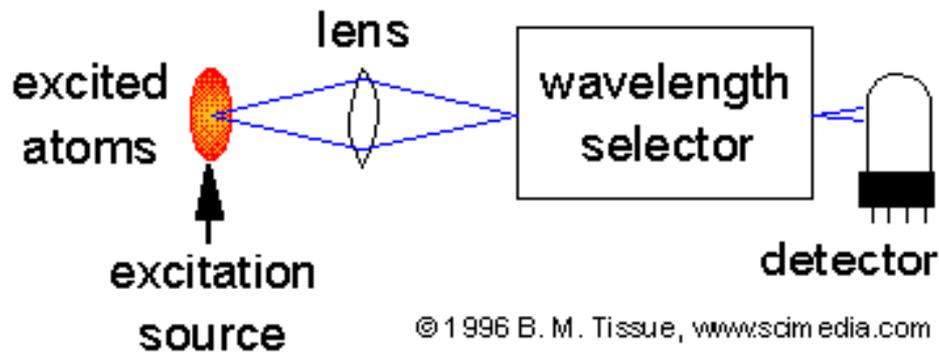


Atomic Emission Spectroscopy (AES, OES)

Introduction:

- Atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration.
- Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomized by a flame, discharge, or plasma.
- These high-temperature atomization sources provide sufficient energy to promote the atoms into high energy levels.
- The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow.
- The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer.
- Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to atomic-absorption (AA) spectroscopy.

Instrumentation:



As in AA spectroscopy, the sample must be converted to free atoms, usually in a high-temperature excitation source

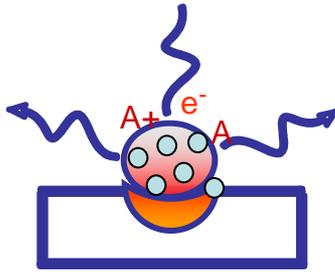
- Sample Introduction:
- Liquid samples are nebulized and carried into the excitation source by a flowing gas.
- Solid samples can be introduced into the source by a slurry or by laser ablation of the solid sample in a gas stream. Solids can also be directly vaporized and excited by a spark between electrodes or by a laser pulse.

Excitation:

- The excitation source must desolvate, atomize, and excite the analyte atoms. A variety of excitation sources are described in separate documents:
 - Flame
 - Arc / Spark
 - Plasma
 - Inductively-coupled plasma (ICP)
 - Direct-current plasma (DCP)
 - Microwave-induced plasma (MIP)
 - Laser-induced plasma, Laser-induced breakdown (LIBS)

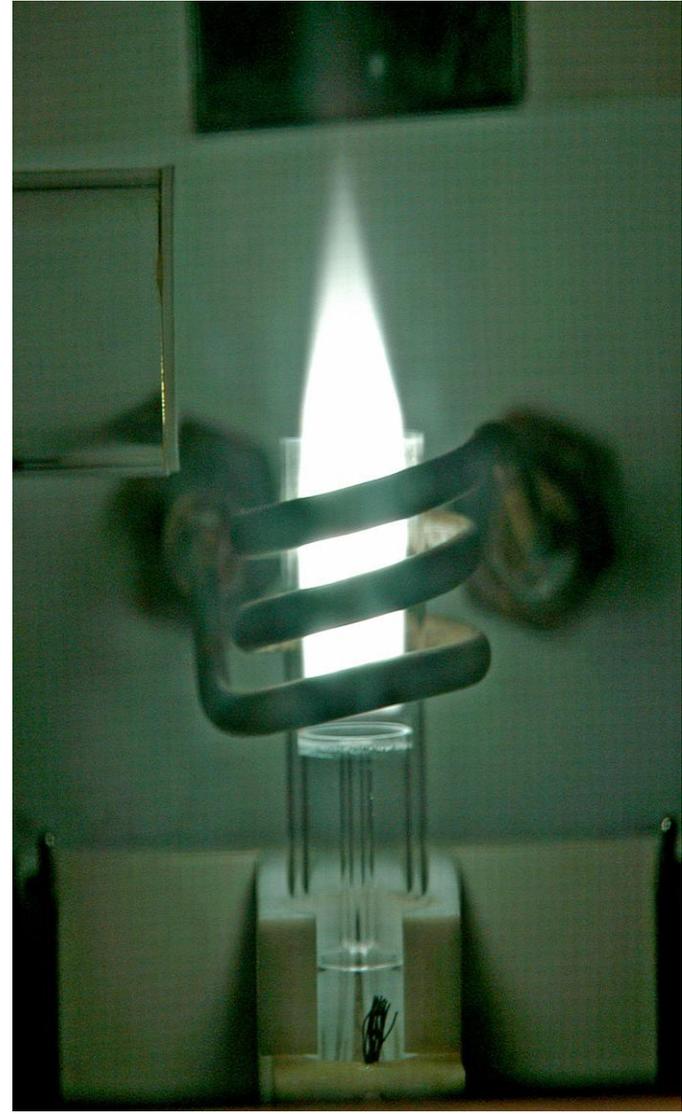
AES based on Plasma Sources:

