ppb (orange):** H, Li, Be, Na, Mg, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.
- < 5 ppb (green):** K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.
- > 10 ppb (blue):** H, Li, Be, Na, Mg, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.
- > 100 ppb (pink):** H, Li, Be, Na, Mg, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

Sampling

Liquids

- Form an aerosol ($<5\ \mu$ droplet size) of the liquid sample
- Eliminate larger droplets
- The use of liquids facilitates automatic sampling

Gases

- May use gasses directly or indirectly, e.g., **form hydrides**

Solids

- May use slurries (if 95% of particles $<5\ \mu$)
- May use spark ablation or laser ablation to generate a small metal vapor

Viewing position

- The plasma generated in an ICP can be viewed by the spectrometer, side-on or end-on.
- These viewing positions are called **radial** and **axial** viewing, respectively.
- Each has advantages and disadvantages, so each tends to be used for different applications: **radial viewing** for normal analysis and complex materials, **axial viewing** for low detection limits in simpler materials.

A Radial Slit

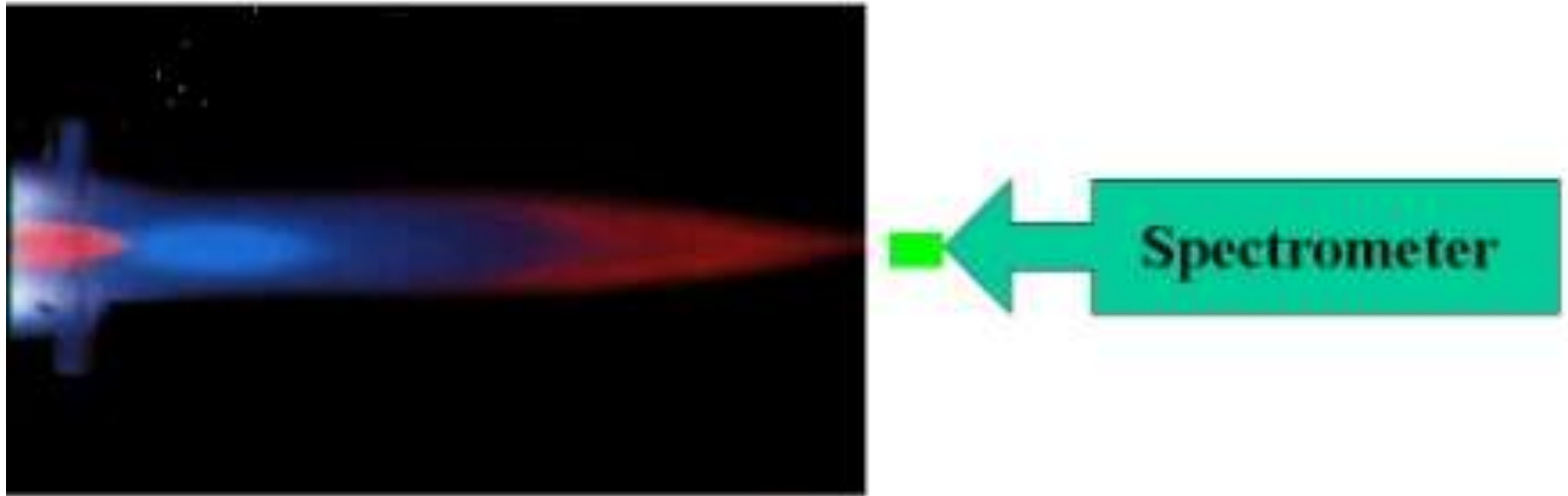


Spectrometer

Advantages of Radial View

- **Should collect signal from the entire normal analytical zone**
 - no torch adjustment for different elements
 - fewer matrix effects and interferences, especially in organics
 - less stray light
 - better detection limits in difficult matrices, especially in alkalis and organics
 - can run any matrix
 - less maintenance of the torch
 - torches last longer especially with dissolved salts
 - lower consumption of argon

