

# Lecture no.1



**IR**  
**And**  
**FTIR**  
**principle and instruments**

## 1. Introduction to IR Spectroscopy

Spectroscopy can be defined as the interaction between matter and light. Infrared spectroscopy is a very powerful technique which uses electromagnetic radiation in the infrared region for the determination and identification of molecular structure as well as having various quantitative applications within analytical chemistry (Figure 1).

We do not aim to provide a mechano-quantic description of light and its interaction with atoms, as this is out of the scope of this module. However, it is important to note that atoms can absorb energy from electromagnetic radiation; this absorbed energy alters the state of the atoms within the molecule. These changes are usually manifest in alterations to the frequency and amplitude of molecular vibrations, which may be measured and plotted to produce an infrared spectrum.<sup>1-4</sup>

Infrared spectrometers use optical devices for dispersing and focusing electromagnetic radiation of IR frequency which is passed through the sample and any changes in absorbance measured against a reference beam.

There are three well defined IR regions (near, mid and far). The boundaries between them are not clearly defined and debate still persists, but broadly they are defined as:

- **Near infrared (12820-4000  $\text{cm}^{-1}$ ):** poor in specific absorptions, consists of overtones and combination bands resulting from vibrations in the mid-infrared region of the spectrum.
- **Mid-infrared (4000-400  $\text{cm}^{-1}$ ):** provides structural information for most organic molecules.
- **Far Infrared (400-33  $\text{cm}^{-1}$ ):** has been less investigated than the other two regions; however, it has been used with inorganic molecules.

The low energies, typically encountered within the infrared region, are not sufficient to cause electronic transitions; however, they are large enough to cause changes in the frequency and amplitude of molecular vibrations.

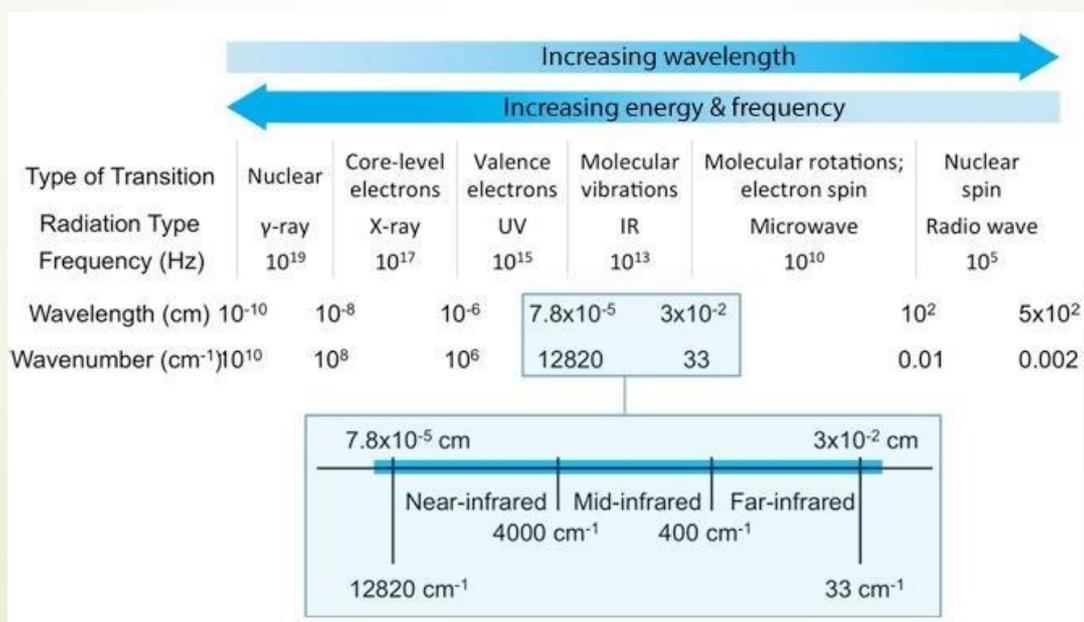


Figure 1: The electromagnetic spectrum and the infrared region.

## 2. Electromagnetic Spectrum

The electromagnetic spectrum is the range of all possible frequencies of electromagnetic radiation, each of which can be considered as a wave or particle travelling at the speed of light, often referred to as a photon. These waves differ from each other in length and frequency.

**Frequency  $\nu$**  - the number of wave cycles that pass through a point in one second. Measured in Hertz (Hz).

**Wavelength  $\lambda$**  - The length of one complete wave cycle (cm).

Frequency and wavelength are inversely related (Equation 1):

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**Where:**

$c$  = speed of light  $3 \times 10^{10}$  cm/sec

The energy of a photon ( $E$  in Joules) is related to wavelength and frequency as follows (Equation 2):

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**Where:**

$h$  = Planck's constant  $6.6 \times 10^{-34}$  Joules-sec

Energy is directly proportional to frequency; therefore, high energy radiation will have a high frequency.

Energy is inversely proportional to wavelength, hence, short wavelengths are high energy and vice versa (Figure 2).

Type of Transition	Nuclear	Core-level electrons	Valence electrons	Molecular vibrations	Molecular rotations; electron spin	Nuclear spin
Radiation Type	$\gamma$ -ray	X-ray	UV	IR	Microwave	Radio wave
Frequency (Hz)	$10^{19}$	$10^{17}$	$10^{15}$	$10^{13}$	$10^{10}$	$10^5$
Wavelength (cm)	$10^{-10}$	$10^{-8}$	$10^{-6}$	$7.8 \times 10^{-5}$	$3 \times 10^{-2}$	$10^2$
Wavenumber ( $\text{cm}^{-1}$ )	$10^{10}$	$10^8$	$10^6$	12820	33	0.01

Figure 2: Electromagnetic spectrum.

### 3. Electromagnetic Radiation and Spectroscopy

The frequency and wavelength of electromagnetic radiation varies over many orders of magnitude. The electromagnetic spectrum is divided according to the type of atomic or molecular transition that gives rise to the absorption or emission of photons; UV, IR, microwave, radio wave etc. (Table 1). Absorption spectroscopy relies on the absorption of energy from a photon which subsequently promotes the analyte from a lower-energy state to a higher-energy, or excited, state. As the energy of the photon changes the type of transition that the analyte undergoes will change. For example in IR spectroscopy, the absorption of relatively low IR radiation results in the vibration of chemical bonds within the analyte; a process which requires a fairly low energy input. Whereas, higher energy photons, such as those found in the UV-visible region of the electromagnetic spectrum, will promote valence electrons to move from their ground state to excited state energy levels within the atoms of an analyte; a process that requires a much greater energy input.



Type of Energy Transfer	Region of the Electromagnetic Spectrum	Spectroscopic Technique
Absorption	$\gamma$ -ray	Mossbauer
	X-ray	X-ray absorption
	UV-Vis	UV-Vis
		Atomic absorption
	Infrared	Infrared (IR)
		Raman
	Microwave	Microwave
		Electron spin resonance (EPR)
	Radio waves	Nuclear magnetic resonance (NMR)
Emission (thermal excitation)	UV-Vis	Atomic emission
Photoluminescence	X-ray	X-ray fluorescence
	UV-Vis	Fluorescence
		Phosphorescence
		Atomic fluorescence

Table 1: Electromagnetic spectrum region, type of energy transfer, and the associated spectroscopic technique.

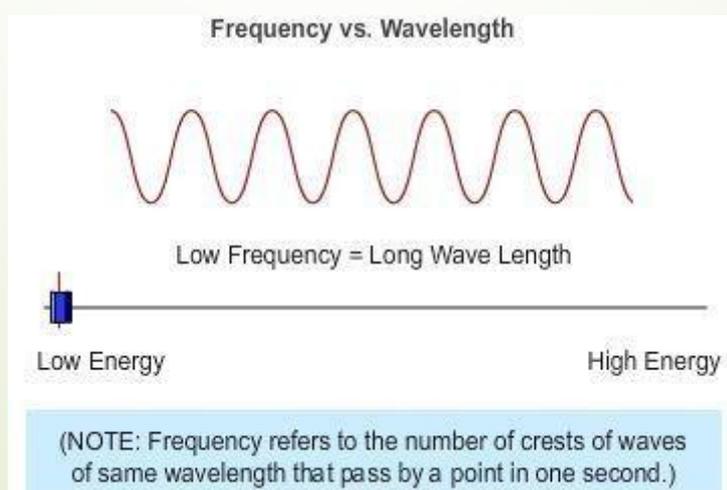


Figure 3: Relationship between frequency and wavelength.

## 4. Infrared Regions

Infrared spectroscopy can be rationalized as the spectroscopy that deals with electromagnetic radiation of infrared frequency. As previously explained, there are three well defined infrared regions; each of them has the potential to provide different information: (Figure 4)

- **Far-Infrared (400-33  $\text{cm}^{-1}$ ):** vibrations of molecules containing heavy atoms, molecular skeleton vibrations and crystal lattice vibrations
- **Mid-Infrared (4000-400  $\text{cm}^{-1}$ ):** useful for organic analysis
- **Near Infrared (12820-4000  $\text{cm}^{-1}$ ):** overtones; very useful for quantitative analysis

Infrared spectroscopy is one of the most useful and widely used methods to perform structural analysis.

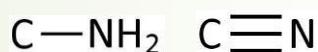
Given that the molecule under investigation is infrared active, (i.e. it absorbs Infrared radiation), then different types of structural information can be obtained.

Information achievable with Infrared spectroscopy includes:

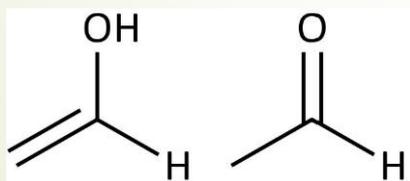
1. The type of atoms within the molecule.



2. The type of bonds between atoms.



3. The molecular structure. More often than not, infrared spectroscopy is insufficient to determine the complete structure and additional techniques (such as NMR, mass spectroscopy, etc.) are used to solve the puzzle.



Both structures have the molecular formula  $\text{C}_2\text{H}_4\text{O}$

4. From a quantitative point of view, infrared spectroscopy has a very well gained reputation for its power, flexibility, and reliability.

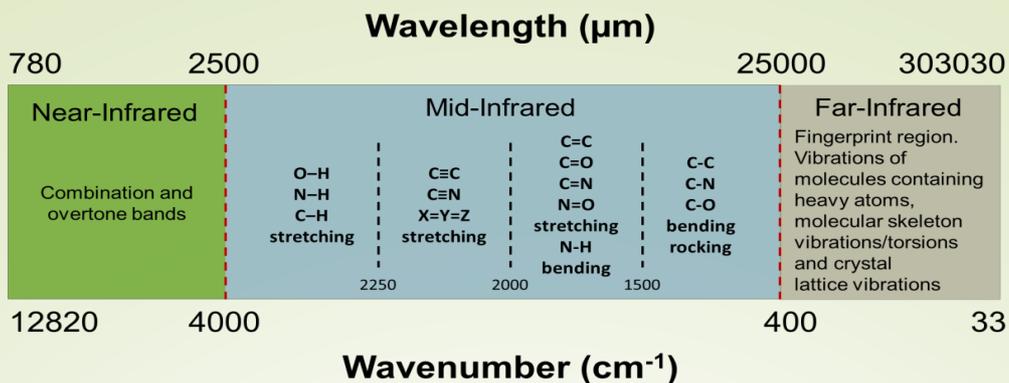
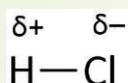


Figure 4: Infrared spectroscopy regions (oversimplified).

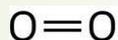
## 5. Molecular Vibrations

The absorption of light will increase both amplitude and frequency of molecular vibrations.<sup>4-5</sup> When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. Molecules with a permanent dipole moment, such as water, HCl, and NO, are infrared active.

The HCl molecule possesses a permanent dipole moment, so it is infrared active.



The O<sub>2</sub> molecule does not possess a permanent dipole moment, so it is not infrared active.



In the case of alkenes (C=C) and alkynes (C≡C) if the bond is symmetrically substituted no band will be seen in the IR spectrum, however, if the bond is asymmetrically substituted a stretching frequency corresponding to the alkene or alkyne bond will be present (Table 2).

Oscillator	Wavenumber ( $\text{cm}^{-1}$ )
C-H	3320-2700
-C=C-	1690-1590
C=O	1870-1590
C-O	1300-1050
C≡C	2250-2150
C-Cl	800-600

Table 2: Wavenumbers for selected diatomic oscillators.

In order to understand molecular vibrations, a bond can be treated as a simple harmonic oscillator composed of two masses (atoms) joined by a spring. Figure 6 depicts a diatomic molecule with two generic atoms (of masses  $m_1$  and  $m_2$ ) connected by a spring.

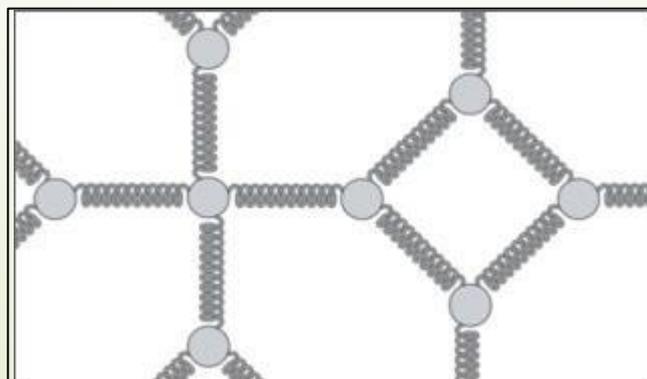


Figure 5: Representation of a polyatomic molecule.

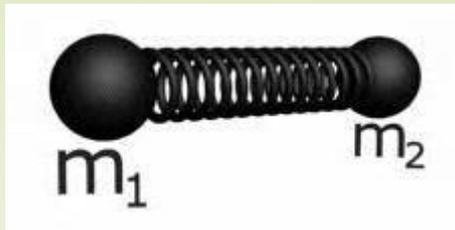


Figure 6: Representation of a diatomic molecule. If masses  $m_1$  and  $m_2$  are equal, no change in the dipole moment will occur as the molecule vibrates.

The classical vibrational frequency for a diatomic molecule (with force constant  $k$  and masses  $m_1$  and  $m_2$ ) has been derived from Hooke's Law (Equation 3):

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

**Where:**

$\mu$  = reduced mass =

In terms of the wavenumber ( $\tilde{\nu}$ ) (Equation 4):

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

**Where:**

$c$  = speed of light =  $3 \times 10^{10}$  cm/sec

## 6. Calculation of Molecular Vibrations

The stretching frequency  $\bar{\nu}$  ( $\text{cm}^{-1}$ ) of C-H can be calculated as follows: k

$$= 5 \times 10^5 \text{ dyne/cm}$$

$$m_1 = \text{C} = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23} \text{ g}$$

$$m_2 = \text{H} = 1/6.02 \times 10^{23} = 0.167 \times 10^{-23} \text{ g}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

The observed values for C-H bonds are in the region 3320-2700  $\text{cm}^{-1}$ , which differ from the calculated values as the calculation does not take into account the environment of the C-H group within the molecule.

### Force constants (k):

$$\text{Single bond} = 5 \times 10^5 \text{ dyne/cm}$$

$$\text{Double bond} = 10 \times 10^5 \text{ dyne/cm}$$

$$\text{Triple bond} = 15 \times 10^5 \text{ dyne/cm}$$

### Remember higher wavenumber = higher frequency

The vibrational frequency of a bond will increase as 1) the strength of the bond increases and/or 2) the reduced mass ( $\mu$ ) decreases.

For example compare the calculated frequencies for the following bonds:

1) Increase in bond strength from single to double to triple bond (Figure 7).

**C-N bond**

$$k = 5 \times 10^5 \text{ dyne/cm}$$

$$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23} \text{ g}$$

$$m_2 = N = 14/6.02 \times 10^{23} = 2.33 \times 10^{-23} \text{ g}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$-\sqrt{\frac{k}{\mu}}$$


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$$-\sqrt{\frac{k}{\mu}}$$


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**C=N bond**

$$k = 10 \times 10^5 \text{ dyne/cm}$$

$$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23} \text{ g}$$

$$m_2 = N = 14/6.02 \times 10^{23} = 2.33 \times 10^{-23} \text{ g}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$-\sqrt{\frac{k}{\mu}}$$


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$$-\sqrt{\frac{k}{\mu}}$$


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**C≡N bond**

$$k = 15 \times 10^5 \text{ dyne/cm}$$

$$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23} \text{ g}$$

$$m_2 = N = 14/6.02 \times 10^{23} = 2.33 \times 10^{-23} \text{ g}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$-\sqrt{\frac{k}{\mu}}$$


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$$-\sqrt{\frac{k}{\mu}}$$


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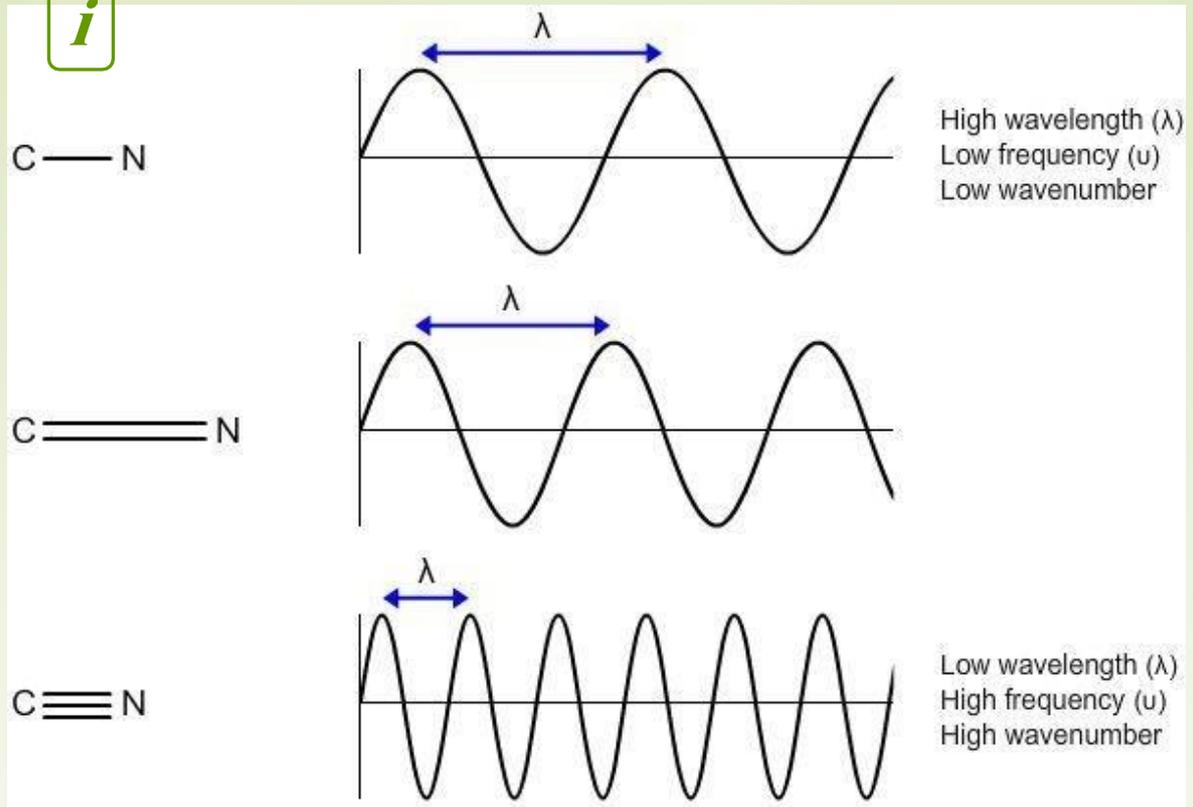
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Figure 7: Comparison of wavelength, stretching frequency, and wavenumber of bonds with different strengths (i.e. single, double, and triple bonds).

## 2) Decrease in reduced mass ( $\mu$ ) (Figure 8).

### C-S bond

$$k = 5 \times 10^5 \text{ dyne/cm}$$

$$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23} \text{ g}$$

$$m_2 = S = 32/6.02 \times 10^{23} = 5.32 \times 10^{-23} \text{ g}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$- \sqrt{\frac{k}{\mu}}$$

$$- \frac{1}{\lambda} \sqrt{\frac{k}{\mu}}$$

-

### C-H bond

$$k = 5 \times 10^5 \text{ dyne/cm}$$

$$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23} \text{ g}$$

$$m_2 = H = 1/6.02 \times 10^{23} = 0.167 \times 10^{-23} \text{ g}$$

$$c = 3 \times 10^{10} \text{ cm/sec}$$

$$- \sqrt{\frac{k}{\mu}}$$

$$- \frac{1}{\lambda} \sqrt{\frac{k}{\mu}}$$

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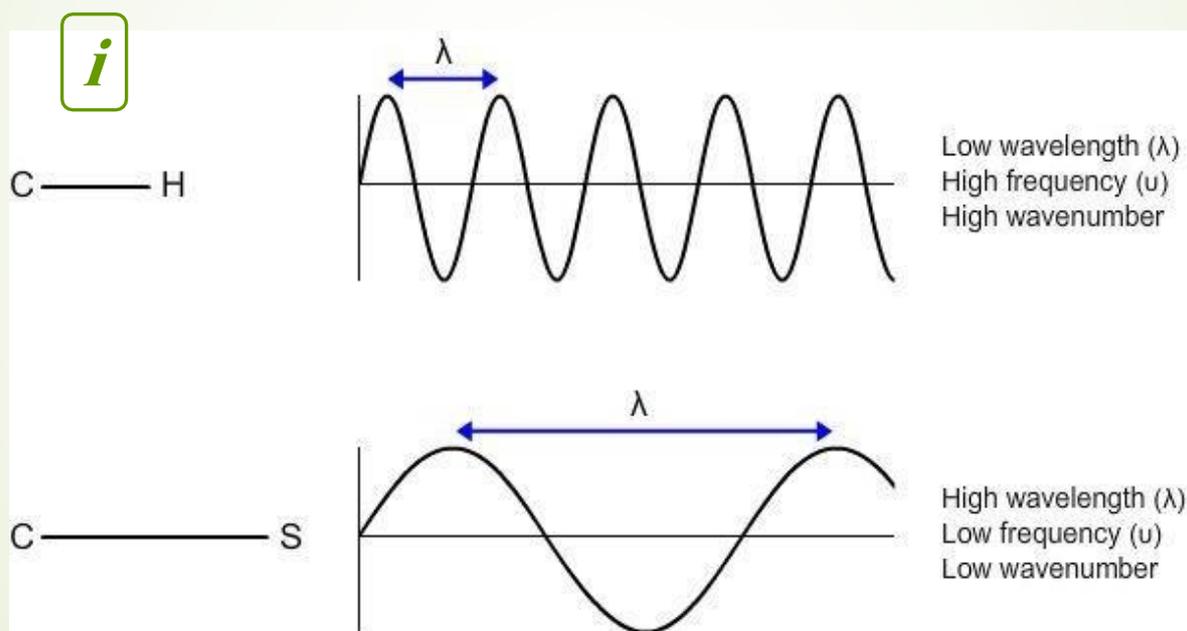


Figure 8: Comparison of wavelength, stretching frequency, and wavenumber of bonds with different reduced masses ( $\mu$ ).

## 7. Infrared Active Modes

A molecule that is infrared active must undergo a change in its dipole moment when vibrating. The simplest modes of vibration that are infrared active are stretching and bending modes (Figure 9).<sup>3-5</sup>

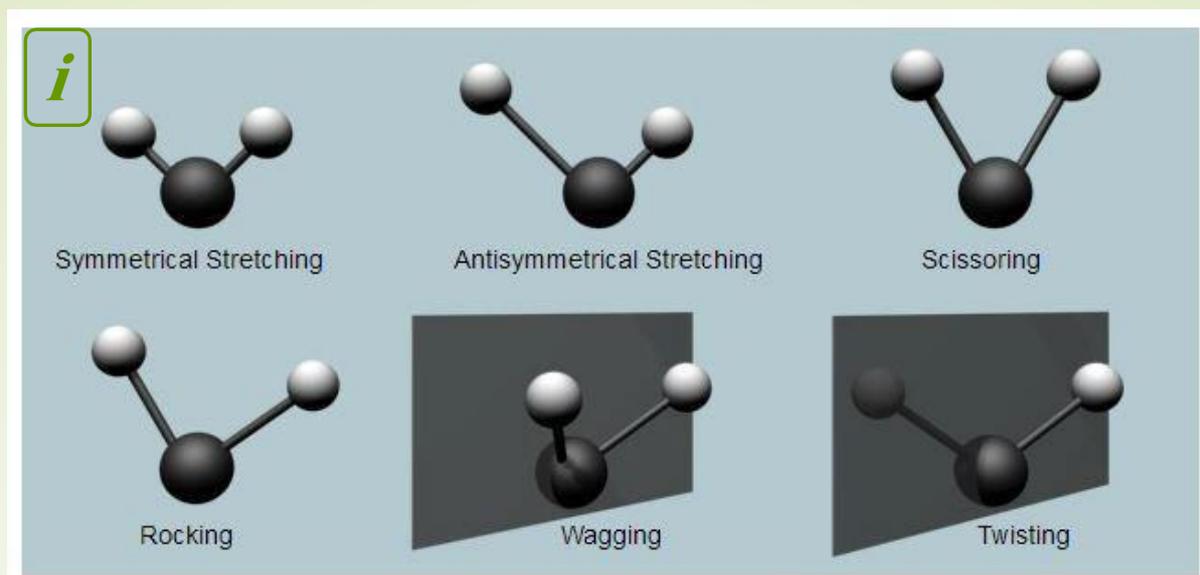
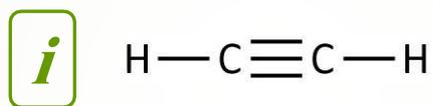


Figure 9: Modes of vibration (oversimplified).

For simplicity, we are going to illustrate the vibration modes in a linear molecule (acetylene in this case).



The symmetric  $\text{C} \equiv \text{C}$  stretching will not alter the acetylene's dipole moment and **it is not** infrared active.

However, substitution of either of the H atoms in acetylene produces an asymmetric alkyne bond which will be IR active.

Homonuclear diatomic molecules such as  $\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , etc. will exhibit no infrared active modes as no change in their dipole moment is experienced during vibration.

## 8. Absorption Considerations

The amount of infrared radiation absorbed by the sample, at any given wavelength, can be measured in different ways. The use of 'transmittance' is common place in infrared spectroscopy.<sup>2- 4, 5-7</sup>

Figure 10 illustrates a beam of infrared radiation of power  $I_0$ , directed at a sample solution.

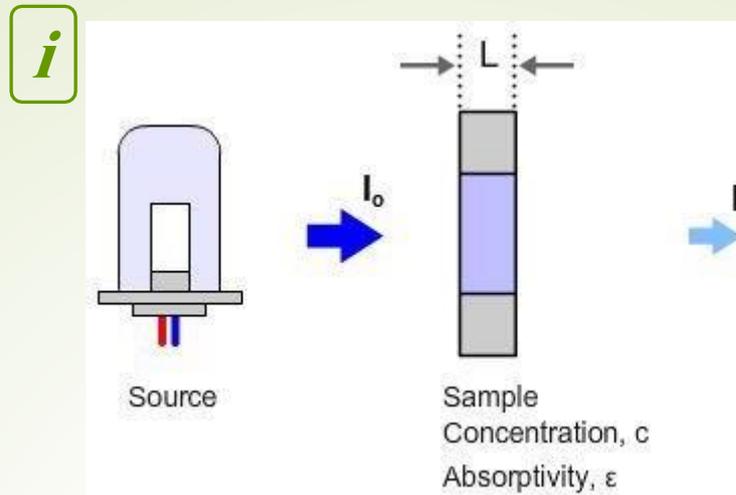


Figure 10: Absorption of infrared radiation of radiant power  $I_0$ . The radiation leaving the sample has radiant power  $I$ .

The transmittance can be calculated as follows (Equation 5):

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### Where:

$I_0$  = intensity of the incident radiation (light)

$I$  = intensity of the radiation (light) leaving the sample

Absorbance is given by Equation 6:

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From the previous expression it follows that (Equation 7):

Absorbance is related to concentration *via* the Beer-Lambert law (Equation 8):

**Where:**

$\epsilon$  = molar absorptivity ( $\text{Lmol}^{-1}\text{cm}^{-1}$ )

$l$  = path length (cm)

$c$  = concentration ( $\text{molL}^{-1}$ )

$\epsilon$  is sometimes referred to as the extinction coefficient.

Infrared (IR) radiation of all wavelengths is transmitted from the source. Some of the wavelengths of IR radiation will be absorbed by the sample and some of them will pass through (they are transmitted). The IR radiation which is transmitted is measured by the detector resulting in a unique IR spectrum for the sample of interest. This spectrum represents the IR absorption and transmission of that molecule. No two unique molecules will produce the same IR spectrum, resulting in IR spectroscopy being a very useful tool for molecular characterization and quantification.

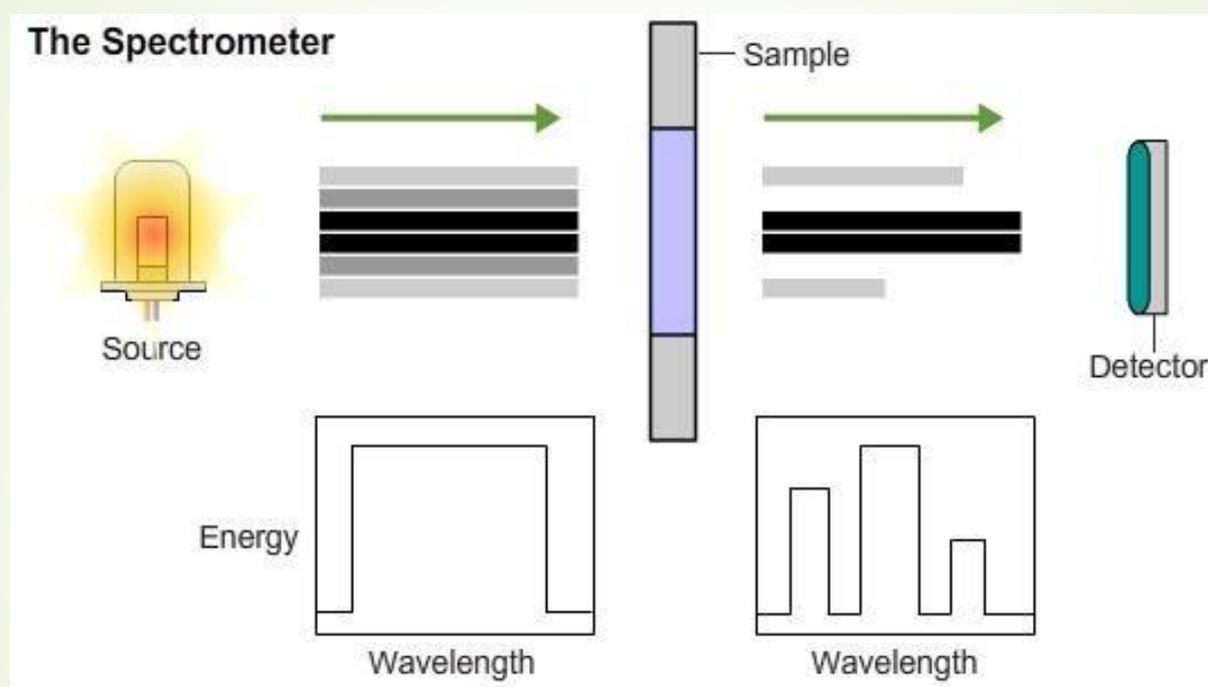


Figure 11: Sample absorption of IR radiation.

## 9. The IR Spectrum

Historically, infrared spectra have been represented as percent of transmittance versus either the wavenumber or the wavelength. The use of wavenumbers, is standard, with the use of wavelength (expressed in nm or  $\mu\text{m}$ ) having fallen out of favor.<sup>4-6, 8-10</sup>

In terms of wavenumbers the infrared region spans from 33 to 12820  $\text{cm}^{-1}$ . However, most infrared analyses are carried out in the mid-infrared region (400 to 4,000  $\text{cm}^{-1}$ ).

By convention, the wavenumbers are plotted in decreasing order from left to right. A typical IR spectrum is illustrated in Figure 12.

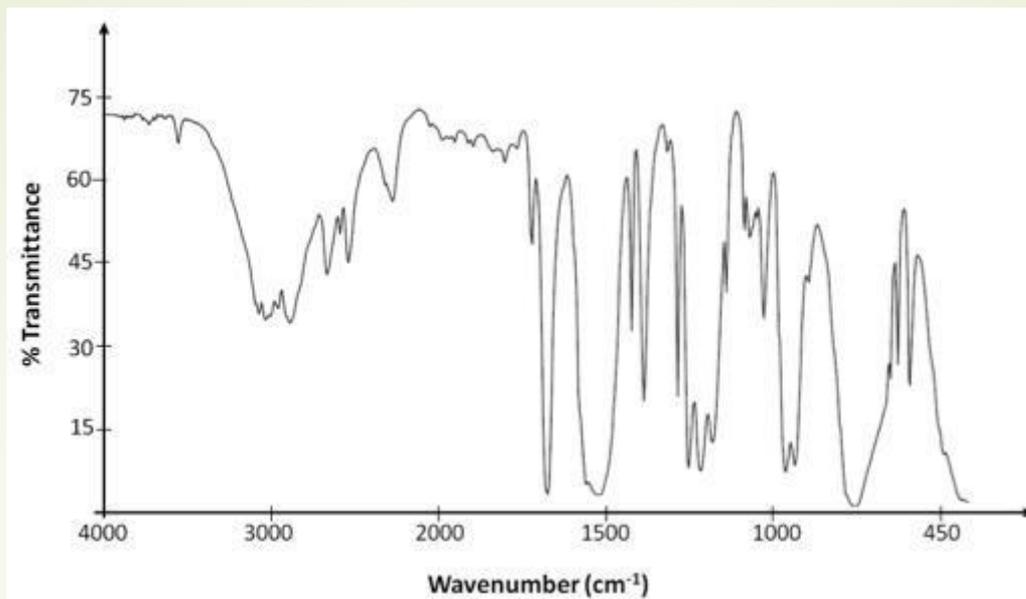


Figure 12: Typical IR spectrum.

The wavenumber  $\bar{\nu}$  can be found by using the following expression (Equation 9):

$$\bar{\nu} = \frac{1}{\lambda}$$

The wavenumber is usually expressed as  $\text{cm}^{-1}$ .

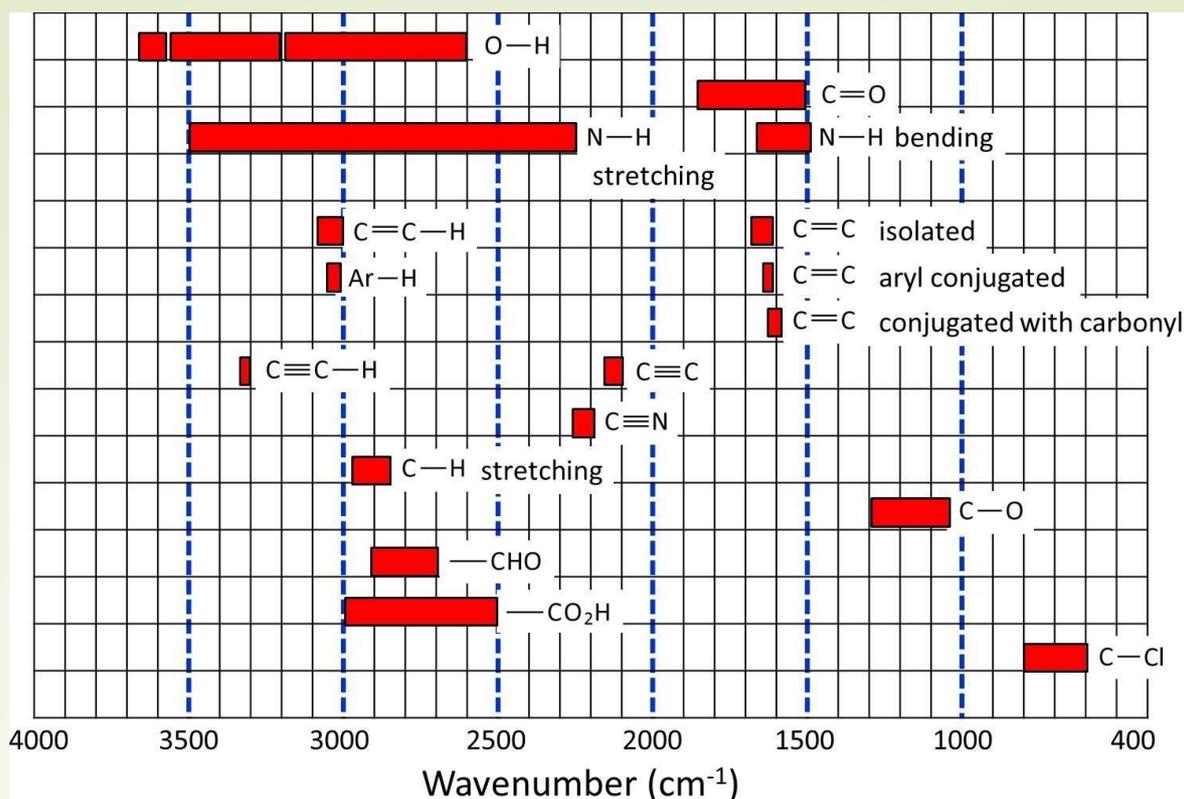
**Example:** Calculate the wavenumber (in  $\text{cm}^{-1}$ ) corresponding to infrared radiation of wavelength 2,500 nm.

$$\bar{\nu} = \frac{1}{\lambda}$$

**Note:** 1 nm =  $1 \times 10^{-7}$  cm

## 10. Infrared Absorption Signals

Selected IR frequencies.<sup>11</sup>



The vibrational frequencies of certain functional groups will correspond to the absorption of certain wavelengths of IR energy. Absorption of these wavelengths by a sample can therefore act as a diagnostic or fingerprint, to indicate the possible presence of these groups within the analyte molecule. Some typical frequencies are shown in the table above.

## 11. Dispersive IR Instruments

Most IR spectrometers can be categorized into two classes: dispersive and Fourier Transform instruments.<sup>2-4</sup>

The basic design of a dispersive single beam instrument includes a source of infrared radiation, a monochromator, and the detector (Figure 13).

After interacting with the sample (or the blank), infrared radiation is dispersed by a monochromator into its individual frequency components and information on which frequencies were absorbed can be obtained using a photodiode array detector.

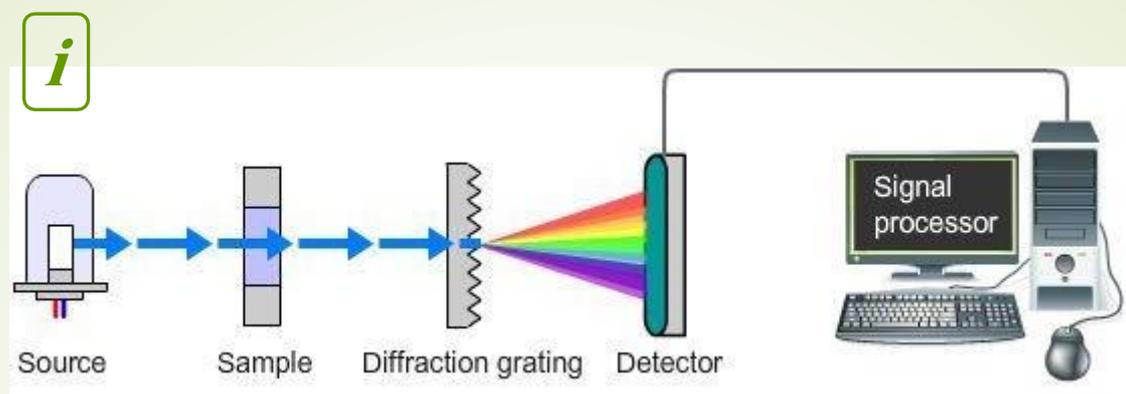


Figure 13: Basic concept of a single beam IR instrument.

Sources and detectors for infrared radiation have limited stability; with light intensity and detector sensitivity changing over time, or with fluctuations in temperature etc. The blank (reference or background) and sample measurements should be made one after the other to ensure they are made under the same analytical conditions. This limitation is minimized by the use of double beam instruments which are capable of measuring the sample and reference simultaneously.

Double beam instruments use 'choppers' to control the path of the radiation, alternating between the sample and the reference (Figure 14). These instruments use the known speed of rotation of the beam chopper to compare and resolve the information reaching the detector.

The use of an opaque surface provides the means for adjusting the 0% transmittance response of the detector.

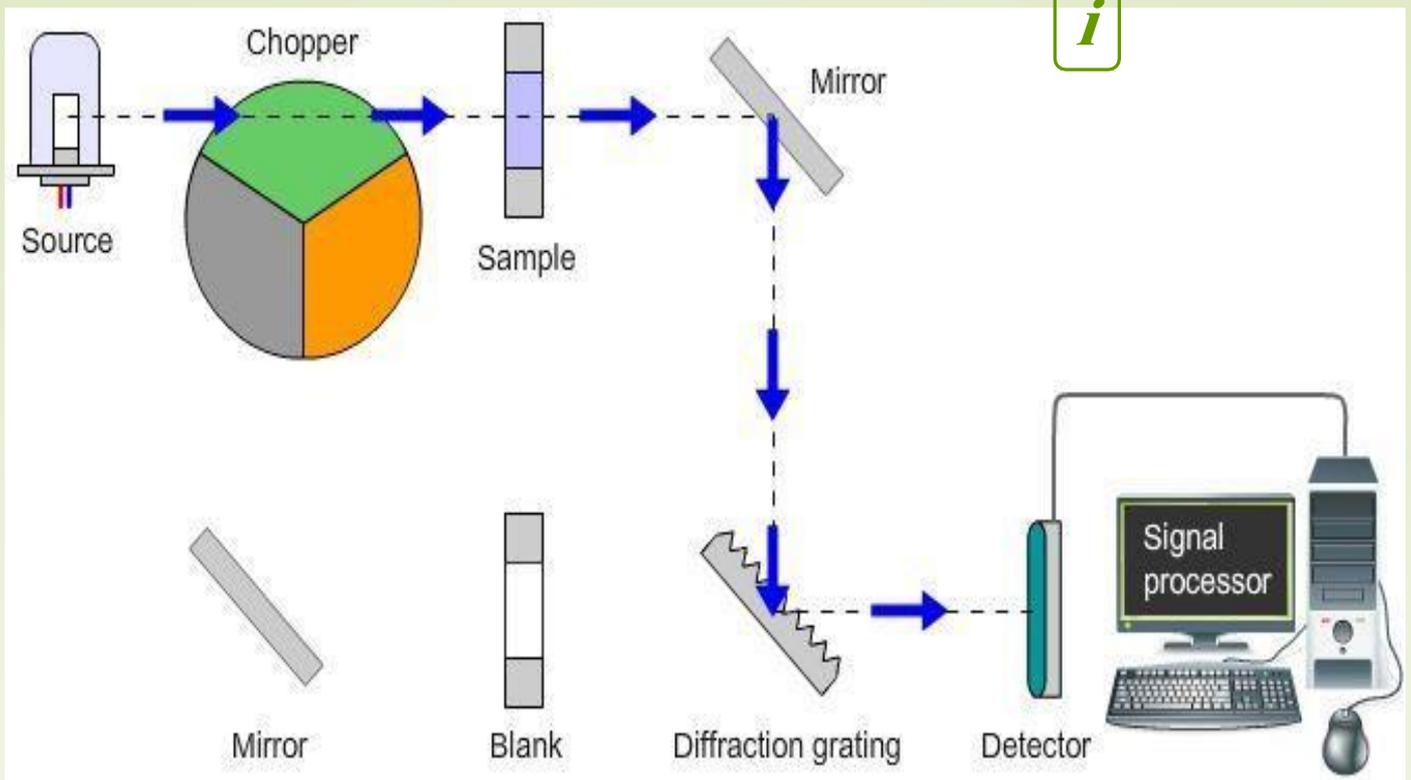


Figure 14: The double beam IR instrument.

Finally, it is easier to correct for absorption of infrared radiation by carbon dioxide and water (present within the instrument background) with double beam instruments than with their single beam counterparts.

## 12. FTIR Instruments

FTIR stands for Fourier Transform Infrared. FTIR spectrometers consist of an IR source, interferometer, sample cell or chamber, detector and a laser.<sup>7,9,11</sup> A schematic of an FTIR instrument is shown below (Figure 15).

### IR source

IR radiation is emitted from a glowing black body source. IR radiation passes through an aperture which controls the amount of radiation that reaches the sample, and therefore, the detector.

Common IR sources are:

1. Silicon carbide rods which are resistively heated and commonly known as a Globar. An electric current is passed through the rod which becomes very hot (1300 K) and emits large amounts of IR radiation. Previously, cooling with water was required to avoid damaging electrical components; however, advances in metal alloys have led to the production of Globars that do not require cooling by water.
2. Nichrome and Kanthal wire coils were once popular IR sources and did not require cooling as they ran at lower temperatures than Globars, however, this also resulted in lower amounts of IR radiation being emitted.
3. Nernst Glowers are manufactured from a mixture of refractory oxides and are capable of reaching hotter temperatures than a Globar; however, they are not capable of producing IR radiation above  $2000\text{ cm}^{-1}$ .

### Interferometer

The first interferometer was invented by Albert Abraham Michelson, who received a Nobel Prize for his work in 1907. Without this essential piece of optical equipment the modern day FTIR system would not exist. The interferometer consists of a beam splitter, a fixed mirror, and a moving mirror.

### Beam Splitter

The beam splitter is made of a special material which transmits half of the incident radiation and reflects the other half. IR radiation from the source strikes the beam splitter and is separated into two beams. One beam is transmitted through the beam splitter to the fixed mirror while the other beam is reflected from the beam splitter to the moving mirror. Both mirrors reflect the radiation back to the beam splitter where the two beams interfere to produce an interferogram.

### Moving Mirror

The moving mirror is a flat highly reflective surface mounted on air bearings that allow for high speed movement of the mirror (movements are made once every millisecond). The moving mirror only moves a few millimeters away from the beam splitter.

### Fixed Mirror

The fixed mirror is a flat highly reflective surface.