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

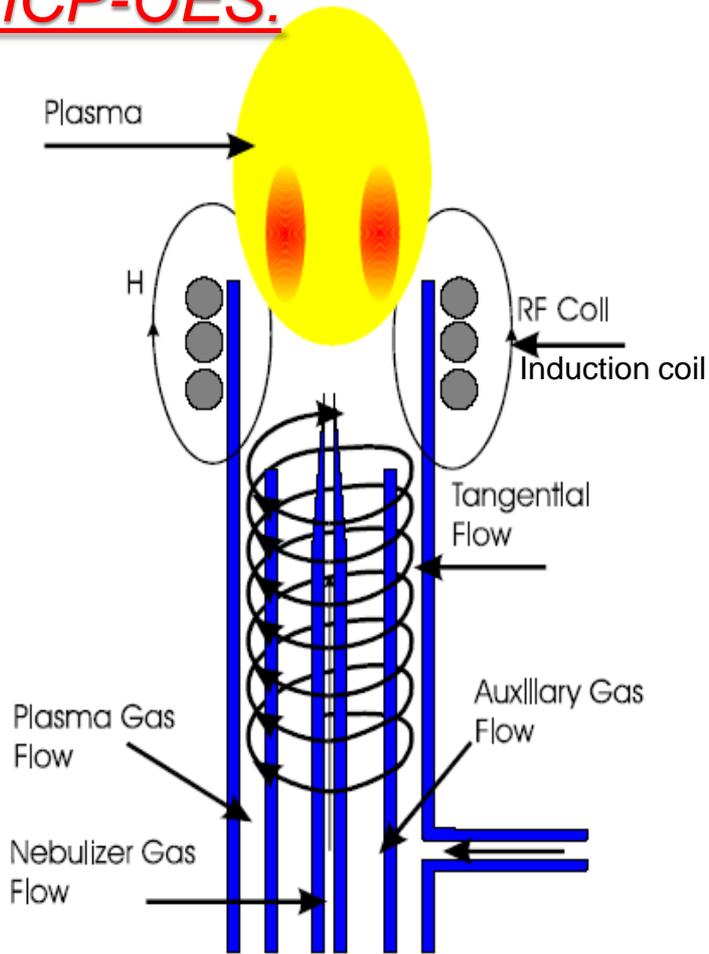


- 1) increased atomization/excitation
- 2) wider range of elements
- 3) simultaneous multielement analysis
- 4) wide dynamic range

1) ICP-OES:



1) ICP-OES:



- Torch up to 1" diameter
- Ar cools outer tube, defines plasma shape
- Radio-frequency (RF) up to 2 kW
- Ar flow up to 20 L/min