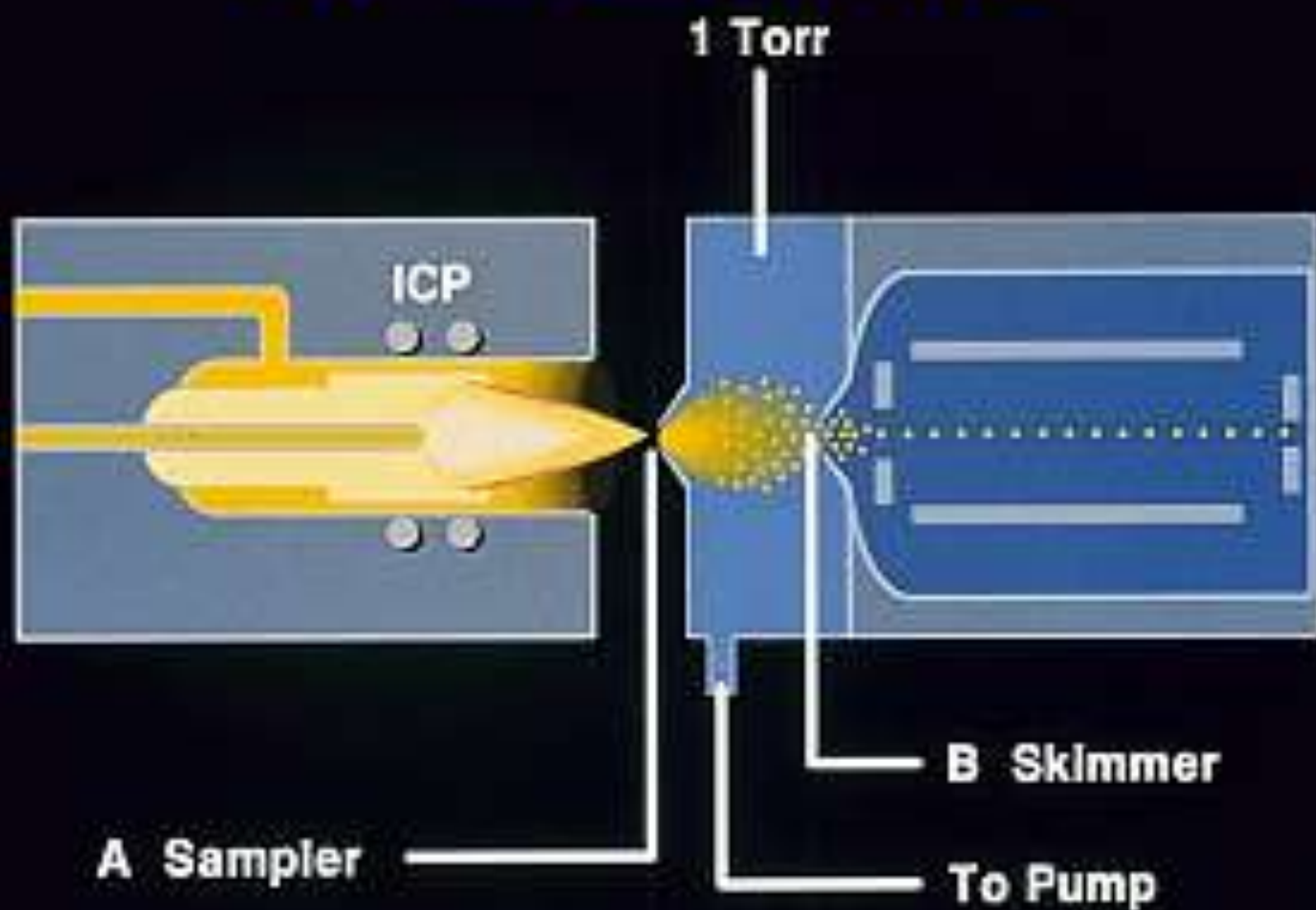
An Axial Slit



Advantages of Axial View:

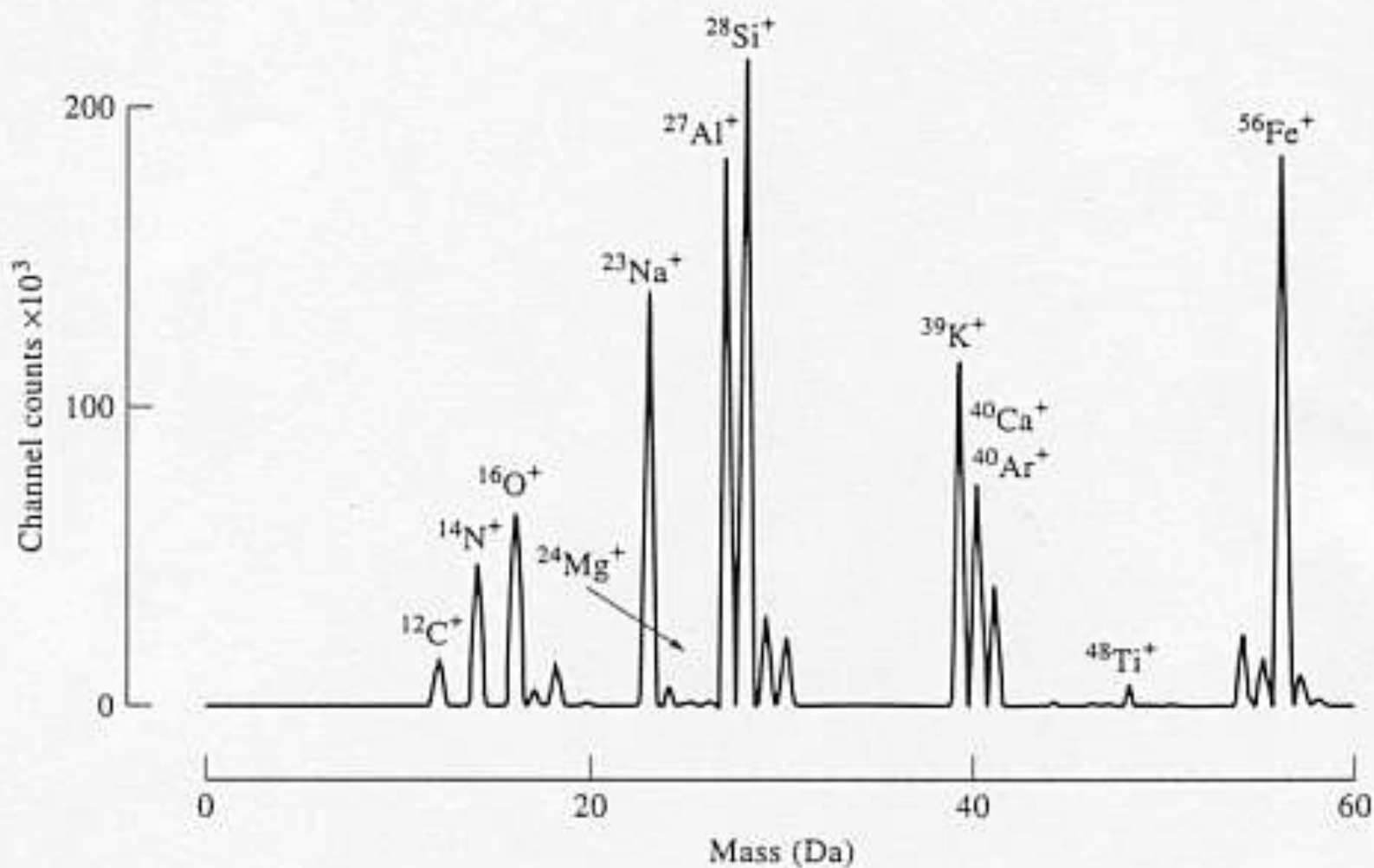
- More intensity
- Better detection limits in simple matrices

ICP / MS INTERFACE



- **> 90% element coverage**
- **0.1 to 10 ppb sensitivity for most elements**
- **RSD ~ 2% to 4%**