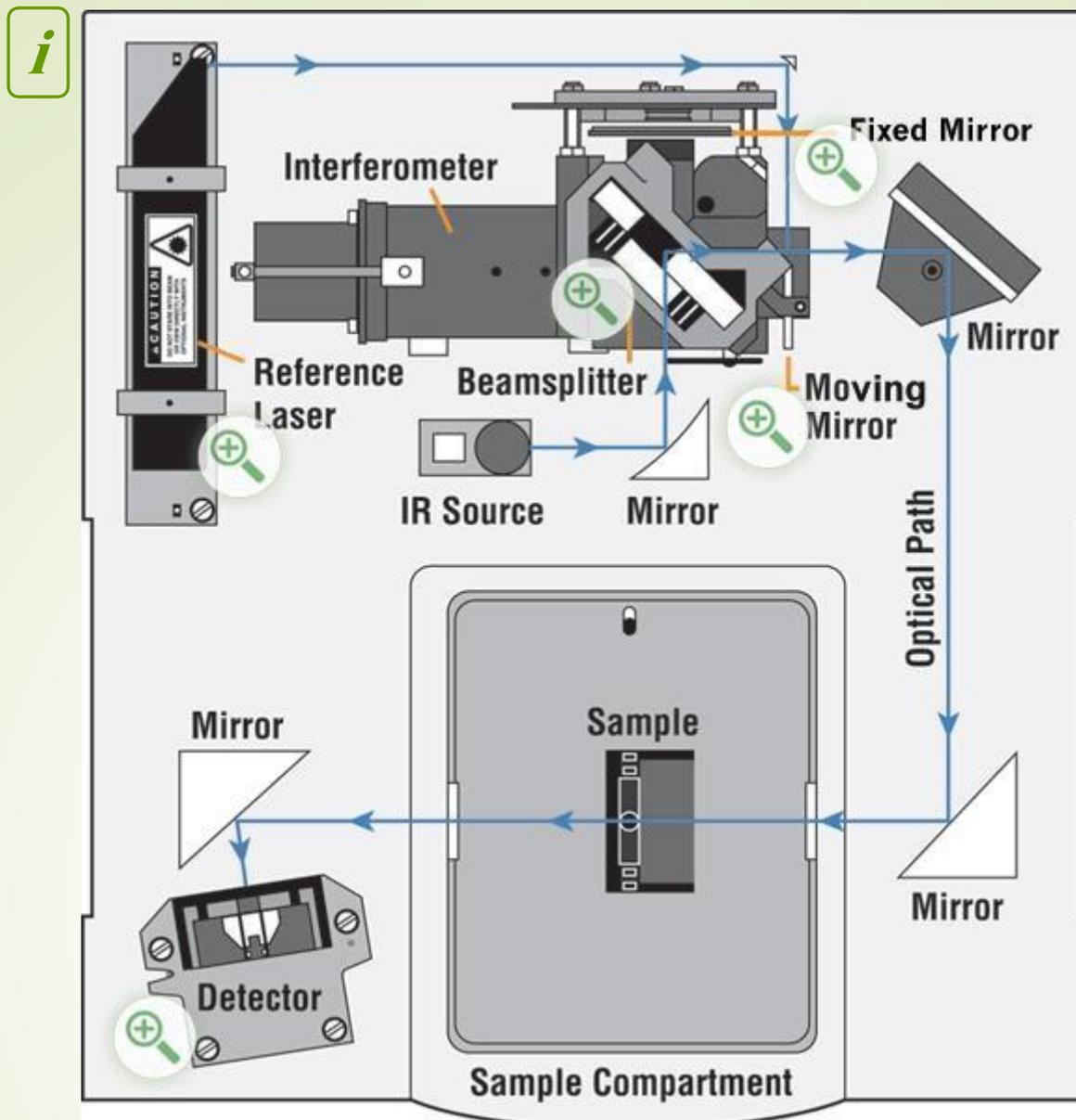


Figure 15: Operational Schematic of a Thermo Nicolet FTIR Instrument. Image reproduced with permission from Thermo Fisher Scientific (Madison, WI, USA).

### Laser

Many instruments employ a Helium-Neon laser as an internal wavelength calibration standard. It is imperative that the position of the moving mirror is known at any given moment. The moving mirror moves back and forth at a precise constant velocity that is timed using a very accurate laser wavelength.

The intensity of the laser beam is measured at two points in the interferometer. As the mirror moves the intensity at these two points will rise and fall due to the enhancement and cancellation of the HeNe beam paths, producing a sine wave of intensity vs. mirror position. The number of “fringes” in the sine wave allows the instrument to know exactly how far the mirror has moved, and the relative phase of the sine wave tells the instrument in which direction the mirror is moving.

## Detector

There are two classes of infrared detectors; thermal and photonic detectors. Thermal detectors use the IR radiation as heat; whereas, quantum mechanical (photonic) detectors use the IR radiation as light which results in a more sensitive detector.

**Thermal detectors:** detect changes in temperature of an absorbing material (lithium tantalate ( $\text{LiTaO}_3$ ), lead selenide ( $\text{PbSe}$ ), germanium etc.). Many temperature dependent phenomena can be followed to measure the effects of the incident IR radiation. Bolometers and microbolometers use changes in resistance, while thermocouple and thermopiles use the thermoelectric effect. Golay cells monitor thermal expansion.

**Photonic Detector:** exhibit faster response times and higher sensitivity in comparison to their thermal counterparts, therefore, they are much more prolific in FTIR instruments. The materials used in these detectors are semiconductors with narrow band gaps. The incident IR radiation causes electronic excitations between the ground and first excited states, which in photoconductive detectors result in a change in resistivity which is monitored.

### 13. FTIR Operation

Prior to the development of FTIR spectrometry, the limitation within IR was the slow scanning process. FTIR allows for all the infrared frequencies to be scanned simultaneously, allowing for data to be collected in a matter of seconds rather than several minutes. This is achieved through the use of an optical device called an interferometer which produces a signal which is made up of all of the infrared frequencies.

Most interferometers consist of a beam splitter which splits the incident infrared beam into two separate optical beams. One beam is reflected from a fixed mirror, while the other beam is reflected from a mirror that is constantly moving in the instrument. The moving mirror typically moves by only a few millimeters from the beam splitter (Figure 16).

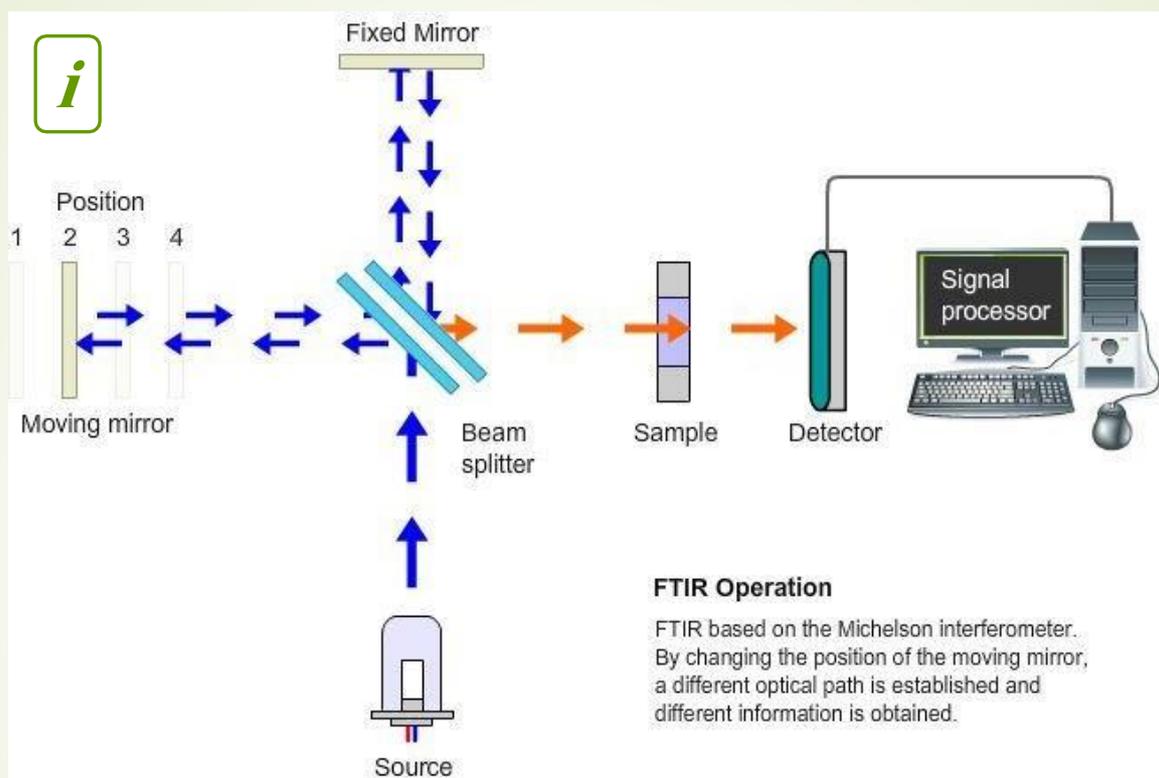


Figure 16: FTIR based on the Michelson interferometer. By changing the position of the moving mirror, a different optical path is established and different information is obtained.

The two beams are reflected from their respective mirrors and recombine at the beam splitter. The path length of the beam that is reflected from the fixed mirror remains constant, while the path length of the beam that is reflected from the moving mirror is constantly changing as the mirror moves. The signal that exits the interferometer is the result of these two beams interfering with each other, and is called an interferogram (Figure 17).

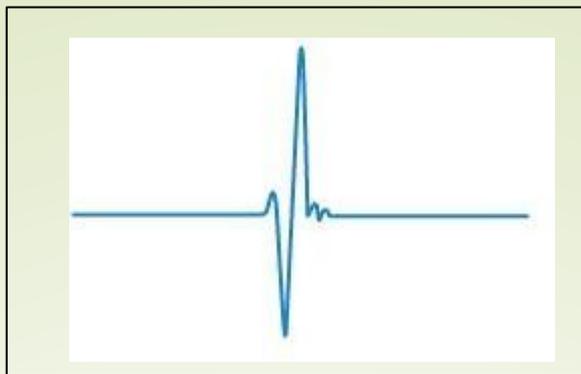


Figure 17: Interferogram.

The interferogram is unique in that every data point, which is a function of the moving mirror position, has information about every infrared frequency emitted from the source. This allows for all frequencies to be measured simultaneously.

The interferogram is converted to a more familiar IR spectrum (wavenumber vs. % transmittance) using the well-known mathematical technique called Fourier transformation. The transformation of the interferogram is carried out by the instrument software.

IR spectra are presented on a relative scale (%T), therefore, a background spectrum must be measured. A background spectrum is taken with no sample in the beam and is then subtracted from the sample spectrum to remove artifacts generated by the instrument or air (i.e. water, carbon dioxide, etc.).

### **FTIR Advantages**

FTIR instruments have several advantages over dispersive IR instruments including:

#### **Speed**

All IR frequencies are measured simultaneously, resulting in measurements being taken in seconds rather than minutes. This is often referred to as the Fellgett Advantage.

#### **Sensitivity**

The detectors utilized in FTIR instruments are highly sensitive which results in lower signal to noise ratios. This is known as the Jacquinot Advantage.

#### **Simplicity**

The only moving part in an FTIR instrument is the mirror in the interferometer; therefore, there is very little need for mechanical maintenance.

#### **Internal calibration**

The internal laser is used to self-calibrate the moving mirror in the FTIR instrument negating any need for timely or complicated external calibration. This is denoted as the Connes Advantage.

## 14. Sample Preparation

Proper sample preparation is required to obtain meaningful spectra with sharp peaks, which have good intensity and resolution. Ideally the largest peaks should be attributable to the compound being analyzed opposed to the background or sample matrix (water, CO<sub>2</sub>, solvent etc.) and should ideally have an intensity of 2-5 %T for the strongest peaks in the spectrum (Figure 18). A transmission of 5 % is equivalent to an absorbance (A) = 1.3 (i.e. the amount of light that is absorbed by the sample), which is the upper detection limit for most detectors.

The equation above is worth remembering as it allows the absorbance of a sample to be calculated from the percentage transmittance data.

Peaks that are of higher intensity will be cut off and the sample will need to be prepared again.

Compounds can be analyzed in the vapor phase, as pure liquids, in solution, and as solids.

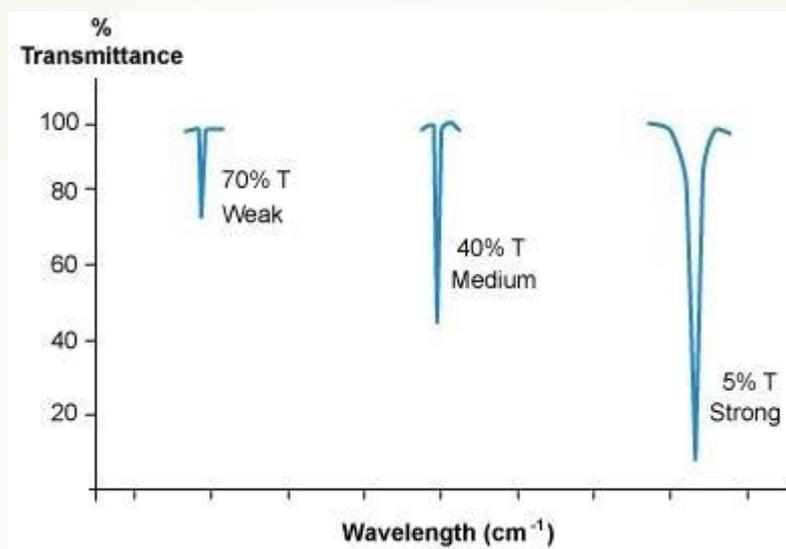


Figure 18: Classification of IR signals.

### 15.1. As a Liquid

A drop of the liquid is squeezed between two sodium chloride (NaCl) plates, which are transparent in the 4000-625 cm<sup>-1</sup> region (Figure 19).

The plates are then placed in a holder and a spectrum is taken.

If the peaks in the spectrum are too intense the liquid can be wiped from one plate, then the spectrum taken again.



Figure 19: Sodium chloride (NaCl) plates in various conditions.

NaCl plates are very fragile and sensitive to water. Samples should never be dissolved in water and placed on a NaCl plate as it will fog up or dissolve. The plates should be held by the edges to avoid moisture from fingers damaging them. After a sample has been run, ethanol can be used to clean the plates. Moisture in the air can also damage NaCl plates; therefore, they should be stored in a desiccator. Cloudy or damaged plates (pitted, fingerprints etc.) will result in **poor spectra** with broad bands and spectra with less than optimum transmission (Figure 20). Cloudy plates can be restored by polishing.

Liquids can also be placed directly on an Attenuated Total Reflectance (ATR) plate which will be discussed later.

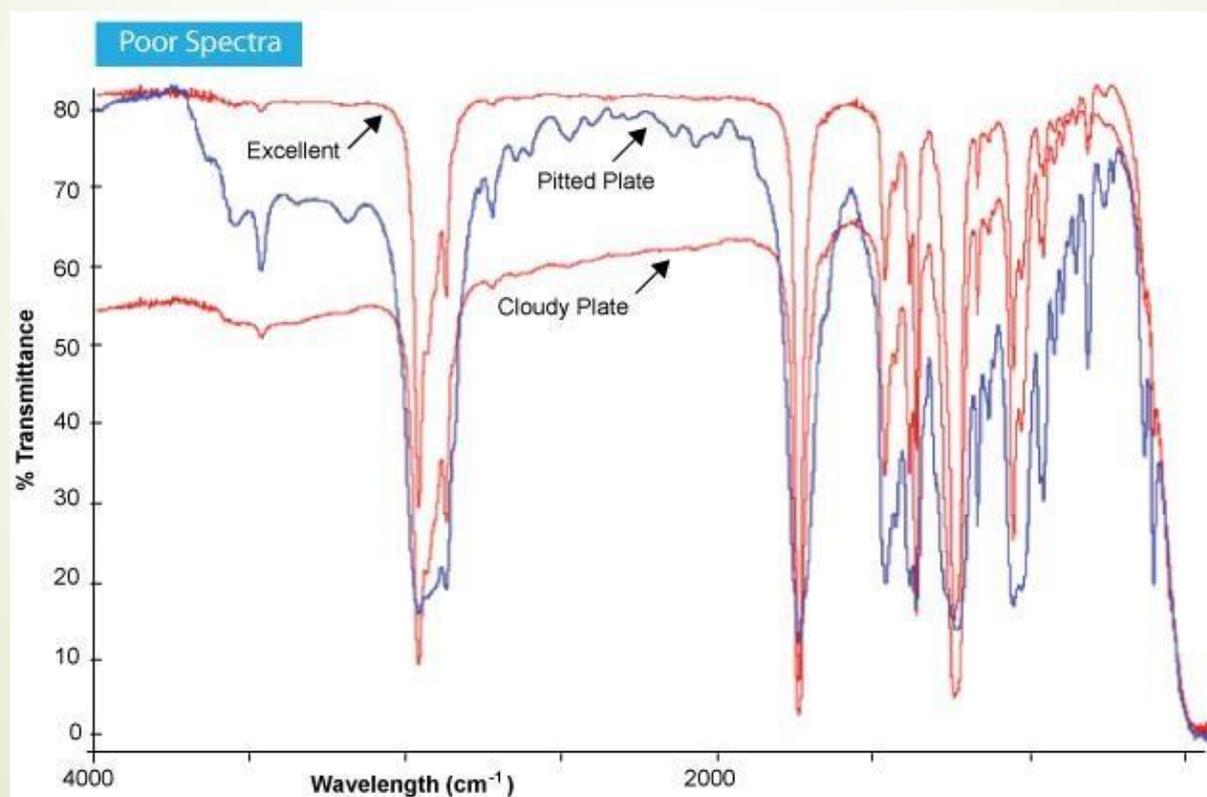


Figure 20: Representative spectra obtained with sodium chloride (NaCl) plates in various conditions.

## 15.2. As a Solution

Samples can be dissolved in an appropriate solvent to give a solution. The spectrum is then taken by placing a drop on a NaCl plate or by using a sodium chloride solution cell (Figure 21). Solvents should be free of water to avoid damaging the sodium chloride cell surfaces. A reference spectrum of the blank solvent should be obtained and subtracted from the sample spectrum.

When solvents absorb ~80% of the incident light, spectra cannot be obtained because insufficient light will be transmitted and detected. The regions in which common solvents absorb too strongly to give meaningful spectral information from a sample are shown in the table below.

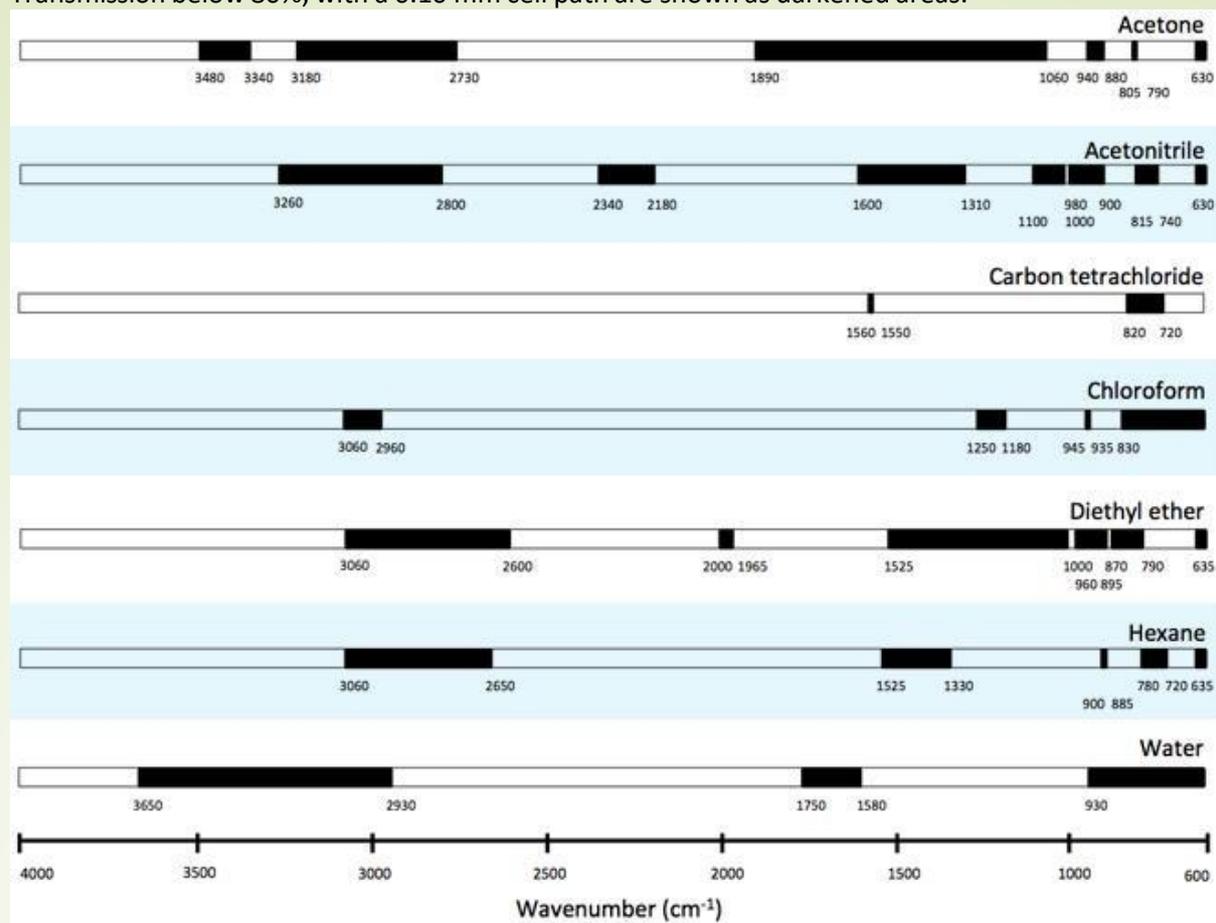
If aqueous solvents must be used for solubility, special calcium fluoride cells can be used.



Figure 21: Sodium chloride solution cell. Image reproduced with permission from International Crystal Laboratories (Garfield, NJ, USA).

## Transmission Characteristics of Common Solvents.

Transmission below 80%, with a 0.10 mm cell path are shown as darkened areas.



## As a Nujol Mull

IR spectra of solid samples can be obtained using a Nujol mull. Nujol is a mineral oil which itself has an IR spectrum (Figure 22).

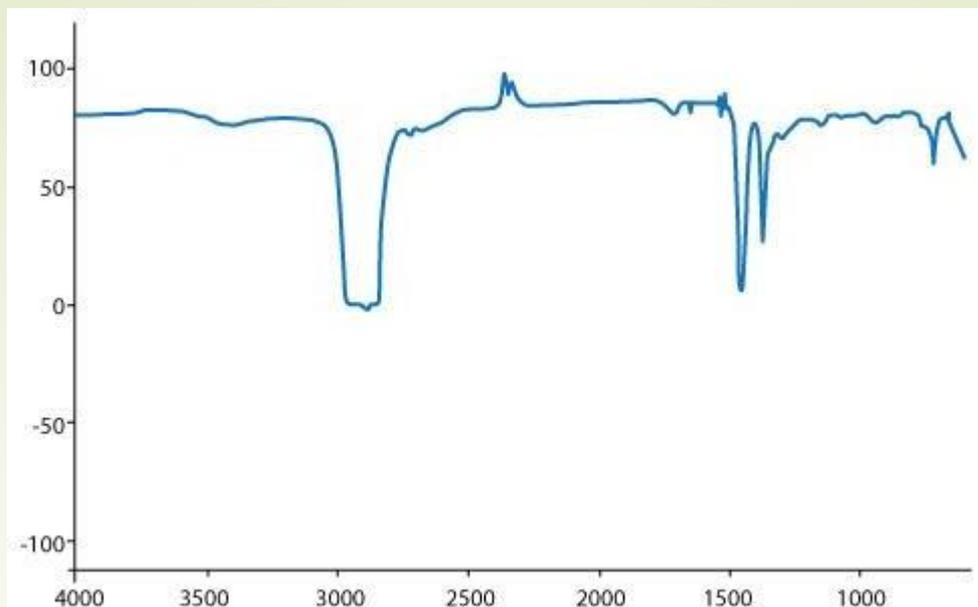


Figure 22: IR spectrum of pure Nujol.

A small amount of sample is ground using a small agate mortar and pestle and a drop of Nujol (Figure 23). The mull is then pressed between two NaCl plates and the spectrum obtained. The mull should appear transparent and free of bubbles when properly prepared. If the peaks in the spectrum are too strong one plate can be wiped clean and the spectrum re-run.



Figure 23: Agate mortar and pestle. Image reproduced with permission from Cole-Parmer (Hanwell, London, UK).

## As a KBr Disc

A solid sample can be ground with 10-100 times its mass of pure potassium bromide (KBr). Solid samples should be finely ground before adding the KBr. This is then pressed into a disc using a special mold and a hydraulic press (Figure 24). The use of KBr eliminates any bands that may obscure analyte signals when using a Nujol mull. A band at  $3450\text{ cm}^{-1}$  will often be present and is attributable to the OH group from traces of water. Water can be minimized by drying the KBr in an oven. Excessive grinding of the hygroscopic KBr can increase the water content.

Solid state spectra can differ greatly from solution state spectra due to intermolecular interactions between functional groups, i.e. hydrogen bonding. Conversely, solid state spectra will often exhibit a greater number of resolved bands which can aid in compound identification.

Material	Wavelength Range ( $\mu\text{m}$ )	Wavelength Range ( $\text{cm}^{-1}$ )	Refractive Index at $2\ \mu\text{m}$
NaCl	0.25-17	40,000-590	1.52
KBr	0.25-25	40,000-400	1.53
KCl	0.30-20	33,000-500	1.5

Table 3: Material used for obtaining solid state IR spectra. Note these materials can also be used to produce plates and solution cells for obtaining spectra with liquids and mulls.

## Reasons for Cloudy Discs

- KBr mixture not properly ground
- Sample was not dry
- Sample:KBr ratio too high
- Disc too thick
- Sample has a low melting point



Figure 24: KBr Press. Image reproduced with permission from Specac (Orpington, Kent, UK).

## 15. Attenuated Total Reflectance (ATR)

As has been discussed previously, IR spectra can be obtained from samples as liquids, solids, or mulls; however, the primary drawback is the sample preparation that is required to obtain good quality spectra. IR instruments which utilize an attenuated total reflectance (ATR) stage negate the necessity for complex and timely sample preparation resulting in good quality, reproducible spectra.

With traditional means of IR spectroscopy the IR radiation is passed through the sample and the resulting radiation which is transmitted is measured. Attenuated total reflectance measure the changes which occur in a totally internally reflected IR beam when it is in contact with a sample (Figure 25).

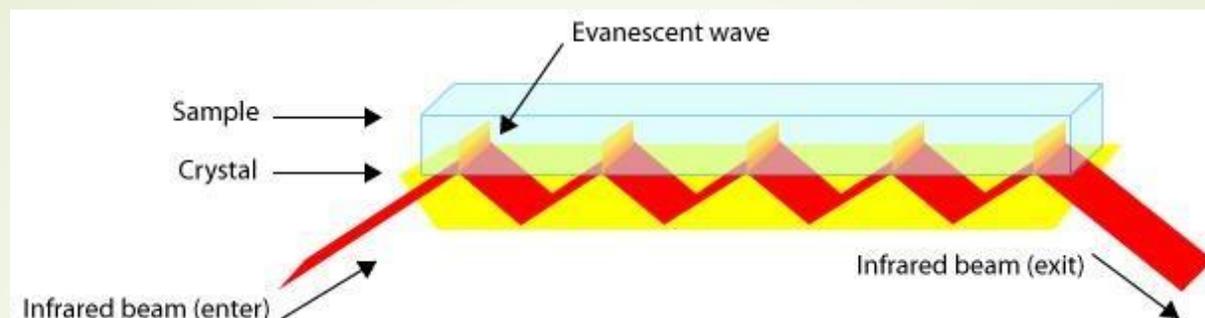


Figure 25: Evanescent wave.

The infrared beam enters the crystal which is made of an optically dense material (i.e. it has a high refractive index) at a particular angle of incidence, the IR beam is internally reflected (usually between five and ten times), this internal reflectance results in the production of an evanescent wave which can extend beyond the crystal surface and into the sample itself. The wave will usually penetrate into the sample with a depth of 0.5-2  $\mu\text{m}$ . The depth to which the wave penetrates is dependent on the angle of the incident IR beam and the refractive index of the crystal material and sample itself.

When a sample absorbs the infrared radiation there is a change in the evanescent wave; in other words the wave is attenuated. The attenuated energy from each of the evanescent waves is then transferred back to the IR beam which exits the crystal and is measured by the detector to produce an IR spectrum.

### Typical ATR Crystal Materials

In ATR instruments the crystal is an optically dense material which has a refractive index that is greater than the sample. Common ATR crystal materials are listed in Table 4. The most common are zinc selenide (ZnSe) and Germanium (Ge).

Zinc selenide is applicable to the analysis of liquids and non-abrasive pastes. It has a working pH range of 5 – 9. Germanium is more robust with a working pH range of 1 – 14 and can be used to analyze weak acids and alkalis. For a greater initial cost, instruments which utilize diamond as the ATR crystal material exhibit greater durability and robustness, with the crystal having to be replaced less in comparison to ZnSe and Ge.

Materials such as ZnSe and Ge can scratch easily; therefore, care must be taken when cleaning the

crystal surface. It is recommended that crystal surfaces are cleaned with lint free tissues soaked with solvents such as water, methanol or isopropanol.

Material	Wavelength Range (cm <sup>-1</sup> )	Refractive Index
ZnSe	20,000-500	2.43
ZnS	22,000-750	2.25
Ge	5,000-600	4.01
Si	10,000-100	3.42
Diamond	45,000-10	2.40

Table 4: Attenuated total reflectance (ATR) crystal materials.

### ATR Instrument

In traditional ATR instruments the sample was clamped against the vertical face of the crystal. This design has now been replaced by horizontal ATR stages where the upper surface of the crystal is exposed (Figure 26). ATR accessory kits can be purchased which can be used to modify existing IR instruments.

Similarly to FT-IR instruments a background spectrum must be collected; this is taken from the clean ATR crystal. The background spectrum which is obtained can be a useful indication of the cleanliness of the ATR crystal; a line at 100% T should be obtained with no spectral features. In order for total internal reflectance to occur there must be good contact between the sample and crystal surface. Liquid samples can be placed directly onto the ATR crystal; the whole crystal must be covered. Similarly pastes or other viscous substances can be spread onto the crystal. In the case of solids, these are more readily analyzed on single reflection ATR instruments which are often made of diamond. High quality spectra can be obtained directly from powder samples placed on the ATR crystal. The amount of sample should entirely cover the crystal and does not need to be more than a few millimeters thick. In order to ensure that there is good contact with the crystal surface the instrument pressure arm is positioned over the sample and tightened; it may be necessary to apply greater pressure when analyzing high density polymers or coatings on metal surfaces, however, the user manual should always be consulted for optimum operating parameters.

The major advantages of ATR instruments are the lack of sample preparation, the ability to obtain high quality reproducible spectra, and due to their ease of use, the variation between users is minimized.

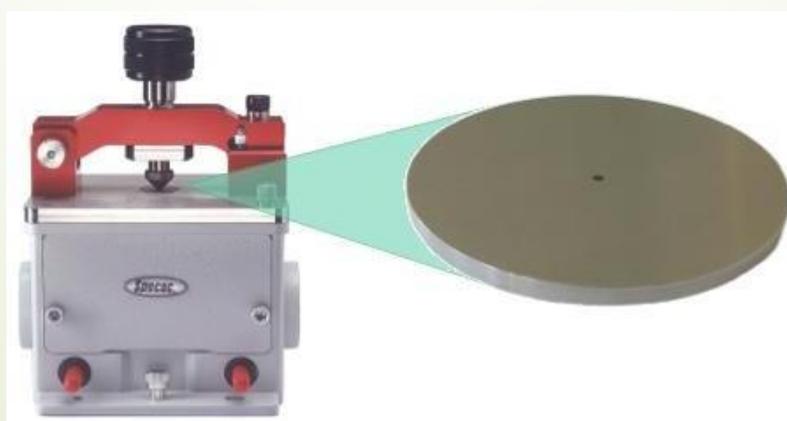


Figure 26: ATR Instrument. Image reproduced with permission from Specac (Orpington, Kent, UK).

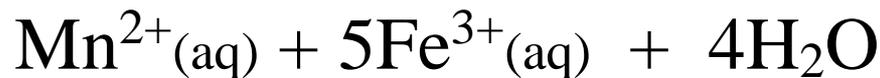
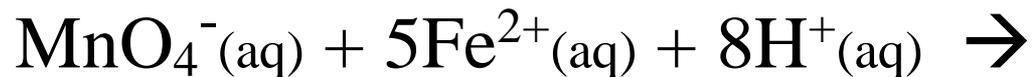
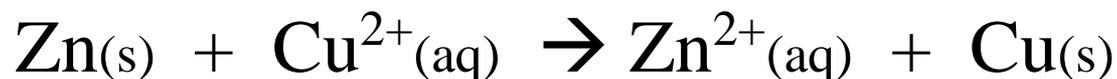
# Lecture no.2

# Electrochemical

- 1. Balancing Oxidation–Reduction Reactions*
- 2. Galvanic Cells*
- 3. Standard Reduction Potentials*
- 4. Cell Potential, Electrical Work, and Free Energy*
- 5. Dependence of Cell Potential on Concentration*
- 6. Batteries*
- 7. Corrosion*
- 8. Electrolysis*
- 9. Commercial Electrolytic Processes*

# Redox Reactions

- Examples of Redox Reactions:



# Balancing Redox Equations

- Review of Terms:
  - Oxidation–reduction (redox) reaction – involves a transfer of electrons from the reducing agent to the oxidizing agent
  - Oxidation – loss of electrons
  - Reduction – gain of electrons
  - Reducing agent – electron donor
  - Oxidizing agent – electron acceptor

# Balancing Redox Equations

- Half-Reactions Method:
- The overall reaction is split into two half-reactions, one involving oxidation and one reduction.



# Balancing Redox Equations

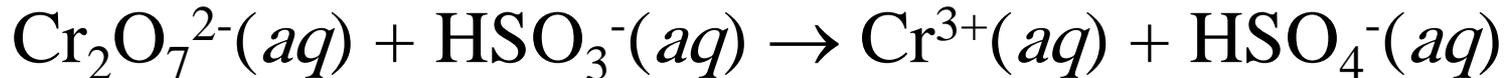
- The Half–Reaction Method for Balancing Equations for Oxidation–Reduction Reactions Occurring in Acidic Solution
  1. Write separate equations for the oxidation and reduction half–reactions.
  2. For each half–reaction:
    - A. Balance all the elements except H and O.
    - B. Balance O using  $\text{H}_2\text{O}$ .
    - C. Balance H using  $\text{H}^+$ .
    - D. Balance the charge using electrons.

# Balancing Redox Equations: The Half-Reaction Method

1. Write separate equations for oxidation and reduction half-reactions.
2. For each half-reaction:
  - Balance all the elements except H and O.
  - Balance O using  $\text{H}_2\text{O}$ .
  - Balance H using  $\text{H}^+$ .
  - Balance the charge using electrons.
3. If necessary, multiply one or both balanced half-reactions by an integer to make the number of electrons in both half-reactions equal.
4. Add half-reactions and cancel identical species.

# Balancing Redox Equations

Example:



- How can we balance this equation?
- First Steps:
  - Separate into half-reactions.
  - Balance elements except H and O.

# Balancing Redox Equation: The Half-Reaction Method

- $\text{Cr}_2\text{O}_7^{2-}(aq) \rightarrow 2\text{Cr}^{3+}(aq)$
- $\text{HSO}_3^-(aq) \rightarrow \text{HSO}_4^-(aq)$
- How many electrons are needed to balance the charge in each half-reaction?

# Balancing Redox Equation: The Half-Reaction Method

- Adding electrons:
- $6e^- + \text{Cr}_2\text{O}_7^{2-}(aq) \rightarrow 2\text{Cr}^{3+}(aq)$
- $\text{HSO}_3^-(aq) \rightarrow \text{HSO}_4^-(aq) + 2e^-$
- How can we balance the oxygen atoms?

# Balancing Redox Equation: The Half-Reaction Method

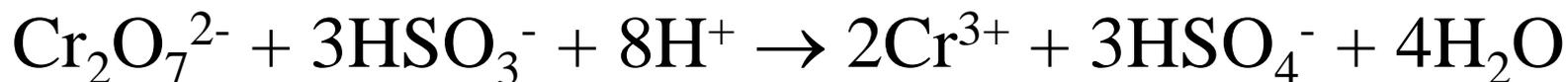
- $6e^- + \text{Cr}_2\text{O}_7^{2-}(aq) \rightarrow \text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}$
- $\text{H}_2\text{O} + \text{SO}_3^{2-}(aq) \rightarrow + \text{SO}_4^{2-}(aq) + 2e^-$
- How can we balance the hydrogen atoms?

# Balancing Redox Equation: The Half-Reaction Method

- This reaction occurs in an acidic solution.
- $14\text{H}^+ + 6\text{e}^- + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
- $\text{H}_2\text{O} + \text{HSO}_3^- \rightarrow \text{HSO}_4^- + 2\text{e}^- + 2\text{H}^+$
- How can we balance the electrons?

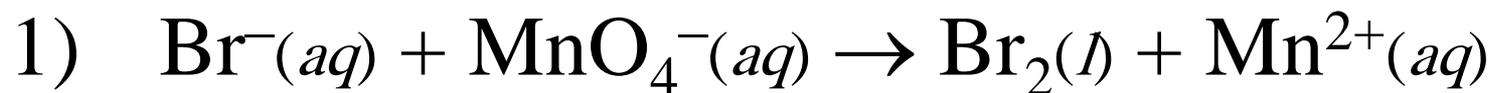
# Balancing Redox Equation: The Half-Reaction Method

- $14\text{H}^+ + 6\text{e}^- + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
- $3[\text{H}_2\text{O} + \text{HSO}_3^- \rightarrow \text{HSO}_4^{2-} + 2\text{e}^- + 2\text{H}^+]$
- The final balanced equation:



# Sample Exercises

Balance the following redox reactions in **acidic** solution.



# The Half–Reaction Method for Balancing Redox Equations in Basic Solution

1. Use the half–reaction method as specified for acidic solutions to obtain the final balanced equation as *if*  $\text{H}^+$  ions were present.
2. To both sides of the equation, add a number of  $\text{OH}^-$  ions that is equal to the number of  $\text{H}^+$  ions present. (You want to eliminate  $\text{H}^+$  by turning it into  $\text{H}_2\text{O}$ )
3. Form  $\text{H}_2\text{O}$  on the side containing both  $\text{H}^+$  and  $\text{OH}^-$  ions, and eliminate the number of  $\text{H}_2\text{O}$  molecules that appear on both sides of the equation.
4. Check that elements and charges are balanced.

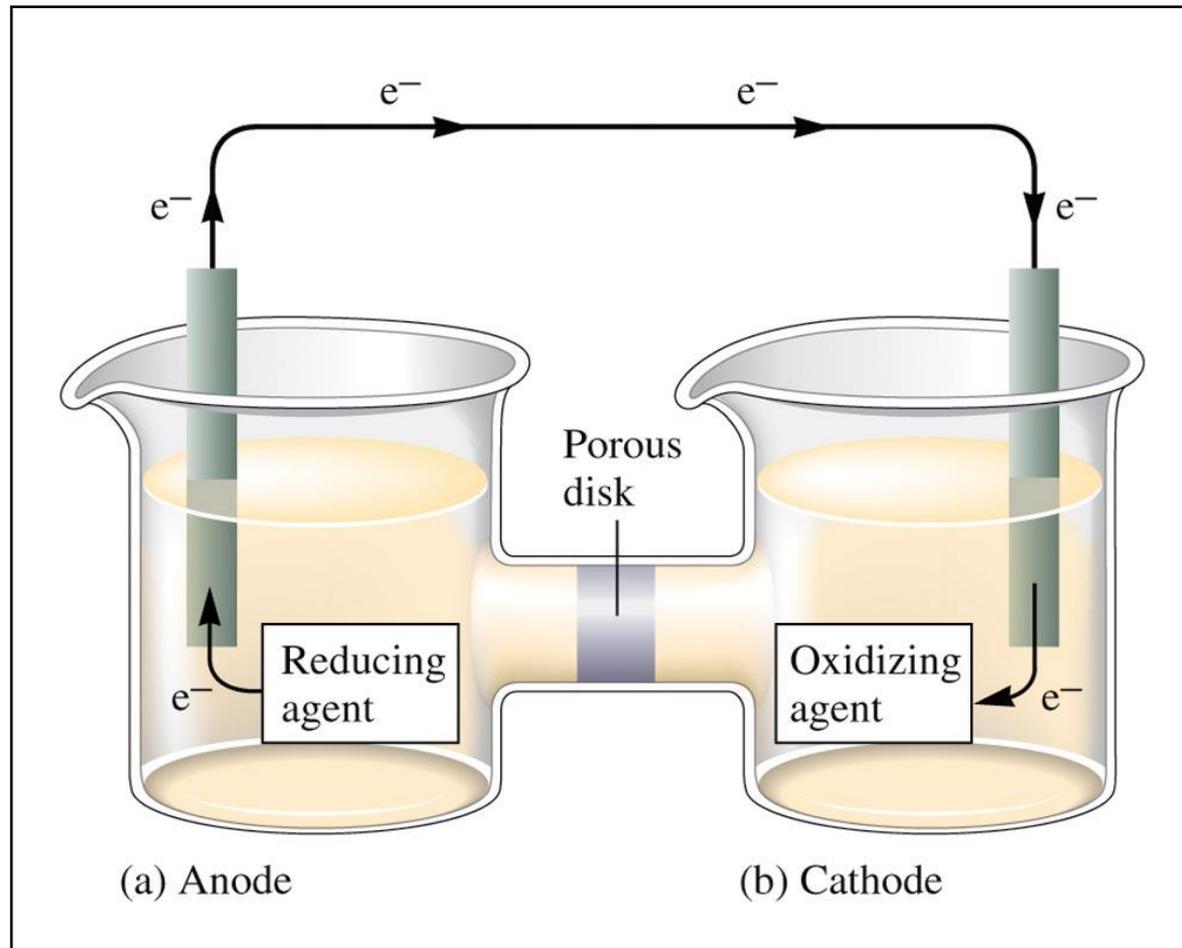
# Sample Exercises

- Balance the following redox reactions in basic solution:
- $\text{Br}_2(aq) + \text{OH}^-(aq) \rightarrow \text{BrO}_3^-(aq) + \text{Br}^-(aq) + \text{H}_2\text{O}$ ;
- $\text{Cr}(\text{OH})_4^-(aq) + \text{OH}^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{H}_2\text{O}$ ;

# Galvanic Cell

- A device in which chemical energy is converted to electrical energy.
- It uses a spontaneous redox reaction to produce a current that can be used to generate energy or to do work.

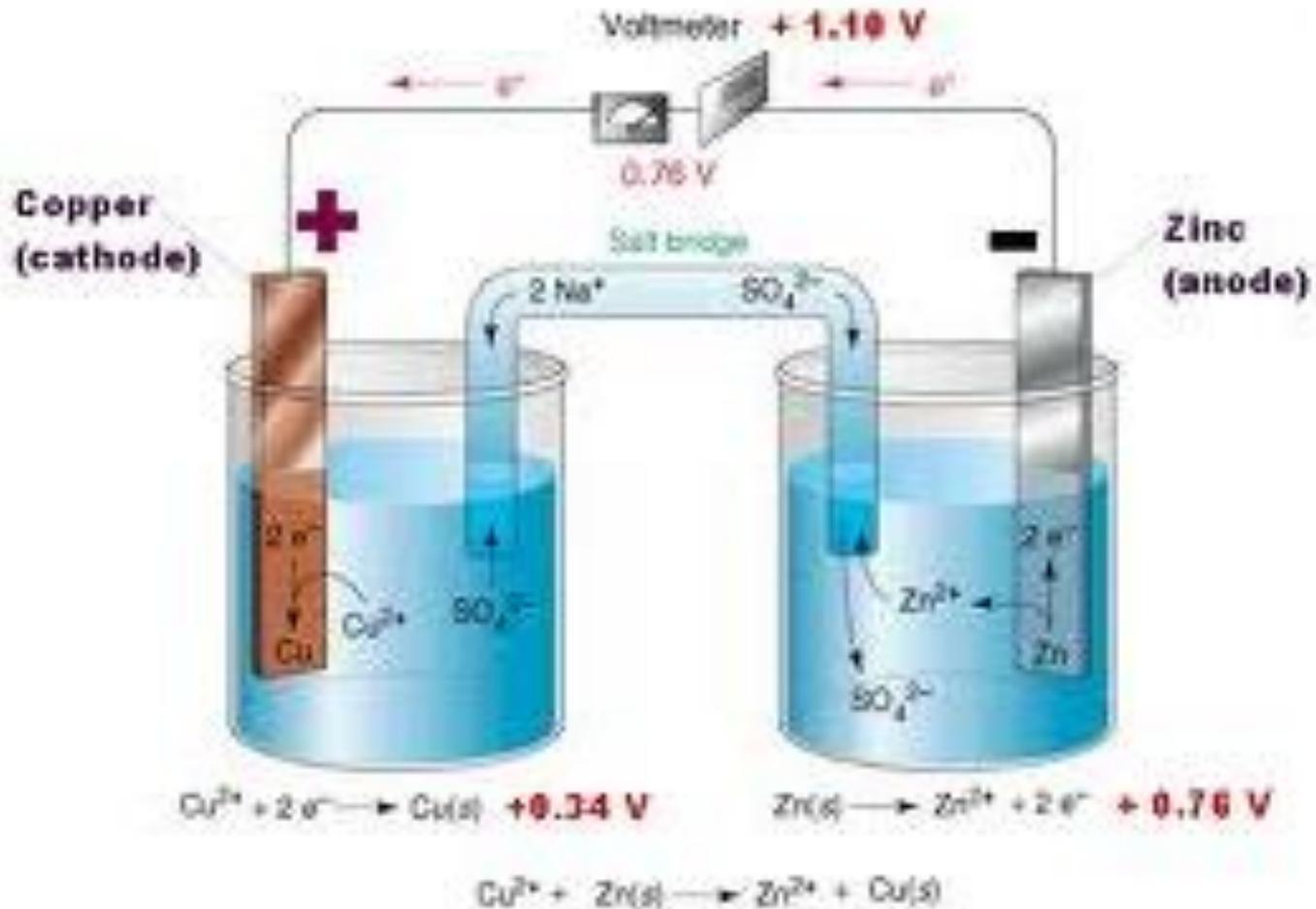
# A Galvanic Cell



# In Galvanic Cell:

- Oxidation occurs at the anode.
- Reduction occurs at the cathode.
- Salt bridge or porous disk allows ions to flow without extensive mixing of the solutions.
  - Salt bridge – contains a strong electrolyte held in a gel-like matrix.
  - Porous disk – contains tiny passages that allow hindered flow of ions.