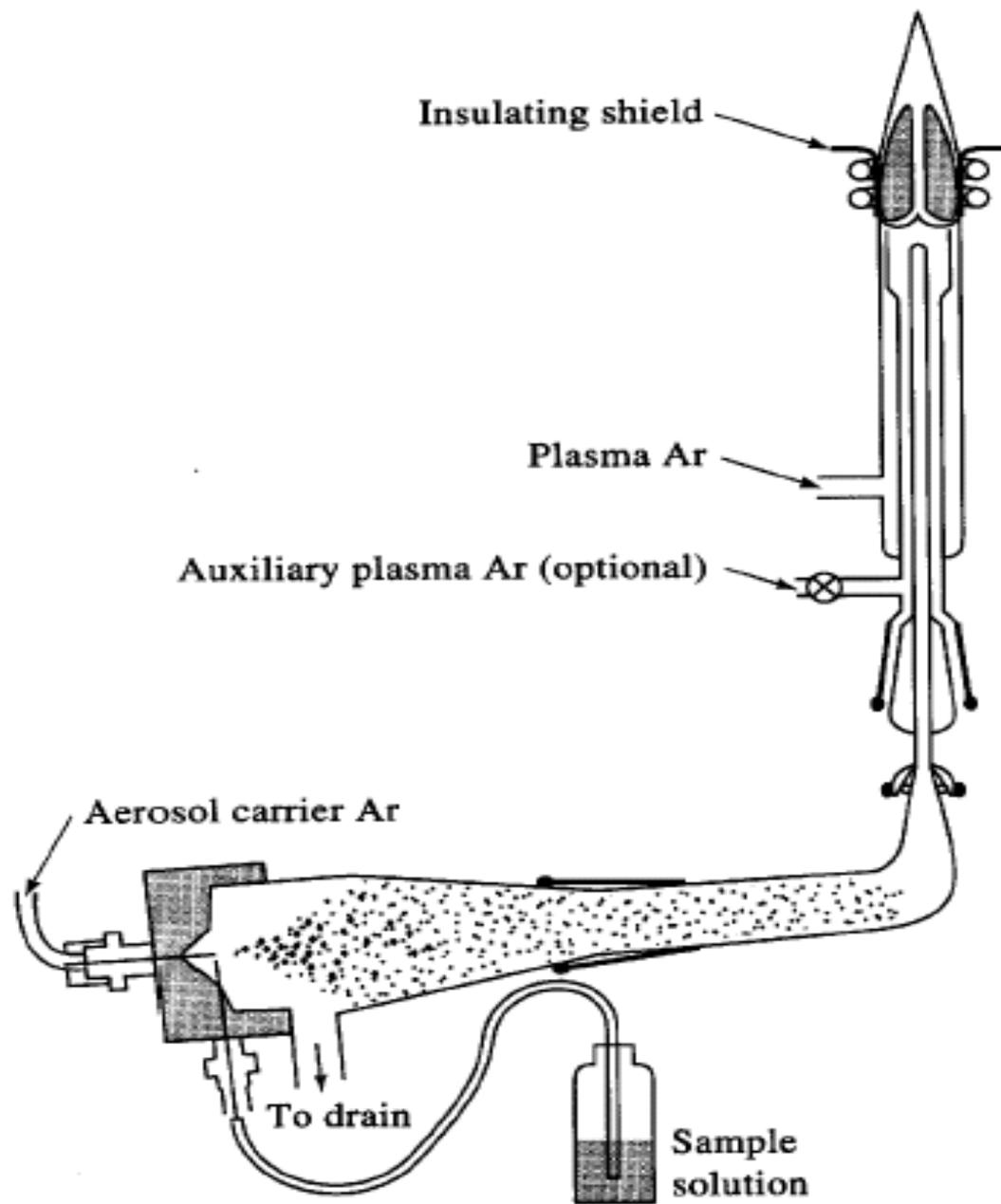
-A typical ICP consists of three concentric quartz tubes through which streams of argon gas flow at a rate in the range from 5-20 L/min.

- The outer tube is about 2.5 cm in diameter and the top of this tube is surrounded by a radiofrequency powered induction coil producing a power of about 2 kW at a frequency in the range from 27-41 MHz. This coil produces a strong magnetic field as well.

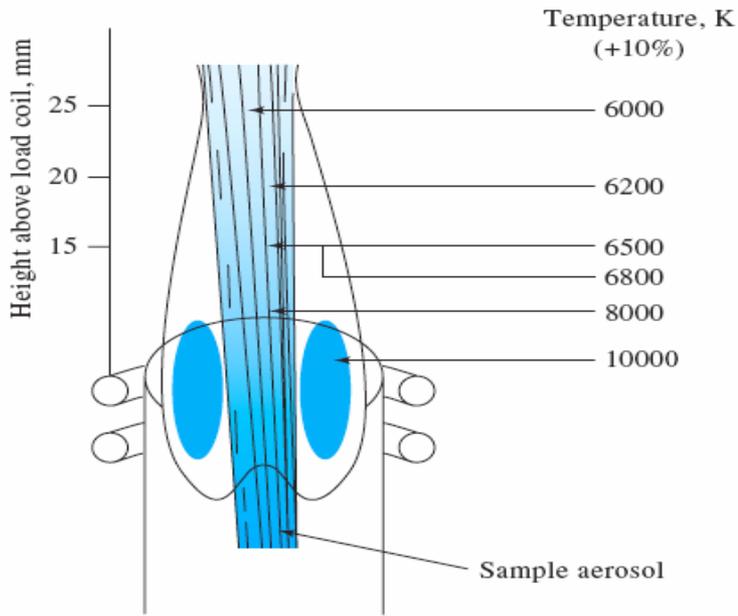
- Ionization of flowing argon is achieved by a spark where ionized argon interacts with the strong magnetic field and is thus forced to move within the vicinity of the induction coil at a very high speed.