Typical laser ablation/ICP-MS mass spectrum of a rock sample

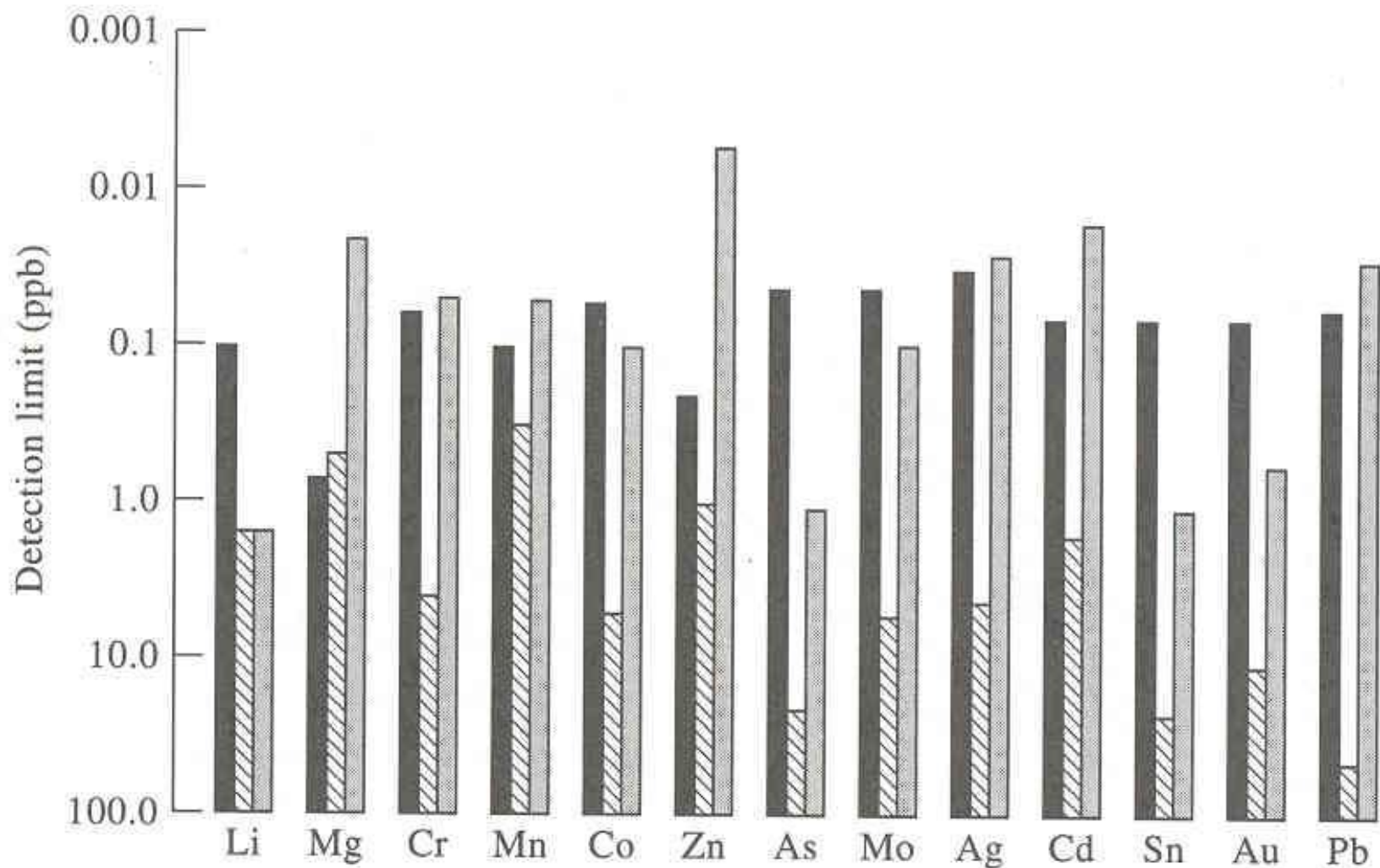


Comparison of Detection Limits

Black = ICP/MS

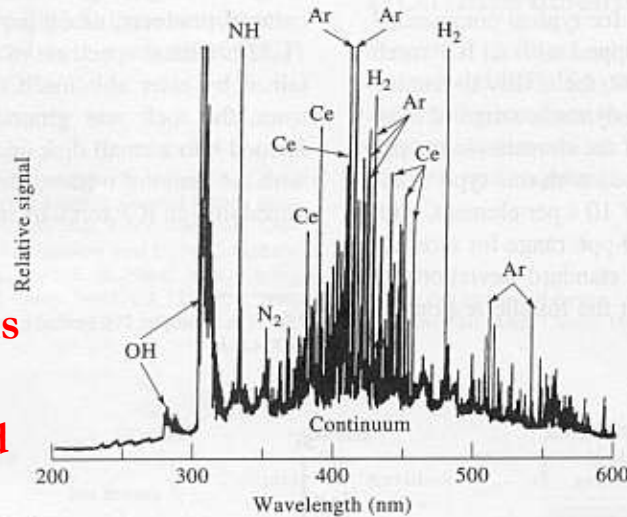
Cross-Hatch = ICP/AES

Gray = Furnance AA

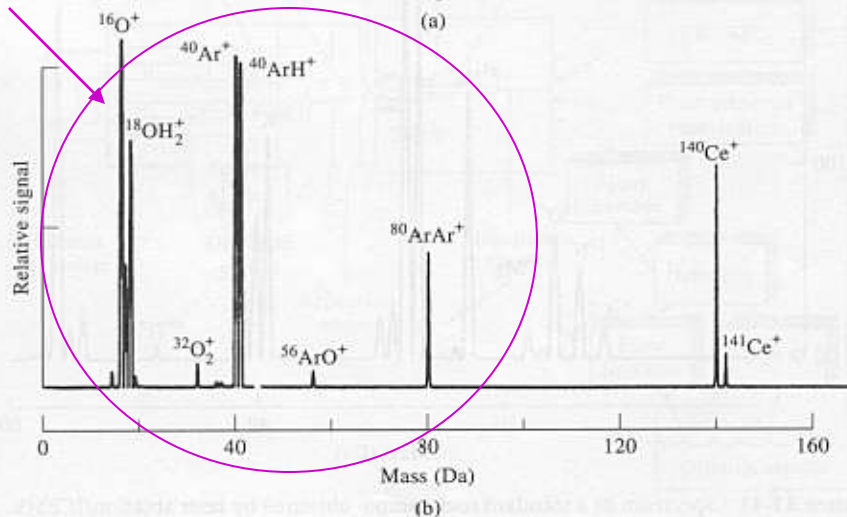


Comparison of ICP/AES & ICP/MS for the analysis of Cerium solutions

ICP/AES (100 ppm Ce)



Background ions originated from the Ar, O, H and N elements



ICP/MS (10 ppm Ce)

- Simple to interpret, especially for rare elements
- Less interference from atmospheric contaminants or molecular bands

Nitric acid is commonly used as acidification agent rather than hydrochloric acid, sulfuric acid and phosphoric acid in sample preparation. Why?

Limitations for ICP/MS Quantitation

- Formation of *monocationic ions*, *doubly-charged ions* and *stable metal oxides ions* in the torch depends on the identity of the element and several experimental conditions, such as the plasma *r.f.* power and the nebulizer gas flow rate.
- Spectroscopic interference:

Isobaric Interference

- isotopes of different elements (or isobaric interference) e.g. $^{87}\text{Rb}^+$ and $^{87}\text{Sr}^+$; $^{40}\text{Ar}^+$ and $^{40}\text{Ca}^+$; $^{58}\text{Ni}^+$ and $^{58}\text{Fe}^+$

Polyatomic Ion Interference

- interactions between species in the plasma and species in the matrix or atmosphere, e.g. molecular ions from the acids of digestion
- e.g. ClO^+ and $^{51}\text{V}^+$

Matrix effect

a. Limited tolerance for salt concentration

(< 1% is acceptable but < 0.1% is preferred!)