# Galvanic Cell



# Cell Potential

- A galvanic cell consists of an oxidizing agent (in cathode half-cell) and a reducing agent (in anode half-cell).
- Electrons flow through a wire from the anode half-cell to the cathode half-cell.
- The driving force that allows electrons to flow is called the electromotive force (emf) or the cell potential ( $E_{\text{cell}}$ ).
  - The unit of electrical potential is *volt* (V).
    - $1 \text{ V} = 1 \text{ J/C}$  of charge transferred.

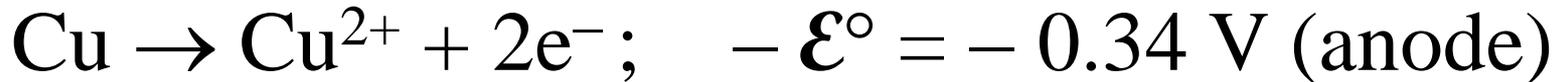
# Standard Reduction Potentials

- Values of  $\mathcal{E}^\circ$  in standard table of half-cell potentials are for reduction half-cell reactions
  - Table 18.1 (or 17.1)
  - 1 *M*, 1 atm, 25°C
- When a half-reaction is reversed, the algebraic sign of  $\mathcal{E}^\circ$  changes.
- When a half-reaction is multiplied by an integer, the value of  $\mathcal{E}^\circ$  remains the same.
- A galvanic cell runs spontaneously in the direction that gives a positive value for  $\mathcal{E}^\circ_{\text{cell}}$

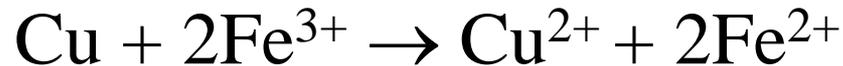


- Half-Reactions:
  - $\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+} \quad \mathcal{E}^{\circ} = 0.77 \text{ V}$
  - $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu} \quad \mathcal{E}^{\circ} = 0.34 \text{ V}$
- To balance the cell reaction and calculate the cell potential, we must reverse reaction 2.
  - $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^{-} \quad -\mathcal{E}^{\circ} = -0.34 \text{ V}$
- Each Cu atom produces two electrons but each  $\text{Fe}^{3+}$  ion accepts only one electron, therefore reaction 1 must be multiplied by 2.
  - $2\text{Fe}^{3+} + 2\text{e}^{-} \rightarrow 2\text{Fe}^{2+} \quad \mathcal{E}^{\circ} = 0.77 \text{ V}$

# Standard Cell Potential



- **Balanced Cell Reaction:**



- **Cell Potential:  $\mathcal{E}$**

$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}(\text{cathode}) - \mathcal{E}^{\circ}(\text{anode})$$

$$\mathcal{E}^{\circ}_{\text{cell}} = 0.77 \text{ V} - 0.34 \text{ V} = 0.43 \text{ V}$$

# Calculating Standard Cell Potential

- Given the following reduction potentials:
- $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}); \quad \mathcal{E}^\circ = 0.80 \text{ V}$
- $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s}); \quad \mathcal{E}^\circ = -0.76 \text{ V}$
- Calculate the cell potential for the following reaction and predict whether the reaction will take place:
- $\text{Zn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$

# Standard Cell Potentials

- Given the following reduction potentials:
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s}); \quad \mathcal{E}^{\circ} = 0.34 \text{ V}$
- $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ni}(\text{s}); \quad \mathcal{E}^{\circ} = -0.23 \text{ V}$
- Predict whether the following reaction will take place:
- $\text{Cu}(\text{s}) + \text{Ni}^{2+}(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Ni}(\text{s})$

# Cell Notations for Galvanic Cells

- Used to describe electrochemical cells.
- Anode components are listed on the left.
- Cathode components are listed on the right.
- Separated by double vertical lines.
- The concentration of aqueous solutions should be specified in the notation when known.
- Example:  $\text{Mg}_{(s)}|\text{Mg}^{2+}_{(aq)}||\text{Al}^{3+}_{(aq)}|\text{Al}_{(s)}$ 
  - $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$  (anode)
  - $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$  (cathode)

# Description of a Galvanic Cell

- The cell potential is always positive for a galvanic cell, where  $\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{(cathode half-cell)}} - \mathcal{E}^{\circ}_{\text{(anode half-cell)}}$  (as given in the table of half-cell potentials)
- Anode is the negative terminal and cathode is the positive terminal.
- Electron flows from the anode (-) to cathode (+).
- Current flows from cathode(+) to anode(-).
- Positive ions flows from anode to cathode half-cells and negative ions flows from cathode to anode though the “salt bridge”.

# Designation of Anode and Cathode

- Write balanced net ionic equation for the spontaneous cell reaction.
- The oxidizing agent (one with the more positive or less negative reduction potential  $\mathcal{E}^\circ$ ) will be the cathode and the other will be the anode.
- Oxidation occurs in anode half-cell and reduction in cathode half-cell.
- Anode is negative(-) and cathode is positive(+).

# Cell Potential, Free Energy, and Electrical Work

## Maximum cell potential and free energy

- Directly related to the free energy difference between the reactants and the products in the cell reaction.

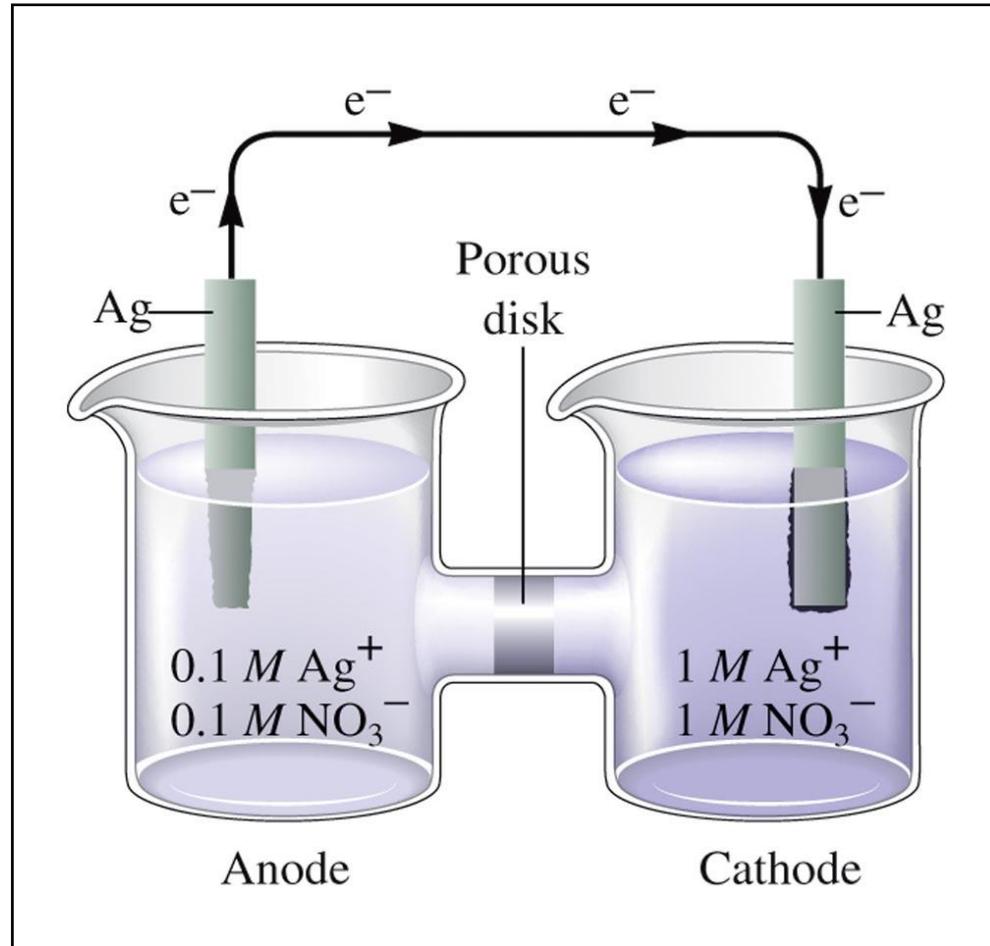
- $\Delta G^\circ = -nF\mathcal{E}^\circ$

- $F = 96,485 \text{ C/mol e}^-$

## Work:

- In any real, spontaneous process some energy is always lost (wasted) – the actual work obtained is always less than the calculated (maximum) value.

# Concentration Cells



# Concentration Cell

- For the concentration cell depicted in the previous diagram, indicate the anode and cathode half-cell.
- Calculate the cell potential for the concentration cell depicted in this diagram.

# Nernst Equation

- At 25°C.

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.0591}{n} \log(Q)$$

$$\mathcal{E}^{\circ} = \frac{0.0591}{n} \log(K)$$

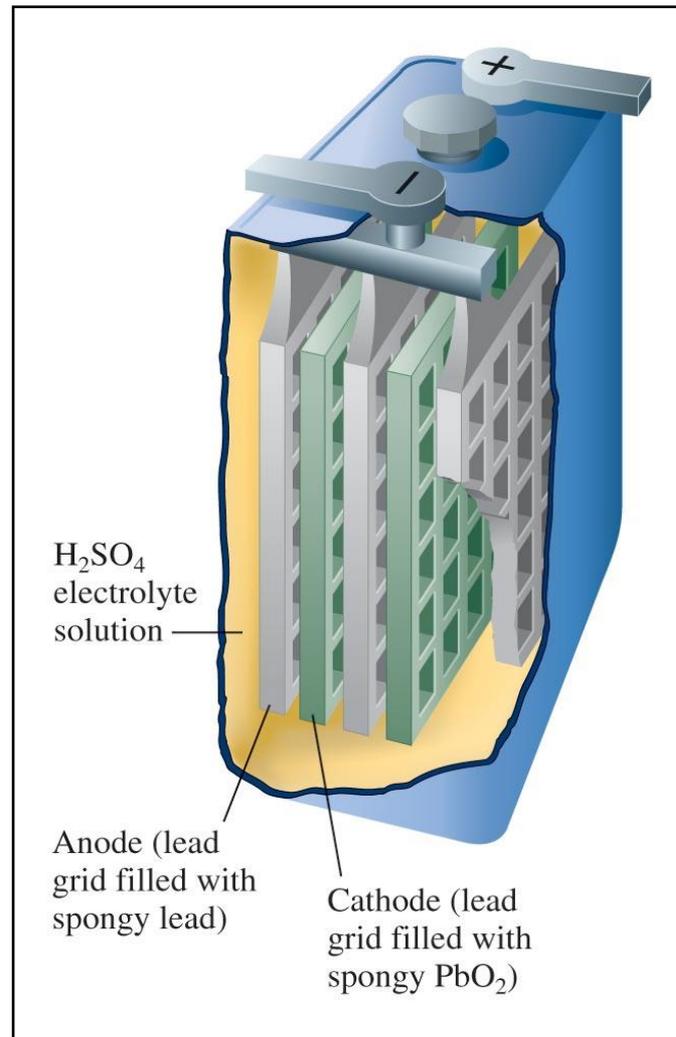
# Cell Potential for Concentration Cells

- A concentration cell is set up with one of the half-cells consists of a silver electrode in 1.0 M  $\text{AgNO}_3$  and other other half-cell contains silver electrode in saturated solution of  $\text{AgCl}$  ( $K_{\text{sp}} = 1.6 \times 10^{-10}$  at  $25^\circ\text{C}$ ). Calculate the cell potential for the concentration cell.
- Identify the anode and cathode half-cell.

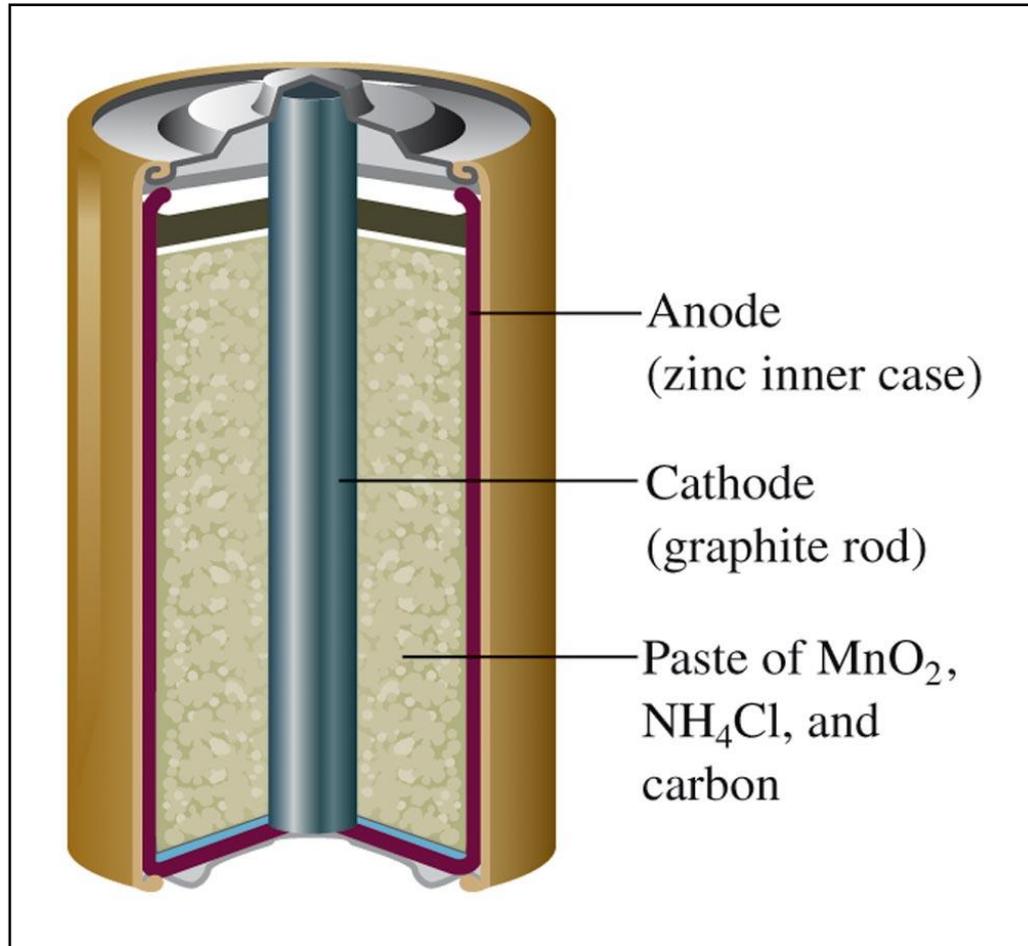
## Concentration Cell and Determination of $K_{sp}$

- In another set up of concentration cell, one of the half-cells contains 1.0 M  $\text{CuSO}_4$  and the other contains saturated solution of  $\text{CuCO}_3$ . Copper metal is used as electrode in each half-cell. If the cell potential at  $25^\circ\text{C}$  is 0.28 V, calculate the concentration of  $\text{Cu}^{2+}$  in the saturated solution. What is the  $K_{sp}$  for  $\text{CuCO}_3$  at  $25^\circ\text{C}$ .

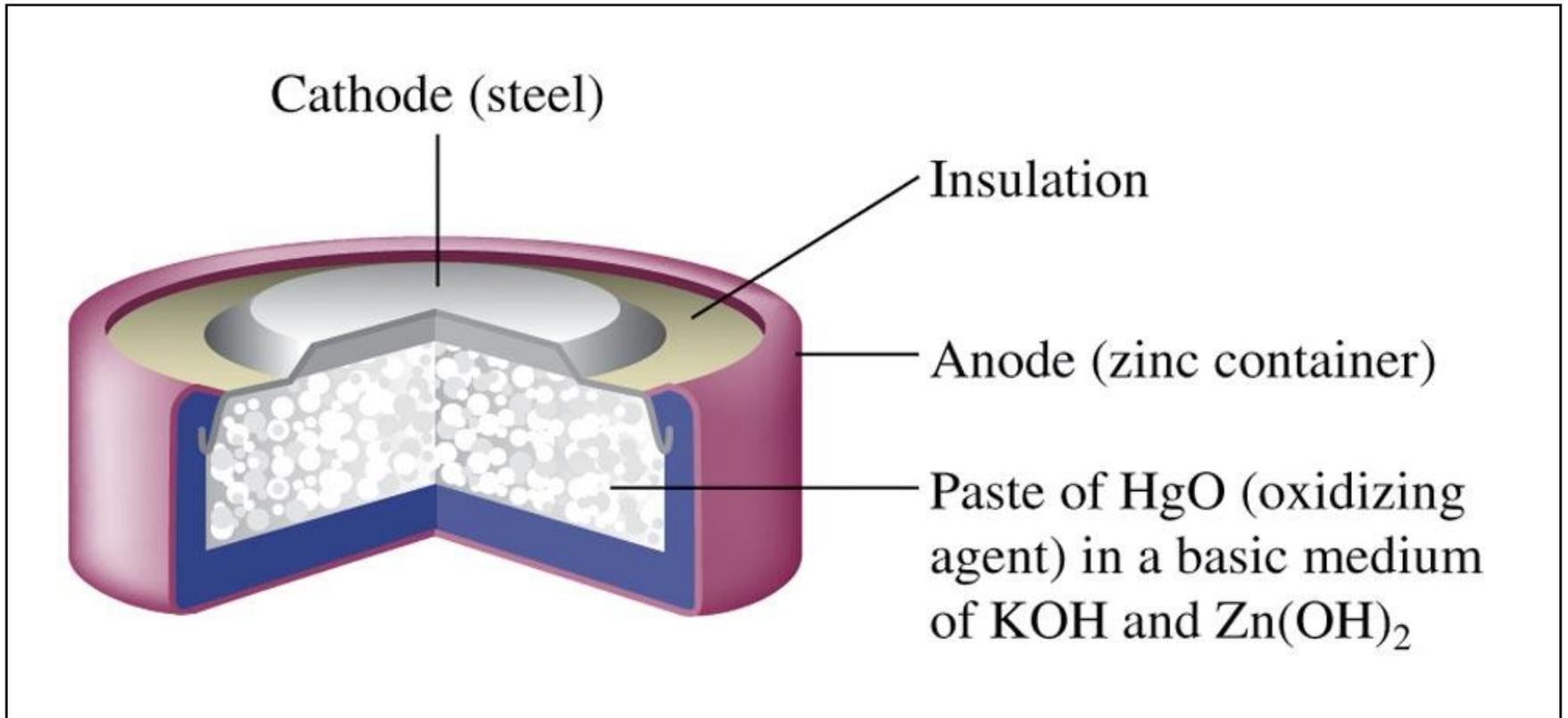
# Lead Storage Battery



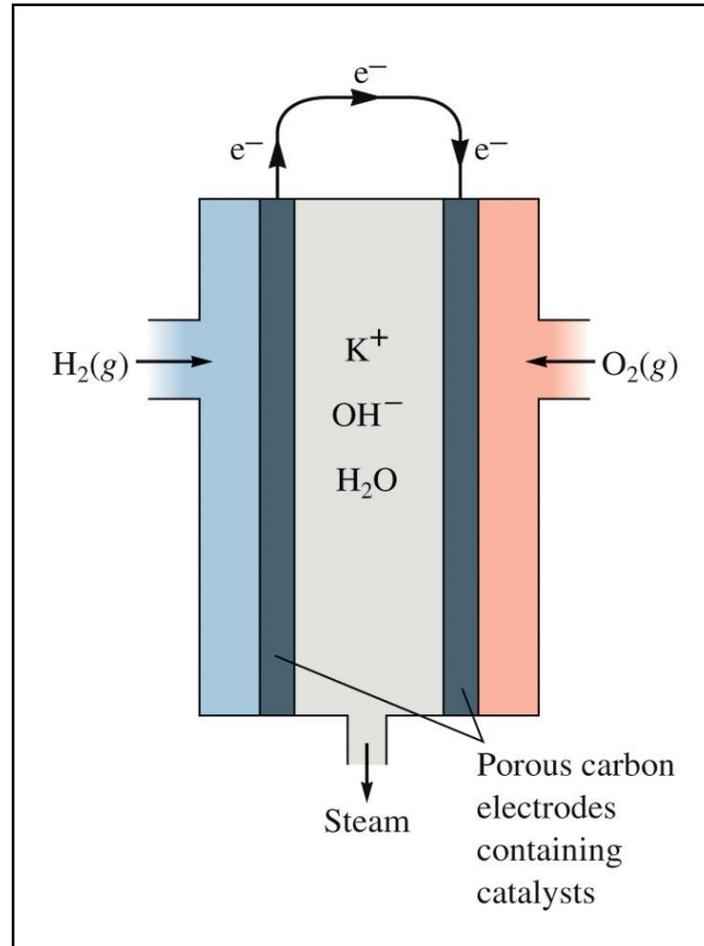
# Nonalkaline Dry Cell



# Mercury Battery



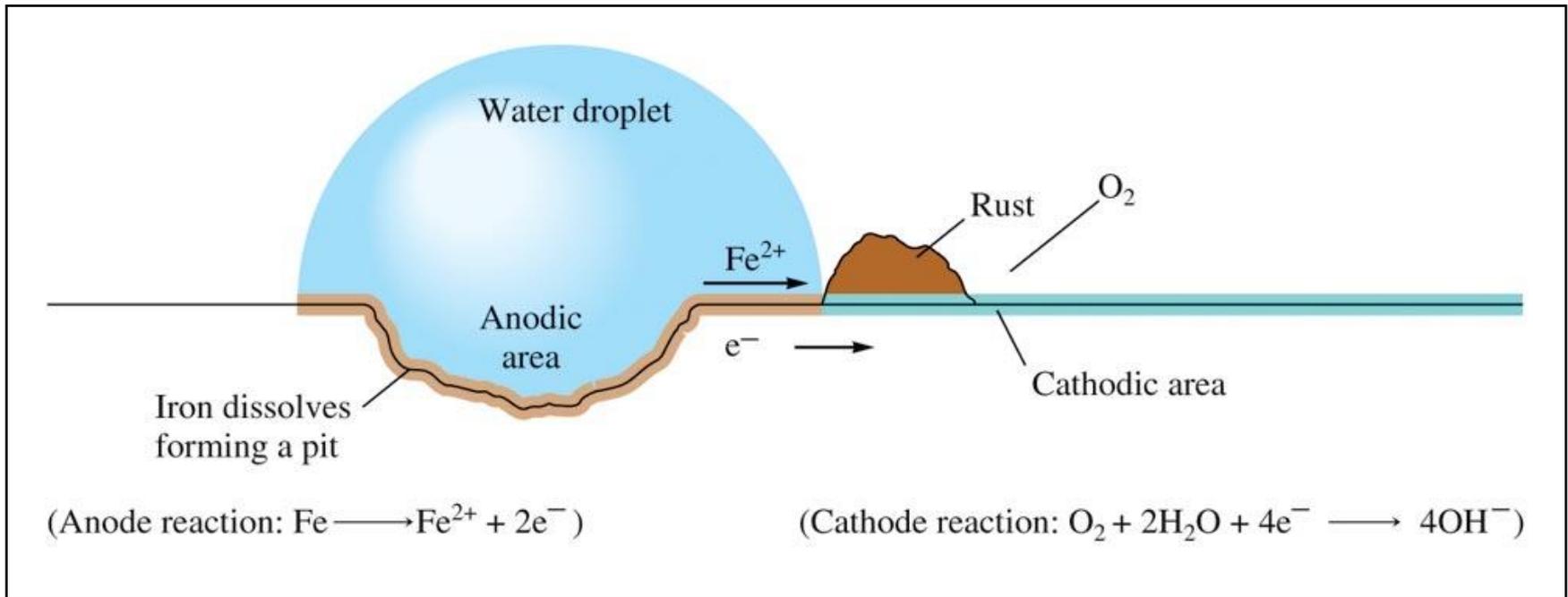
# Fuel Cell



# Corrosion

- The process that returns metals to their oxidized state.
- Involves oxidation of the metal.

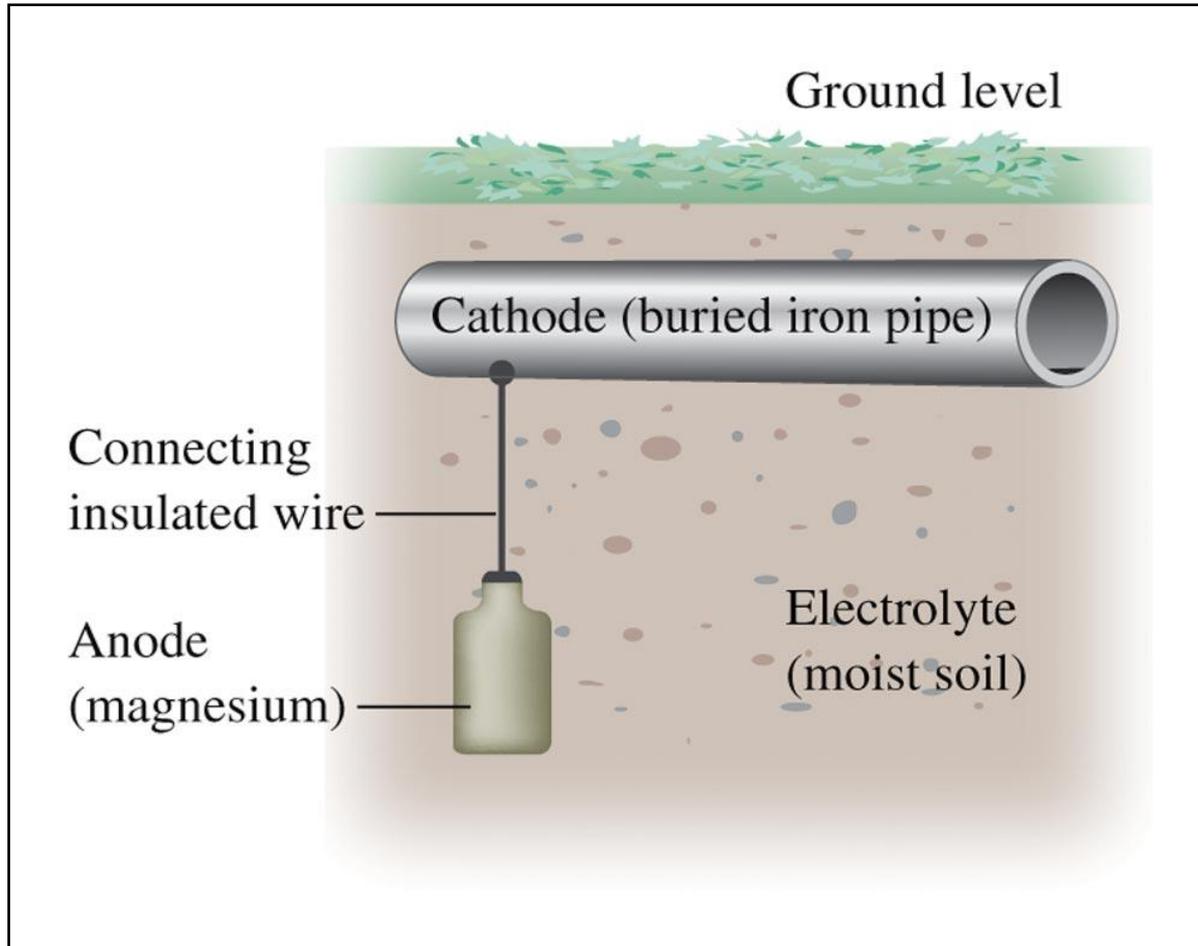
# Electrochemical Corrosion of Iron



# Corrosion Prevention

- Apply coating (such as paint or metal plating)
  - Galvanizing
- Alloying
- Cathodic Protection
  - Protects steel in buried fuel tanks and pipelines.

# Cathodic Protection



# Electrolysis

- A process that forces a current through a cell to produce a chemical change for which the cell potential is negative.

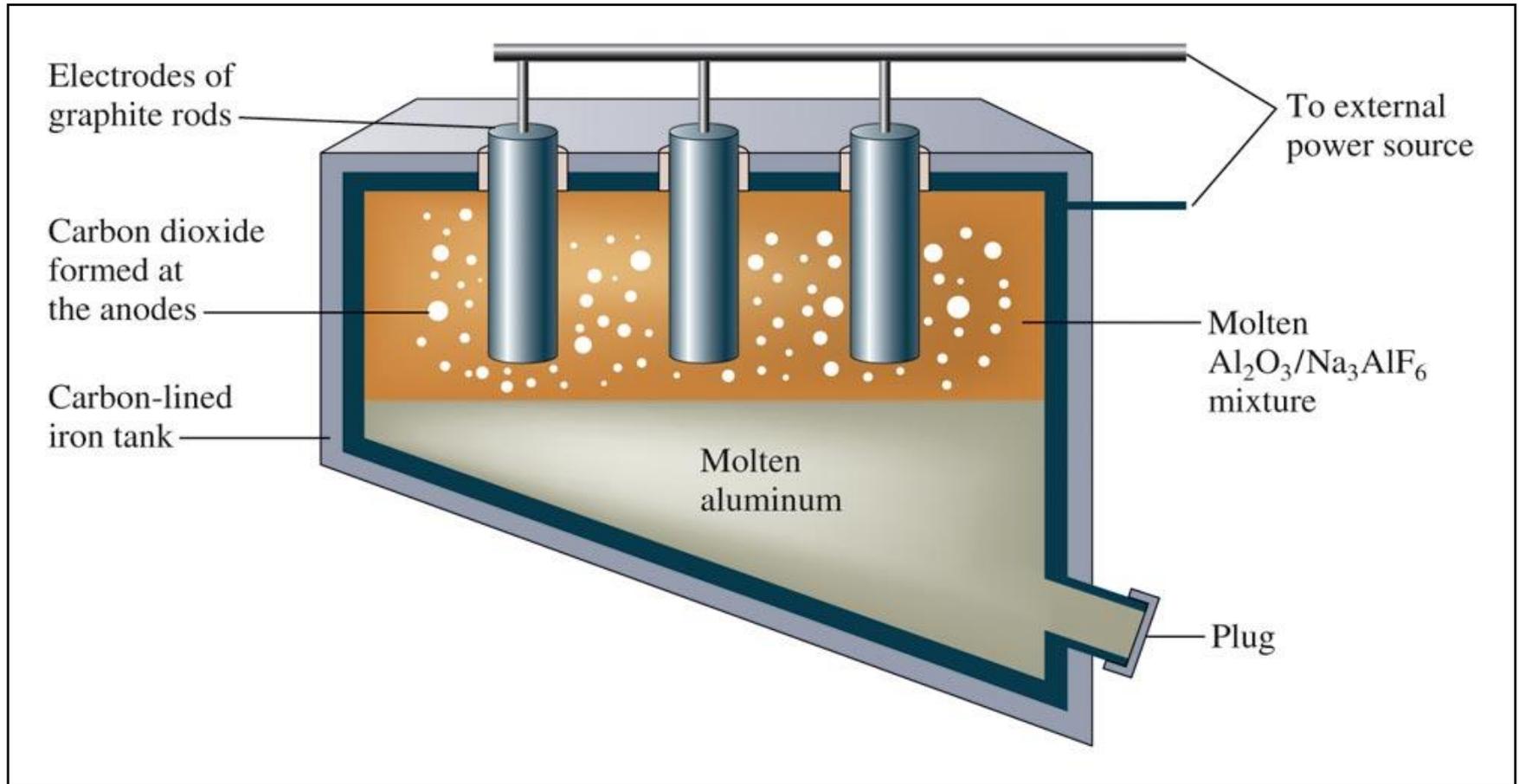
# Electrolysis

- Consider a solution containing 0.10 *M* of each of the following:  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Pb}^{2+}$ .
- Predict the order in which the metals plate out as the voltage is applied.
- Do the metals form on the **cathode** or the **anode**?  
Explain.

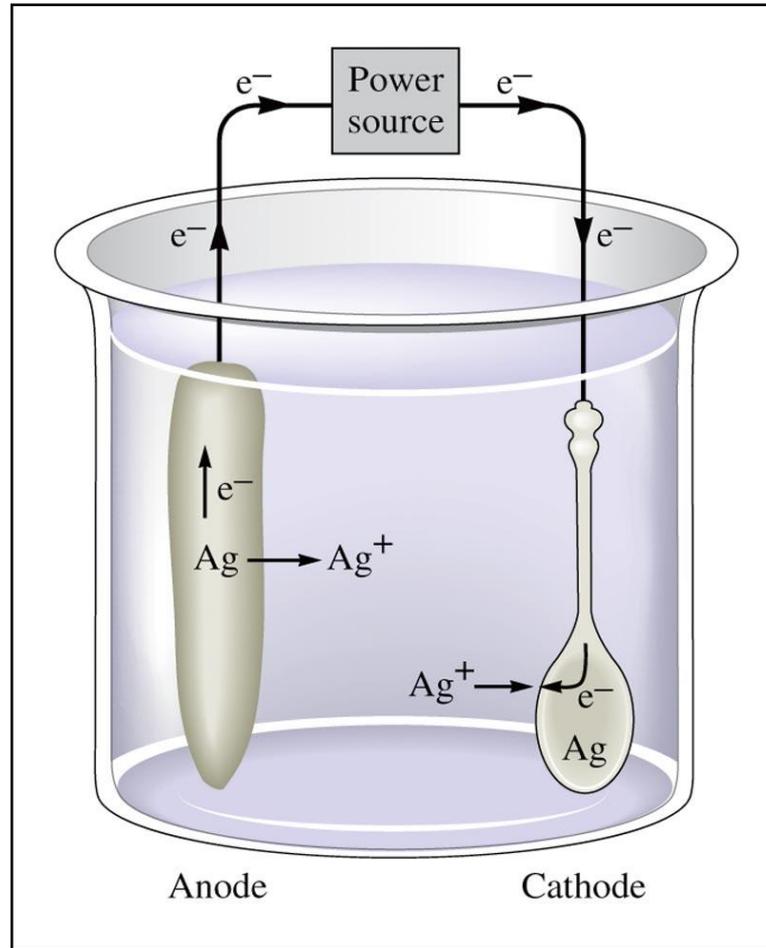
# Commercial Electrolytic Processes

- Production of aluminum
- Purification of metals
- Metal plating
- Electrolysis of sodium chloride
- Production of chlorine and sodium hydroxide

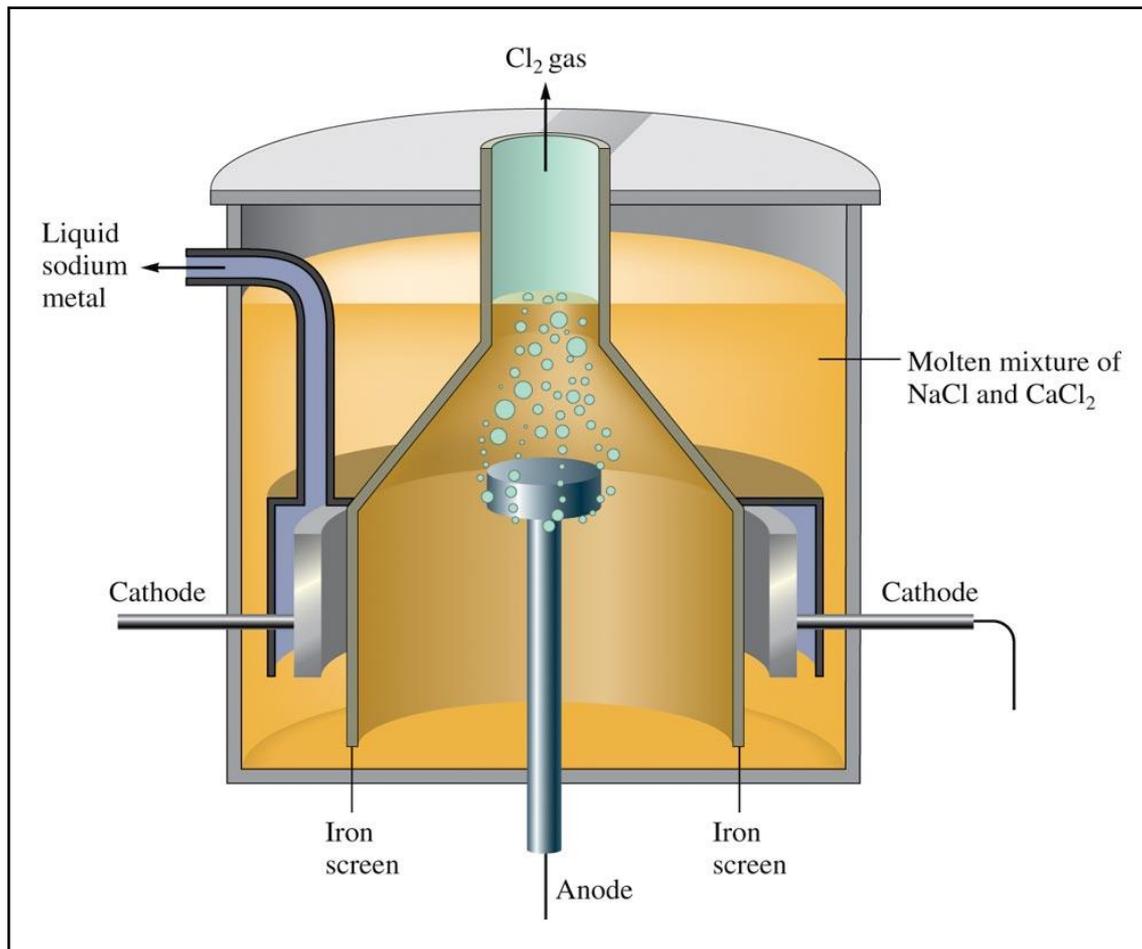
# The Hall-Heroult Process for Al Production



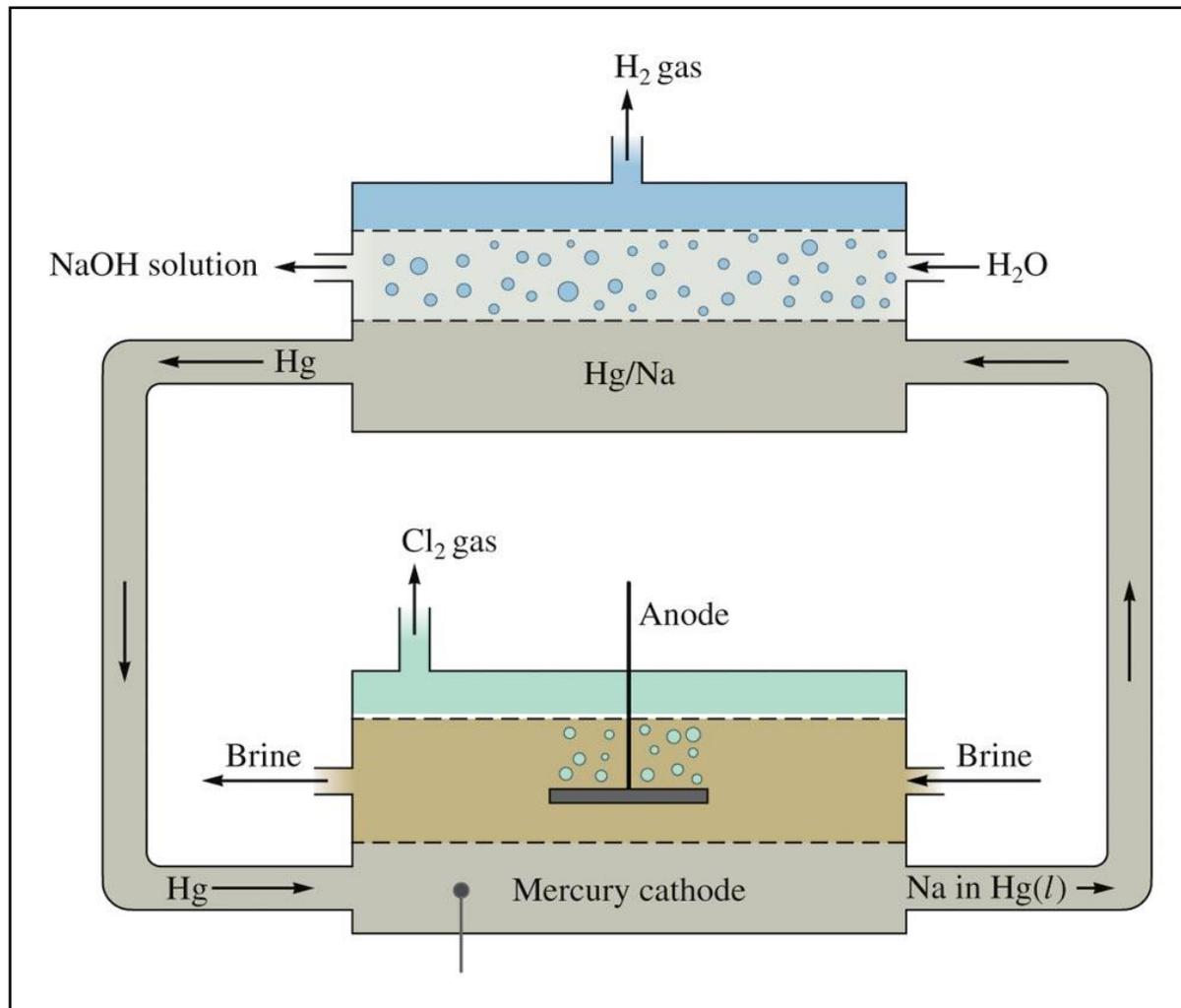
# Electroplating/Silver Plating a Spoon



# The Downs Cell for the Electrolysis of Molten Sodium Chloride



# The Mercury Cell for Production of Chlorine and Sodium Hydroxide



# Lecture no.3

# **Flow injection Analysis**

# Introduction...

- By IUPAC terminology, automatic devices do not modify their operation as a result of feedback from an analytical transducer. For example, an automatic acid/base titrator adds reagent to a solution and simultaneously records pH as a function of volume of reagent

# *Advantages and Disadvantages of Automatic Analyses...*

- Automated instruments offer a major economic advantage because of their savings in labor costs.
- Their speed, which is frequently significantly greater than that of manual devices.
- A well-designed analyzer can usually produce more reproducible results over a long period of time than can an operator employing a manual instrument.

# *Unit Operations in Chemical Analysis...*

- All analytical methods can be broken down into a series of eight steps, or unit operations, any one of which can be automated. The next table lists the steps in the order in which they occur in a typical analysis.

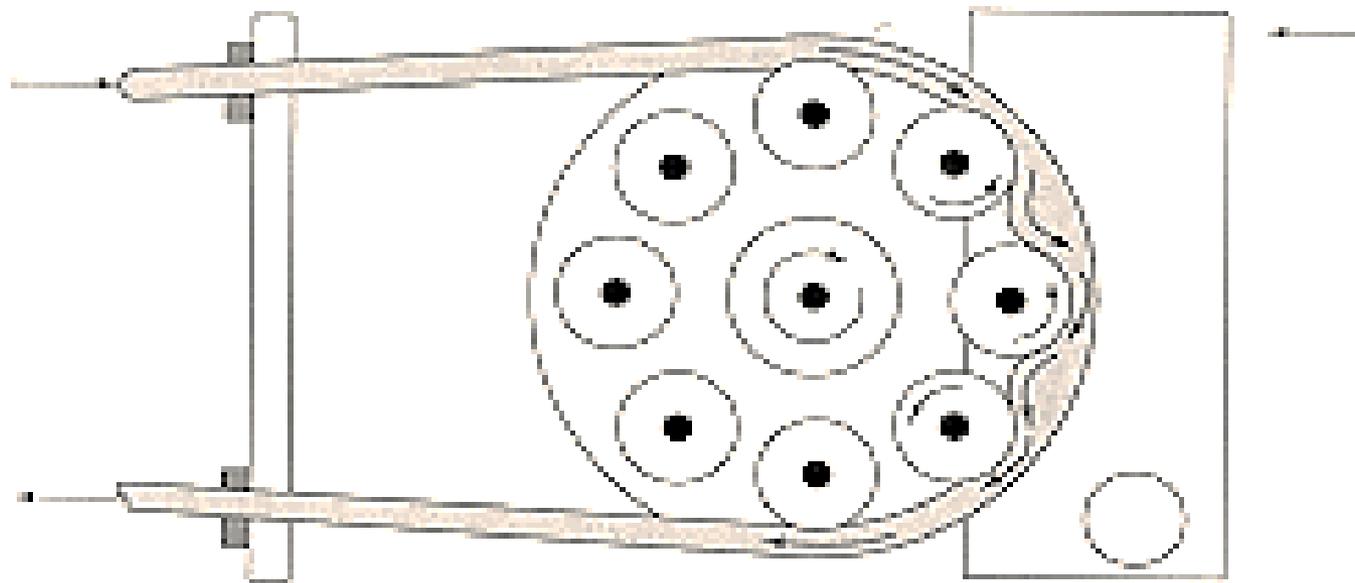
Automatic analytical systems are of two general types:

- *discrete analyzers*
- *continuous-flow analyzers*

# **FLOW-INJECTION ANALYSIS...**

Flow-injection methods, in their present form, were first described in the mid 70s. Flow-injection methods are and outgrowth of segmented-flow procedures, which were widely used in clinical laboratories in the 1960s and 1970s for automatic routine determination of a variety of species in blood and urine samples for medical diagnostic purposes.

## *Instrumentation...*



**Figure 33-2** Diagram showing one channel of a peristaltic pump. Usually, several additional tubes may be located under the one shown (below the plane of the paper). (From D. Karberg and G. E. Faley, *Flow Injection Analysis, A Practical Guide*, p. 34. New York: Elsevier, 1989. With permission of Elsevier Science Publishers.)

# Sample and Reagent Transport System...

- Ordinarily, the solution in a flow-injection analysis is moved through the system by a peristaltic pump, a device in which a fluid (liquid or gas) is squeezed through plastic tubing by rollers.