- A very high temperature is obtained as a result of the very high resistance experienced by circulating argon (ohmic heating).

-The top of the quartz tube will experience very high temperatures and should, therefore, be isolated and cooled. This can be accomplished by passing argon tangentially around the walls of the tube



ICP Plasma Structure



➤ A plasma torch looks very much like a flame but with a very intense nontransparent brilliant white color at the core (less than 1 cm above the top).

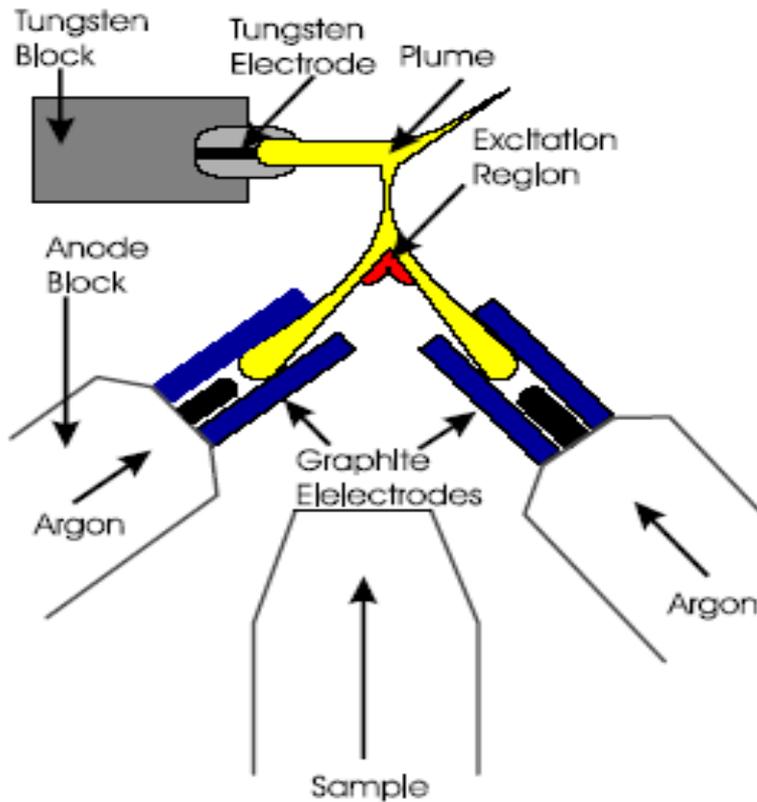
➤ In the region from 1-3 cm above the top of the tube, the plasma becomes transparent.

➤ The temperatures used are at least two to three orders of magnitude higher than that achieved by flames which may suggest efficient atomization and fewer chemical interferences.

- Brilliant **white core** - Ar continuum and lines
- **Flame-like tail** up to 2 cm
- **Transparent region** - measurements made
- **Hotter than flame** (10,000 K) - more complete atomization/excitation
- **Atomized in "inert" atmosphere**
- **Little ionization** - too many electrons in plasma

- The viewing region used in elemental analysis is usually about 6000 °C, which is about 1.5-2.5 cm above the top of the tube.
- It should also be indicated that argon consumption is relatively high which makes the running cost of the ICP torch high as well.
- Argon is a unique inert gas for plasma torches since it has few emission lines. This decreases possibility of interferences with other analyte lines.

2) Direct Current DC-Plasma



- The DCP is composed of three electrodes arranged in an inverted Y configuration.
- A tungsten cathode resides at the top arm of the inverted Y while the lower two arms are occupied by two graphite anodes.
- Argon flows from the two anode blocks and plasma is obtained by momentarily bringing the cathode in contact with the anodes.
- Argon ionizes and a high current passes through the cathode and anodes.