- *The deposition of salts leads to a decrease in the aperture diameter, so the sensitivity worsens and the signal gradually decreases as a function of time*

b. Organic solvents tend to quench the plasma torch

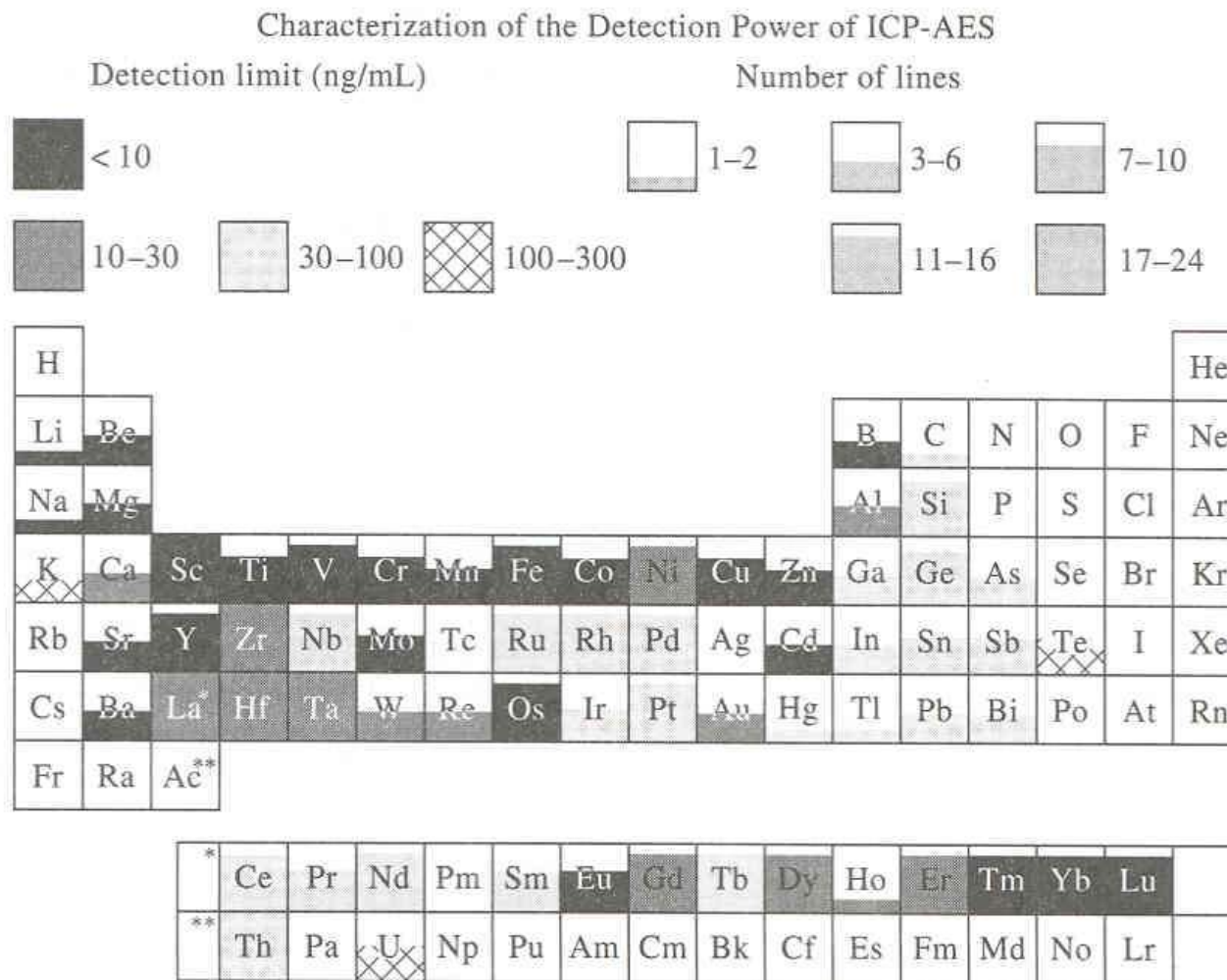
Approaches to reduce the occurrence of polyatomic interferences

- Adjust the plasma conditions to minimize the formation of polyatomic species
e.g. use 5-10% N_2 in Ar, the axial temperature of the plasma increases by ~ 1000 K and the electron density increases by 30%. A marked reduction of MO^+ ions
- Minimizing the amount of water vapor introduced into the plasma in order to limit the signal intensity of oxygen-containing species
e.g. reduce the spray chamber temperature(?)
- Use He instead of Ar as plasma gas to avoid interference from polyatomic ions containing argon
- Use electrothermal volatilization for sample introduction
- Use high resolution ICP/MS