# Sample Injectors and Detectors...

- The injectors and detectors employed in flow-injection analysis are similar in kind and performance requirements to those used in HPLC. For successful analysis, it is vital that the sample solution be injected rapidly as a pulse or plug of liquid

# Separations in FIA...

- Separations by dialysis, by liquid/liquid extraction, and by gaseous diffusion are readily carried out automatically with flow-injection systems.

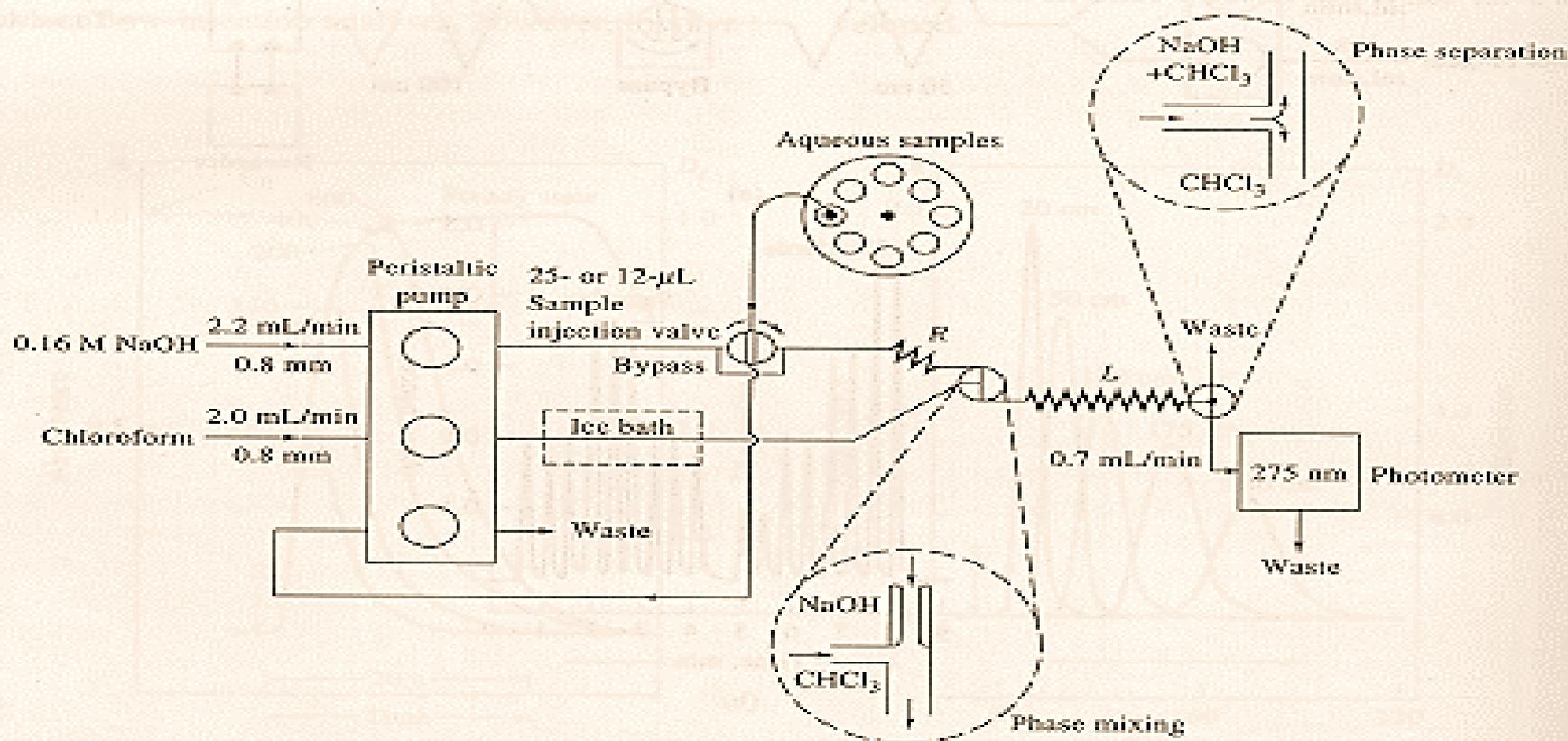
# Dialysis and Gas Diffusion...

- Dialysis is often used continuous-flow methods to separate inorganic ions, such as chloride or sodium or small organic molecules, such as glucose, from high-molecular-weight species such as proteins.

# Extraction...

- Another common separation technique readily adapted to continuous-flow methods is extraction. It is important to reiterate that none of the separation procedures in FIA methods is ever complete. The lack of completeness is of no consequence, however, because unknowns and standards are treated an identical way.

# Principles of Flow-Injection Analysis...



**Figure 33-8** Flow-injection apparatus for the determination of caffeine in acetylsalicylic acid preparations. With valve rotated at 90 deg, the flow in the bypass is essentially zero because of its small diameter. *R* and *L* are Teflon coils with 0.8-mm inside diameters; *L* has a length of 2 m, while the distance from the injection point through *R* to the mixing point is 0.15 m. (Adapted from B. Karlberg and S. Threlander, *Anal. Chim. Acta*, 1978, 98, 2. With permission.)

# Dispersion...

Dispersion  $D$  is defined by the equation

$$D = c_o/c$$

where  $c_o$  is the analyte concentration of the injected sample and  $c$  is the peak concentration at the detector. Dispersion is influenced by three interrelated and controllable variables: sample volume, tube length, and pumping rate.

# *Applications of Flow-Injection Analysis*

- In the flow-injection literature, the terms limited dispersion, medium dispersion, and large dispersion are frequently encountered where they refer to dispersions of 1 to 3, 3 to 10, and greater than 10, respectively.

# Limited-Dispersion Applications...

- Limited-dispersion flow-injection techniques have found considerable application for high-speed feeding of such detector systems as flame atomic absorption and emission as well as inductively coupled plasma.

# *DISCRETE AUTOMATIC SYSTEMS...*

- A wide variety of discrete automatic systems are offered by numerous instrument manufacturers. Some of these devices are designed to perform one or more.

# *Automatic Sampling and Sample Definition of Liquids and Gases...*

- This device consists of a movable probe, which is a syringe needle or a piece of fine plastic tubing supported by an arm that periodically lifts the tip of the needle or tube from the sample container and positions it over a second container in which the analysis is performed.

# Lecture no.4

# **LASER SPECTROSCOPY**

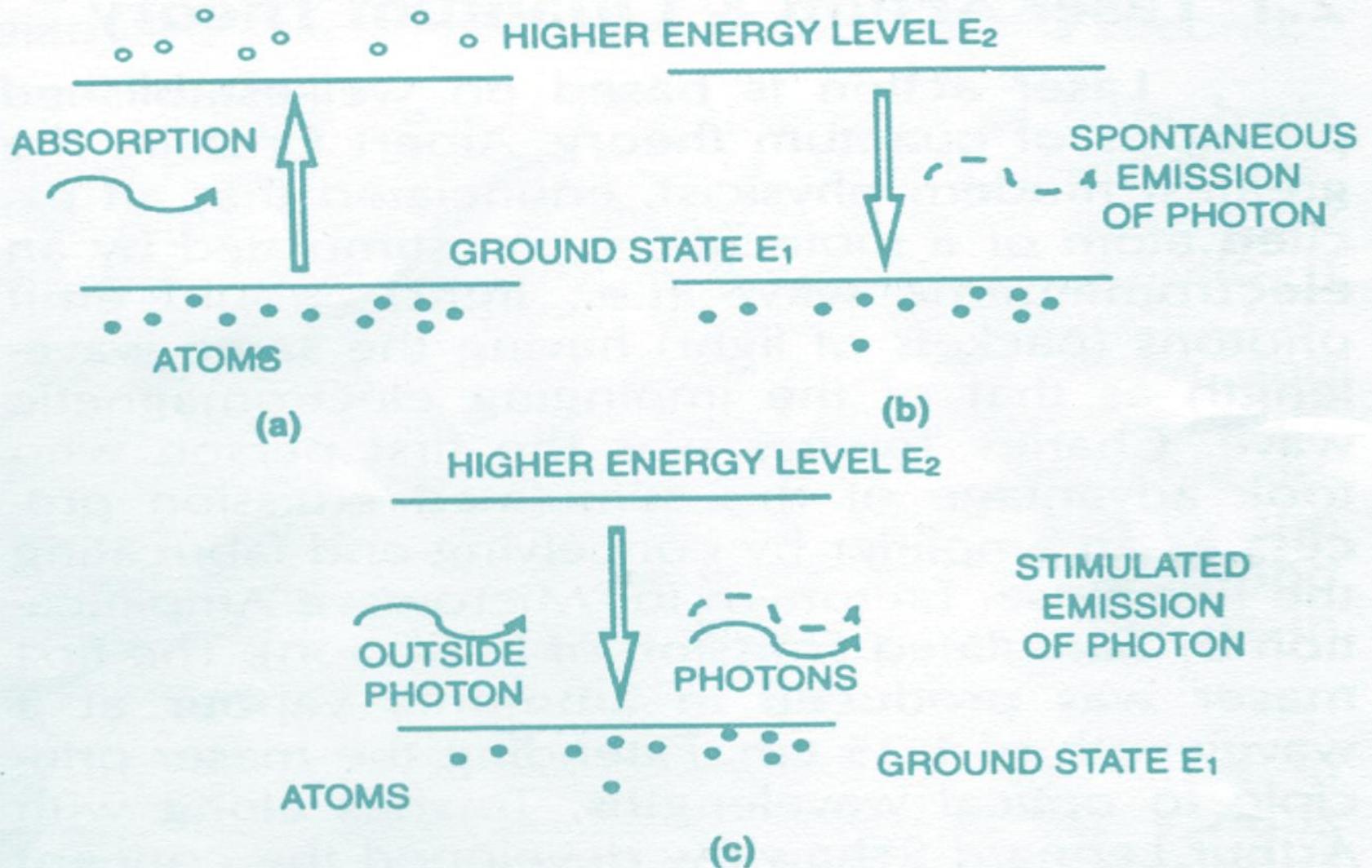
## **Principle and TYPES OF LASERS**

Laser is a powerful source of light having extraordinary properties which are not found in the normal light sources like tungsten lamps, mercury lamps, etc. The unique property of laser is that its light waves travel very long distances with a very little divergence. In case of a conventional source of light, the light is emitted in a jumble of separate waves that cancel each other at random and hence can travel very short distances only. An analogy can be made with a situation where a large number of pebbles are thrown into a pool at the same time. Each pebble generates a wave of its own. Since the pebbles are thrown at random, the waves generated by all the pebbles cancel each other and as a result they travel a very short distance only. On the other hand, if the pebbles are thrown into a pool one by one at the same place and also at constant intervals of time, the waves thus generated strengthen each other and travel long distances. In this case, the waves are said to travel coherently. In laser, the light waves are exactly in step with each other and thus have a fixed phase relationship. A high degree of directionality and monochromaticity is also associated with these light beams. Therefore, in a laser beam the light waves not only are in the same phase but also have the same color (wavelength) throughout their journey. The beam of the ordinary light spreads out very quickly. On the other hand, the laser beam is highly collimated and spreads very little as it travels through space; even after traveling to the surface of the moon the spread of laser light has been found to be only about 3 km across. Hypothetically, if ordinary light was able to travel to the moon, its beam would have fanned out to such an extent leading to a diameter of the light on the moon as much as 40,000 km.

# Laser Action & Quantum Theory

Laser action is based on well-established principles of quantum theory. Albert Einstein, the greatest modern physicist, enunciated that an excited atom or a molecule, when stimulated by an electromagnetic wave (i.e., light), would emit photons (packets of light) having the same wavelength as that of the impinging electromagnetic wave. Charles Townes was the first person who took advantage of this stimulated emission process as an amplifier by conceiving and fabricating the first maser (acronym for Microwave Amplification by Stimulated Emission of Radiation). The first maser was produced in ammonia vapour at a wavelength of 1.25 cm. Extending the maser principle to optical wavelengths, Townes along with Arthur Leonard Schawlow developed the concept of using a laser amplifier and an optical mirror cavity to provide the multiple reflections necessary for rapid growth of light signal into an intense visible beam.

# Principle of Laser Action



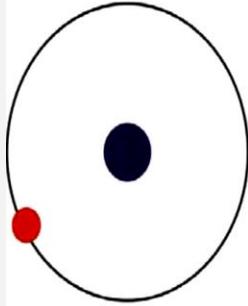
# Amplification & Population Inversion

When favorable conditions are created for the stimulated emission, more and more atoms are forced to give up photons thereby initiating a chain reaction and releasing vast amount of energy. This results in rapid build up of energy of emitting one particular wavelength (monochromatic light), traveling coherently in a precise, fixed direction. This process is called amplification by stimulated emission.

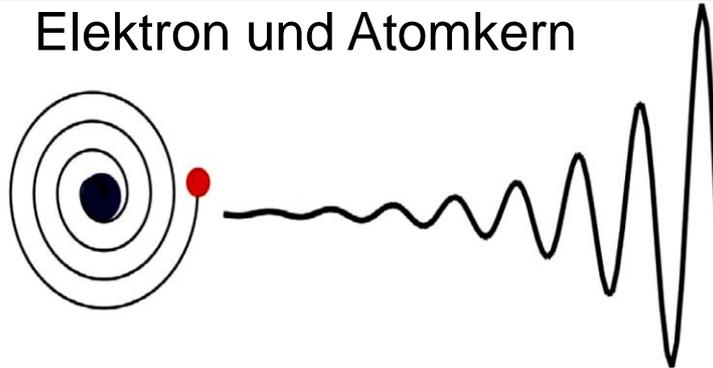
The number of atoms in any level at a given time is called the population of that level. Normally, when the material is not excited externally, the population of the lower level or ground state is greater than that of the upper level. When the population of the upper level exceeds that of the lower level, which is a reversal of the normal occupancy, the process is called population inversion. This situation is essential for a laser action. For any stimulated emission, it is necessary that the upper energy level or metastable state should have a long life time, i.e., the atoms should pause at the metastable state for more time than at the lower level. Thus, for laser action, pumping mechanism (exciting with external source) should be from a such, as to maintain a higher population of atoms in the upper energy level relative to that in the lower level.

# Atomic emission spectra

Planet und Sonne



Elektron und Atomkern

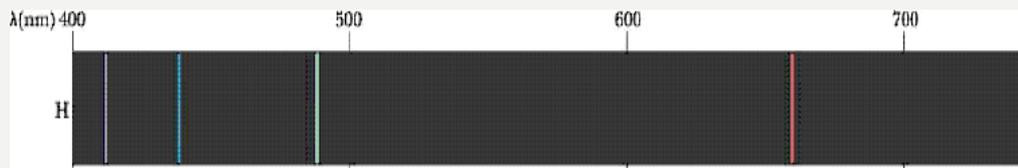


since Rutherford: positively charged nucleus and negatively charged electron.

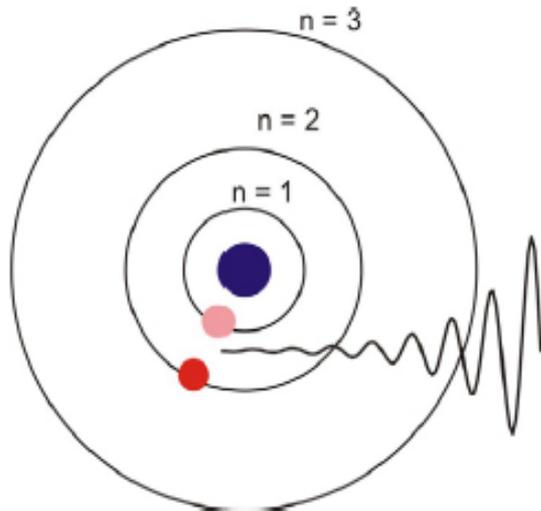
Classical physics:

Accelerated electron should emit light and collapse into nucleus. Broad emission spectrum.

Emission spectrum exhibits sharp lines



# Bohr's quantized electronic orbits



a) circular orbits have to fulfil Quantum condition.

$$\oint p dq = \oint m \dot{x} dx = J (= n h).$$

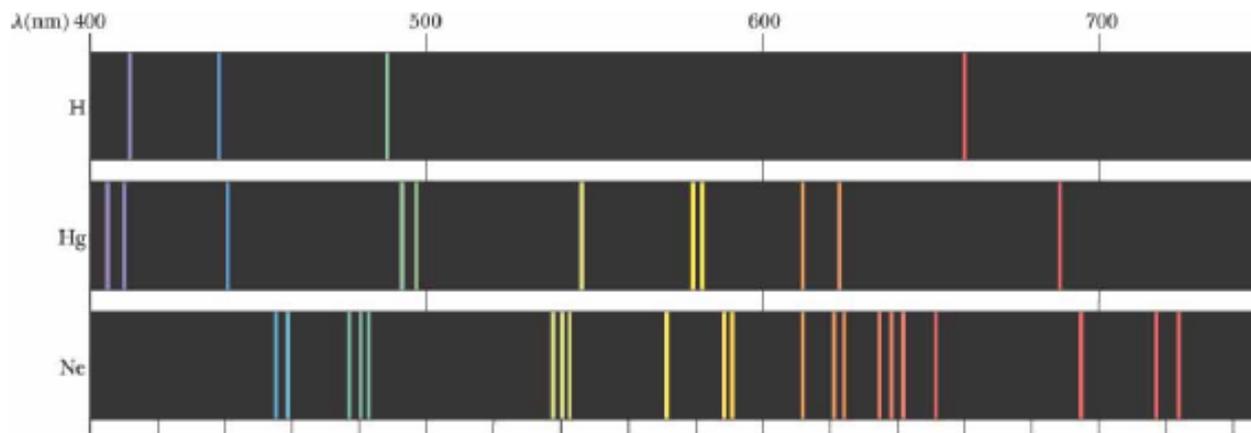
Planck's constant appears !!

b) energy difference of orbits is emitted as light quantum.

Electron orbit for  $n=1$  is stabil.

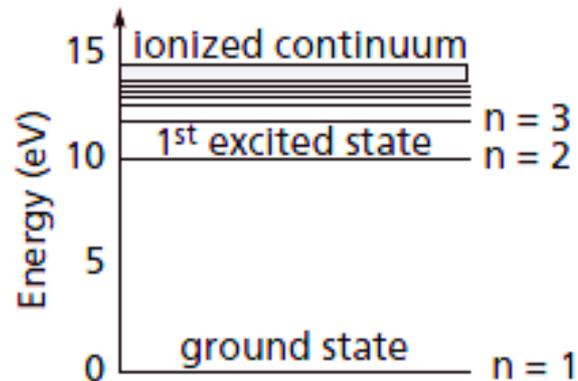
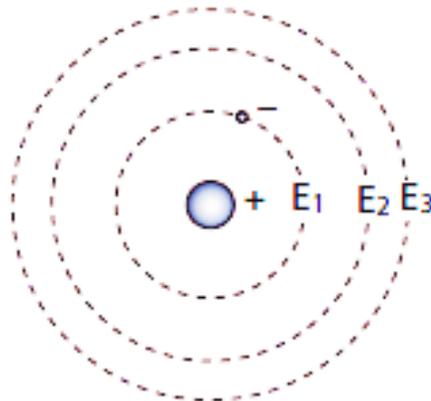
## other emission spectra

Nobelprize 1922



# PHOTONS AND ENERGY

In the 1600s and 1700s, early in the modern study of light, there was a great controversy about light's nature. Some thought that light was made up of particles, while others thought that it was made up of waves. Both concepts explained some of the behavior of light, but not all. It was finally determined that light is made up of particles called "photons" which exhibit both particle-like and wave-like properties

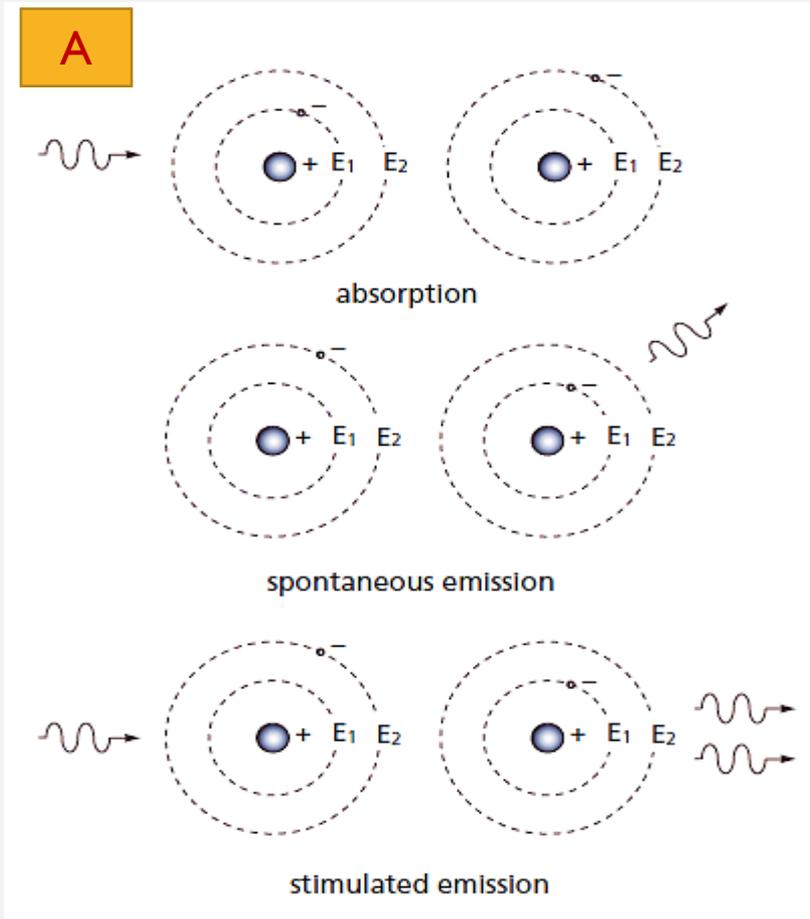


# SPONTANEOUS AND STIMULATED EMISSION

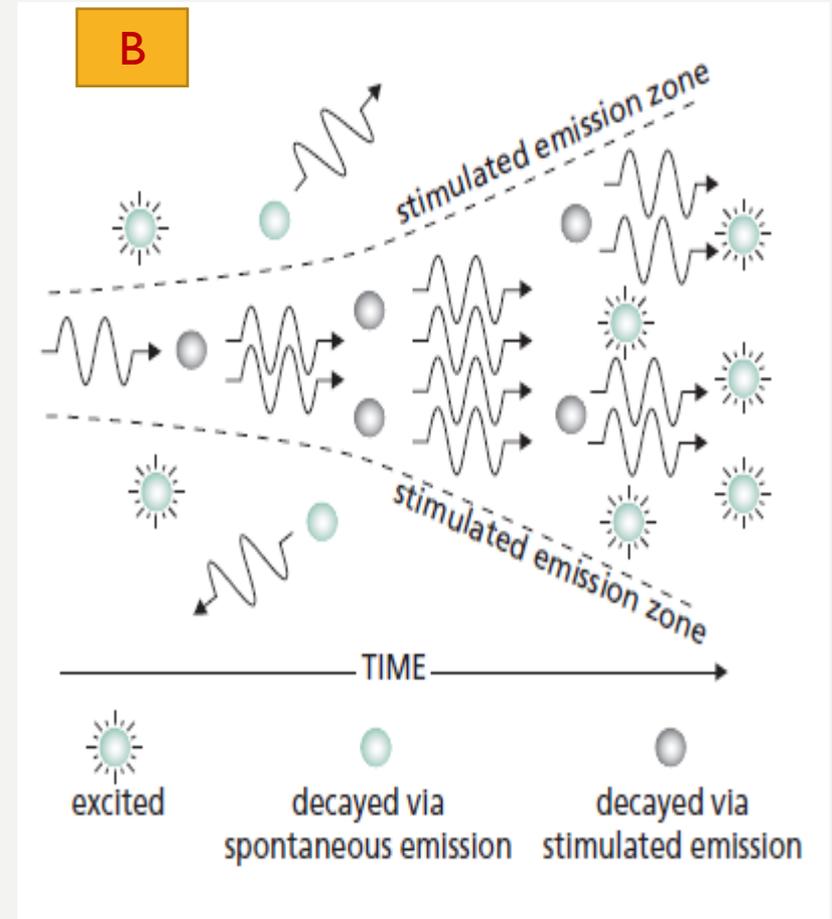
In general, when an electron is in an excited energy state, it must eventually decay to a lower level, giving off a photon of radiation. This event is called “spontaneous emission,” and the photon is emitted in a random direction and a random phase. The average time it takes for the electron to decay is called the time constant for spontaneous

emission, and is represented by  $t$ . On the other hand, if an electron is in energy state  $E_2$ , and its decay path is to  $E_1$ , but, before it has a chance to spontaneously decay, a photon happens to pass by whose energy is approximately  $E_2 - E_1$ , there is a probability that the passing photon will cause the electron to decay in such a manner that a photon is emitted at exactly the same wavelength, in exactly the same direction, and with exactly the same phase as the passing photon. This process is called “stimulated emission.” Absorption, spontaneous emission, and stimulated emission are illustrated in figure **A**

Now consider the group of atoms shown in figure **B** all begin in exactly the same excited state, and most are effectively within the stimulation range of a passing photon. We also will assume that  $t$  is very long, and that the probability for stimulated emission is 100 percent. The incoming (stimulating) photon interacts with the first atom, causing stimulated emission of a coherent photon; these two photons then interact with the next two atoms in line, and the result is four coherent photons, on down the line. At the end of the process, we will have eleven coherent photons, all with identical phases and all traveling in the same direction. In other words, the initial photon has been “amplified” by a factor of eleven. Note that the energy to put these atoms in excited states is provided externally by some energy source which is usually referred to as the “pump” source.



Spontaneous and stimulated emission

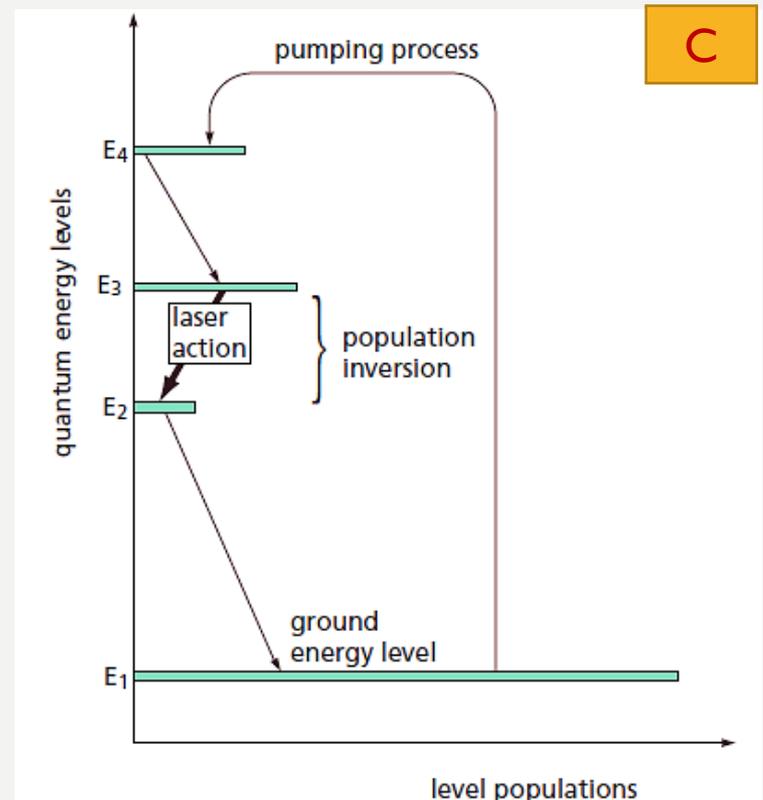


Amplification by stimulated emission

# POPULATION INVERSION

Atomic energy states are much more complex than indicated by the description above. There are many more energy levels, and each one has its own time constants for decay. The four-level energy diagram shown in figure C is representative of some real lasers. The electron is pumped (excited) into an upper level  $E_4$  by some mechanism (for example, a collision with another atom or absorption of high-energy radiation). It then decays to  $E_3$ , then to  $E_2$ , and finally to the ground state  $E_1$ . Let us assume that the time it takes to decay from  $E_2$  to  $E_1$  is much longer than the time it takes to decay from  $E_3$  to  $E_2$ . In a large population of such atoms, at equilibrium and with a continuous pumping process, a population inversion will occur between the  $E_3$  and  $E_2$  energy states, and a photon entering the population will be amplified coherently.

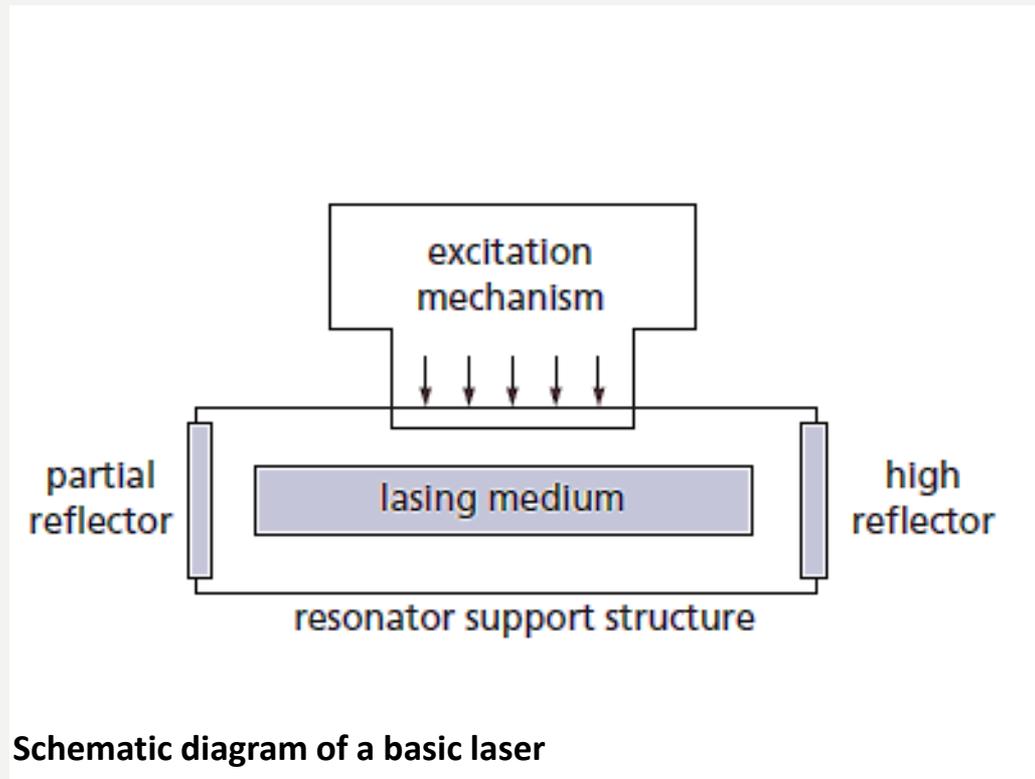
A four-level laser pumping system



# THE RESONATOR

Although with a population inversion we have the ability to amplify a signal via stimulated emission, the overall single-pass gain is quite small, and most of the excited atoms in the population emit spontaneously and do not contribute to the overall output. To turn this system into a laser, we need a positive feedback mechanism that will cause the majority of the atoms in the population to contribute

to the coherent output. This is the resonator, a system of mirrors that reflects undesirable (off-axis) photons out of the system and reflects the desirable (on-axis) photons back into the excited population where they can continue to be amplified..

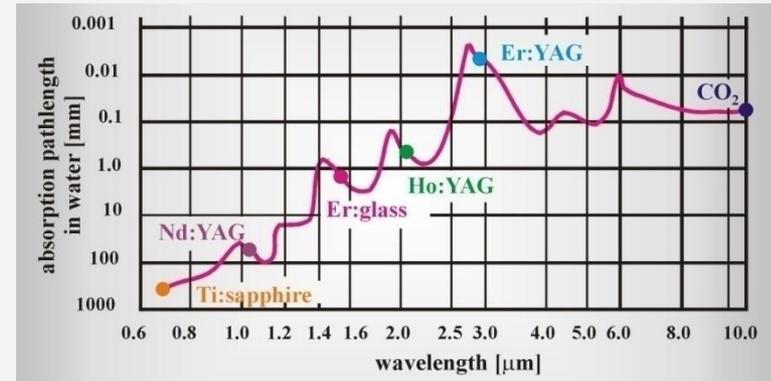


Schematic diagram of a basic laser

# GAS LASERS, LIQUID LASERS

- Lasers can be classified according to the active medium or the wavelength of the emitted radiation. The most general division based on the first criterion consists of gas lasers, liquid lasers and solid-state lasers. Gas lasers include all lasers in which the gain medium is a gas. The most well-known gas lasers are:
  - a) *CO<sub>2</sub> laser* (10.6 μm) (near infrared),
  - b) *CO laser* (5–6.5 μm) (near infrared),
  - c) *N<sub>2</sub>O laser* (10.6 μm),
  - d) *molecular gas lasers* (CH<sub>3</sub>OH, C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>, CH<sub>3</sub>F) (40 μm–1 mm) (far infrared),
  - e) *chemical lasers* (in which one of the reaction products are: I, HF, HCl, HBr, CO, CO<sub>2</sub>), near infrared (1.3–11 μm),
  - f) *ion argon laser* (a few lines in the range of 476.5 – 514.5 nm) (visible region),
  - g) *krypton laser* (503.9–752.5 nm) (visible region),
  - h) *helium–neon laser* (632.8 nm) (visible region),
  - i) *excimer lasers* such as: ArF, XeCl, KrF emitting radiation at the wavelength of 193, 248, 308 nm (UV),
  - j) *nitrogen laser N<sub>2</sub>* (337 nm) (UV).
- Liquid lasers* include all lasers in which the gain medium is a liquid. Dye lasers emitting in the visible region belong to the most often used liquid lasers. Output spans the spectrum from the near-UV to the near-IR depending on the dye used.

# SOLID STATE LASERS



- *Solid-state lasers* are optically pumped, the gain medium is a solid state material. The most well-known solid-state lasers are:
  - *ruby laser* (694.3 nm) (visible region),
  - *Nd:YAG* laser with neodymium doped *yttrium-aluminum garnet* matrix, (1064 nm)
  - *Titanium-sapphire laser* (670–1070 nm) and other solid-state tunable vibronic lasers,
  - **rare earth elements** other than neodymium (holmium, erbium, thulium) lasers like *Ho:YAG*, *Er:glass*, *Er:YAG*, *Tm:YAG* emitting at about 2 mm depending on a matrix and a doped material used.

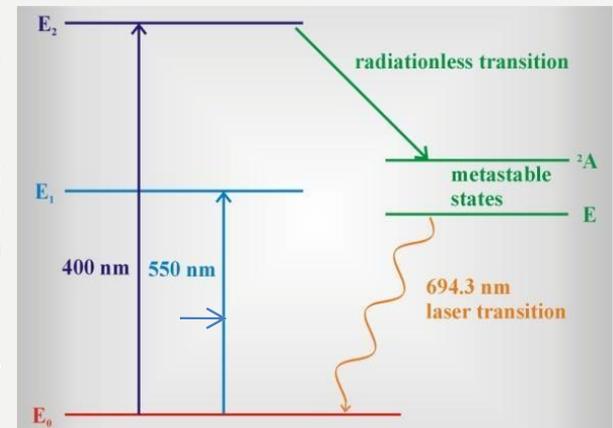
# SEMICONDUCTOR LASERS

- Semiconductor lasers do not belong to the category of solid–state lasers although the gain medium is also a solid. Traditionally, they form separate category because diode lasers are usually electrically pumped and different physical processes are responsible for emission that occurs over a broad spectral range of visible and infrared region.

# RUBY LASER

- Theodore Maiman constructed the world's first laser from a ruby crystal. Since that first ruby laser, researchers have discovered many other materials as the gain medium, but the oldest laser still find some applications. The large energy pulses and the red visible (694.3 nm) light radiation of ruby laser still find the applications in **holography and dermatology**. The ruby laser is a pulsed laser of low repetition rate. (The repetition rate is the number of pulses that are sent by a laser per 1 second). The pulse duration is on the order of **milliseconds**, energy of **1 J** and the average pulse power on the **order of kilowatts**. The active medium of a ruby laser is a rod made of a synthetic **shapphire** ( $\text{Al}_2\text{O}_3$ ) doped with **chromium** (0.01–0.5 %) having the same valence number (+3) as the aluminum. The ruby laser can also work in the **modelocking regime** emitting pulses of **20–30 picosecond** duration, energy of **1 mJ** and the repetition rate of **20–30 Hz**. The electronic transitions in ruby laser are presented in figure

The ruby laser is pumped with a **xenon flash lamp**. When the chromium  $\text{Cr}^{+3}$  ions in a ruby crystal absorb photons of visible light at 400 nm or 550 nm, some electrons jump from their ground-state  $E_0$  to the excited states  $E_1$  or  $E_2$ . The electron excited to those states almost immediately (ca. 100 ns) dissipate their excess energy to the surrounding crystal lattice. As a result of the radiationless transitions the electrons jump to one of two closely **spaced metastable states:  $E$  or  ${}^3A$**  where they stay for a long time of **3 ms** at room temperature. This time is long enough to achieve population inversion. Stimulated emission occurs on the  $E \rightarrow E_0$  transition generating the light at a wavelength of 694.3 nm. Because the whole cycle of excitation, relaxation and stimulated emission involves transitions between three energy levels, the ruby laser is known as a **three-level laser**.



Electronic transitions in ruby laser

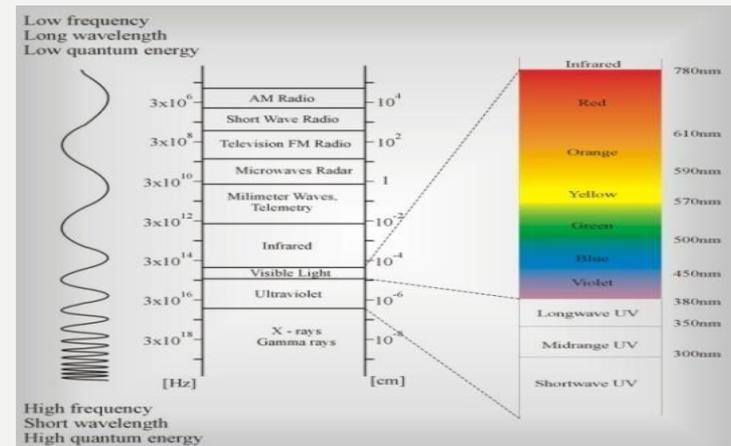
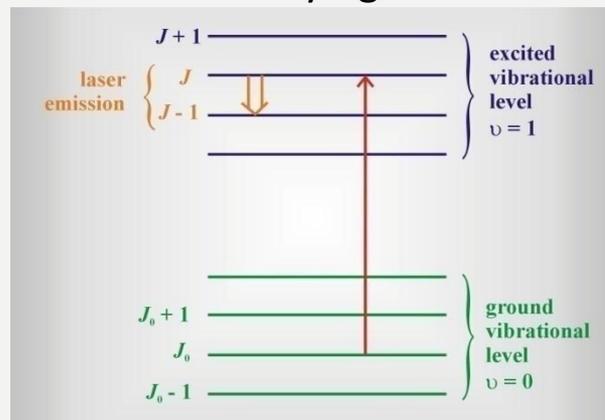
# RUBY LASER

- **APPLICATIONS**

- The ruby lasers find wide applications in holography, plasma diagnostics and dermatology. In dermatological applications the  $Q$ -switched ruby lasers generating pulses of energy of 2–3 J and the repetition rate of 0.5–1 Hz are utilized. Such an energy is sufficient to remove black, blue and green pigments of skin tattoos as well as stains caused by melanin excess. The laser beam destroys cells containing the pigment by inducing photochemical reactions whereas the surrounding non pigmented areas of skin do not absorb the energy of the light and experience only negligible damage. Then the lymphatic system slowly removes dead cells during the next several months. The ruby laser does not remove red pigments since they do not absorb the red light at 694.3 nm.

# LASERS OPERATING ON ROTATIONAL TRANSITIONS – FAR INFRARED LASERS

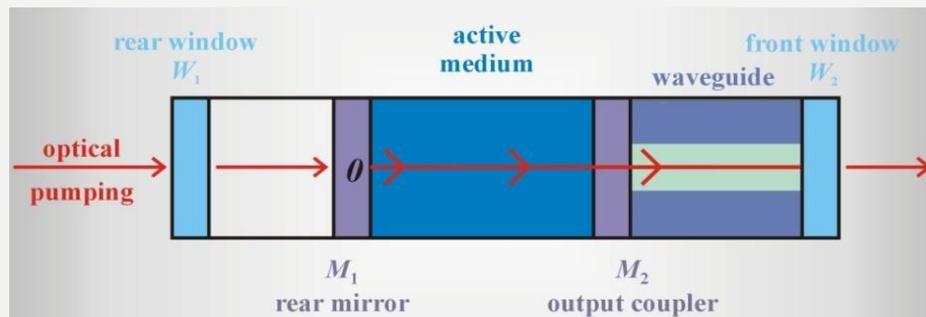
- Lasers emitting light as a result of rotational transitions generate far infrared radiation. Powers of the lasers operating on rotational transitions in commercially available models are comprised in the range from milliwatts to 1 W. Far infrared lasers are pumped with radiation at  $10\text{ }\mu\text{m}$  from  $\text{CO}_2$  or  $\text{N}_2\text{O}$  lasers. The optical pumping causes the molecules are transferred from the rotational state characterized by the rotational quantum number  $J_0$  in the ground vibrational state ( $\nu = 0$ ) to the rotational state  $J$  in the excited vibrational state ( $\nu > 0$ ) for a given vibrational mode. The symbol  $\nu$  indicates the vibrational quantum number. The laser action occurs between the two rotational levels  $J$  and  $J-1$  in the excited vibrational state. The pumping laser should deliver strongly monochromatic radiation in a narrow spectral range to avoid filling neighboring rotational levels lying close to each other.

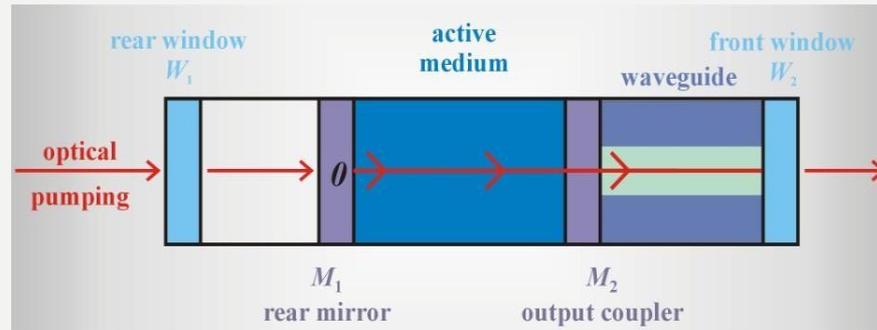


Schematic diagram of quantum transitions in lasers emitting as a result of rotational transitions

# LASERS OPERATING ON ROTATIONAL TRANSITIONS FAR INFRARED LASERS

- Active medium in the far infrared lasers are simple organic substances e.g. alcohols and hydrocarbons. In commercial models the optical resonator contains a gas reservoir which can be exchanged and replaced by another one making possible to obtain far infrared radiation from **40  $m\mu$  to 2000  $m\mu$** . Since the rotational energy depends strongly on molecular mass, so the isotopic substitution may provide additional lines. For example,  $CD_3OD$  emit at **41.0  $m\mu$** ,  $CH_3OD$ —at **46.7  $m\mu$** ,  $CH_3OH$ —at **70.6  $m\mu$** .





- Optical resonator of the far infrared laser consists not only of two mirrors,  $Z_1$  and  $Z_2$ , and an active medium, but also a vacuum waveguide, which leads the emitted waves. The vacuum waveguide must be used because air absorption at the wavelength of 30 and 50  $\mu\text{m}$  would attenuate effectively the light propagation on longer distances. The optical resonator consists of the mirrors  $Z_1$  and  $Z_2$  between which the laser action occurs as well as the windows  $W_1$  and  $W_2$  protecting the tube under vacuum from environment influence. The optical elements inside the resonator have to obey several requirements, which sometimes exclude each other:
  - The resonator mirrors  $Z_1$  and  $Z_2$  have to reflect both the radiation from the range of 10 mm (the pumping radiation) and from the far infrared (the generated radiation). The reflection of the pumping radiation inside the resonator increases the feedback due to the increase of the optical path which is very important taking into account small energies of the rotational transitions.
  - The rear window  $W_1$  has to transmit the pumping radiation and is usually made of zinc selenide. There is a hole  $O$  of 1–2 mm diameter in the rear mirror  $Z_1$  that allows to introduce the radiation at 10  $\mu\text{m}$  into the cavity.
  - The front window  $W_2$  has to transmit the far infrared radiation generated in the resonator. Most of materials are opaque for radiation at wavelengths longer than 50  $\mu\text{m}$ . Only some materials such as silicon, germanium, crystalline quartz, diamond as well as polyethylene can be used in the window  $W_2$  as they are transparent for the far infrared light.

# APPLICATIONS OF FAR IR LASERS

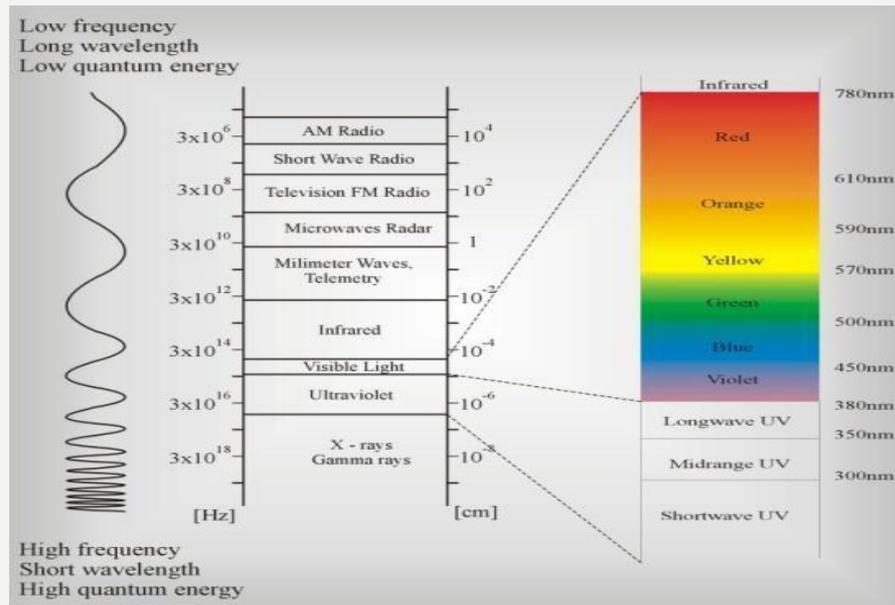
Although commercially available, the far infrared gas lasers are less popular than the gas lasers such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$  that emit shorter wavelengths in the near infrared. This results from technical problems in the far infrared range which are related to propagation in waveguides as well as requirements imposed on optical elements.