- It is this current which ionizes more argon and sustains the current indefinitely.
- Samples are aspirated into the vicinity of the electrodes (at the center of the inverted Y) where the temperature is about 5000 °C.
- DCP sources usually have fewer lines than ICP sources, require less argon/hour, and have lower sensitivities than ICP sources.
- In addition, the graphite electrodes tend to decay with continuous use and should thus be frequently exchanged.

- DC current (10-15 A) flows between C anodes and W cathode
- Plasma core at 10,000 K, **viewing region at ~5,000 K**
- **Simpler, less Ar than ICP - less expensive**

Comparison of DCP and ICP

A DCP has the advantage of less argon consumption,

- simpler instrumental requirements, and
- less spectral line interference.

However,

- ICP sources are more convenient to work with,
- free from frequent consumables (like the anodes in DCP's which need to be frequently changed), and
- are more sensitive than DCP sources.

Advantages of Plasma Sources over Flame and Electrothermal Atomization

1. No oxide formation as a result of two factors including
 - Very high temperature
 - Inert environment inside the plasma (no oxygen)
2. Minimum chemical interferences
3. Minimum spectral interferences except for higher possibility of spectral line interference due to exceedingly large number of emission lines (because of high temperature)
4. Uniform temperature which results in precise determinations
5. No self-absorption is observed which extends the linear dynamic range to higher concentrations
6. No need for a separate lamp for each element
7. Easily adaptable to multichannel analysis

Plasma Emission Instruments

Three classes of plasma emission instruments can be presented including:

1. Sequential instruments

In this class of instruments a single channel detector is used where the signal for each element is read using the specific wavelength for each element sequentially. Two types of sequential instruments are available:

a) Linear sequential scan instruments where the wavelength is linearly changed with time. Therefore, the grating is driven by a single speed during an analysis of interest

b) Slew scan instruments where the monochromator is preset to provide specific wavelengths; moving very fast in between wavelengths while moving slowly at the specific wavelengths. Therefore, a two-speed motor driving the grating is thus used.

Sequential MC

Sequential monochromators:

Slew-scan spectrometers - even with many lines, much spectrum contains no information

- rapidly scanned (**slewed**) across blank regions
- slowly **scanned** across lines
- computer control/preselected lines to scan

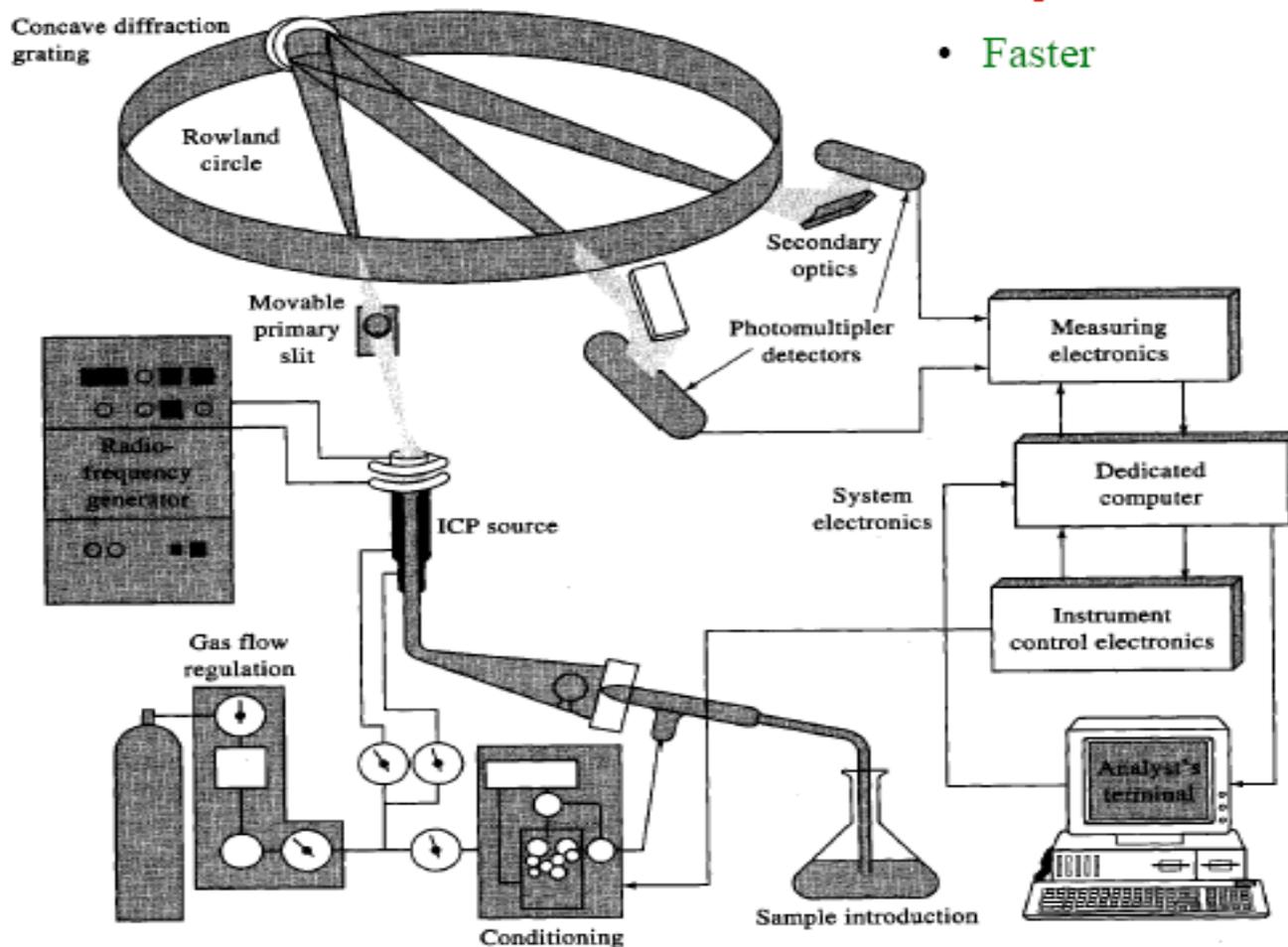
Sequential instrument - PMT moved behind aperture plate, or grating+prism moved to focus new λ on exit slit