Approaches to correct for or overcome matrix effect

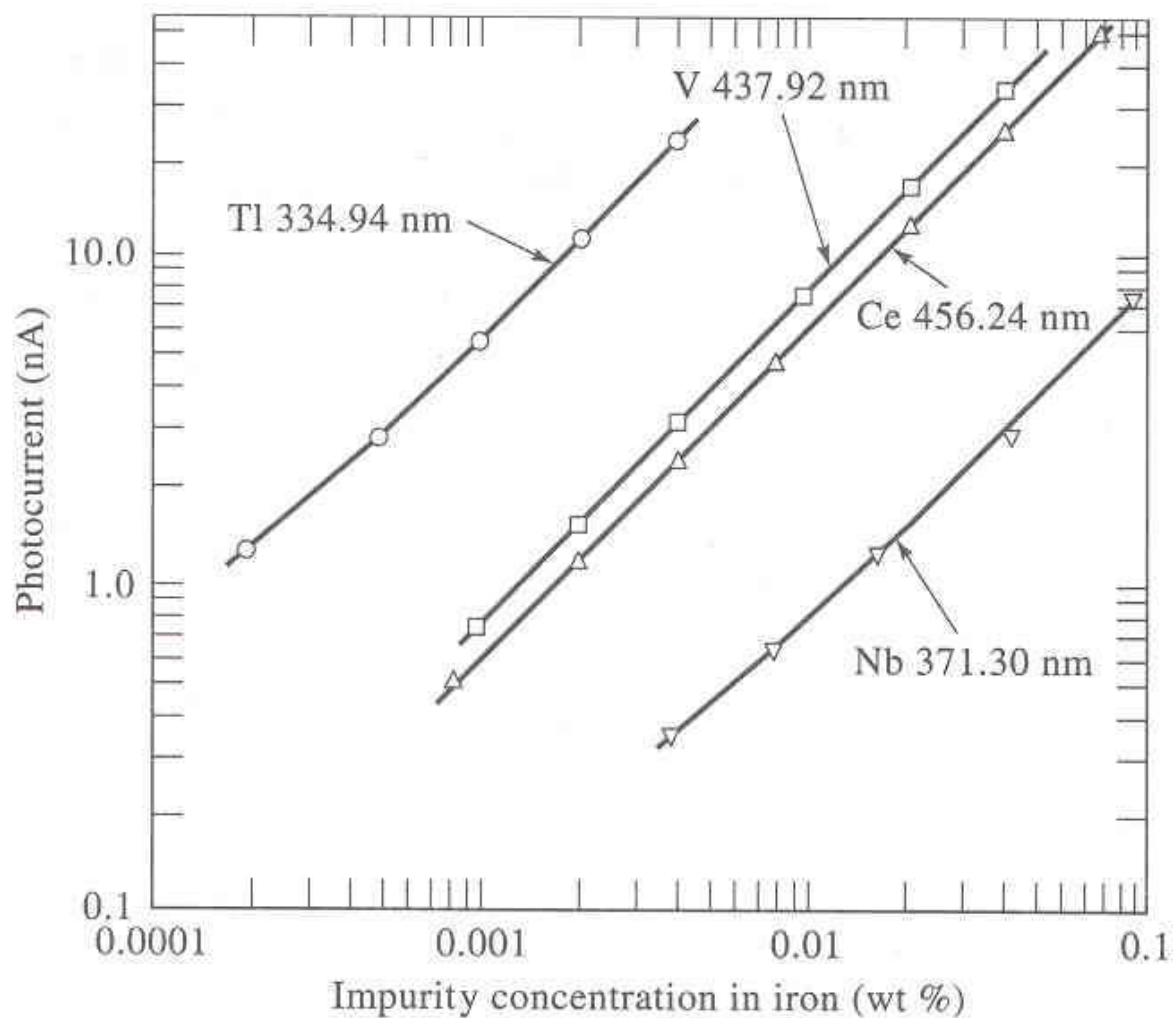
- Dilution
- Matrix matching
- Use of internal standards
 - Addition of a known and preferably an equal concentration of an internal standard to all samples (& standards). The analytical signal is taken as the ratio of the signals for the analyte elements in the sample (& standards) and the signal for the internal standard
- Standard addition
 - A known amount of the element(s) of interest is added to the sample and hence suffers the same matrix effect as the analyte

Detection limit and number of useful lines for ICP with pneumatic nebulizer.



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

AES Calibration Curve



Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

“S”-shaped Calibration Curves

Low concentrations, curvature due to increased degree of ionization (especially in flames).

High concentrations, self-absorption

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods*

Method	Number of Elements Detected at Concentrations of				
	<1 ppb	1–10 ppb	11–100 ppb	101–500 ppb	>500 ppb
Inductively coupled plasma emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	19
Flame atomic fluorescence	4	14	16	4	6
Flame atomic absorption	1	14	25	3	14

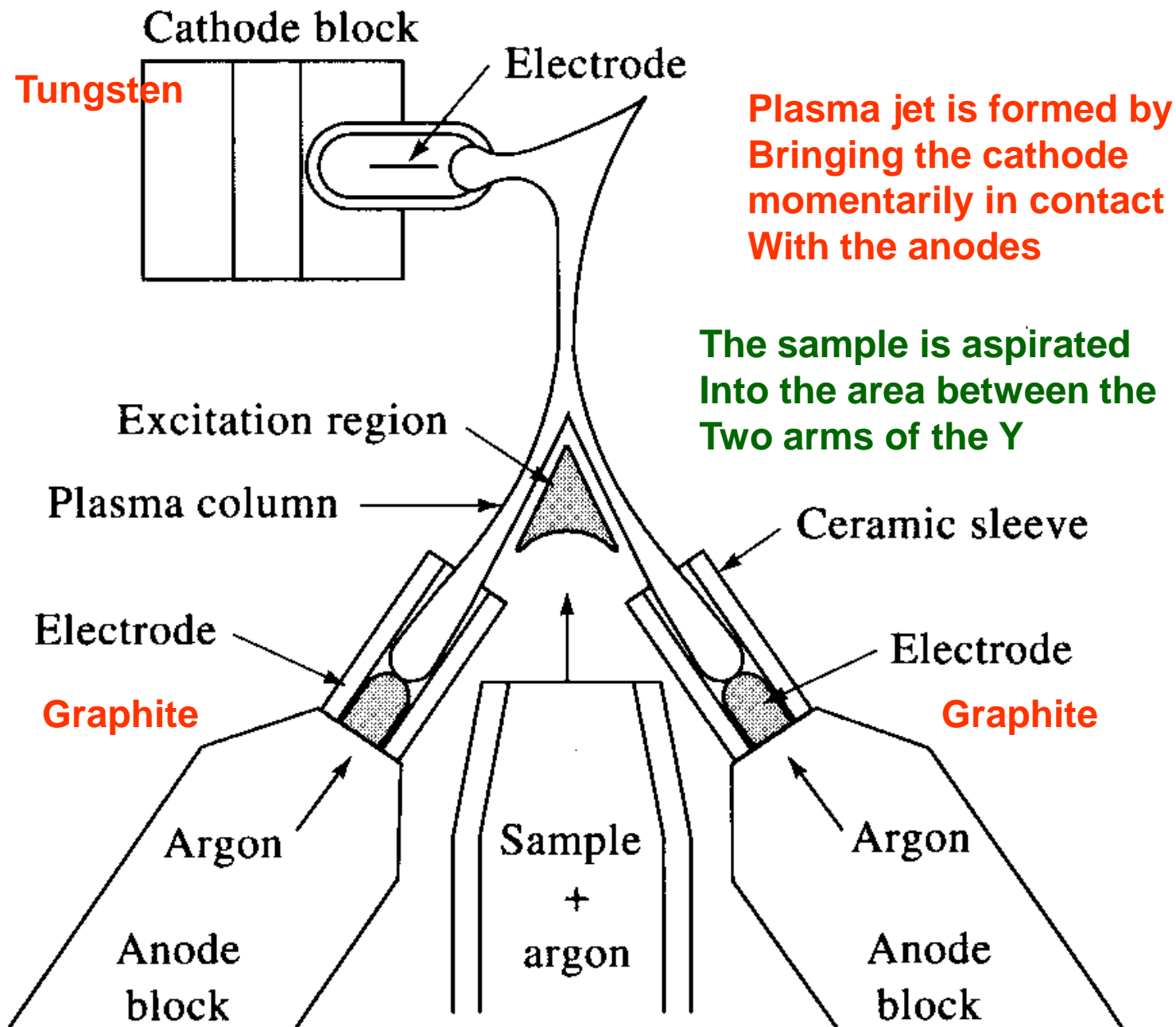
*Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise. Data abstracted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, **1974**, *46*(13), 1111A. Copyright 1974 American Chemical Society.