# LASERS OPERATING ON VIBRATIONAL-ROTATIONAL TRANSITIONS: CO<sub>2</sub> AND CO – NEAR IR LASERS

The **active medium** in CO<sub>2</sub> laser - carbon dioxide, nitrogen N<sub>2</sub> and helium He.

A ratio 1 : 2 : 3 for the CO<sub>2</sub> : N<sub>2</sub> : He mixture is typical

**Pumping** - RF (radio frequency) or direct-current electrical discharge in the gas medium

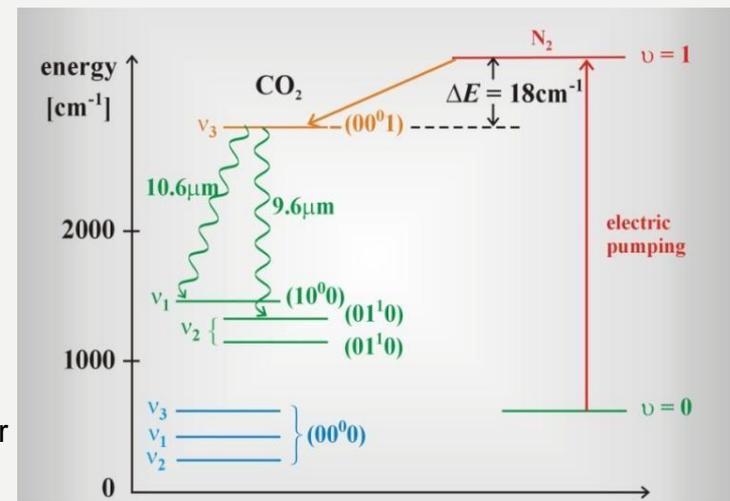


# MECHANISM OF LASING IN CO<sub>2</sub> LASER

- Electrons produced as a result of ionization excite the stretching mode of N<sub>2</sub> molecules promoting them from the ground vibrational state ( $\nu = 0$ ) to the first excited vibrational state ( $\nu = 1$ ). Nitrogen has a very long-lived first-excited vibrational state that almost exactly matches the upper level of CO<sub>2</sub>. Therefore, the process of transferring the excess energy via collisions to carbon dioxide is very efficient. The energy of the N<sub>2</sub> molecule in the first-excited vibrational state is practically the same as the energy of the first excited vibrational state (00<sup>0</sup>1) of the asymmetric stretching mode  $\nu_3$  of CO<sub>2</sub> molecule. Small energy gap ( $\Delta E = 18 \text{ cm}^{-1}$ ) between the excited levels makes possible the energy transfer from the N<sub>2</sub> molecule to the CO<sub>2</sub> molecule, return of N<sub>2</sub> molecule to the ground vibrational state ( $\nu = 0$ ) and the excitation of the mode  $\nu_3$  from the ground vibrational state denoted in fig. as (00<sup>0</sup>0) to the excited vibrational state (00<sup>0</sup>1) in CO<sub>2</sub> molecule. The main laser transitions in CO<sub>2</sub> occur between the excited states of the mode  $\nu_3$  (00<sup>0</sup>1) and the symmetric stretching mode  $\nu_1$  (10<sup>0</sup>0) (10.6  $\mu\text{m}$ ) or the bending mode  $\nu_2$  (01<sup>1</sup>0) (9.6  $\mu\text{m}$ ). Helium molecules do not take part in the excitation of CO<sub>2</sub> molecules directly but they play an important role in heat transfer out of the gas mixture to the tube walls as well as facilitate depopulation of the lower vibrational levels in CO<sub>2</sub> contributing in this way to the population inversion maintenance.

The numbers in the brackets denote the quantum vibrational numbers of the mode  $\nu_1$ , the  $\nu_2$ , and  $\nu_3$ , respectively. The upper indices define the vibrational level degeneration. For example the symbol (01<sup>1</sup>0) denotes the ground vibrational state for the mode  $\nu_1$ , the first excited vibrational state for the mode  $\nu_2$ , which is twice degenerated and the ground vibrational state for the mode  $\nu_3$ .

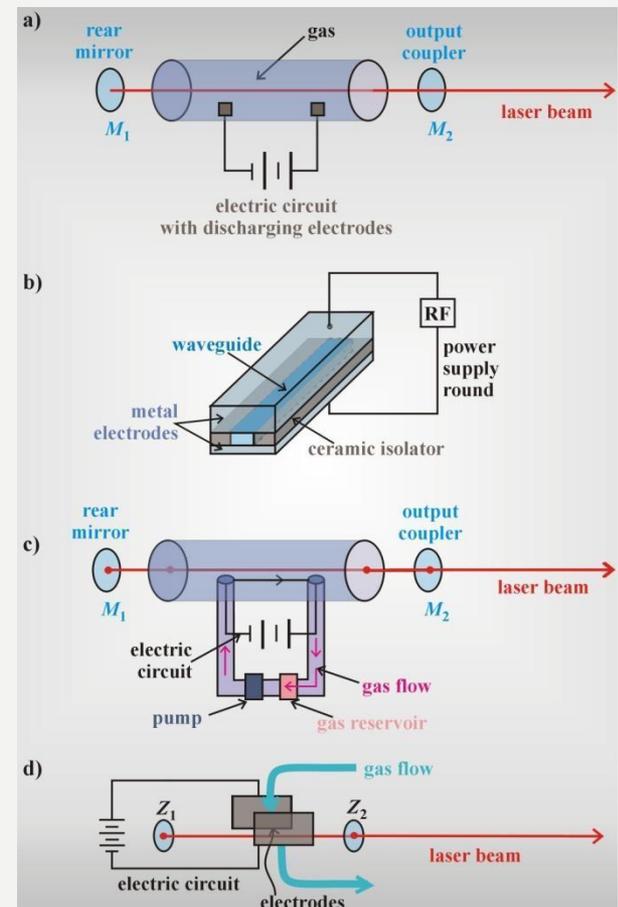
Quantum transitions in CO<sub>2</sub> laser



# CO<sub>2</sub> LASERS

One can distinguish the following types of CO<sub>2</sub> lasers:

- *conventional laser with longitudinal direct-current discharge excitation,*
- *waveguide laser with RF excitation,*
- *longitudinal flowing-gas laser,*
- *transverse flowing-gas laser,*
- *transversely excited atmospheric lasers (TEA).*

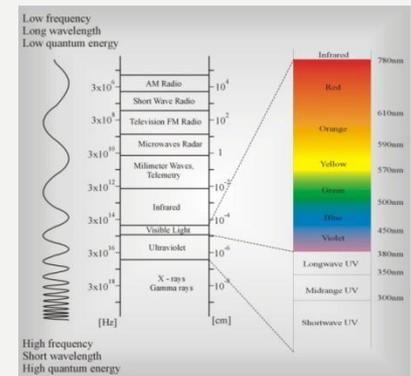
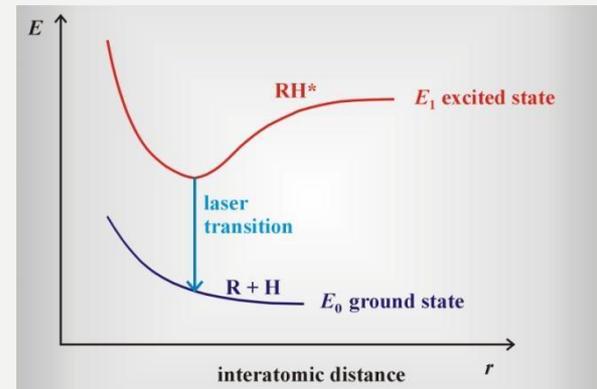


# CHEMICAL LASERS

- *Chemical lasers* emit radiation in the far infrared and infrared regions (1.3–11 m $\mu$ )
- Pumping- the energy released during chemical reaction

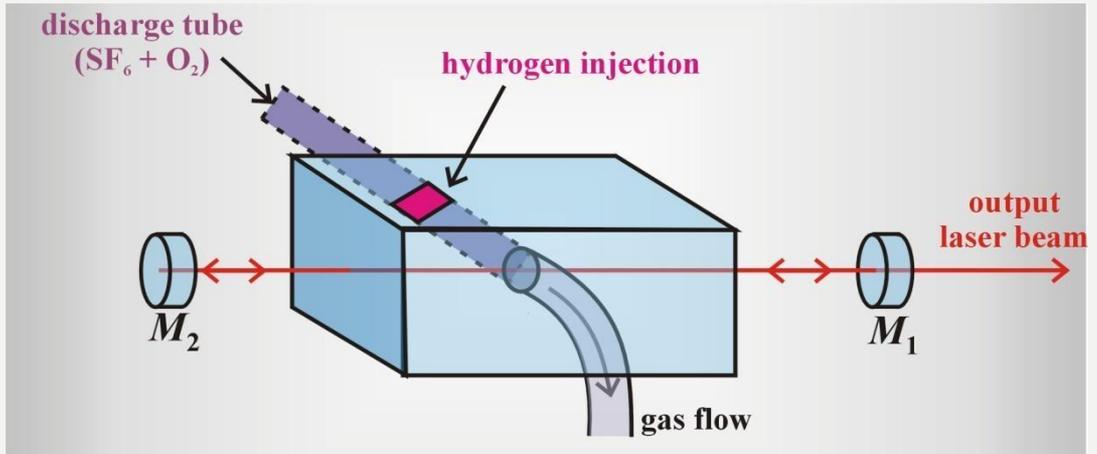
*Typical chemical lasers*

Laser	Reaction	Radiation wavelength [ $\mu$ m]
CO <sub>2</sub>	DF* + CO <sub>2</sub> → CO <sub>2</sub> + DF	10.0–11.0
CO	CS + O → CO* + S	4.9–5.8
HBr	H + Br <sub>2</sub> → HBr* + Br	4.0–4.7
DF	F + D <sub>2</sub> → DF* + D	3.5–4.2
HCl	H + Cl <sub>2</sub> → HCl* + Cl	3.5–4.1
HF	F + H <sub>2</sub> → HF* + H	2.6–3.3
I	O <sub>2</sub> * + I <sub>2</sub> → O <sub>2</sub> + 2I*	1.3



# CHEMICAL LASERS

- In commercially available lasers HF/DF, the hydrogen fluoride is produced by electric discharge in a tube *via* a reaction of sulfur hexafluoride  $\text{SF}_6$  dissociation. Oxygen is added to react with sulfur. Hydrogen, which is injected to the tube, reacts with fluoride generating the hydrogen fluoride  $\text{HF}^*$  in vibrationally excited states. Gas flows quickly through the resonator cavity perpendicularly to the axis



# APPLICATION OF CHEMICAL LASERS

There is no other group of lasers where interest is almost entirely dominated by military and defense applications. High-energy laser weapon projects date back to the 1970s. In the seventies the US Navy built a 2.2 MW deuterium-fluoride chemical laser called MIRACL. In eighties the star wars shifted strategic defense to study prospects for space-based laser battle stations and large financial means were invested in development of HF lasers. In nineties the military interest has been shifted to the 1.315  $\mu\text{m}$  oxygen-iodine laser known as COIL.

As early as 2005 the Airborne Laser program in US plans to generate a megawatt beam that can destroy ballistic missiles several hundred kilometers away. They plan to mount a chemical oxygen iodine laser on the board of Boeing 747.

There is some interest in shifting applications of the chemical oxygen-iodine laser from military to civilian use. A high power COIL emitting at the wavelength of 1.315  $\mu\text{m}$  that can be easily transmitted by standard fused-silica fiber optics may soon be used for general industrial use such as cutting and welding. They show promise to be used as a powerful tool to dismantle obsolete nuclear-weapon production facilities and nuclear-power reactors.

# SOLID-STATE LASERS

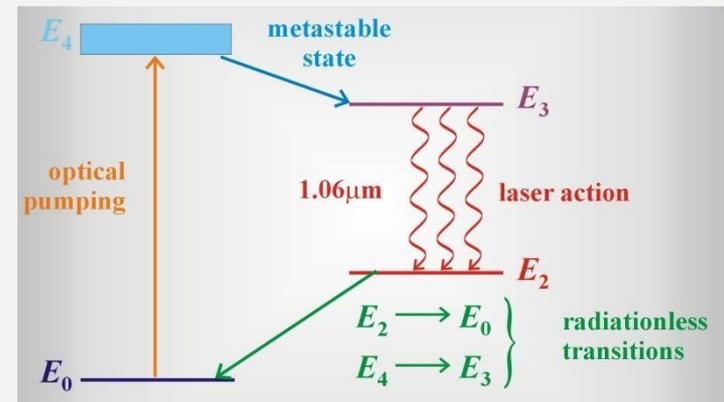
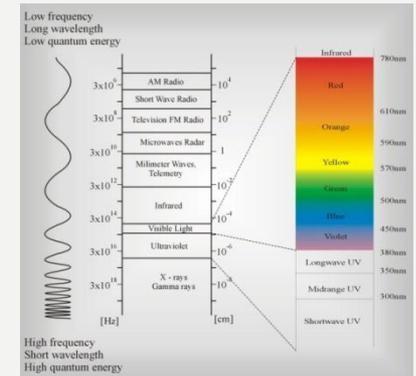
- **Pumping** – flash lamps, cw lasers, *diode-pumped solid-state lasers (DPSSL)*
- **active medium** - a solid-state host, most often a single crystal, doped with about 1 % of different species, such as neodymium ion or other ions like holmium, erbium or thulium.
- Solid-state lasers can be divided into two broad groups of **non-tunable and tunable** lasers
- Most solid-state lasers belong to the class of four-level lasers and they operate on **electronic transitions**

# NEODYMIUM LASER AND OTHER RARE EARTH LASERS

- **active medium** - rare earth elements belonging to lanthanide series: **neodymium, holmium, erbium and thulium**. The neodymium ion can be added as an impurity to crystalline solids or to glasses.
- *Nd:YAG laser*, host - yttrium aluminum garnet  $Y_3Al_5O_{12}$  - YAG),
- *Nd:YLF* (YLiF<sub>4</sub>-yttrium lithium fluoride)
- *Nd:YVO<sub>4</sub>* (yttrium orthovanadate).
- *Nd:glass laser*

# MECHANISM OF LASING IN *ND:YAG LASER*

The neodymium ions are pumped optically by a flash lamp or a laser diode from the ground state  $E_0$  to the excited state  $E_4$  characterized by a short lifetime and not involved directly in a laser transition. Radiationless transitions promote the ion to the metastable state  $E_3$  where it stays for longer time of about 100 ms. The population inversion takes place between the states  $E_3$  and  $E_2$ . The laser action between these states produces radiation from the range of near infrared at the wavelength of 1.064  $\mu\text{m}$ . The lower laser state  $E_2$  relaxes quickly to the ground state  $E_0$ .

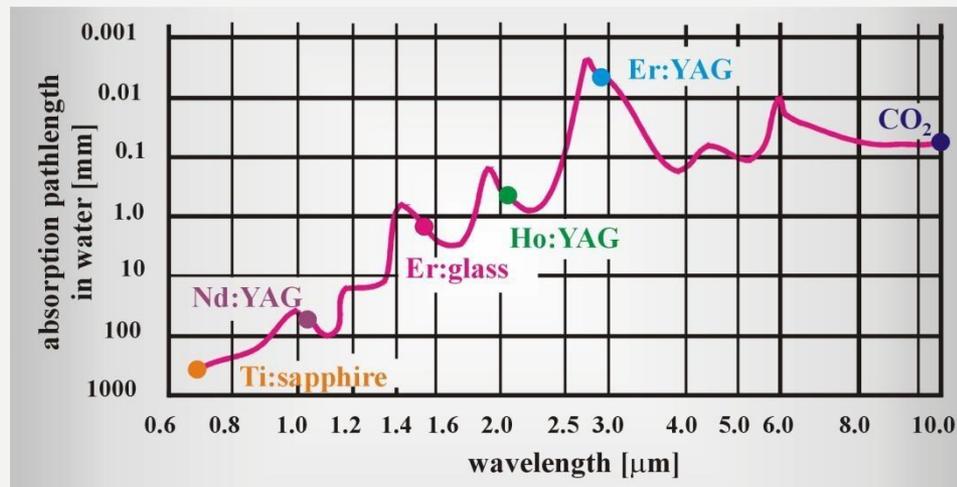


# ND:YAG LASER

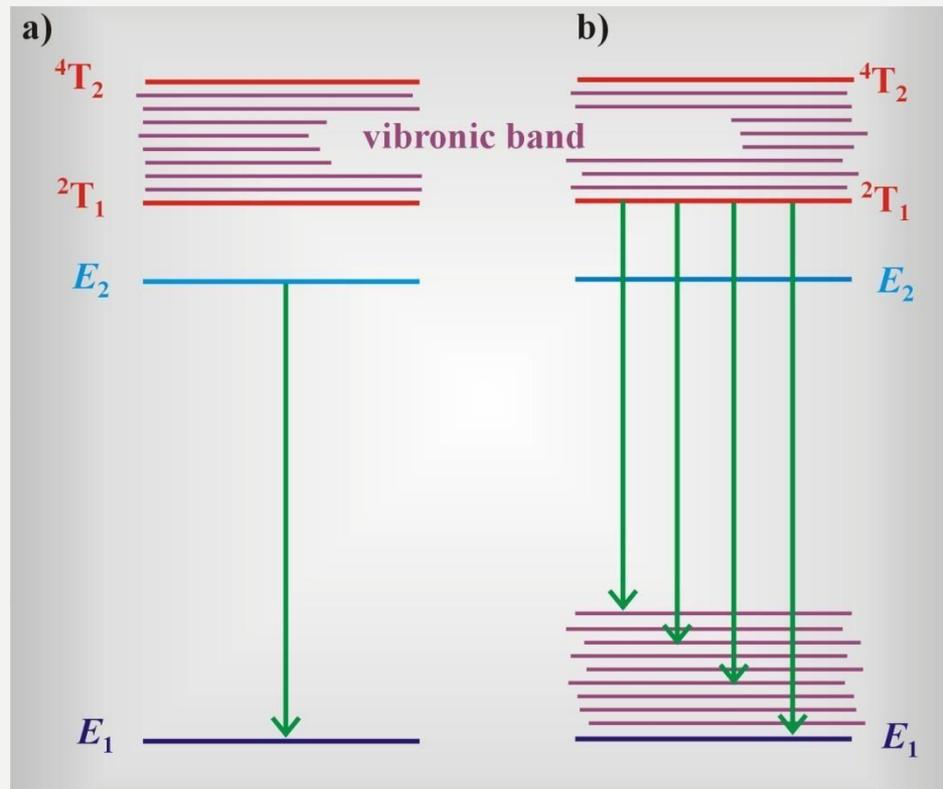
- The neodymium laser can work in the continuous and pulsed regimes. The shortest pulses of tens picoseconds can be achieved in the modelocking regime combined with the  $Q$ -switching.  $Q$ -switching without modelocking provides pulses of nanoseconds. The neodymium laser belongs to the group of non-tunable lasers. The typical construction of the lamp-pumped laser resonator is shown in fig.

# ND:YAG LASER APPLICATIONS

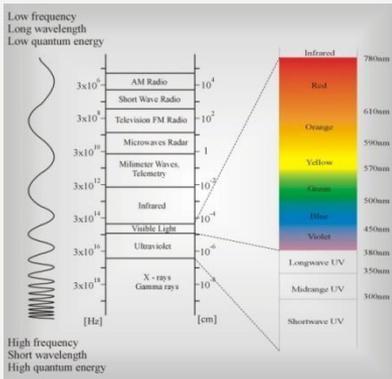
- There are many industrial applications of Nd:YAG lasers. Metals processing including **cutting, welding or marking** is almost always associated with Nd:YAG lasers. This kind of applications needs usually large, lamp-pumped lasers. **Spectroscopic research or surgical procedures** usually need smaller, diode-pumped systems with frequency doubling. The neodymium lasers are utilized to pump another lasers or to pump the regenerative amplifiers. For example, Ti:sapphire laser can be pumped by the second harmonic of the neodymium laser (Nd:YVO<sub>4</sub>, *cw*, 5.5 W, 532 nm). The regenerative amplifier seeded by the Ti:sapphire laser (82 MHz, 80 fs, 12 nJ, modelocked) can be pumped with the neodymium lasers (Nd:YLF, 1 kHz, 10 mJ, 250 ns, 527 nm, *Q*-switched). The specifications in brackets illustrate typical commercial parameters. **Since the mid-seventies, Nd:YAG lasers have been workhorses in laboratories around the world for pumping dye lasers. The advent of tunable solid-state laser systems and optical parametric oscillators reduced significantly this application.**
- The neodymium lasers found many diverse applications in medicine although their applicability is limited by small water absorption, the main component of the human tissue, in the spectral range of 1 mm.



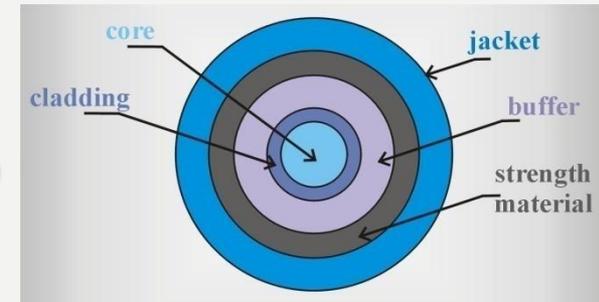
# TUNABLE SOLID-STATE LASERS (VIBRONIC LASERS)



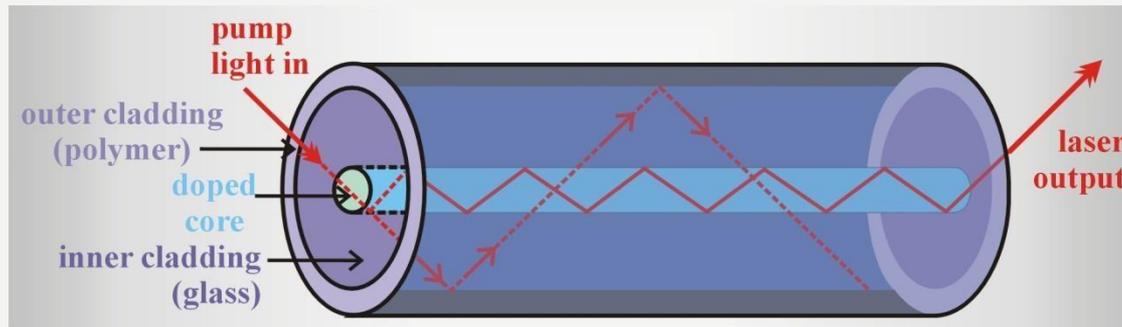
Scheme of electronic levels involved in a laser transition in a) non-tunable lasers, b) tunable lasers



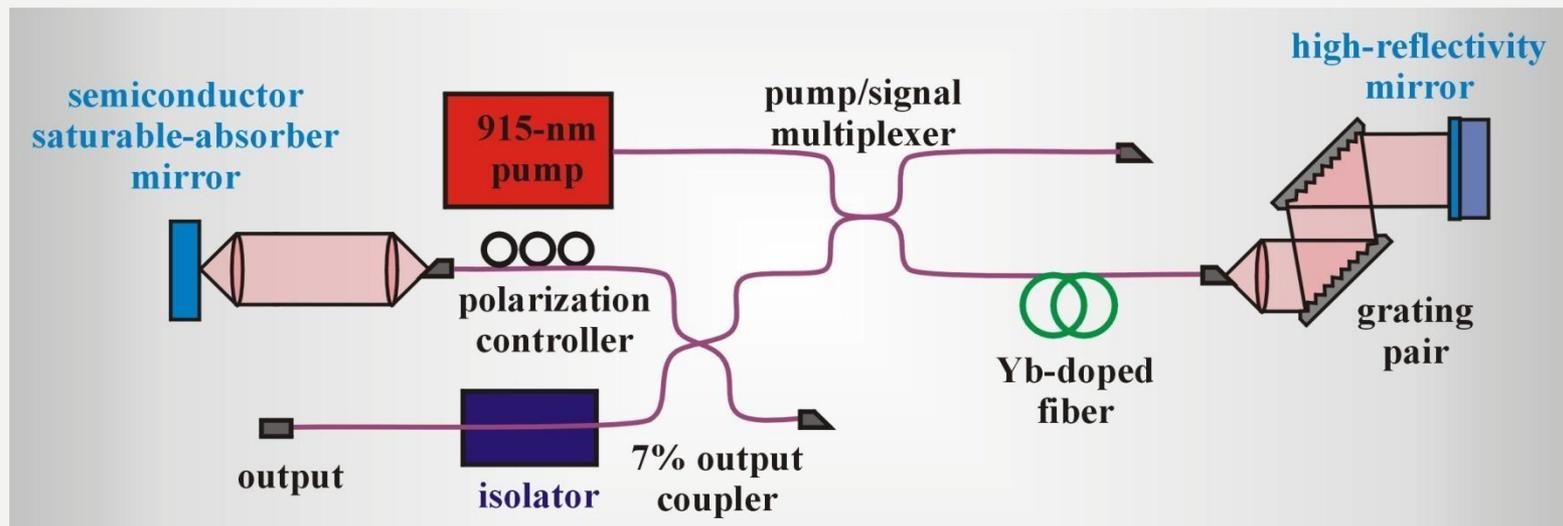
# FIBER LASERS



A *fiber laser* consists of a piece of a fiber cable as a resonator cavity sealed with coated ends that is optically pumped. The cavity length can be tens or even hundred of meters long in contrast to much shorter conventional lasers, but the size of the fiber laser does not create a problem at all as the flexible fiber cable can be rolled up into a small box of a few centimeters. In contrast to conventional lasers based on optical elements that are prone to contamination or misalignment, the fiber lasers cavity is nearly perfectly immune to these drawbacks. The fiber cable used in a fiber laser is modified by doping core with erbium or another earth element (neodymium, erbium, thulium) and adding additional cladding layer. Such a double-cladding consists of an inner cladding (glass) and an outer cladding (polymer). This allows for trapping both of light inside a cavity (core) and the pump light in the inner layer of cladding through total internal reflection. In this fiber configuration, multimode diode pump radiation is injected into a fiber through an end facet, then trapped in the inner cladding, propagating along the fiber and producing a population inversion in the core fiber.



The Yb-doped fiber is pumped with a single diode laser operating at 915 nm and average power of around 130 mW. A semiconductor saturable-absorber mirror, described in chapter 3, passively modelocks the laser. The semiconductor mirror uses an AlGaAs/GaAs distributed Bragg reflector, which usually has a bandwidth of 100 nm. A grating pair compensates for dispersion in the fiber. The laser can be tuned over more than 100 nm from 980 to 1100 nm. The wavelength tuning is achieved by adjusting the angular orientation of the high-reflectivity mirror. The duration of the modelocked pulses varies typically from 1.6 to 2.0 ps across the tuning range. The typical output average power is around 3 mW.



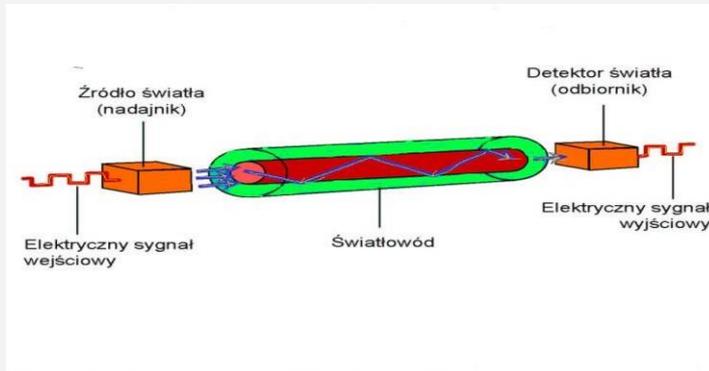
The mode-locked Yb: fiber laser configuration

# APPLICATIONS OF FIBER LASERS

- Fiber lasers are being developed in laboratories around the world as alternatives to traditional solid-state lasers. For many laser applications, however, average power of watts rather than milliwatts is required. Therefore, the Ti:sapphire laser has remained largely unchallenged as a source of broadly tunable, ultrashort pulses with routinely provided average power up to 2 W from a modelocked oscillator, with pulse duration on the order of 100 fs. The previous generation of high-power fiber systems has never exceeded these limits. However, this situation is changing due to improvements in amplification methods. Continuous wave—2 kW fiber lasers for industrial purposes have recently been developed. Powers as large as 13 W were reported as an output from a modelocked fiber laser emitting 2–5 ps pulses amplified as a result of an induced chirp from the non-linearity and positive dispersion.

# APPLICATIONS OF FIBER LASERS

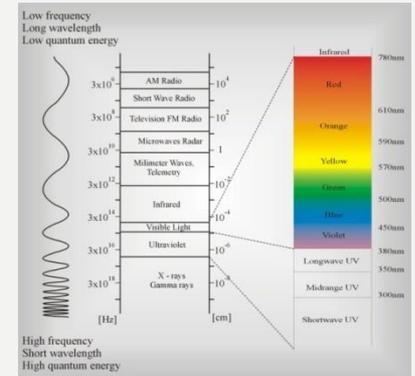
- Rare-earth-doped fibers are well suited to ultrafast applications for several reasons. Their 6-THz amplification bandwidth is broad enough to produce pulses shorter than 100 fs. Now, novel ultrafast fiber lasers are emerging that are capable of delivering average power and pulse duration that may compete with solid-state lasers in certain configurations. Optical communication is a main potential beneficiary of these ultrafast fiber lasers which can be useful in wavelength division multiplexing (WDM). The development of WDM schemes has created a growing market of higher-power devices. In the case of optical amplifiers, the gain must be divided among a large number of channels. Thus, the fiber amplifier power must increase.



Time frame	WDM Type	Channels	Wavelength	Channel Spacing
1980's	Wideband	2	1310nm, 1550nm	-
Early 90's	Narrowband	2 - 8	C-band	200-400 GHz
Mid 90's	Dense	16 - 40	C-band	100-200 GHz
Late 90's	Dense	64 - 160	C-band	25-50 GHz
Current	Dense	160 - 320	C/L-Band	12.5-25 GHz

# GAS LASERS IN VISIBLE RANGE

In *gas lasers* the gain medium is a gas. Here we will discuss gas lasers operating on electronic transitions like solid-state lasers. Gas lasers are facing stiff competition from solid-state lasers, but they are still powerful tools in many scientific, medical and industrial applications.



- **Helium–Neon Laser (632.8 nm)**
- **Ionic Gas Lasers. Argon Laser (514 nm) and Krypton (647.1 nm) Laser**
  - **Nitrogen Laser (337 nm)**

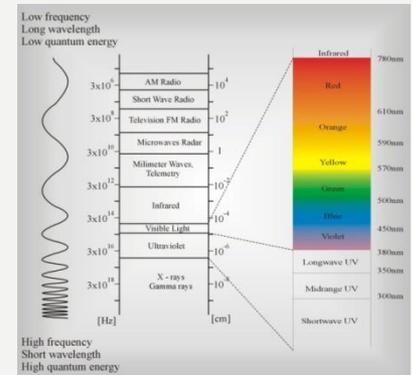
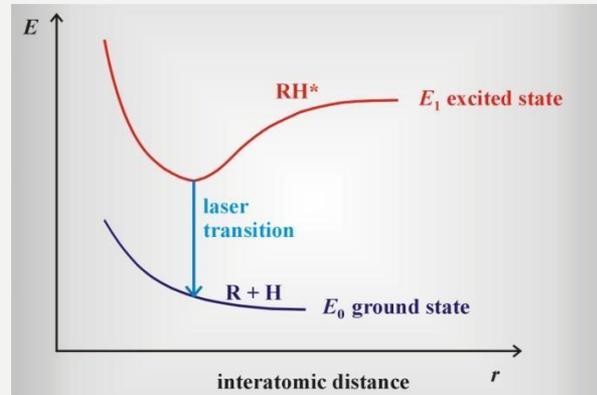
# HELIUM–NEON LASER. APPLICATIONS

Generally, there are several laser transitions possible, but most HeNe lasers are designed to favor **632.8 nm** emission. The transitions in infrared at wavelength of **1523.5 nm and 3392 nm** are not usually used in mass production due to higher prices related to special optics in IR. However, they have several specific uses. For example, the 1523.5 nm line is successfully used for testing of silicon–glass optical fibers due to minimal losses in this spectral area. Although laser diodes provide an alternative to helium–neon lasers, they are still used in **alignment, interferometry, metrology, medical diagnosis like flow cytometry, holography, in malls to read product codes due to good beam coherence and quality. They are also used to determine position of patient under X irradiation.** They serve in industrial alignment to determine straight line with laser beam in buildings, tunnels, sewer pipes construction. The compact laser diodes, however, partially relegated the helium–neon lasers as hand–held barcode readers, but they still dominate **industrial code readers** because of their low divergence.

# GAS LASERS FROM ULTRAVIOLET RANGE

## • Excimer Lasers

- Excimer lasers, beside nitrogen laser, are the most popular gas lasers generating radiation from the ultraviolet range. Active medium is a mixture of a noble gas, halogen gas and a buffer gas, usually neon. Gas mixture in a typical excimer laser consists of 2–9% of a noble gas, 0.2% of a halogen gas, and 90–98% of a buffer gas which serves as a medium to transport energy. The mixture is confined in a pressure vessel, typically at a pressure of 3500–5000 millibars. The gas mixture is usually excited by means of a fast electric discharge lasting a few tens of nanoseconds.
- Short living, unstable in the ground state, halides of noble gases such as: ArF, KrF, XeF, XeCl are created in the gas mixture
- The excimer medium has a very high gain, and output coupler reflectivity of 10–30% is sufficient to achieve an adequate output. The most often used emission lines of excimer lasers are: 193 nm (ArF), 248 nm (KrF), 308 nm (XeCl) and 351 nm (XeF). The powers of these lasers are from 1 W to 100 W (for KrF and XeCl and even more).



# EXCIMER LASERS

- One should remember, that the excimer lasers, although often used in laboratories, industry and medicine, contain a toxic active medium. So, the special safety should be kept. In the early days of the excimer laser development the corrosion of the gas vessel due to halogens presence was a serious problem. In all modern lasers this problem was removed by careful selection of materials, such as electrodes made of nickel or bromine, elimination of organic materials such as lubricants, seals or insulators. These technical improvements extended the lifetime between exchanges of laser gas to  $10^8$  pulses.

# APPLICATIONS OF EXCIMER LASERS

- Excimer lasers produce high pulse energies, high average and peak powers. One of the biggest excimer lasers is Aurora in Los Alamos National Laboratory (5 ns, 5 kJ, KrF) used for plans of nuclear fusion control tests. The excimer lasers were used in scientific laboratories to pump dye lasers as well as to generate higher harmonic to reach vacuum ultraviolet range. Excimer lasers are particularly significant in application such as metrology and systems alignment. They are important tools to monitor pollution and ozone concentrations in upper layers of the atmosphere. Excimer lasers emitting in deep ultraviolet currently dominate the lithography industry. They serve to draw patterns, marks, trade codes on ceramics, glass, plastic and metal.

- Krypton and argon fluoride (KrF and ArF) lasers used in deep-UV microlithography facilitates chip designs generating circuit features smaller than 0.18  $\mu\text{m}$ .

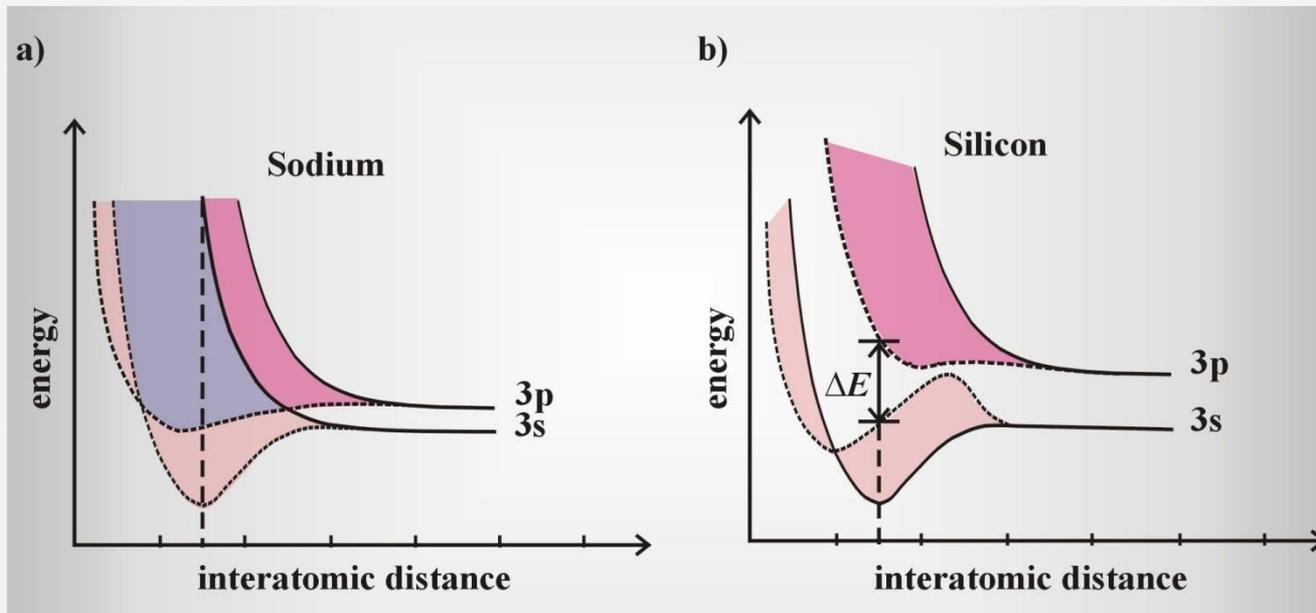
# NITROGEN LASER

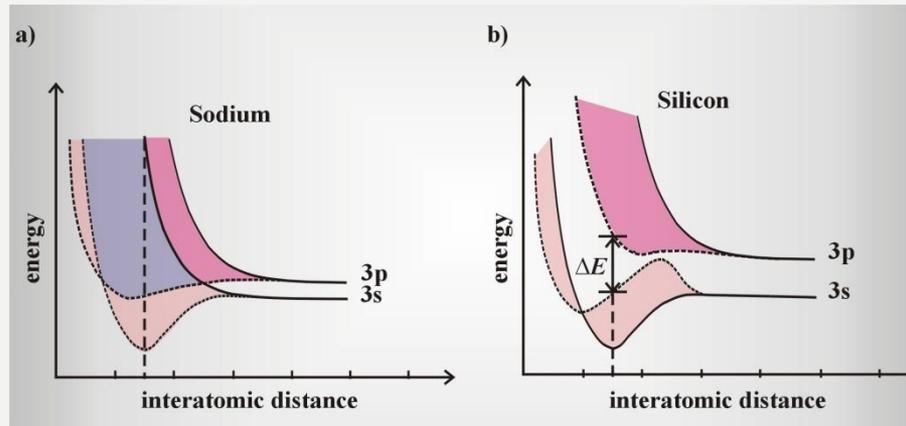
- The nitrogen laser emits radiation at 337 nm. The active medium of nitrogen lasers is a gas nitrogen. The gas is confined within a pressure vessel, usually at total pressure between 101 Pa and 2700 Pa. The nitrogen laser generates pulses of duration between 300 ps (at atmospheric pressure) to 10 ns (at 2700 Pa). The repetition rate changes from 1 to 100 Hz. Low repetition rate lasers use a configuration of sealed-off devices and high repetition rate lasers employ flowing version. The pulse energy changes from microjoules to 10 milijoules. During many years it was used to pump dye lasers and as a source for many other applications requiring UV radiation. The nitrogen laser is well suited to UV laser-induced fluorescence applications in clinical, pharmaceutical, environmental, and process control work.

# **SEMICONDUCTOR DIODE LASERS**

# INTRINSIC SEMICONDUCTORS. DOPED SEMICONDUCTORS. *N-P* JUNCTION

Every material has characteristic properties related to electric current conductivity. Three main classes can be distinguished: a) metals, b) semiconductors, c) insulators. Atoms in a solid are packed into a dense crystalline arrangement, and electron energy levels are no longer narrow discrete lines. They are significantly broadened due to interactions with condensed environment. However, there is a fundamental difference in the energy gap in metals, *semiconductors* and *insulators*





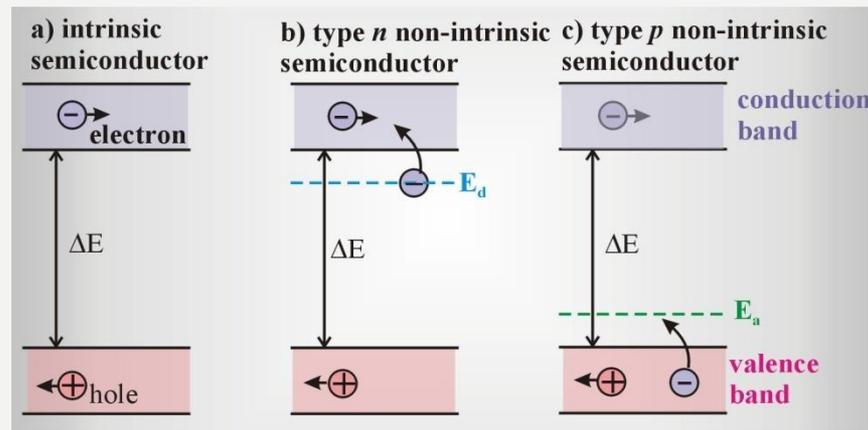
Let us take for example a metal, e.g. sodium ( $^{11}\text{Na}$ ) with the electronic structure:  $(1s)^2(2s)^2(2p)^6(3s)^1$ . The outer electron level 3s is broadened considerably like the first upper lying electron level 3p, unoccupied for an isolated atom. This results in overlapping between the neighboring levels (fig. 4.22a) and the electron can be found either on the 3s or 3p levels. This area of overlapping levels is called *the conduction band* because the electrons occupying 3s or 3p orbitals are common for all the atoms and can wander freely through the solid from one atom to another.

In semiconductors, e.g. in silicon  $^{14}\text{Si}$ :  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$  the outer electron levels are also broadened in a dense crystalline matrix but they do not overlap (fig. 4.22b). The 3s and 3p orbitals broaden into two distinct bands separated by the energy gap  $\Delta E$ . We say that the four electrons (originally two from 3s and two from 3p) occupying 3s (or more precisely  $sp^3$  orbital) are in *the valence band*, while the level 3p (conduction band) remains empty.

A material, in which the energy gap  $\Delta E$  becomes very large is called an *insulator*. In the *insulators* the energy gap  $\Delta E$  is on the order of 3 eV or more, which indicates that the collision energy as well as another forms of thermal energy of molecules are insufficient to transport an electron from the valence band to the conduction band. In semiconductors the energy gap  $\Delta E$  is much smaller (1 eV for silicon) allowing a fraction of electrons to jump to the conduction band at room temperature. At absolute zero temperature, semiconductors become insulators.

# A) INTRINSIC SEMICONDUCTOR, B) SEMICONDUCTOR OF *N*-TYPE, c) semiconductor of *p*-type

- When silicon matrix  $^{14}\text{Si}$  ( $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$ ) is doped with phosphorus  $^{15}\text{P}$  atoms ( $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3$ ), which have the energy of the electrons in the 3s ( $E_d$ ) state approximately the same as the energy of the silicon electrons in the conduction band 3p, the phosphorus electron (donor) can easily jump to the conduction band of the silicon (acceptor) (fig. 4.24b). The semiconductors that are doped in such a way get additional excess electrons and they are called the *semiconductors of n-type*. On the other hand, if silicon matrix is doped with aluminum atoms  $^{13}\text{Al}$  ( $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$ ), which have the electron energy ( $E_a$ ) close to the energy of the silicon valence band 3s, the electrons from the silicon jump to the level  $E_a$  of aluminum leaving a hole in the valence band of the silicon (fig. 4.24c). Semiconductors that are doped in such a way are called the *semiconductors of p-type*.



**Fig. 4.24** Scheme of intrinsic and extrinsic semiconductors: a) intrinsic semiconductor, b) extrinsic semiconductor of *n*-type, c) extrinsic semiconductor of *p*-type

# P-N JUNCTION

- If  $n$ -type and  $p$ -type semiconductors are brought together to form a  $p$ - $n$  junction, holes migrate from the  $p$ -region to the  $n$ -region and conduction electrons move in the opposite direction. As a result of this migration an area in the direct neighborhood of the junction becomes depleted of mobile charge carriers (fig. 4.25), with an excess of negative charges on one side and an excess of positive charges on the other side of the semiconductor. Consequently, such a charge distribution induces an internal electric field  $E$  directed towards  $p$ -region. This internal field prevents charges from further migration across the junction. The  $p$ - $n$  junction is called the *photodiode*.
- When the  $p$ - $n$  junction is irradiated, new electron–hole pairs are generated, which are moved by the internal field  $E$ . The holes move towards the area  $p$ , electrons – towards the area  $n$  causing decrease of the internal voltage potential.