- **Cheaper**
- **Slower**
- Pre-configured exit slits to detect up to 20 lines, slew scan

2. Multichannel instruments

Multichannel instrument - multiple PMT's

- Expensive
- Faster



Since the atomic emission lines are very narrow, a high-resolution [polychromator](#) is needed to selectively monitor each emission line.

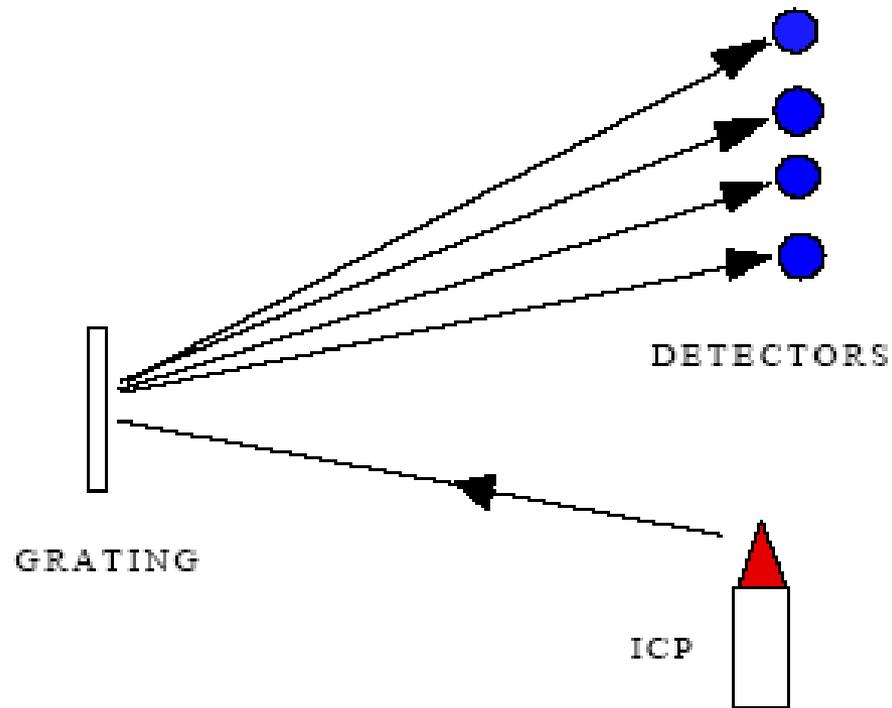


FIGURE 13. A POLYCHROMATOR FOR SIMULTANEOUS ANALYSIS OF RADIATION.