Source: Skoog, Holler, and Nieman, *Principles of Instrumental Analysis*, 5th edition, Saunders College Publishing.

Direct Current Plasma

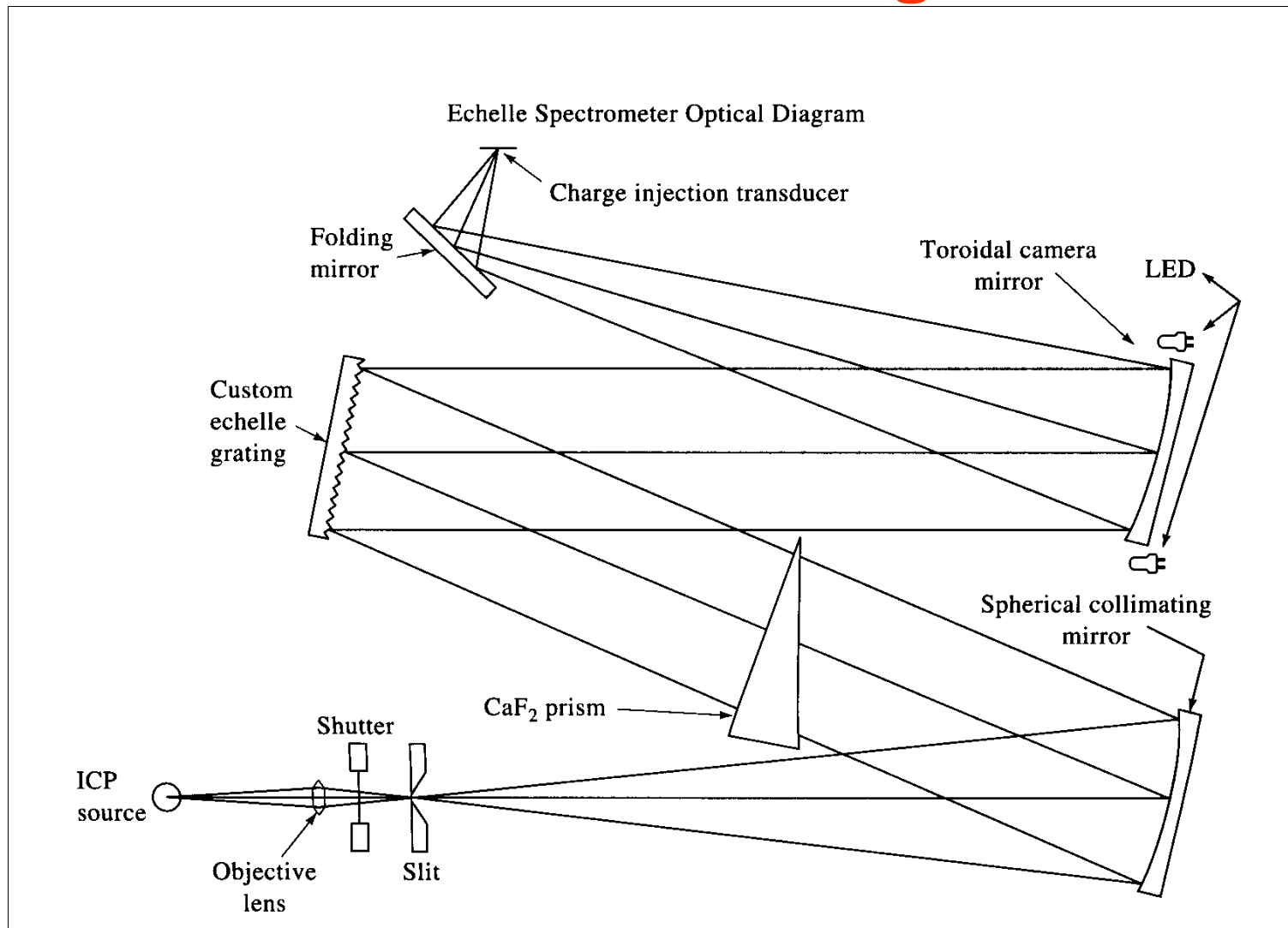
- **Spectra produced have fewer lines, largely from atoms not ions.**
- **Sensitivities from order-of-magnitude lower up to that of ICP.**
- **Reproducibility similar to ICP.**
- **Requires less argon, less expensive.**
- **Graphite electrodes must be replaced frequently (little maintenance with ICP).**

Direct Current (DC) Plasma



ICP spectrometer

Echelle Grating



General ICP-AES

Optics

- There are basically two different types of ICP-ES spectrometers on the market:
 - sequential
 - simultaneous
- These terms relate to the way optics separate the characteristic wavelengths for analysis

General ICP-AES

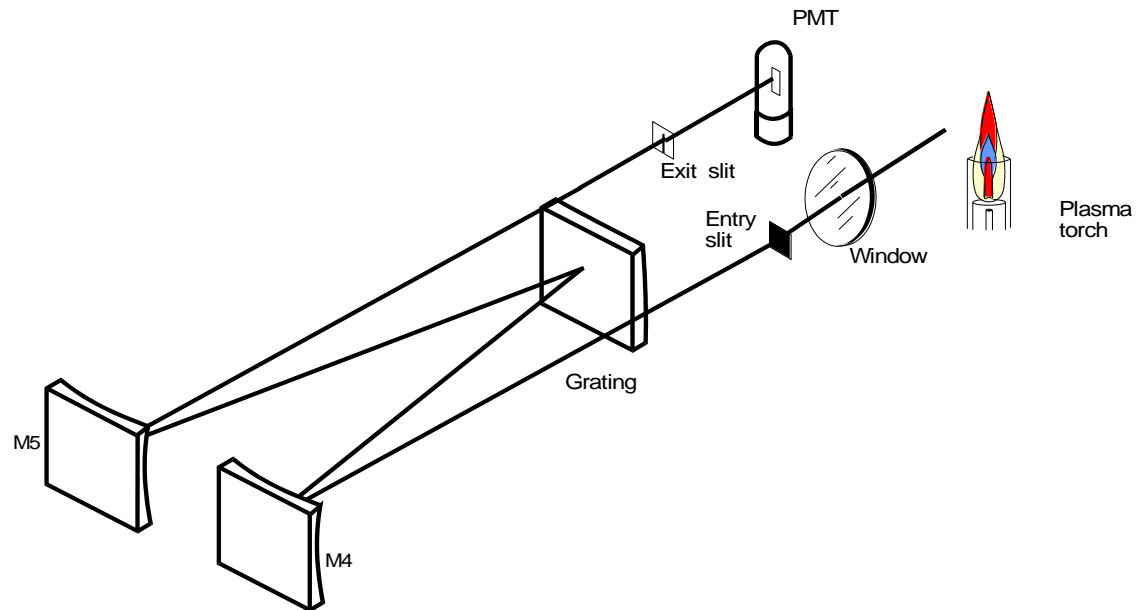
Optics

– Sequential

- A sequential ICP-ES uses a scanning monochromator that gathers the radiant emissions and focuses this incident light onto a diffraction grating.
- The grating is rotated into a position to direct only the characteristic wavelength of interest onto a detector for analysis.
- Most commercially available sequential ICP-ES instruments use a Czerny-Turner configuration.