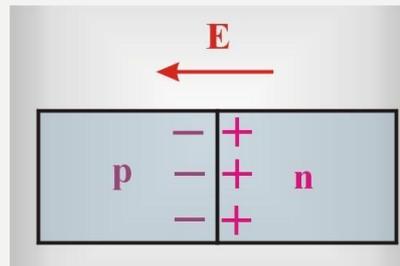
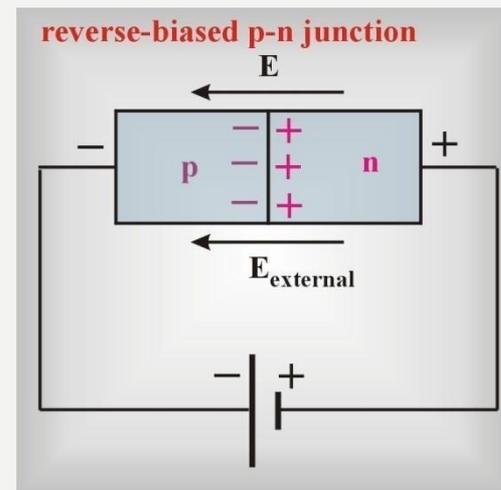
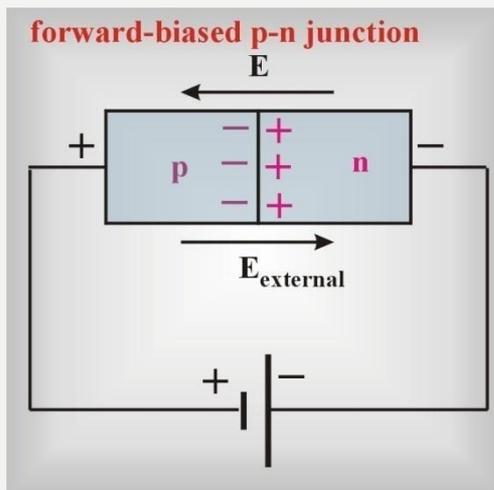


Fig. 4.25  $p$ - $n$  junction

# FORWARD BIASED JUNCTION AND REVERSE BIASED JUNCTION

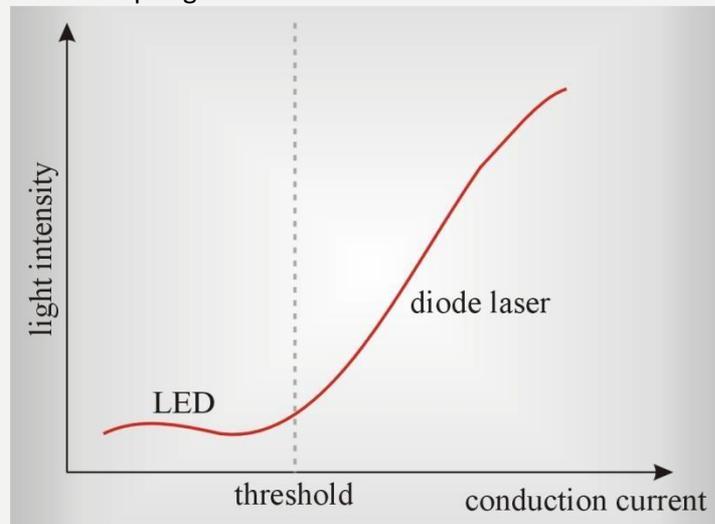
Detection on the junction can be improved by applying an external voltage supply. When a negative terminal of the external voltage source becomes connected to the  $n$  region, and the positive one to the  $p$  region, the  $p$ - $n$  junction is said to be *forward biased*. This means that the charge carriers, both holes from the area  $p$  and electrons from the area  $n$ , flow towards the junction under the external field  $E_{\text{ex}}$  (fig. 4.27). The external field  $E_{\text{ex}}$  is directed just opposite to the internal field  $E$ . The semiconductor lasers, which will be discussed in the next chapter use the forward biased junction. On the other hand, when *the negative* terminal of the external voltage source is connected to the  $p$  region, and the positive one to the  $n$  region, the  $p$ - $n$  junction is said to be *reverse biased* (fig. 4.28).



# DIODE LASER

- The simplest light-emitting diode (LED) is the forward biased  $p$ - $n$  junction. The external forward biased voltage applied to the  $p$ - $n$  junction force holes from the  $p$ -region and conduction electrons from the  $n$ -region towards the junction. The movement of the charge carriers in the opposite directions creates an electric current through the device and recombination of the electrons and the holes at the junction. The energy gained in the recombination can be released as non-selective heat (silicon and germanium semiconductors) or as light (GaAs) at energy of photons equal to the gap  $DE$  between the valence band and the conduction band. The different patterns of relaxation by means of radiative or radiationless decay depend on the band-gain structure. Semiconductor materials with a *direct band gap* dissipate the recombination energy mostly by light, in contrast to semiconductors with an *indirect band gap* in which the energy is released mostly by heat. Radiative way of energy releasing is observed in materials that belong to the III–V groups of elements as well as in some materials from the II–VI groups. The distinct paths of relaxation originate from the fact that the conduction electrons and the holes experience separate dynamics in various materials. In the direct-band gain semiconductor the momentum of an electron returning from the bottom of the conduction band to the top of the valence band changes very little in contrast to a semiconductor with the indirect band gap, in which this electron transition is accompanied by a significant shift in momentum.
- In principle, a semiconductor laser (also known as a diode laser) can be obtained from a LED in which population inversion is achieved. The diode laser requires much higher current densities than LED to reach laser threshold (fig. 4.29). The population inversion between the conduction and valence bands is achieved by applying a strong forward bias across the device to inject a large number of electrons and holes into the junction. Operating under the conditions of population inversion means that the number of recombination events exceeds considerably the number of electron-hole pair generation.

**Fig. 4.29** Scheme illustrating the difference between the light-emitting diode (LED) and the diode laser



# DIODE LASER

- To achieve a greater efficiency some kind of optical feedback is needed like in other lasers that we described so far. Usually, two opposing facets cleaved perpendicularly to the junction play a role of an optical cavity like mirrors in conventional lasers. Therefore, light emitted on the  $p$ - $n$  junction is reflected on the diode edge and turns back to the junction again, additional electrons and holes are produced with electrons jumping from the valence band to the conduction band. The electrons recombine again with the holes under applied forward bias voltage and return to the valence band emitting light of the energy equal to the difference between the valence band and the conduction band  $DE$ . Moreover, the optical feedback between the parallelly cleaved facets produces a more directional, coherent beam of light from the junction plane in contrast to LED that emits in nearly all directions. The simplest laser diode is presented in fig. 4.30.

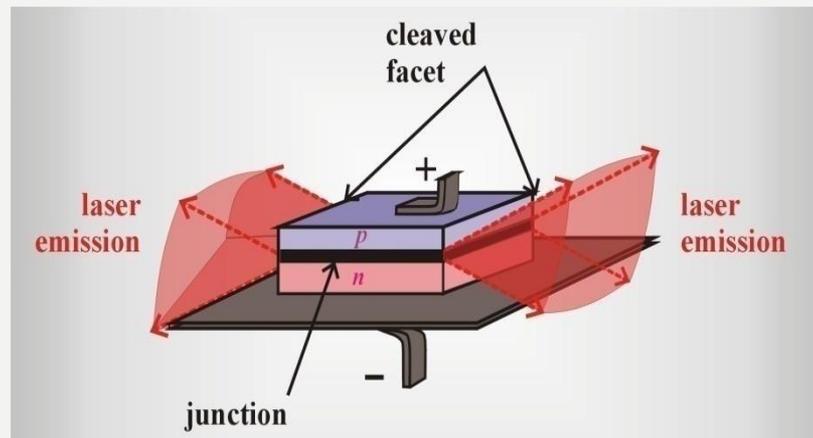
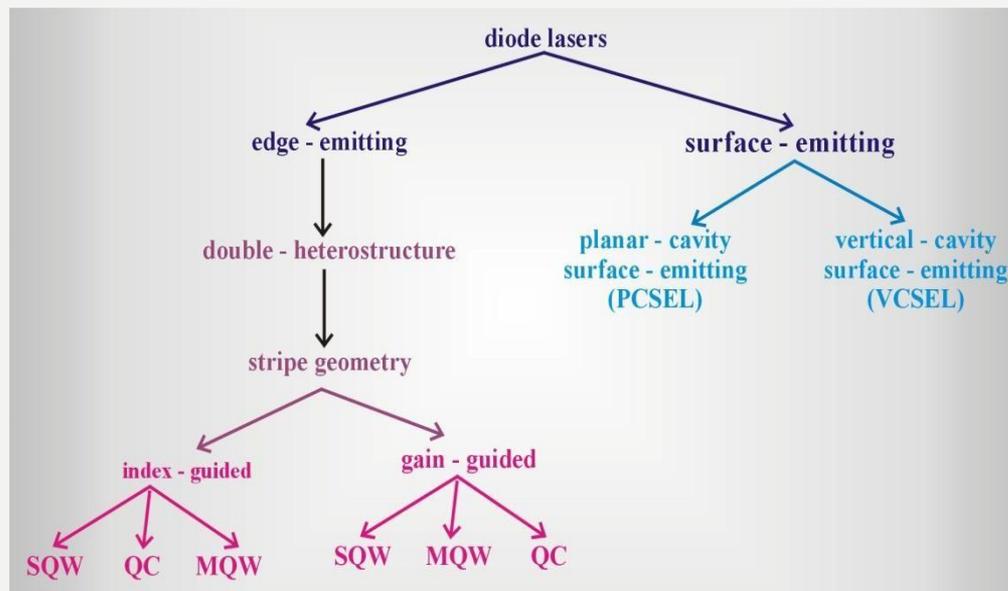


Fig. 4.30 Laser diode scheme

# DIODE LASER

• The earliest diode lasers presented in fig. 4.30 that were a simple  $p$ - $n$  junction required extremely high current densities to reach laser threshold. Although the first semiconductor laser was built in 1962, many years elapsed before the technology matured enough to meet the demands of real-world applications. The first diode lasers had to operate only in pulsed regime under cryogenic cooling. Better performance of diode lasers was attained by inserting a few layers of a semiconductor material instead of the simple  $p$ - $n$  junction described above. The first continuous wave operation at room temperature was achieved in 1970. The  $cw$  operation becomes possible through the advent in the technology of *double heterostructures*.

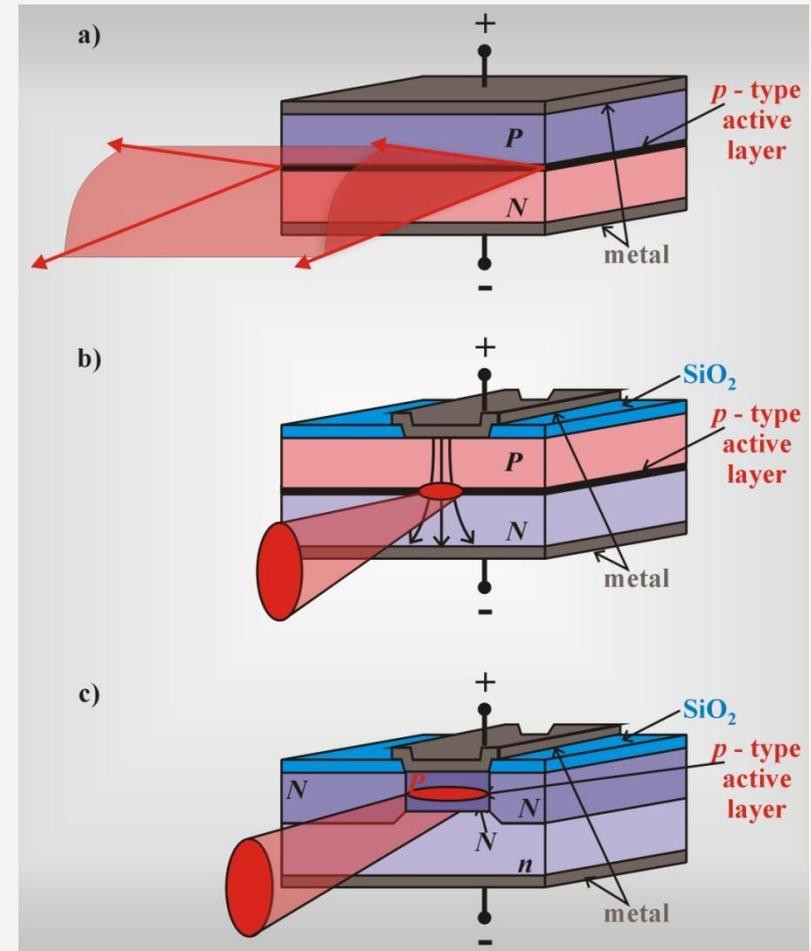


# DIODE LASER

- In order to achieve a goal of performance equal to reliability and stability of other lasers, diode lasers required a few important improvements.
- First, they needed to reduce heat while maintaining a population inversion.
- Second, to improve the beam quality and its divergence.
- Third, to provide higher power levels while maintaining a single transverse mode output.
- Forth, to control output wavelength.

# DIODE LASER

- The first goal can be achieved by increasing effectiveness of inversion population at a given current or/and by reducing the current flow into a small region. Double heterostructure architecture, presented in fig. 4.32a, helps to confine charge carriers, enhancing population inversion. A double heterostructure junction consists of a very thin  $p$ -type layer (approximately 0.2  $\mu\text{m}$ ) of a direct-band-gap material having a smaller band-gap than the thicker  $p$ -type and  $n$ -type layers above and below it. When a forward biased voltage is applied to this  $p$ - $p$ - $n$  junction, holes and electrons are injected from the outer regions into a central active layer, where they become trapped in the potential well created by the wider-band-gap materials. "Carriers confinement" into a small volume increases population inversion, which means higher efficiency, lower threshold current, less heat and more light.
- This effect can be enhanced by adding "current confinement" to the double heterostructure. One way to introduce the current confinement is to use a stripe electrode instead of wide area of the diode's surface. Confining the current into a small region perpendicular to the plane of a junction leads to higher current density, higher concentration of charge carriers inside a diode, higher gain and less heat. A number of techniques can be used to confine the current flow to a small area, but the simplest method is presented in fig. 4.32b. A thin ribbon of positively charged metal is put between two insulator layers such as silicon-dioxide ( $\text{SiO}_2$ ) and cover the  $p$ - $p$ - $n$  junction instead of a monolithic layer of a metal as in fig. 4.32a.

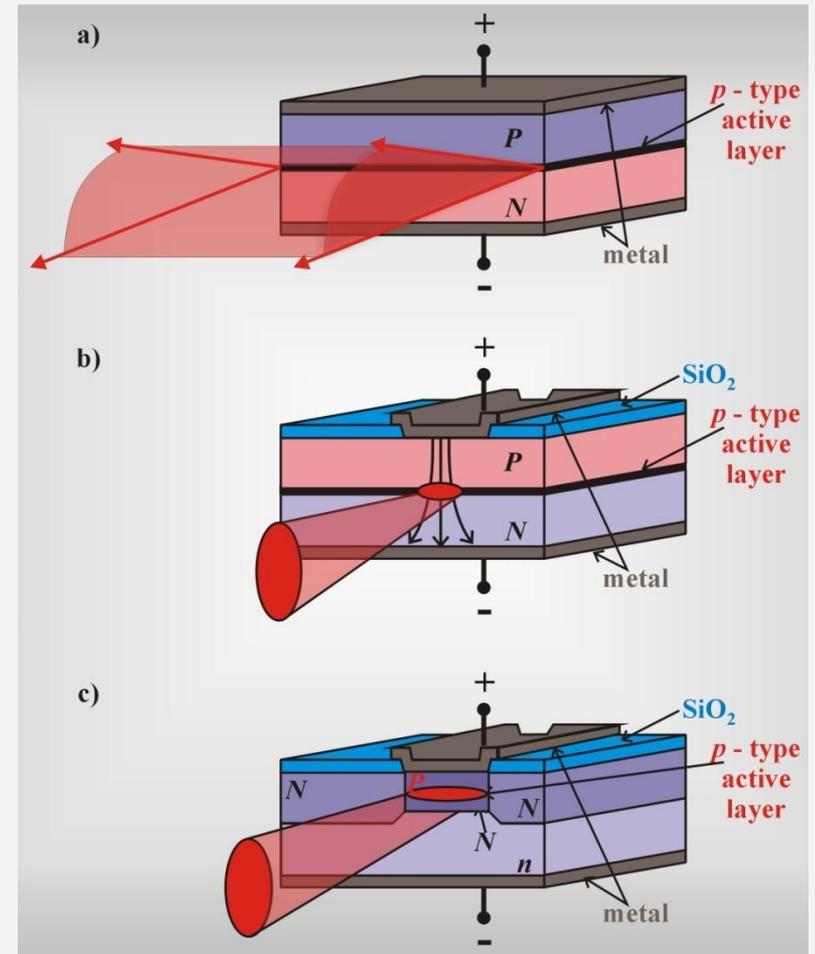


**Fig. 4.32** a) the basic double heterostructure diode; b) gain-guided, striped geometry diode; c) index-guided, striped geometry diode

# DIODE LASER

The effects of “carriers confinement” and “current confinement” can be additionally enhanced by introducing “photons confinement”. Index-guided technique is commonly applied to trap photons inside the optical cavity to increase the density of the cavity optical power. The principle of index-guided diodes is illustrated in fig. 4.32c. A thin active layer of *p*-type small-band-gain material is surrounded on four sides by the wider-band-gain materials characterized by refractive index lower than that for the active layer. This architecture is a gain-guiding, but additionally it takes advantages of trapping light inside a narrow area through total internal reflection due to higher refractive index inside the cavity. This architecture helps to confine the generated photons into a narrow region, enhancing optical feedback and population inversion.

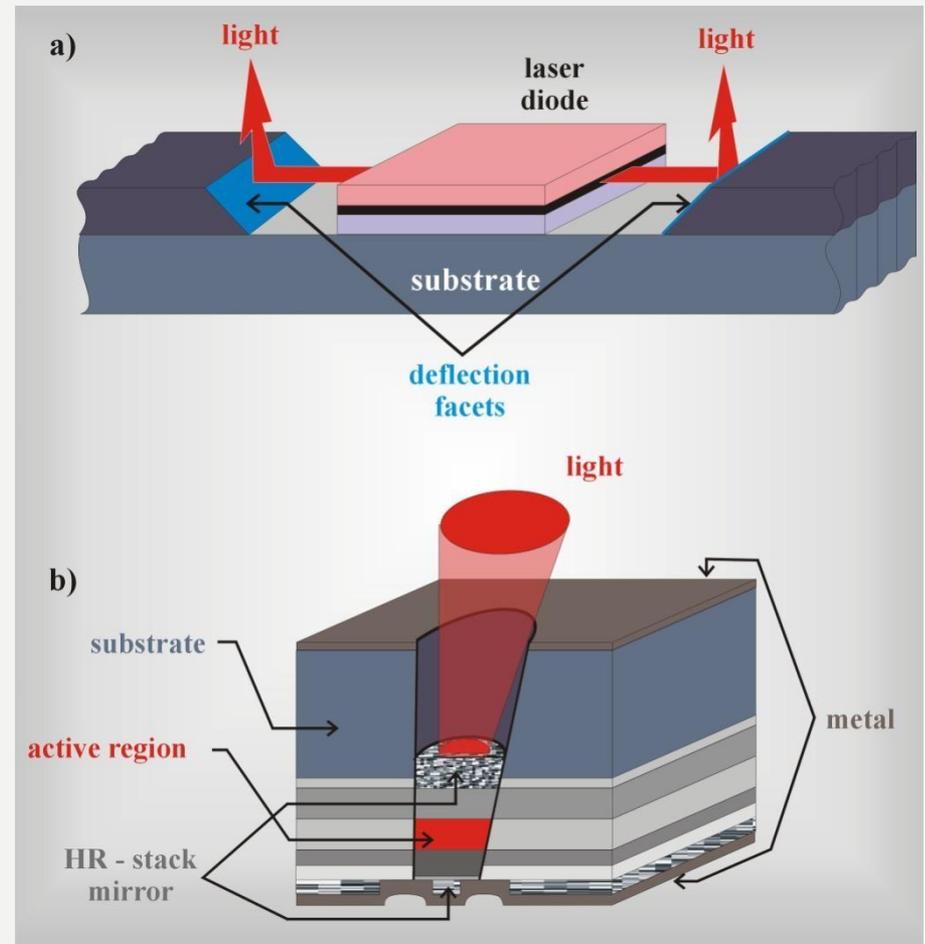
One can notice that both the gain-guided diode laser and the index-guided diode laser produce a tighter coherent beam of light from the narrow active area in contrast to the double heterostructure in fig. 4.32a that emits a broad beam across the entire junction area. The index-guided diodes generate a narrower, more coherent beam than the gain-guided diodes, but the latter can reach higher powers.



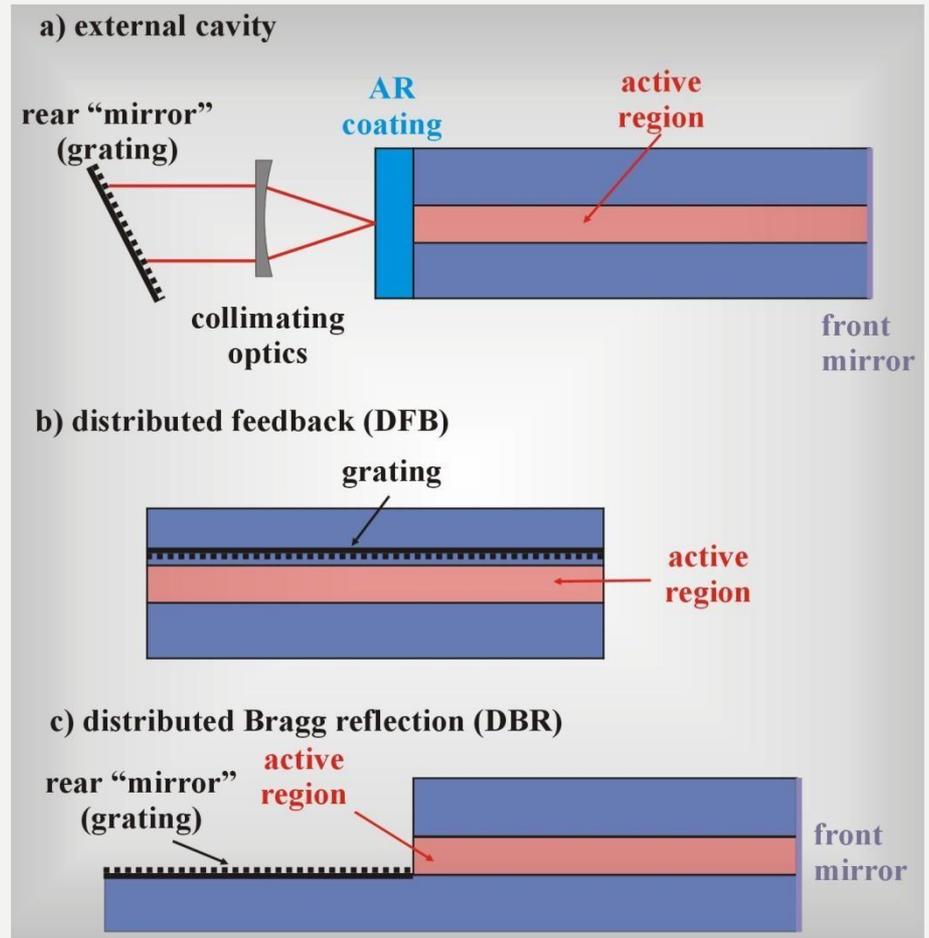
# QUANTUM WELLS

- If we reduce the thickness of the  $p$ -type active layer in the double heterostructure down to 50 nm and less, which is feasible with the development of advanced semiconductor fabrication techniques, additional quantum effects occur in the active layer of the junction. Both the valence and the conduction bands split into discrete sublevels, with energy and momentum of the charge carriers depending on the thickness of the layer. Such double heterostructures with an active layer thicker than 50 nm are called *quantum wells*. When only one thick active layer is employed, the diode laser is called a *single-quantum-well (SQW)* in contrast to a *multiple-quantum-well (MQW)*, where SQW heterostructure layers are stacked. SQW and MQW have both gain-guided and index-guided versions. They have higher gain and lower current threshold and the output beam is much more coherent than in conventional double heterostructure architectures.

# PLANAR-CAVITY SURFACE-EMITTING DIODE LASER (PCSEL); VERTICAL-CAVITY SURFACE-EMITTING DIODE LASER (VCSEL)

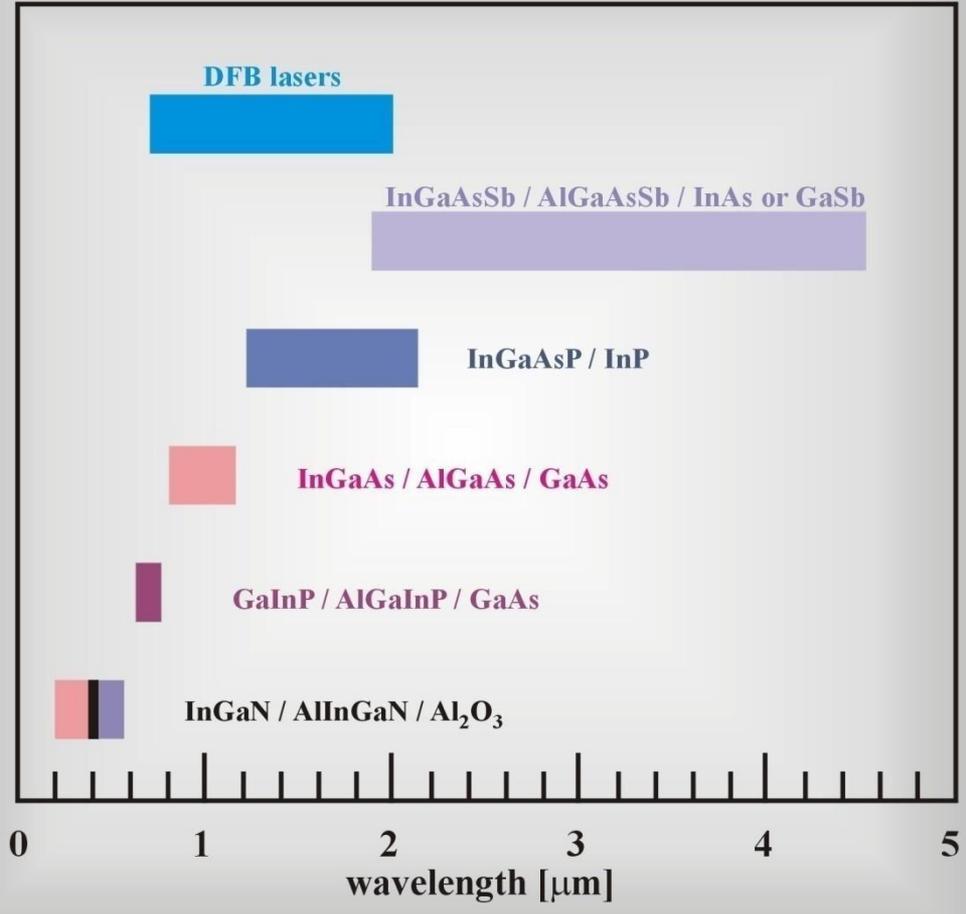


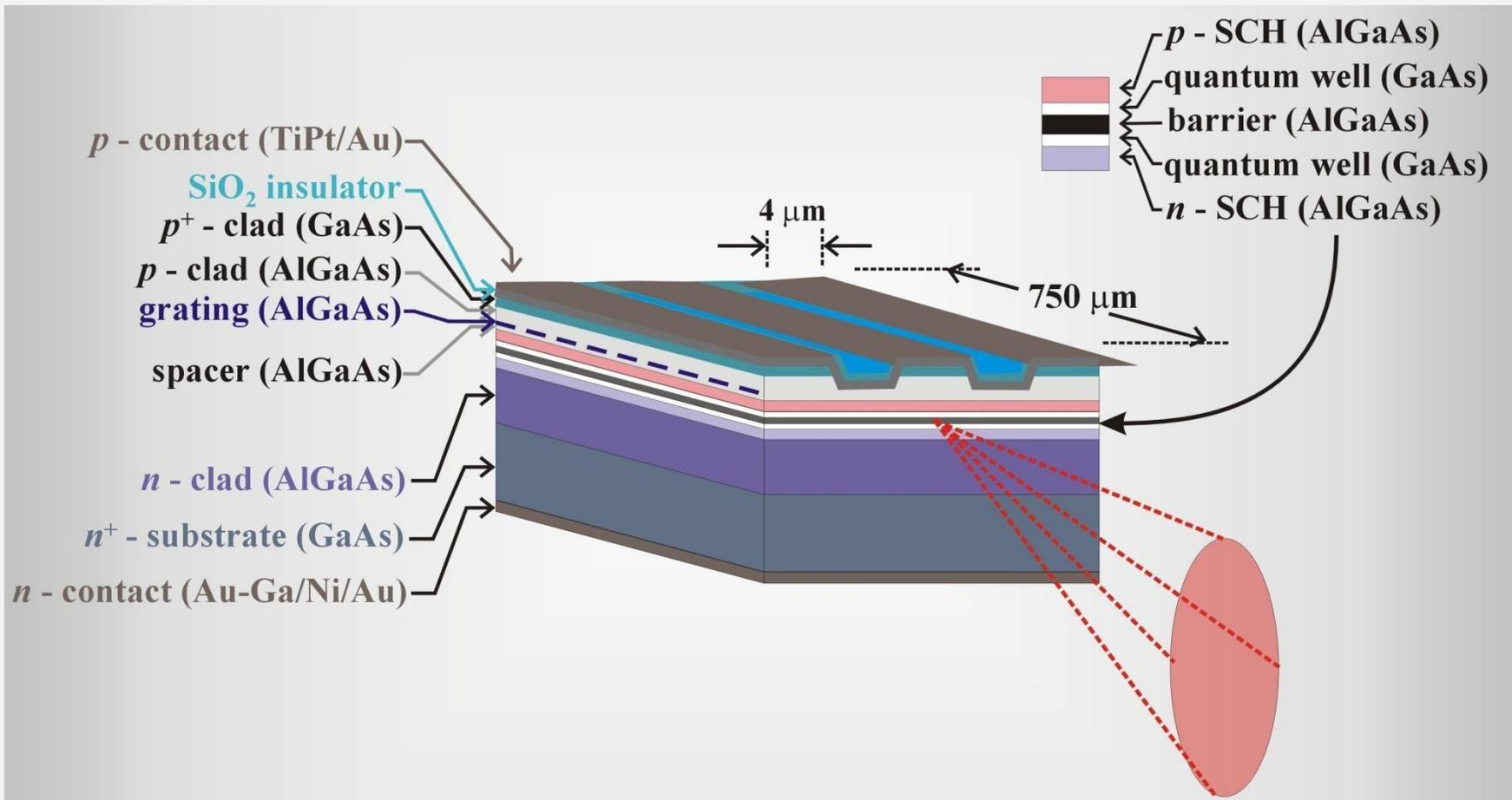
**Fig. 4.33** a) planar-cavity surface-emitting diode laser (PCSEL); b) vertical-cavity surface-emitting diode laser (VCSEL)



**Fig. 4.34** Configurations used for narrow band light output from laser diodes, a) external cavity; b) distributed-feedback (DFB); c) distributed-Bragg-reflection (DBR)

III - V materials system

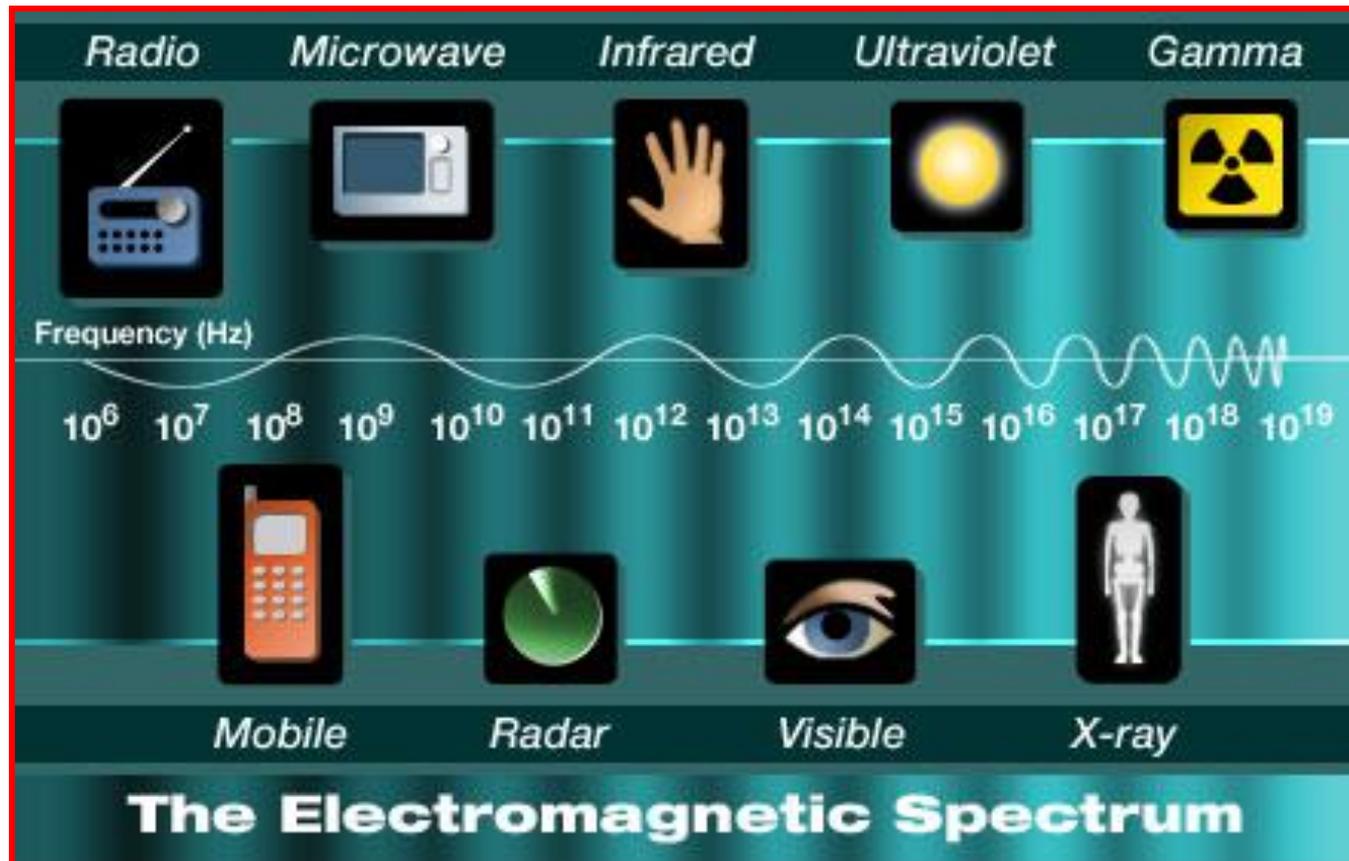




# Lecture no.5

- **Microwaves**
- **Properties**
- **Advantages**
- **Limitations**
- **Applications**
- **Magnetron oscillator**

# Electro Magnetic Spectrum



# Microwaves

- Microwaves are electromagnetic waves whose frequencies range from about **300 MHz – 300 GHz** (1 MHz =  $10^6$  Hz and 1 GHz =  $10^9$  Hz) or wavelengths in air ranging from 100 cm – 1 mm.
- The word *Microwave* means *very short wave*, which is the shortest wavelength region of the radio spectrum and a part of the electromagnetic spectrum.

# Properties of Microwaves

1. Microwave is an electromagnetic radiation of short wavelength.
2. They can reflect by conducting surfaces just like optical waves since they travel in straight line.
3. Microwave currents flow through a thin outer layer of an ordinary cable.
4. Microwaves are easily attenuated within short distances.
5. They are not reflected by ionosphere

# Advantages and Limitations

## 1. Increased bandwidth availability:

- Microwaves have large bandwidths compared to the common bands like short waves (SW), ultrahigh frequency (UHF) waves, etc.
- For example, the microwaves extending from  $\lambda = 1$  cm -  $\lambda = 10$  cm (i.e) from 30,000 MHz – 3000 MHz, this region has a bandwidth of 27,000 MHz.

## 2. Improved directive properties:

- The second advantage of microwaves is their ability to use high gain directive antennas, any EM wave can be focused in a specified direction (Just as the focusing of light rays with lenses or reflectors)

# Advantages and Limitations

## **3. Fading effect and reliability:**

- Fading effect due to the variation in the transmission medium is more effective at low frequency.
- Due to the Line of Sight (LOS) propagation and high frequencies, there is less fading effect and hence microwave communication is more reliable.

## **4. Power requirements:**

- Transmitter / receiver power requirements are pretty low at microwave frequencies compared to that at short wave band.

# Advantages and Limitations

## 5. Transparency property of microwaves:

- Microwave frequency band ranging from 300 MHz – 10 GHz are capable of freely propagating through the atmosphere.
- The presence of such a transparent window in a microwave band facilitates the study of microwave radiation from the sun and stars in radio astronomical research of space.

# Applications

- Microwaves have a wide range of applications in modern technology, which are listed below
- 1. **Telecommunication:** Intercontinental Telephone and TV, space communication (Earth – to – space and space – to – Earth), telemetry communication link for railways etc.
- 2. **Radars:** detect aircraft, track / guide supersonic missiles, observe and track weather patterns, air traffic control (ATC), burglar alarms, garage door openers, police speed detectors etc.

# 3. Commercial and industrial applications

- Microwave oven
- Drying machines – textile, food and paper industry for drying clothes, potato chips, printed matters etc.
- Food process industry – Precooling / cooking, pasteurization / sterility, hot frozen / refrigerated precooled meats, roasting of food grains / beans.
- Rubber industry / plastics / chemical / forest product industries
- Mining / public works, breaking rocks, tunnel boring, drying / breaking up concrete, breaking up coal seams, curing of cement.
- Drying inks / drying textiles, drying / sterilizing grains, drying / sterilizing pharmaceuticals, leather, tobacco, power transmission.
- Biomedical Applications ( diagnostic / therapeutic ) – diathermy for localized superficial heating, deep electromagnetic heating for treatment of cancer, hyperthermia ( local, regional or whole body for cancer therapy).

## Other Applications

4. Identifying objects or personnel by non – contact method.
5. Light generated charge carriers in a microwave semiconductor make it possible to create a whole new world of microwave devices, fast jitter free switches, phase shifters, HF generators, etc.

# Magnetron oscillator

- Magnetrons provide microwave oscillations of very high frequency.

## Types of magnetrons

1. Negative resistance type
2. Cyclotron frequency type
3. Cavity type

# Description of types of magnetron

## Negative resistance Magnetrons

- Make use of negative resistance between two anode segments but have low efficiency and are useful only at low frequencies ( $< 500$  MHz).

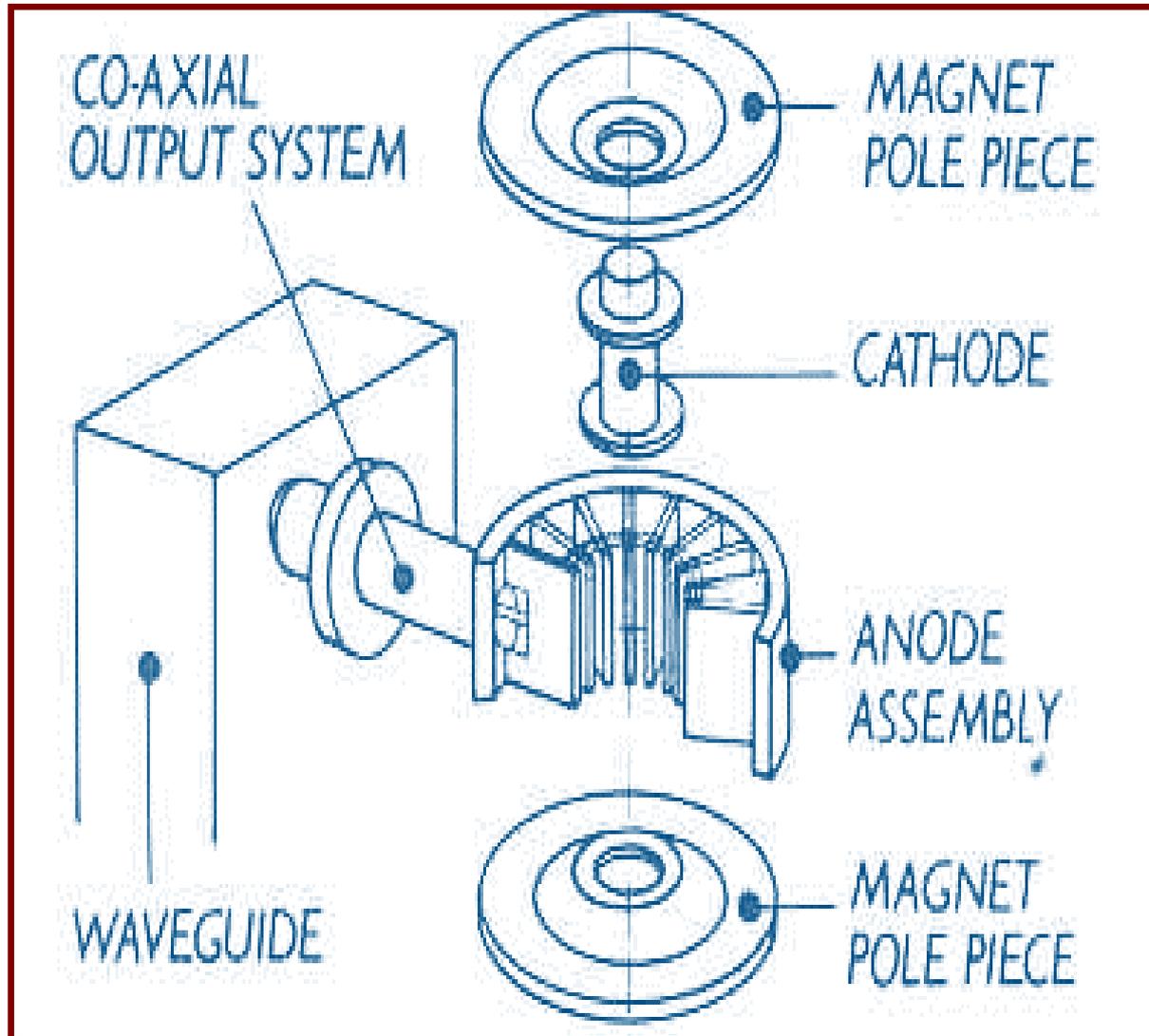
## Cyclotron frequency Magnetrons

- Depend upon synchronization between an alternating component of electric and periodic oscillation of electrons in a direction parallel to this field.
- Useful only for frequencies greater than 100 MHz.