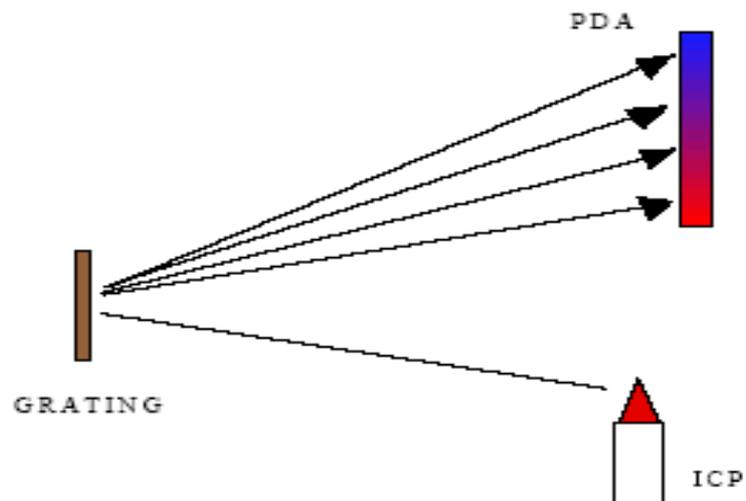


FIGURE 14. A PHOTODIODE ARRAY FOR SIMULTANEOUS ANALYSIS OF RADIATION.

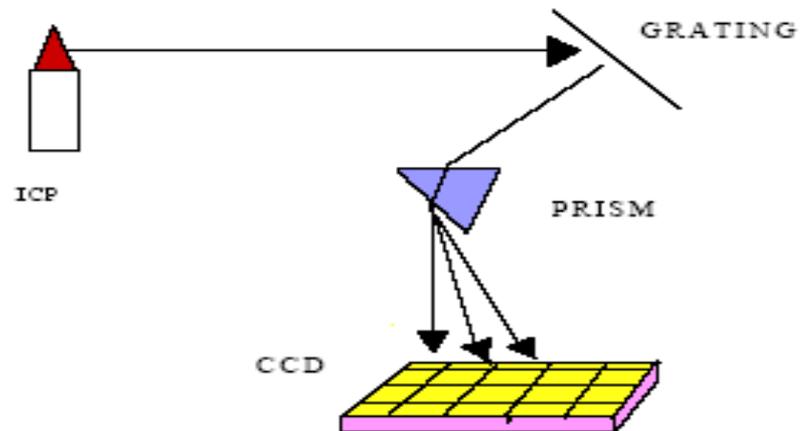


FIGURE 15. TWO-DIMENSIONAL DISPERSION AND DETECTION OF RADIATION USING A CHARGE-COUPLED DEVICE (CCD).

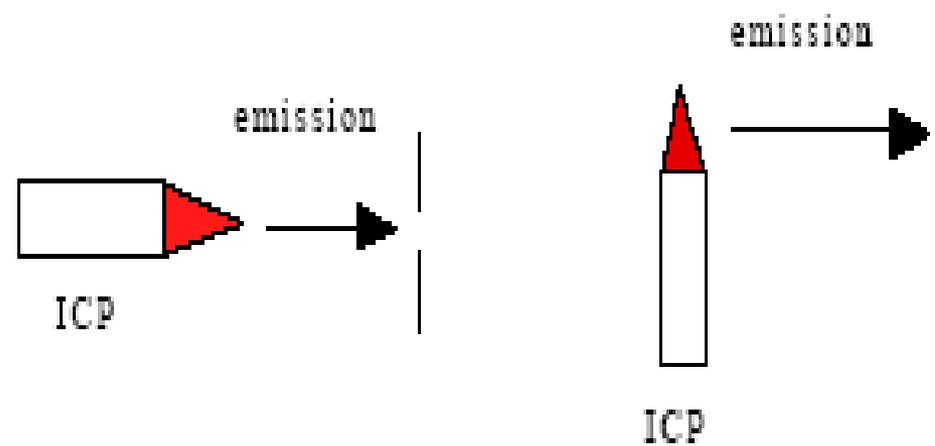


FIGURE 16. ICP TORCH POSITIONS INCLUDE A HORIZONTAL MOUNT (LEFT) AND THE MORE TRADITIONAL VERTICAL MOUNT (RIGHT).