General ICP-AES

— Sequential

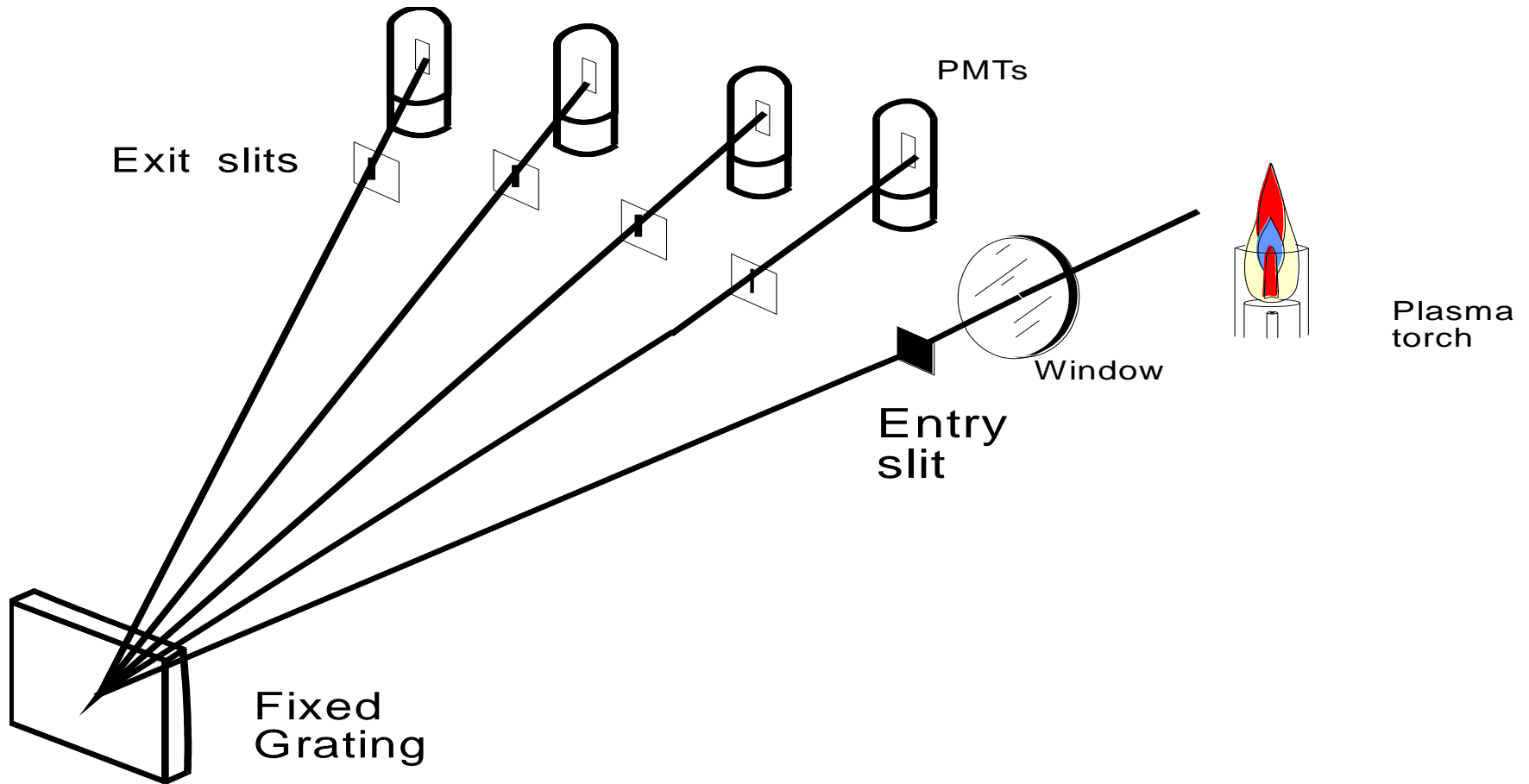


General ICP-AES

– Simultaneous

- There are two basic simultaneous configurations currently commercially available:
 - Rowland circle
 - Echelle