## Cavity Magnetrons

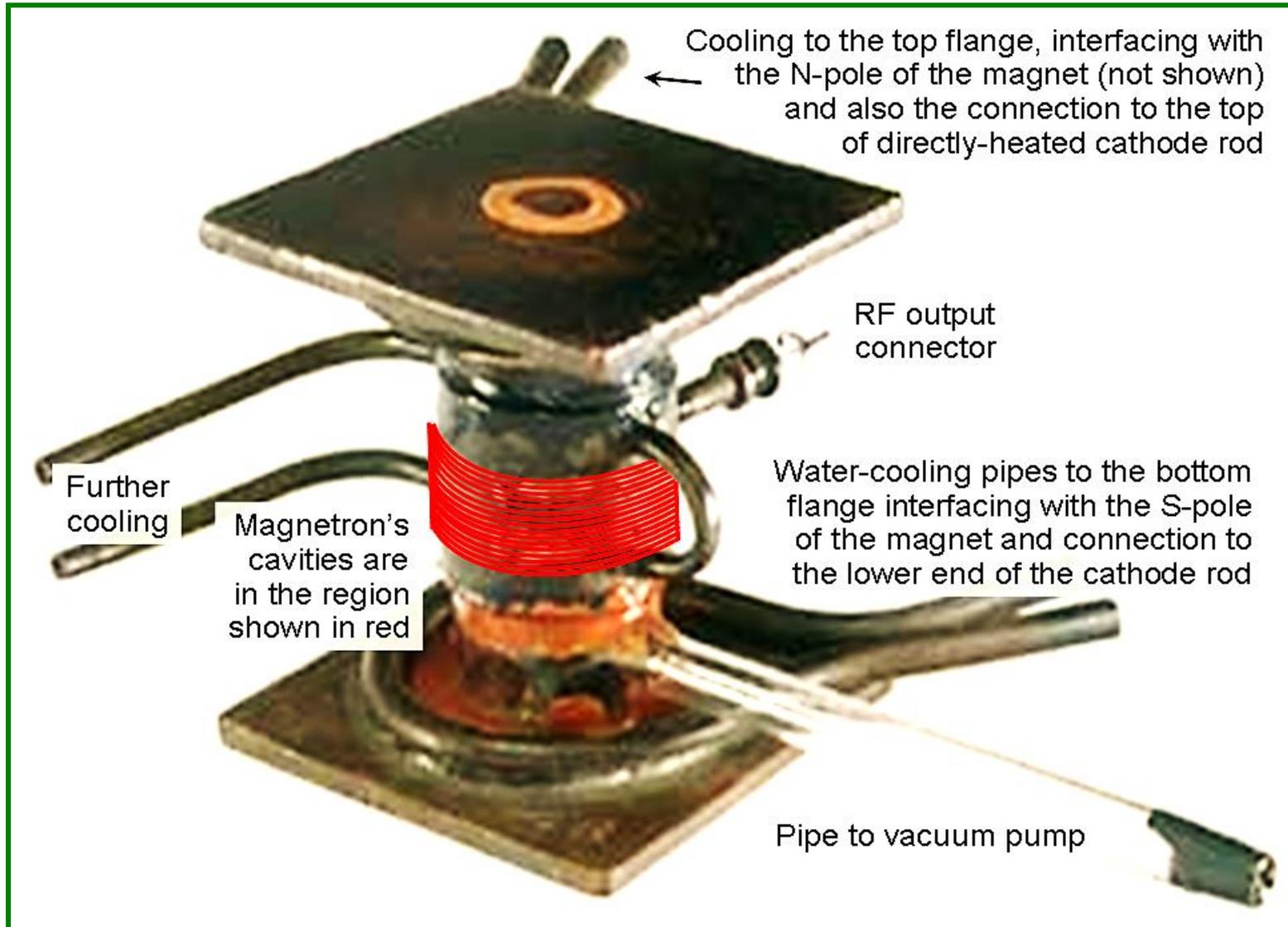
- Depend upon the interaction of electrons with a rotating electromagnetic field of constant angular velocity.
- Provide oscillations of very high peak power and hence are useful in radar applications

# Cavity Magnetrons

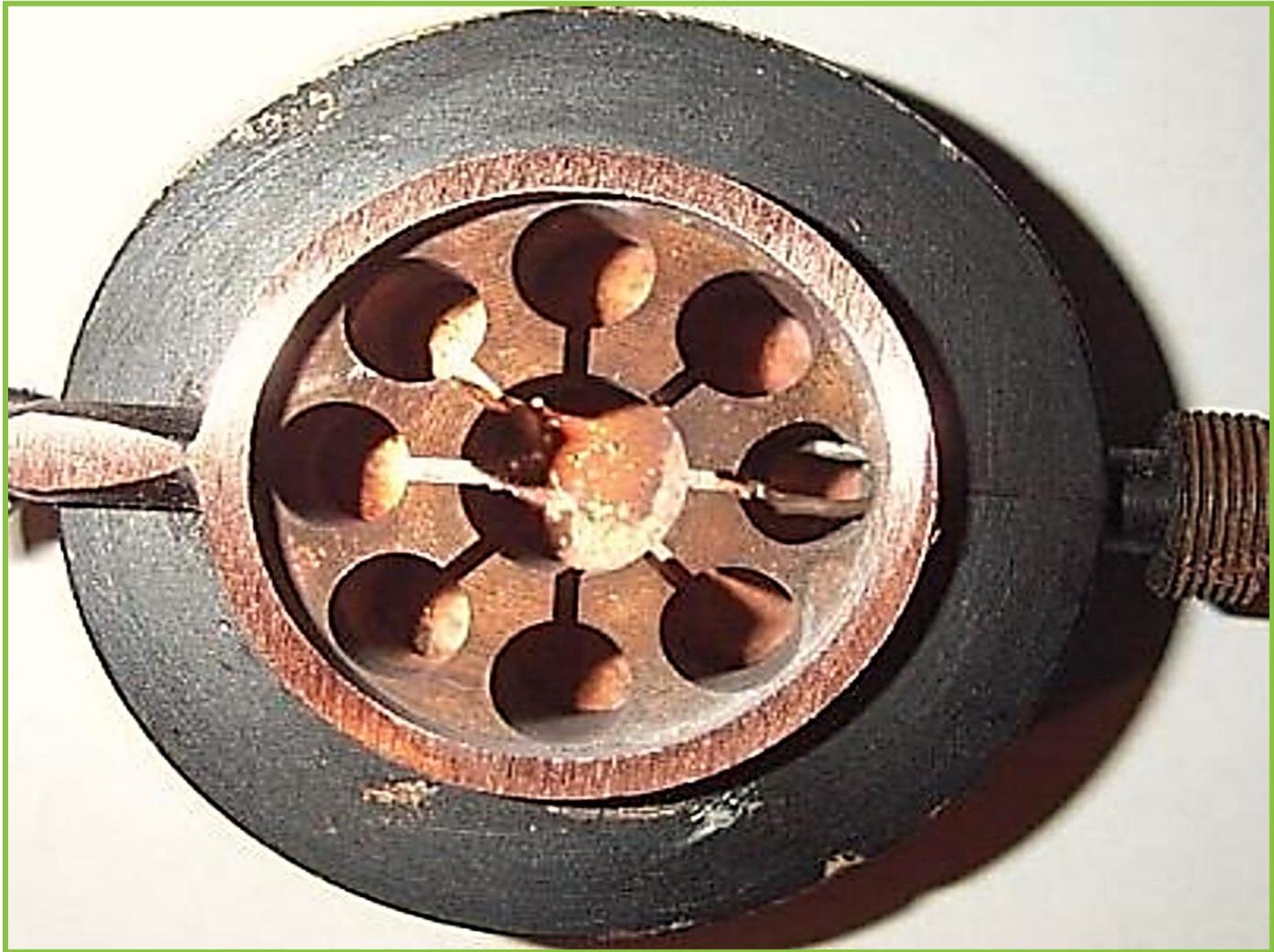


**Fig (i) Major elements in the Magnetron oscillator**

# Cavity Magnetron



# Anode Assembly



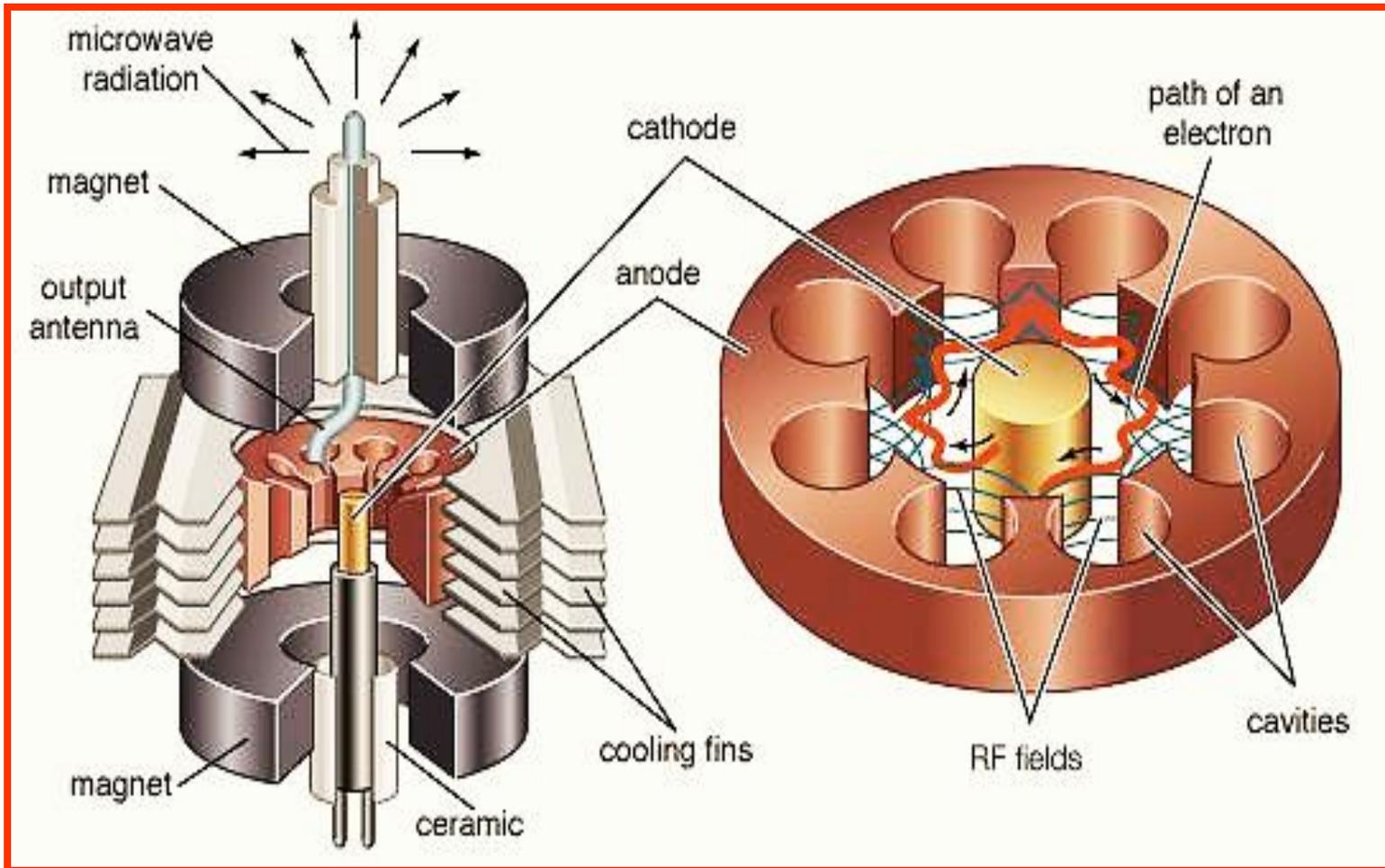
# Construction

- Each cavity in the anode acts as an inductor having only one turn and the slot connecting the cavity and the interaction space acts as a capacitor.
- These two form a parallel resonant circuit and its resonant frequency depends on the value of  $L$  of the cavity and the  $C$  of the slot.
- The frequency of the microwaves generated by the magnetron oscillator depends on the frequency of the RF oscillations existing in the resonant cavities.

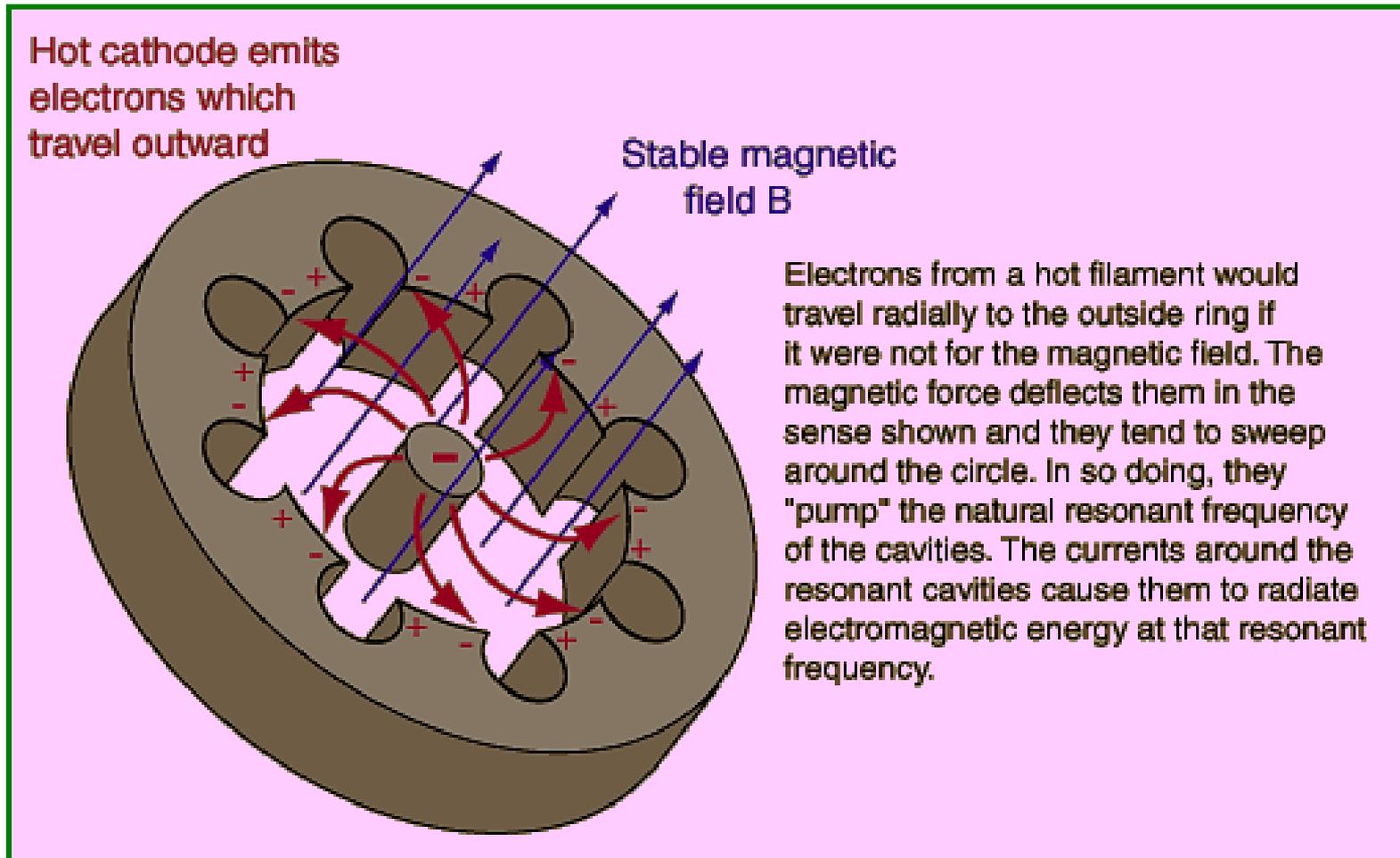
## Description

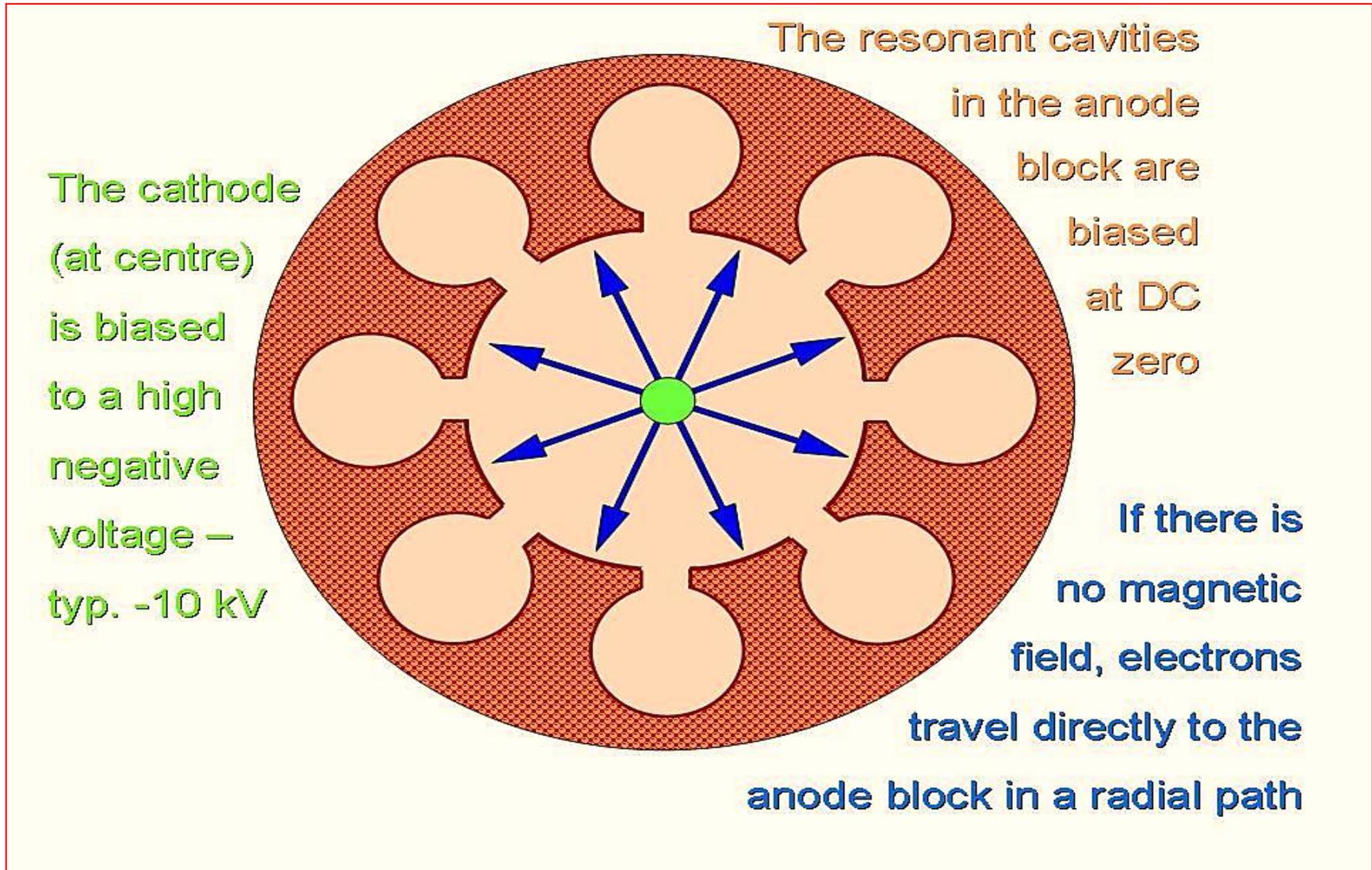
- Magnetron is a cross field device as the electric field between the anode and the cathode is radial whereas the magnetic field produced by a permanent magnet is axial.
- A high DC potential can be applied between the cathode and anode which produces the radial electric field.
- Depending on the relative strengths of the electric and magnetic fields, the electrons emitted from the cathode and moving towards the anode will traverse through the interaction space as shown in Fig. (iii).
- In the absence of magnetic field ( $B = 0$ ), the electron travel straight from the cathode to the anode due to the radial electric field force acting on it, Fig (iii) a.

# Cavity Magnetrons

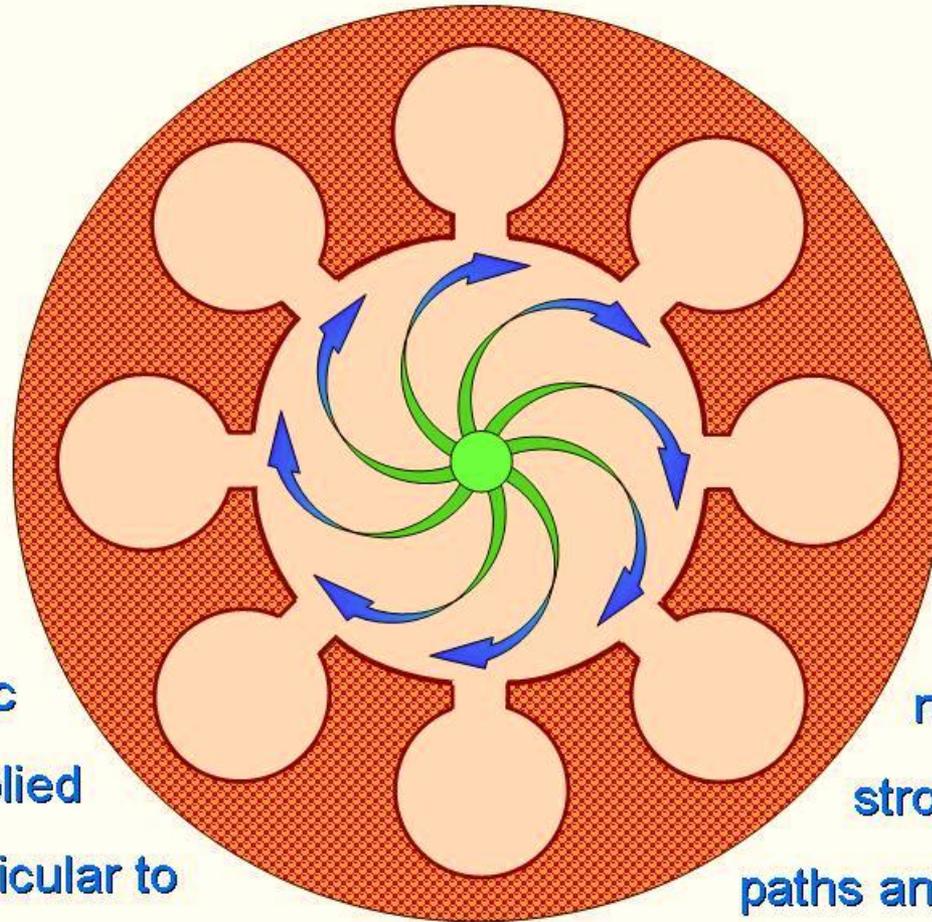


## Fig (ii) Cross sectional view of the anode assembly





With a magnetic field applied perpendicular to plane of the drawing



electrons now travel in strongly curved paths and induce an

EM field in the anode block

## Description

- If the magnetic field strength is increased slightly, the lateral force bending the path of the electron as given by the path 'b' in Fig. (iii).
- The radius of the path is given by, If the strength of the magnetic field is made sufficiently high then the electrons can be prevented from reaching the anode as indicated path 'c' in Fig. (iii)),
- The magnetic field required to return electrons back to the cathode just grazing the surface of the anode is called the critical magnetic field ( $B_c$ ) or the cut off magnetic field.
- If the magnetic field is larger than the critical field ( $B > B_c$ ), the electron experiences a greater rotational force and may return back to the cathode quite faster.

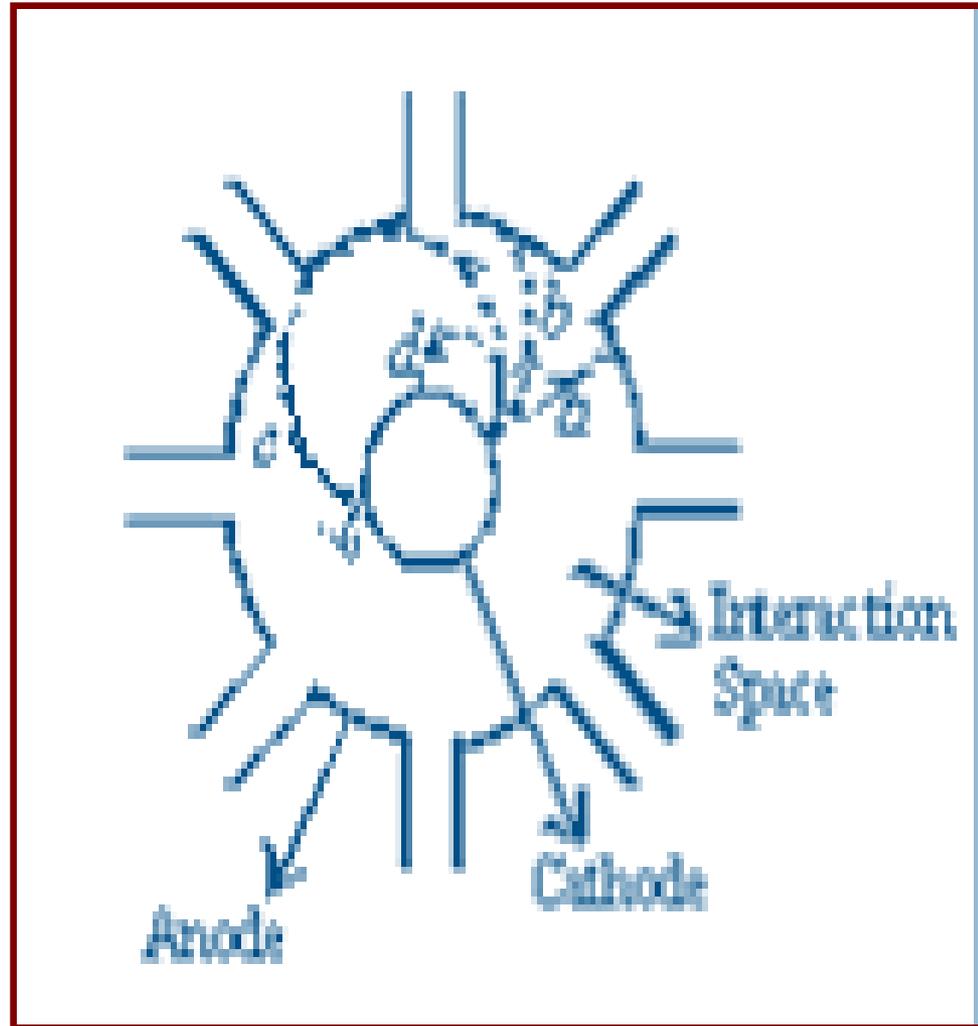
Fig (iii) Electron trajectories in the presence of crossed electric and magnetic fields

(a) no magnetic field

(b) small magnetic field

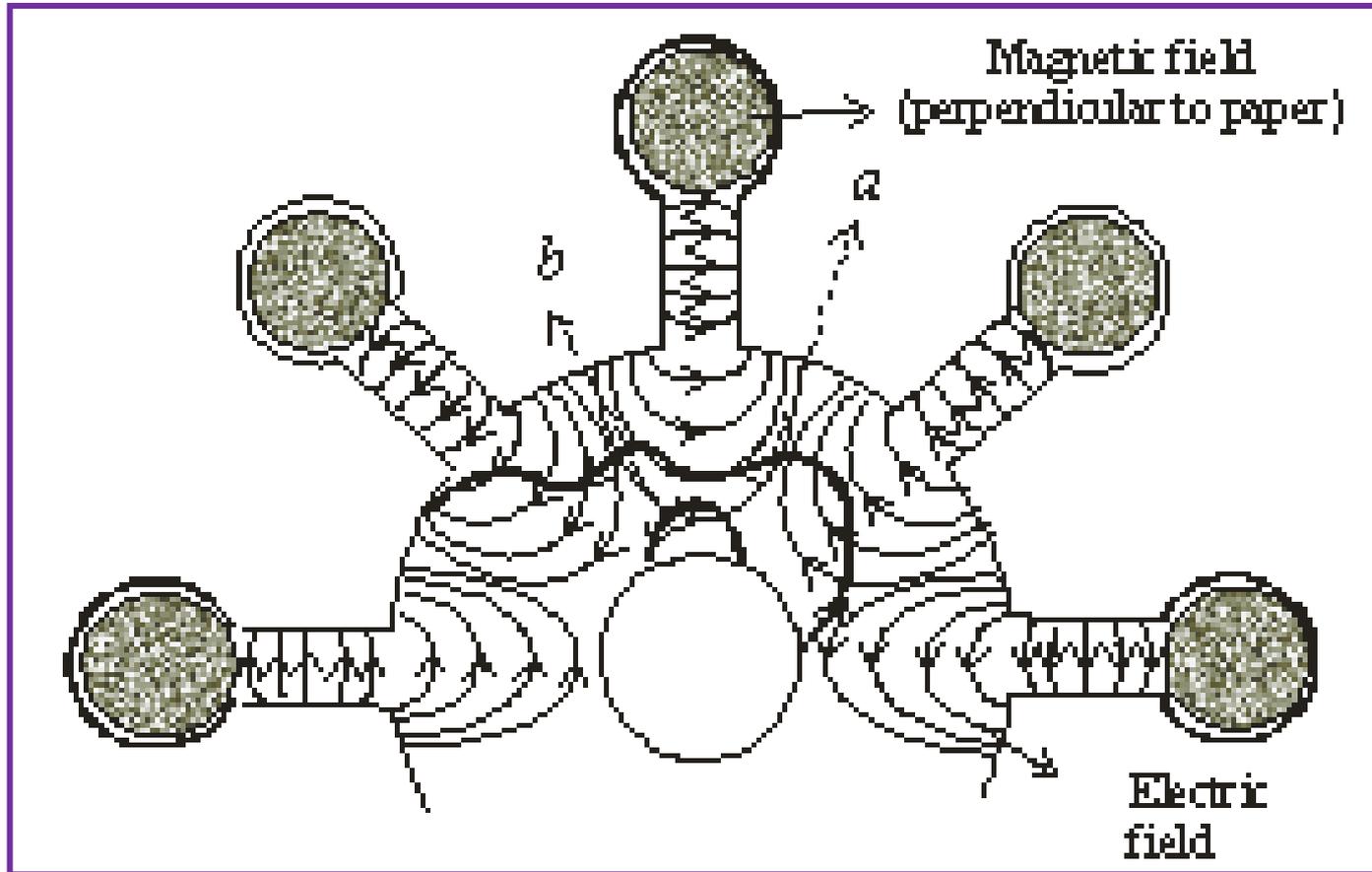
(c) Magnetic field =  $B_c$

(d) Excessive magnetic field



## Working

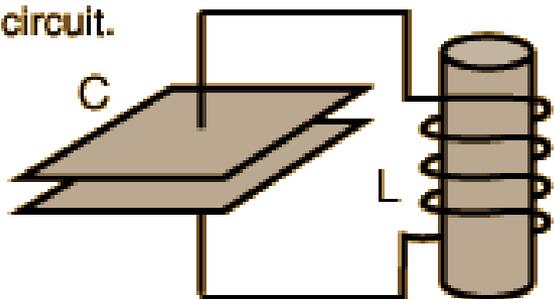
**Fig (iv) Possible trajectory of electrons from cathode to anode in an eight cavity magnetron operating in  $\pi$  mode**



# Working

- The RF Oscillations of transient nature produced when the HT is switched on, are sufficient to produce the oscillations in the cavities, these oscillations are maintained in the cavities reentrant feedback which results in the production of microwaves.
- Reentrant feedback takes place as a result of interaction of the electrons with the electric field of the RF oscillations existing in the cavities.
- The cavity oscillations produce electric fields which fringe out into the interaction space from the slots in the anode structure, as shown in Fig (iv).
- Energy is transferred from the radial dc field to the RF field by the interaction of the electrons with the fringing RF field.

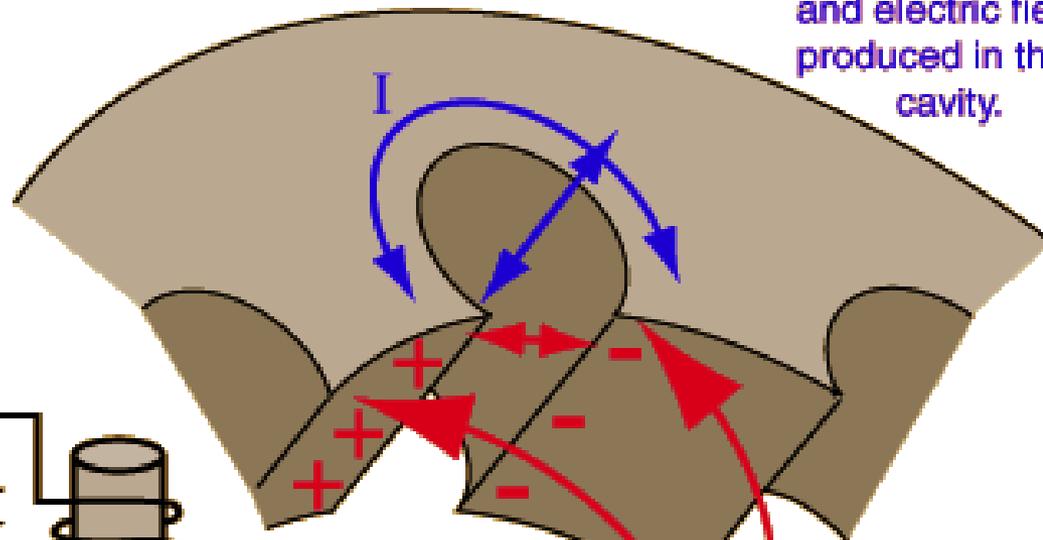
The cavity exhibits a resonance analogous to a parallel resonant circuit.



$$f_{\text{resonance}} \approx \frac{1}{2\pi} \sqrt{\frac{1}{LC}}$$

Current around the cavity plays the role of an inductor.

Oscillating magnetic and electric fields produced in the cavity.



Charge at ends of cavity plays the role of a capacitor.

Electrons from the hot center cathode arriving at a negatively charged region tend to drive it back around the cavity, "pumping" the natural resonant frequency.

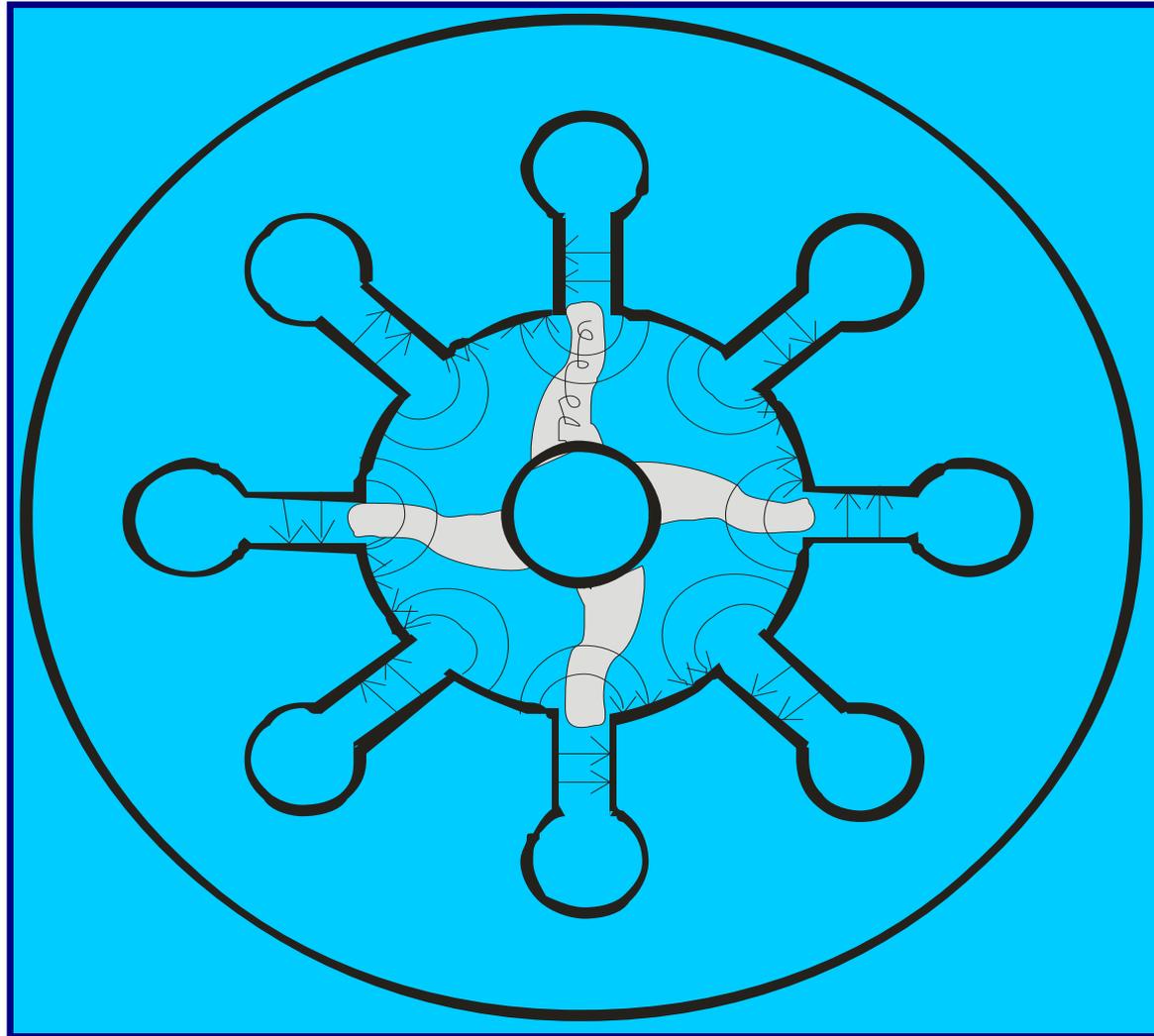
# Working

- Due to the oscillations in the cavities, the either sides of the slots (which acts as a capacitor) becomes alternatively positive and negative and hence the directions of the electric field across the slot also reverse its sign alternatively.
- At any instant the anode close to the spiraling electron goes positive, the electrons gets retarded and this is because; the electron has to move in the RF field, existing close to the slot, from positive side to the negative side of the slot.
- In this process, the electron loses energy and transfer an equal amount of energy to the RF field which retard the spiraling electron.
- On return to the previous orbit the electron may reach the adjacent section or a section farther away and transfer energy to the RF field if that part of the anode goes positive at that instant.

## Working

- This electron travels in a longest path from cathode to the anode as indicated by 'a' in Fig (iv), transferring the energy to the RF field are called as *favoured electrons* and are responsible for bunching effect and give up most of its energy before it finally terminates on the anode surface.
- An electron 'b' is accelerated by the RF field and instead of imparting energy to the oscillations, takes energy from oscillations resulting in increased velocity, such electrons are called *unfavoured electrons* which do not participate in the bunching process and cause back heating.
- Every time an electron approaches the anode "in phase" with the RF signal, it completes a cycle. This corresponds to a phase shift  $2\pi$ .
- For a dominant mode, the adjacent poles have a phase difference of  $\pi$  radians, this called the  $\pi$  - mode.

Fig (v) Bunching of electrons in multicavity magnetron



## Working

- At any particular instant, one set of alternate poles goes positive and the remaining set of alternate poles goes negative due to the RF oscillations in the cavities.
- AS the electron approaches the anode, one set of alternate poles accelerates the electrons and turns back the electrons quickly to the cathode and the other set alternate poles retard the electrons, thereby transferring the energy from electrons to the RF signal.
- This process results in the bunching of electrons, the mechanism by which electron bunches are formed and by which electrons are kept in synchronism with the RF field is called *phase focussing effect*. electrons with the fringing RF field.

# Working

- The number of bunches depends on the number of cavities in the magnetron and the mode of oscillations, in an eight cavity magnetron oscillating with  $\pi$  - mode, the electrons are bunched in four groups as shown in Fig (v).
- Two identical resonant cavities will resonate at two frequencies when they are coupled together; this is due to the effect of mutual coupling.
- Commonly separating the *pi mode* from adjacent modes is by a method called *strapping*. The straps consist of either circular or rectangular cross section connected to alternate segments of the anode block.

# Performance Characteristics

1. **Power output:** In excess of 250 kW ( Pulsed Mode), 10 mW (UHF band), 2 mW (X band), 8 kW (at 95 GHz)
2. **Frequency:** 500 MHz – 12 GHz
3. **Duty cycle:** 0.1 %
4. **Efficiency:** 40 % - 70 %

# Applications of Magnetron

1. Pulsed radar is the single most important application with large pulse powers.
2. Voltage tunable magnetrons are used in sweep oscillators in telemetry and in missile applications.
3. Fixed frequency, CW magnetrons are used for industrial heating and microwave ovens.

# Lecture no.6

# *Statistics of Data*

- **What is Statistics?**
- **Data**
- **Data Sources**
- **Descriptive Statistics**
- **Statistical Inference**
- **Computers and Statistical Analysis**

# What is Statistic of data?

- **Main purpose of statistics, among others, is to develop and apply methodology for extracting useful knowledge from data. (Fisher 1990)**
- **Major activities in statistics involve:**
  - exploration and visualization of sample data
  - summary description of sample data
  - hypothesis testing and statistical inference
  - design of experiments and surveys to test hypotheses
  - stochastic modeling of uncertainty (e.g. flipped coin)
  - forecasting based on suitable models
  - development of new statistical theory and methods

# Statistical data analysis

## ■ **Starts with data**

- Nominal, Ordinal, Interval, and Ratio

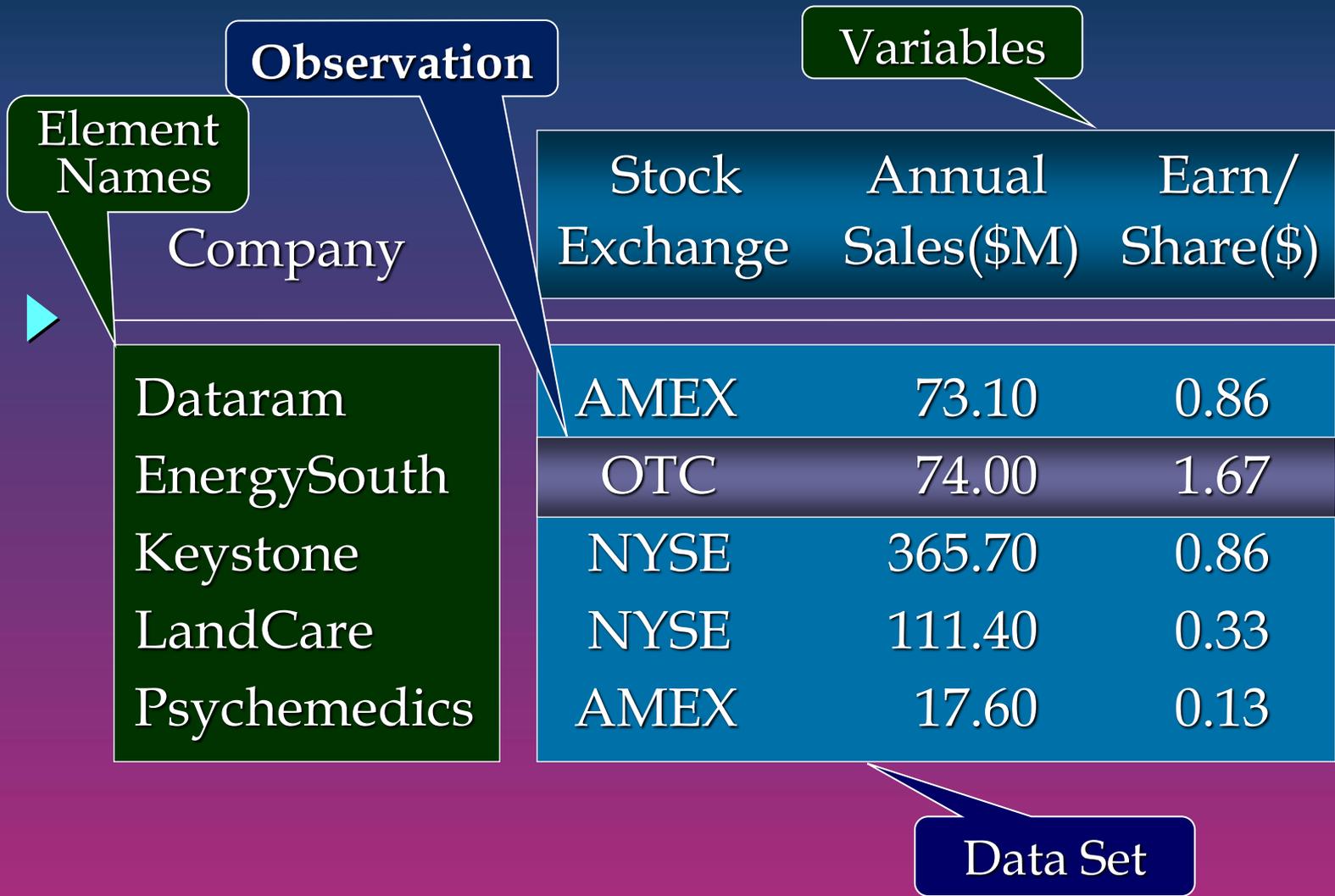
## ■ **Descriptive statistics**

- Exploring, visualizing, and summarizing data without fitting the data to any models

## ■ **Inferential statistics**

- Identification of a suitable model
- Testing either predictions or hypotheses of the model

# Data, Data Sets, Elements, Variables, and Observations



# Scales of Measurement

- ▶ Scales of measurement include:

**Nominal**

**Interval**

**Ordinal**

**Ratio**

- ▶ The scale determines the amount of information contained in the data.
- ▶ The scale indicates the data summarization and statistical analyses that are most appropriate.

# Scales of Measurement

## ■ Nominal

- ▶ Data are labels or names used to identify an attribute of the element.
- ▶ A nonnumeric label or numeric code may be used.

# Scales of Measurement

## ■ Nominal

### ▶ Example:

Students of a university are classified by the school in which they are enrolled using a nonnumeric label such as Business, Humanities, Education, and so on.

Alternatively, a numeric code could be used for the school variable (e.g. 1 denotes Business, 2 denotes Humanities, 3 denotes Education, and so on).

# Scales of Measurement

## ■ Ordinal

- ▶ The data have the properties of nominal data and the order or rank of the data is meaningful.
- ▶ A nonnumeric label or numeric code may be used.

# Scales of Measurement

## ■ Ordinal

### ▶ Example:

Students of a university are classified by their class standing using a nonnumeric label such as Freshman, Sophomore, Junior, or Senior.

Alternatively, a numeric code could be used for the class standing variable (e.g. 1 denotes Freshman, 2 denotes Sophomore, and so on).

# Scales of Measurement

## ■ Interval

- ▶ The data have the properties of ordinal data, and the interval between observations is expressed in terms of a fixed unit of measure.
- ▶ Interval data are always numeric.

# Scales of Measurement

## ■ Interval

### ▶ Example:

Melissa has an SAT score of 1205, while Kevin has an SAT score of 1090. Melissa scored 115 points more than Kevin.

# Scales of Measurement

## ■ Ratio

- ▶ The data have all the properties of interval data and the ratio of two values is meaningful.
- ▶ Variables such as distance, height, weight, and time use the ratio scale.
- ▶ This scale must contain a zero value that indicates that nothing exists for the variable at the zero point.

# Scales of Measurement

## ■ Ratio

### ▶ Example:

Melissa's college record shows 36 credit hours earned, while Kevin's record shows 72 credit hours earned. Kevin has twice as many credit hours earned as Melissa.

## In-class Exercise

- Consider items 1.1, 1.3, 1.4, 1.6, S.4, 3.1, and 3.3 in the handout of an example questionnaire.
  - Comment on what scale of measurement the item uses.
  - Comment on any potential special attention needed when these items will be statistically analyzed.

# Qualitative and Quantitative Data

▶ Data can be further classified as being qualitative or quantitative.

▶ The statistical analysis that is appropriate depends on whether the data for the variable are qualitative or quantitative.

▶ In general, there are more alternatives for statistical analysis when the data are quantitative.

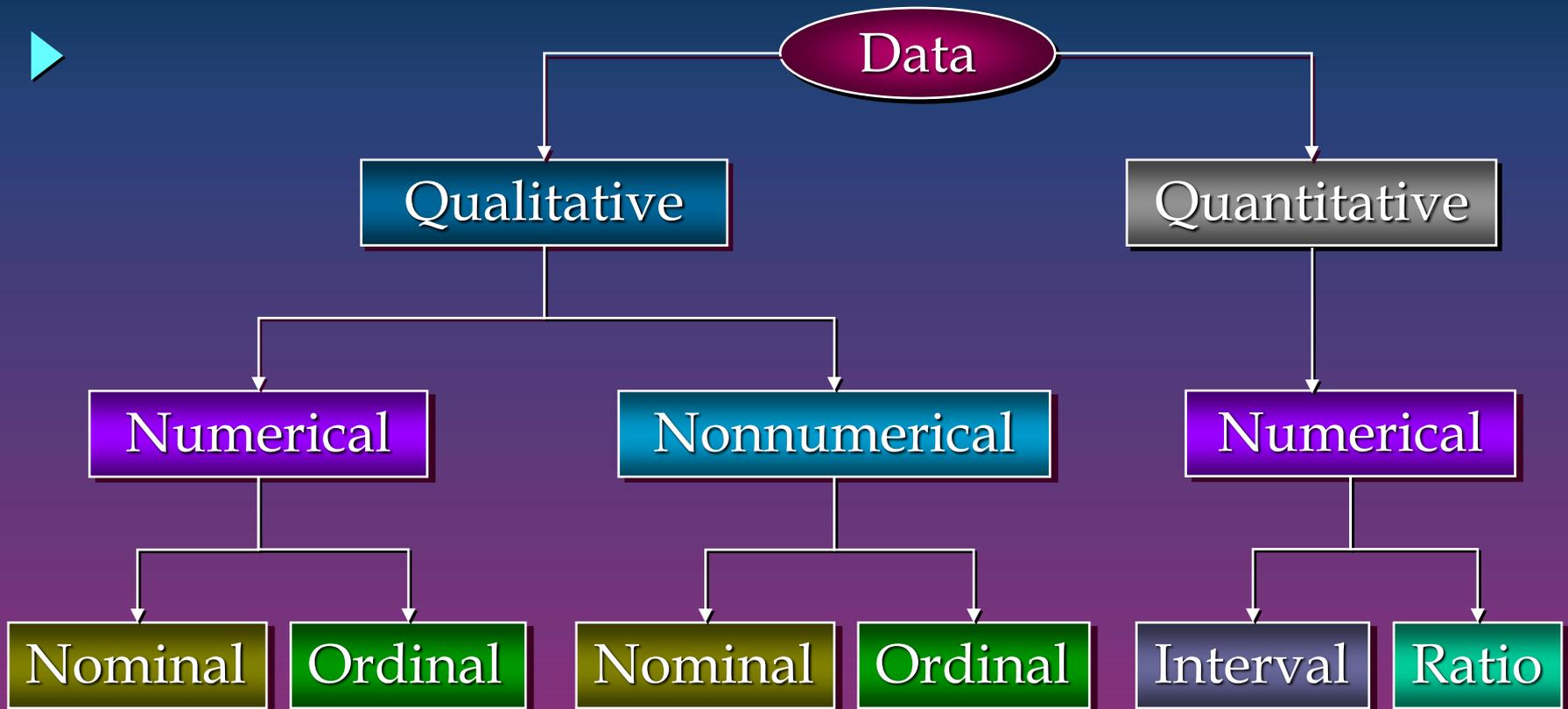
# Qualitative Data

- ▶ Labels or names used to identify an attribute of each element
- ▶ Often referred to as categorical data
- ▶ Use either the nominal or ordinal scale of measurement
- ▶ Can be either numeric or nonnumeric
- ▶ Appropriate statistical analyses are rather limited

# Quantitative Data

- ▶ Quantitative data indicate how many or how much:
  - discrete, if measuring how many
  - continuous, if measuring how much
- ▶ Quantitative data are always numeric.
- ▶ Ordinary arithmetic operations are meaningful for quantitative data.