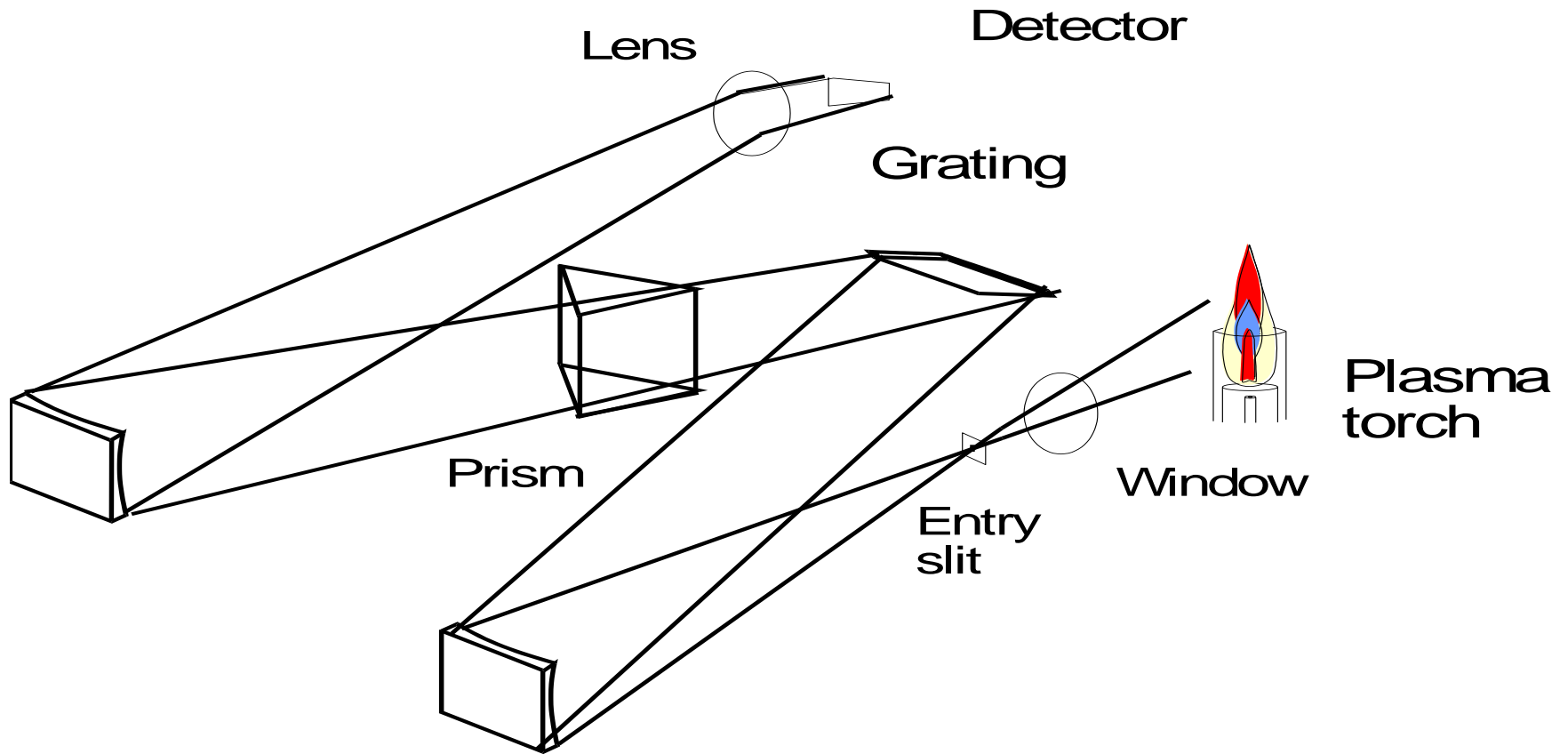
- Simultaneous
 - Rowland circle



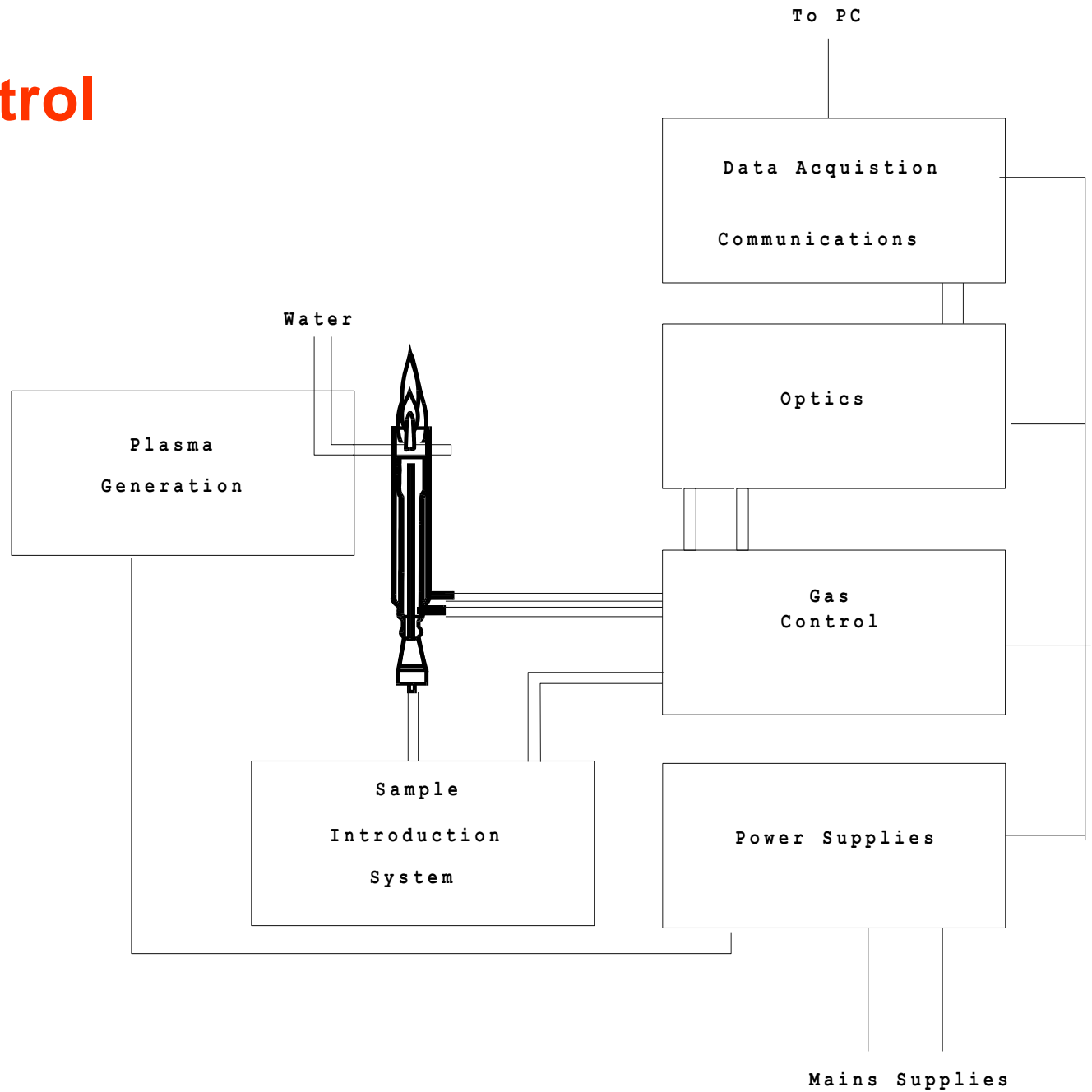
– Rowland circle

- » A Rowland simultaneous ICP-ES uses a stationary monochromator that gathers radiant emissions and focuses incident light onto a single spherical diffraction grating**
- » The grating is designed to direct the spectrum of light to a number of PMT detectors which are arranged in a circle.**
- » Each PMT is physically placed for each characteristic wavelength that is to be analyzed.**
- » Therefore for each wavelength of interest a detector in a specific location must be used.**

- Echelle



Gas control



- **Gas control**
 - The purpose of a gas control assembly is to regulate and control the supply of required gas flows throughout the ICP-ES
 - Most gas control assemblies supply the gas required for
 - torch/plasma
 - nebulizer
 - optics
 - Commercial ICP-ES instruments use argon for the plasma
 - Nitrogen is used on some instruments as an optics purge
 - Oxygen is often used as carrier gas additive when organic solvents are being analyzed