# Scales of Measurement



# Cross-Sectional Data

- ▶ Cross-sectional data are collected at the same or approximately the same point in time.
- ▶ Example: data detailing the number of building permits issued in June 2003 in each of the counties of Ohio

# Time Series Data

- ▶ Time series data are collected over several time periods.
- ▶ Example: data detailing the number of building permits issued in Lucas County, Ohio in each of the last 36 months

# Data Sources

## ■ Existing Sources (often called secondary data)

- ▶ Within a firm – almost any department
- ▶ Business database services – Dow Jones & Co.
- ▶ Government agencies – U.S. Department of Labor
- ▶ Industry associations – Travel Industry Association of America
- ▶ Special-interest organizations – Graduate Management Admission Council
- ▶ Internet – more and more firms

# Data Sources

## ■ Statistical Studies (often called primary data)

▶ In experimental studies the variables of interest are first identified. Then one or more factors are controlled so that data can be obtained about how the factors influence the variables.

▶ In observational (nonexperimental) studies no attempt is made to control or influence the variables of interest.

a survey is a good example

# Data Acquisition Considerations

## ▶ Time Requirement

- Searching for information can be time consuming.
- Information may no longer be useful by the time it is available.

## ▶ Cost of Acquisition

- Organizations often charge for information even when it is not their primary business activity.

## ▶ Data Errors

- Using any data that happens to be available or that were acquired with little care can lead to poor and misleading information.

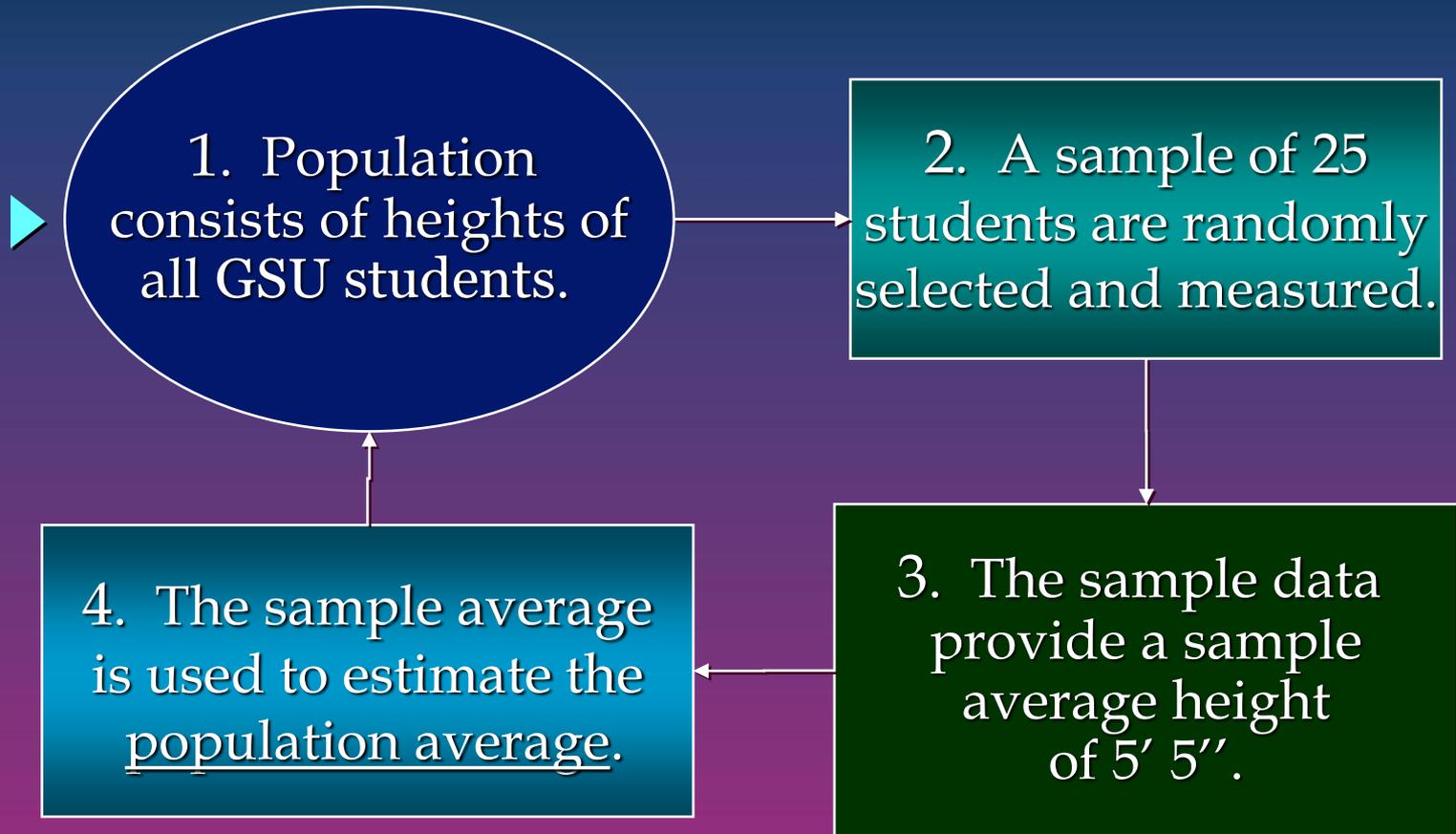
# Descriptive Statistics

- Descriptive statistics are the tabular, graphical, and numerical methods used to summarize data.
- Examples
  - Frequency table
  - Histogram
  - Mean
  - Variance

# Statistical Inference

- ▶ **Population** – the set of all elements of interest in a particular study
- ▶ **Sample** – a subset of the population
- ▶ **Statistical inference** – the process of using data obtained from a sample to make estimates and test hypotheses about the characteristics of a population
- ▶ **Census** – collecting data for a population
- ▶ **Sample survey** – collecting data for a sample

# Process of Statistical Inference: example



## In-class exercise

- Q21 (old book: p24; new book: p26)
- Q22 (old book: p24 or see below)
  
- Q22. In the fall of 2003, Arnold Schwarzenegger challenged Governor Gray Davis for the governorship of California. A Policy Institute of California survey of registered voters reported Arnold Schwarzenegger in the lead with an estimated 54% over the vote (*Newsweek*, September 8, 2003).
  - a. **What was the population of this survey?**
  - b. **What was the sample for this survey?**
  - c. **Why was a sample used in this situation? Explain.**

# Comparison between Excel and SPSS

## ■ Excel

- Good at data manipulation, such as transpose, transformation, etc.
- Powerful graph
- Easy to use
- Not for serious statistical use (data limit, lack of statistical functions, etc.)

## ■ SPSS

- Widely used statistical software in research community
- More comprehensive statistical package than Excel
- Easy to use
- Often Excel and SPSS are used together. Data can be shared between Excel and SPSS easily.
- Excel is often used due to its flexible graphic ability.

# Lecture no.7

# Thermal Methods

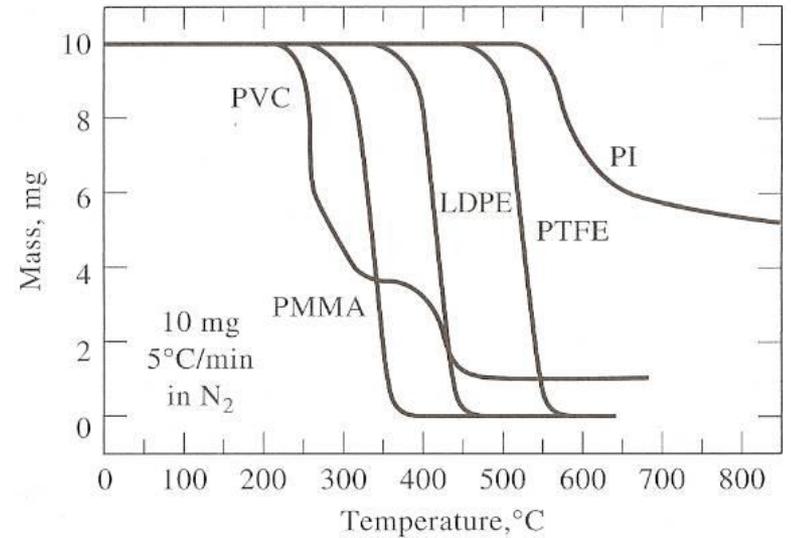
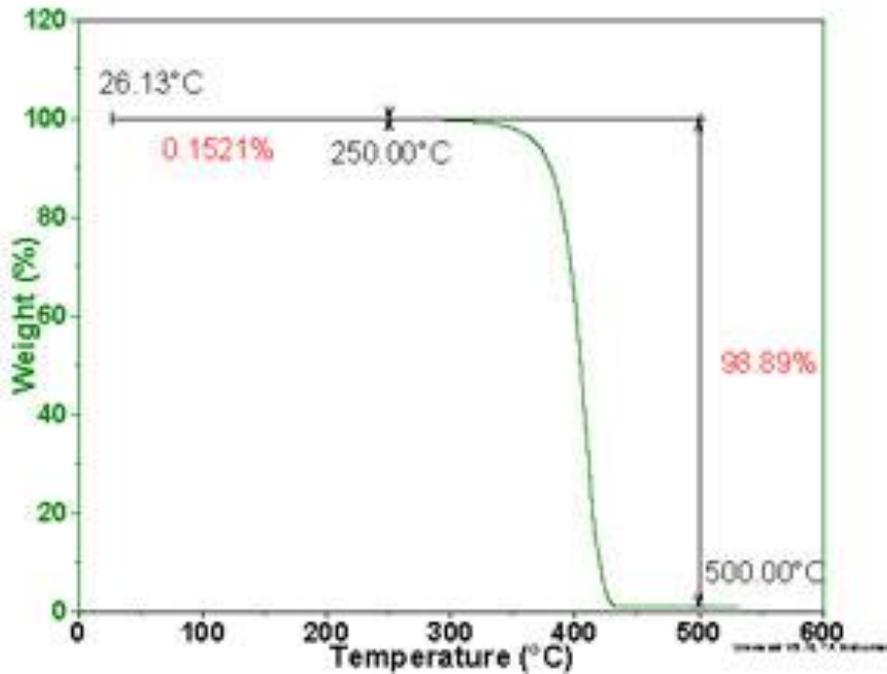
- **Theory**
- **Instrumentation**
- **Thermal methods**
  - **Physical properties of a substance are evaluated as a function of temperature**
    - May include reaction products
    - Temperature is controlled
  - **Methods**
    - Thermogravimetry
    - Differential thermal analysis
    - Differential scanning calorimetry

# Thermogravimetric (TGA)

- **Thermogravimetry is one of the oldest thermal analytical procedures**
  - **has been used extensively in the study of polymeric systems**
- **involves monitoring the weight loss of the sample in a given atmosphere as a function of temperature**
  - **N<sub>2</sub>, O<sub>2</sub>, air, He**
  - **Ambient to 1000 °C**
  - **Can record the first derivative of the mass loss**

# Thermogravimetric

- **MS can be coupled to TGA**
  - **On line analysis**
  - **Evolution of gas**
- **evaluation of the thermal decomposition kinetics of materials**
  - **Polymers**
  - **Resins**
  - **rubbers**
  - **provides information on thermal stability**
- **provide information on the bulk composition of compounds**
  - **Oxidation**
  - **heat resistance**
  - **the amount of water**
  - **compositional analysis**
  - **measurement of ash content in a sample**



**Figure 31-3** Thermograms for some common polymeric materials. PVC = polyvinyl chloride; PMMA = polymethyl methacrylate; LDPE = low density polyethylene; PTFE = polytetrafluoroethylene; PI = aromatic polypyromellitimide. (From J. Chiu, in *Thermoanalysis of Fiber-Forming Polymers*. R. F. Schwenker, Ed., p. 26. New York: Interscience, 1966. Reprinted by permission of John Wiley & Sons, Inc.)

# Analysis of Resin

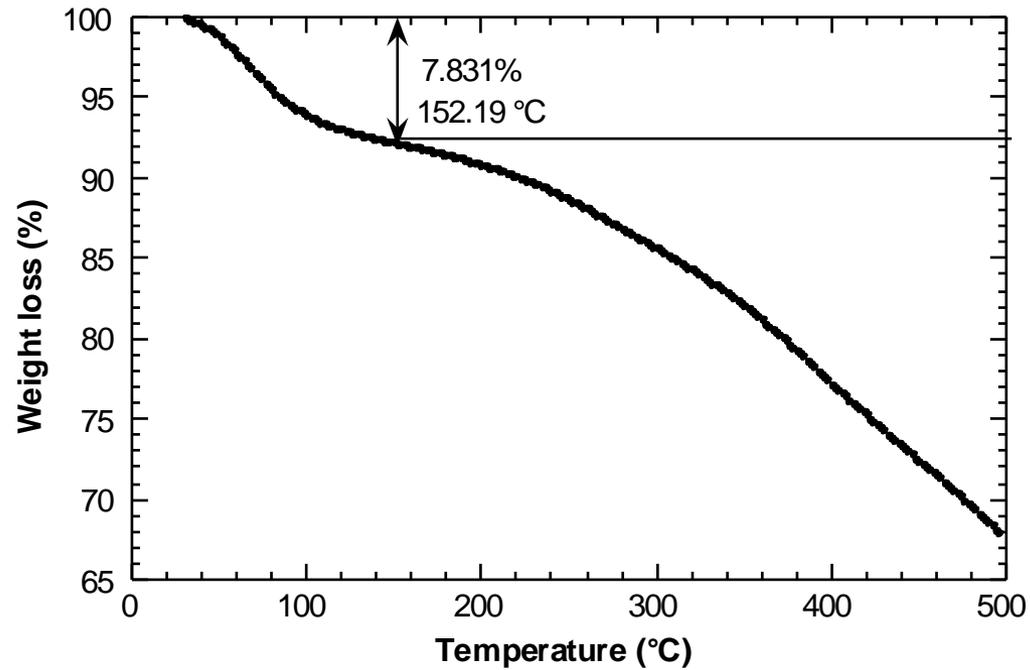


Table 10. Phenomenological data on the thermal decomposition of the phenolic resins

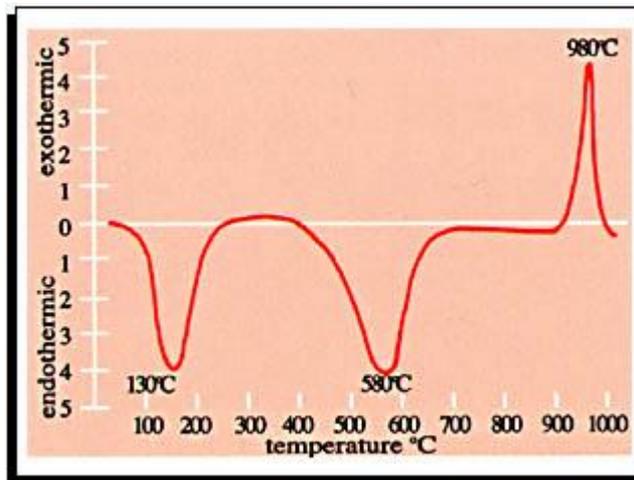
Resin	T <sub>1</sub> , °C	T <sub>2</sub> , °C	Weight loss at 500°C, %
PF	241.62	-	17
CF	148.84	-	40
RF	152.19	-	32
CQF	145.48	221.53	30
RQF	155.54	292.51	24

Table 11. Phenomenological data on the thermal decomposition of the metal complexes of phenolic resins

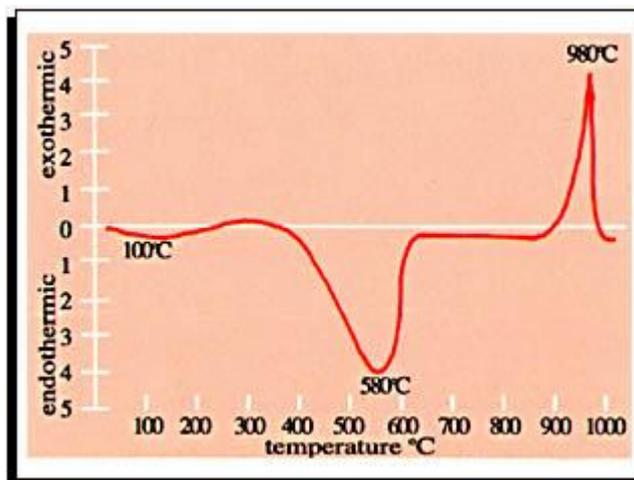
Resin complex	T <sub>1</sub> , °C	T <sub>2</sub> , °C	T <sub>3</sub> , °C	T <sub>4</sub> , °C	Weight loss at 500°C, %
PF-Eu	243.42	-	-	-	18
CF-Eu	172.31	445.06	-	-	29
RF-Eu	193.55	457.36	-	-	32
CQF-Eu	163.37	290.80	361.22	431.65	25
RQF-Eu	172.31	300.00	361.22	451.77	26

# Differential thermal analysis

- temperature difference between a substance and a reference material is measured as a function of temperature
  - substance and reference material are subjected controlled temperature
    - emissions of heat (exothermic)
    - absorptions of heat (endothermic)
      - \* comparison with a passive material such as alumina
- Can be used to identify samples
  - Clay materials
- Peak areas depend upon sample mass and enthalpy
  - $A = -kGm\Delta H$ 
    - A = peak area, G is geometry factor, k is constant related to thermal conductivity

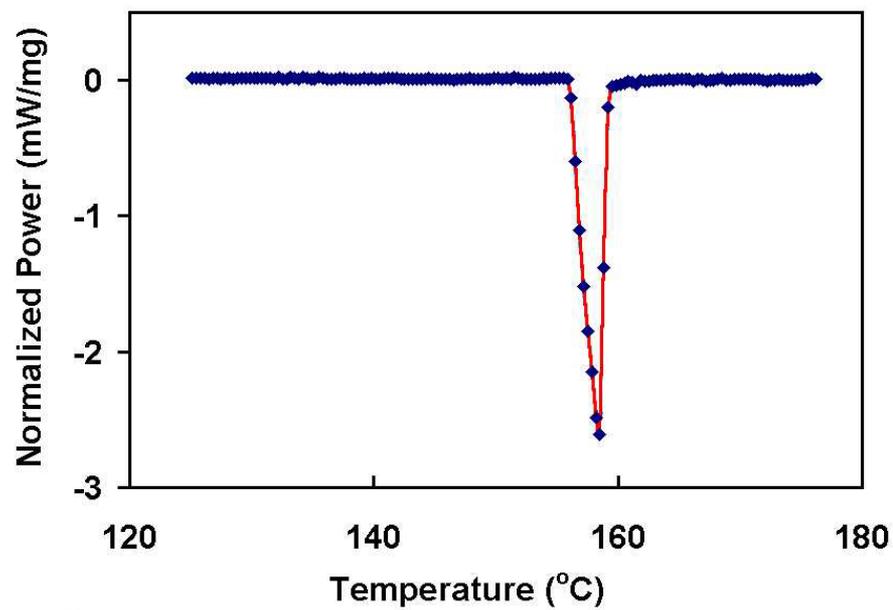


## New Zealand Halloysite. Premium

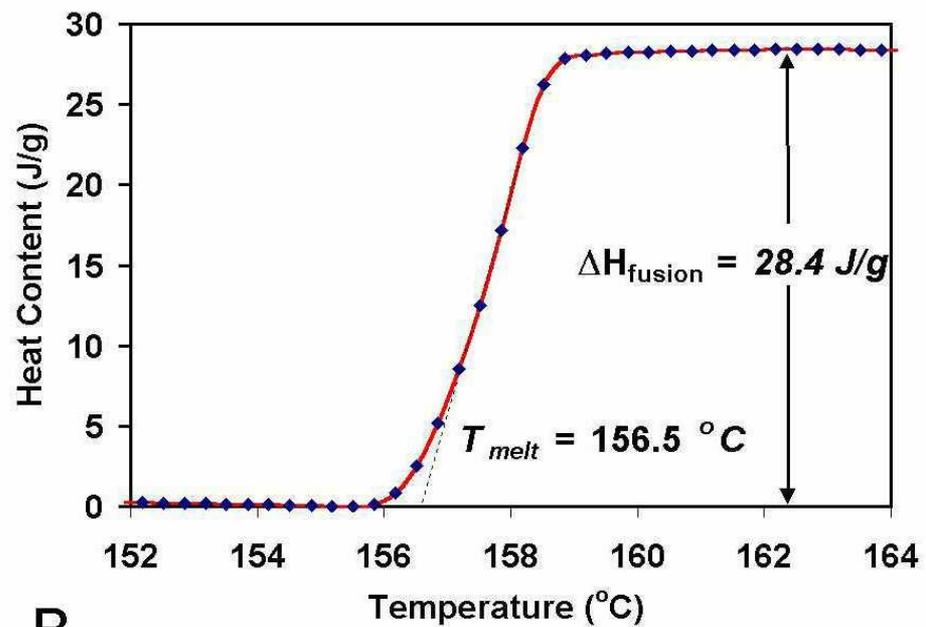


# Differential Scanning Calorimetry

- Differences in heat flow are measured as a function of temperature
  - **Sample and reference**
    - Energy difference measured
- Power Compensated DSC
  - **Two furnaces**
  - **Heat flow evaluated**
  - **Difference in power input monitored**
    - In watts
- Useful for glass transition temperatures
- Purity of drug samples



A



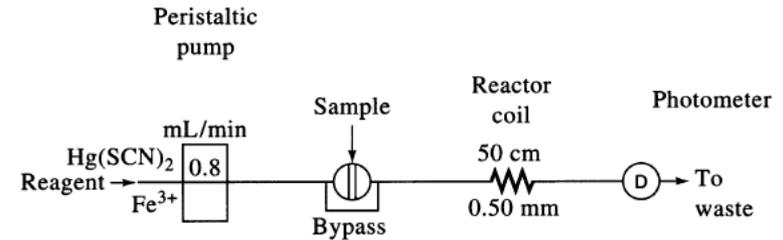
B

# Automated methods

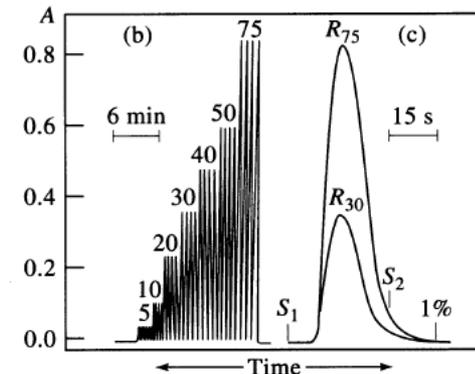
- **Automatic**
  - **No feedback**
- **Automated**
  - **Includes feedback**
- **Different methods**
  - **Discrete/batch**
    - sample remains isolated throughout
  - **Continuous**
    - sample introduced into stream
      - \* **Simpler instrumentation**
      - \* **more efficient**

# Flow Injection Analysis

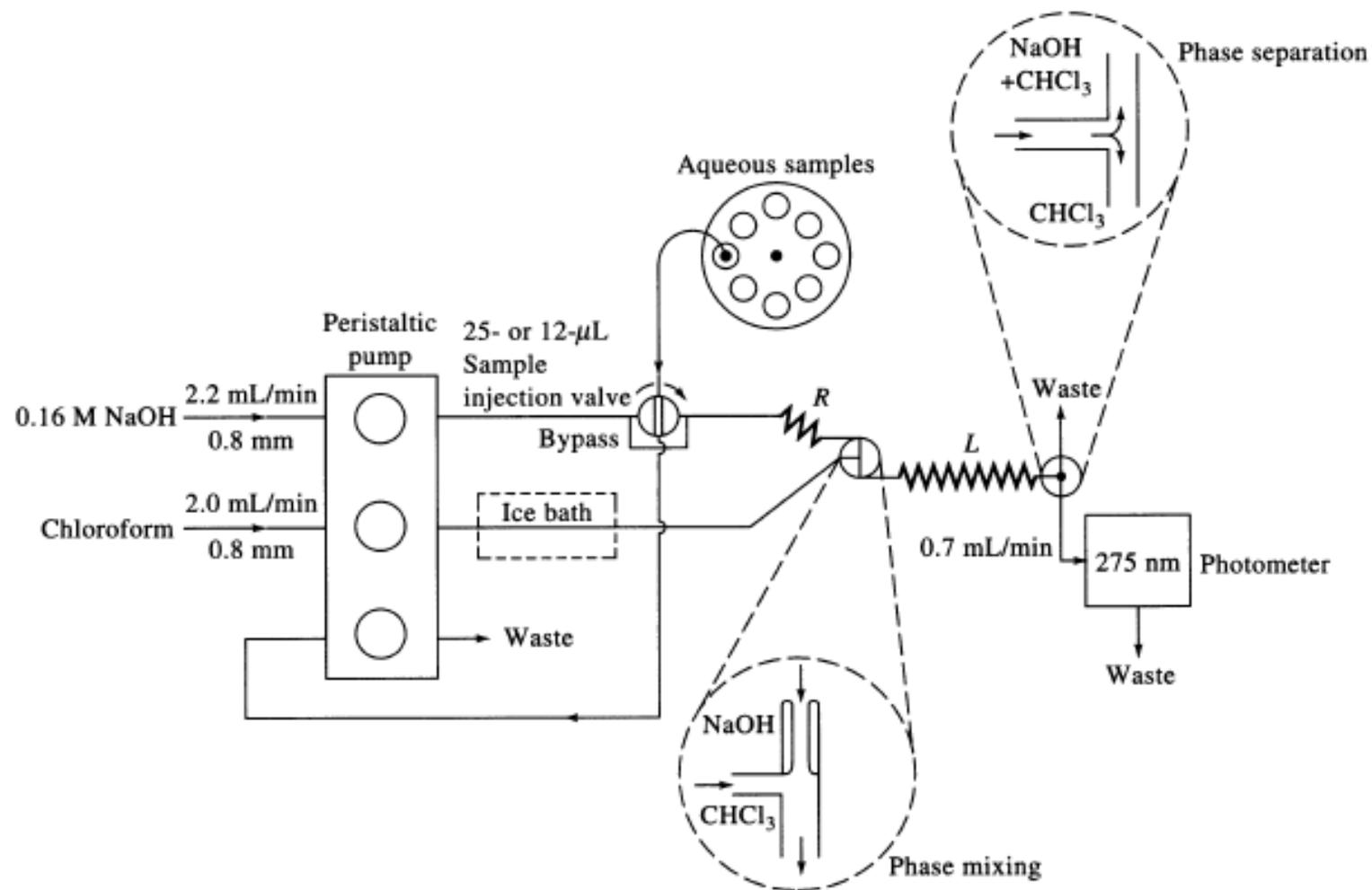
- Samples carried by flow
- Flow can have chromatographic properties
  - Good behavior in system



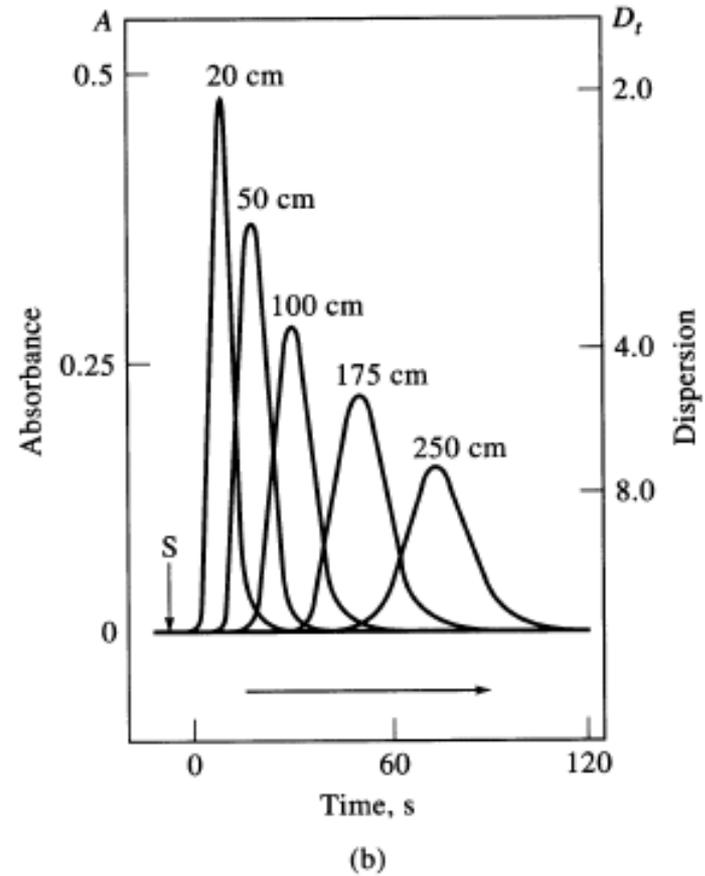
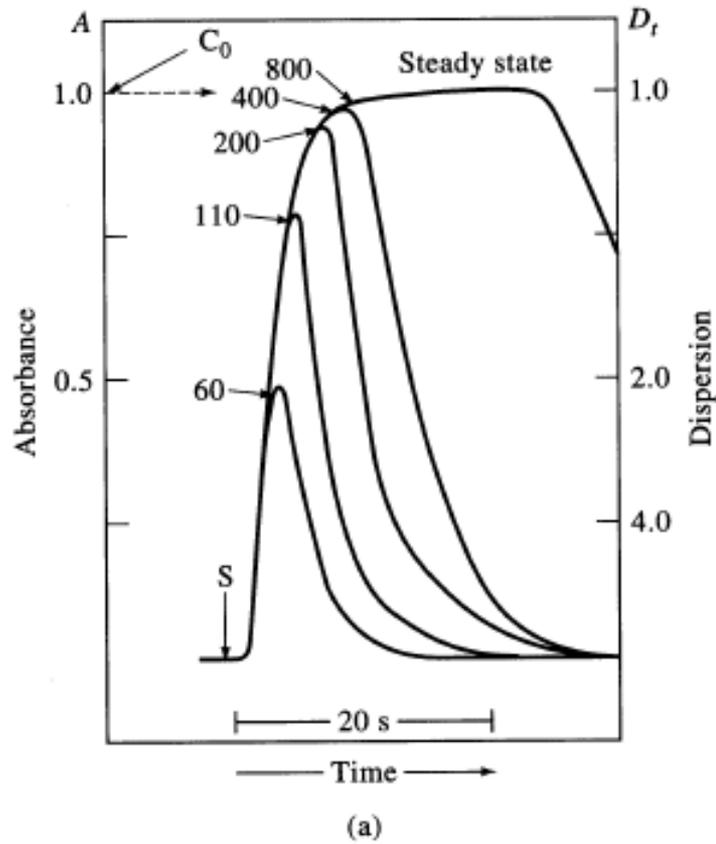
(a)



(b)



# Diffusion processes



# Lecture no.8

# **X-Ray**

**Slide Show 1:**

**Some Background Concepts**

**This slide show will examine:**

- 1. The formation of X-rays**
- 2. X-ray spectra**

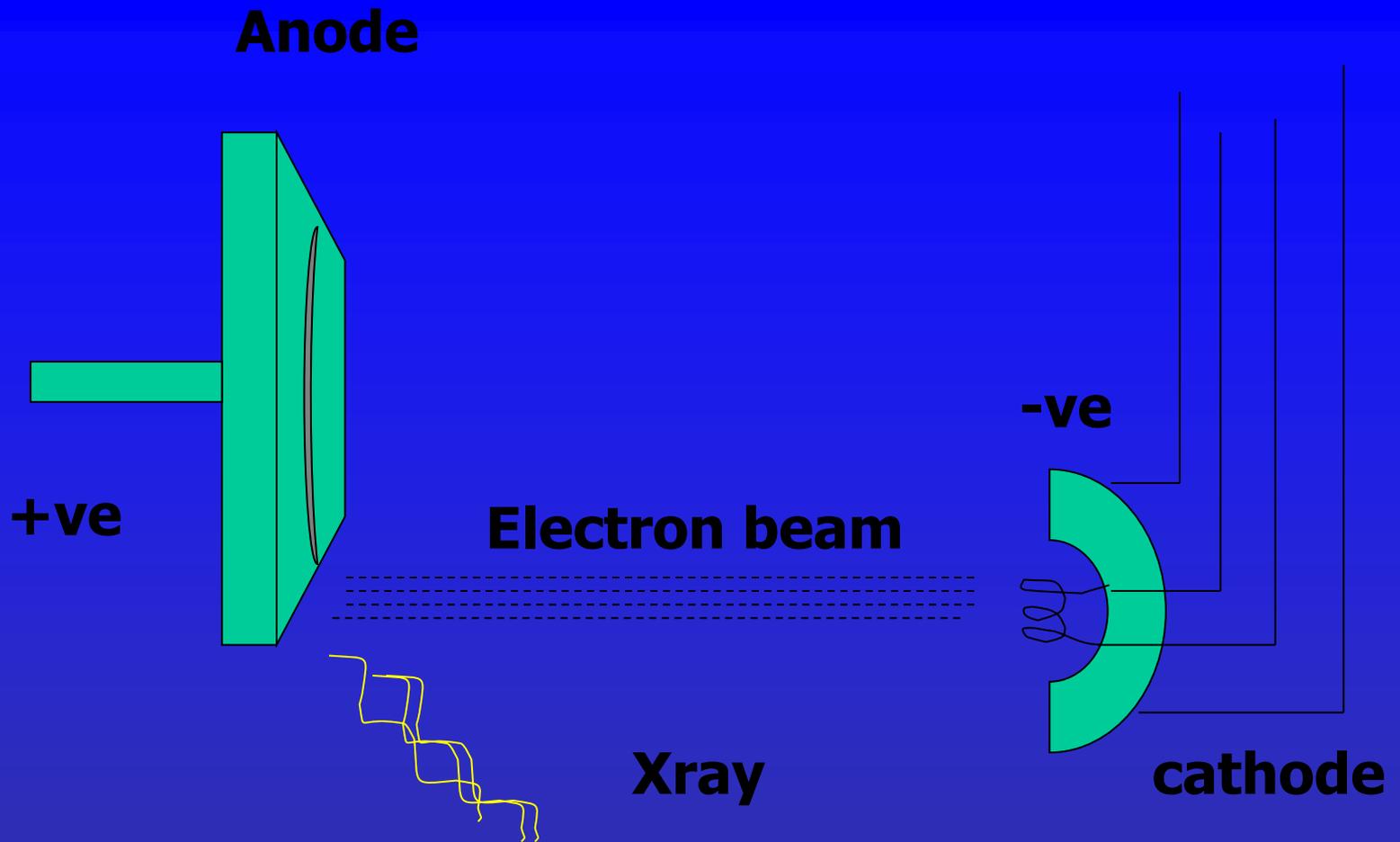
# **X-rays**

**X-rays and gamma rays are both forms of ionising radiation. Both are forms of electromagnetic radiation But they differ in their source of origin.**

- X-rays are produced through interactions in electron shells.**
- Gamma rays are produced in the nucleus.**

- **X-rays are sometimes defined as having wavelengths between  $10^{-10}$  and  $10^{-12}$  m. A more robust definition of X-rays, however, is their mode of production.**
- **X-rays are produced through interactions in electron shells**

# The Formation of X-rays



**To produce x-rays projectile electrons are accelerated from the negative cathode to the positive anode.**

**When the electrons from the cathode are accelerated at high voltage to the anode:**

- **99% of the energy is dissipated as heat**

**(anode materials are selected to withstand the high temperatures they are able to withstand)**

- **1% is given off as x-rays.**

**The x-ray radiation is emitted as:**

- **bremsstrahlung x-ray radiation (about 80%)**

**and/or**

- **characteristic x-ray radiation.**

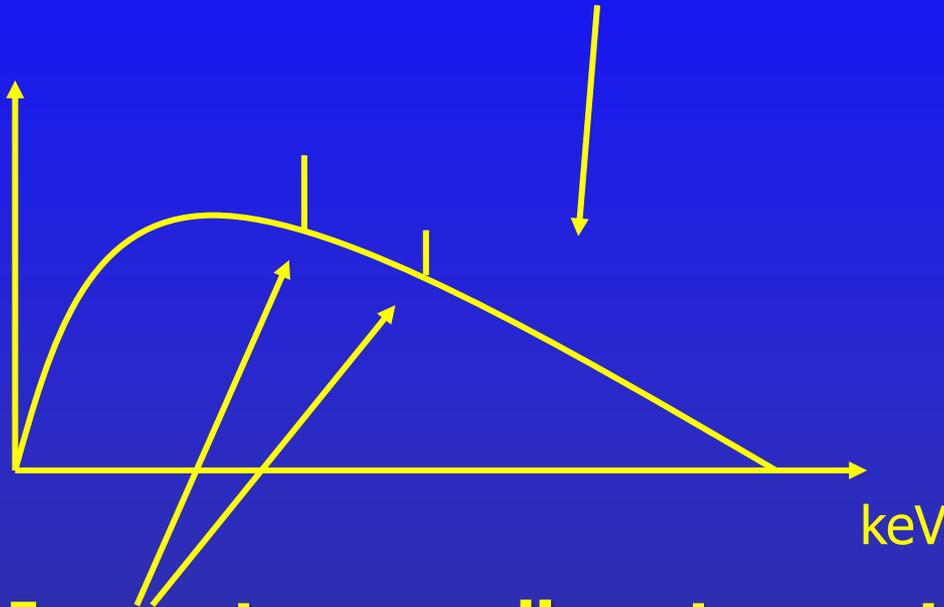
- **The energy of the x-rays (keV) is determined by the voltage applied (kVp).**

- **The amount of x-rays is determined by the current (mA).**

# **X-ray Spectra**

# X-ray spectra are composed of:

## 1. Continuous bremsstrahlung spectra

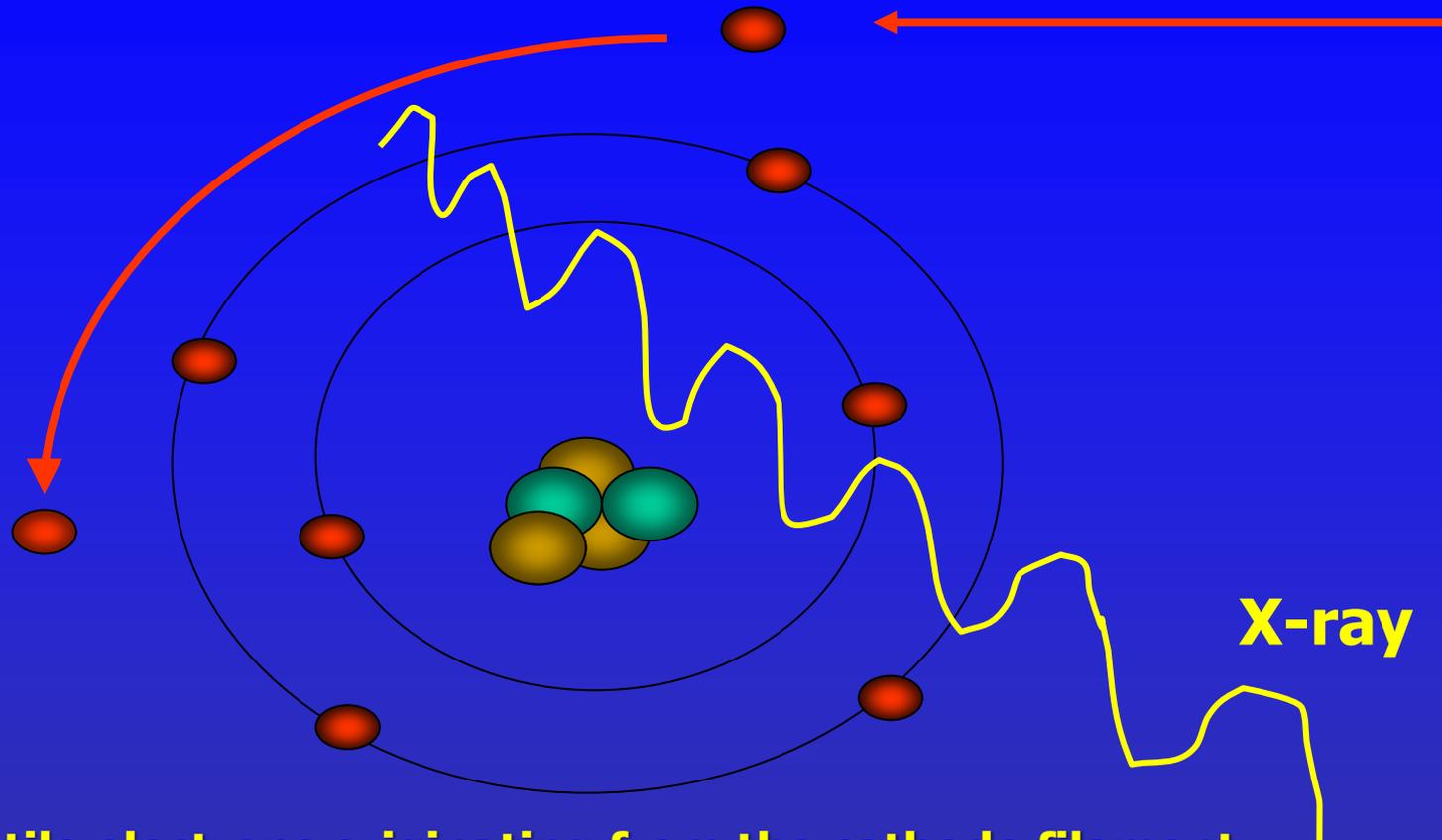


2. In most cases, discrete spectra peaks known as characteristic x-rays.

Bremsstrahlung radiation makes up approximately 80% of the x-ray beam

# **Bremsstrahlung Radiation**

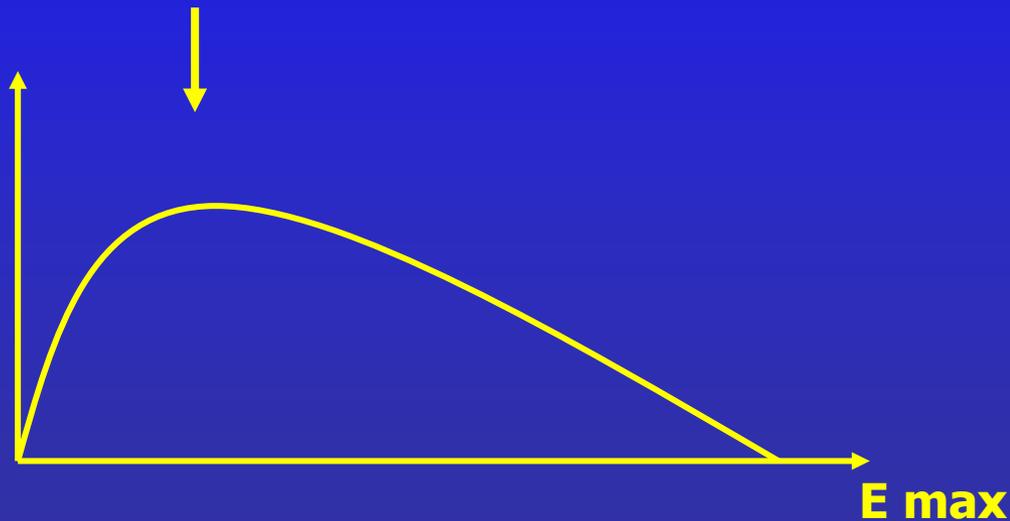
# Bremsstrahlung radiation

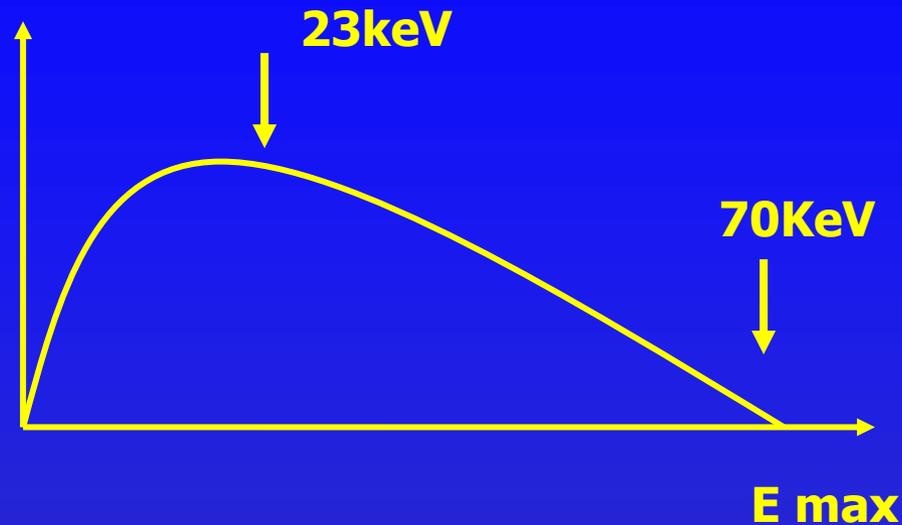


Projectile electrons originating from the cathode filament impinge on atoms in the anode and will often pass close by the nucleus of these atoms.

As the electrons pass through the target atom they slow down, with a loss in kinetic energy. This energy is emitted as x-rays. The process is known as *bremsstrahlung* or "braking energy".

**Bremsstrahlung x-rays form a continuous energy spectra. The frequency distribution is continuous and shows that the Bremsstrahlung process produces more low energy than higher energy x-rays. The average energy is approximately 1/3 of the  $E_{max}$ .**





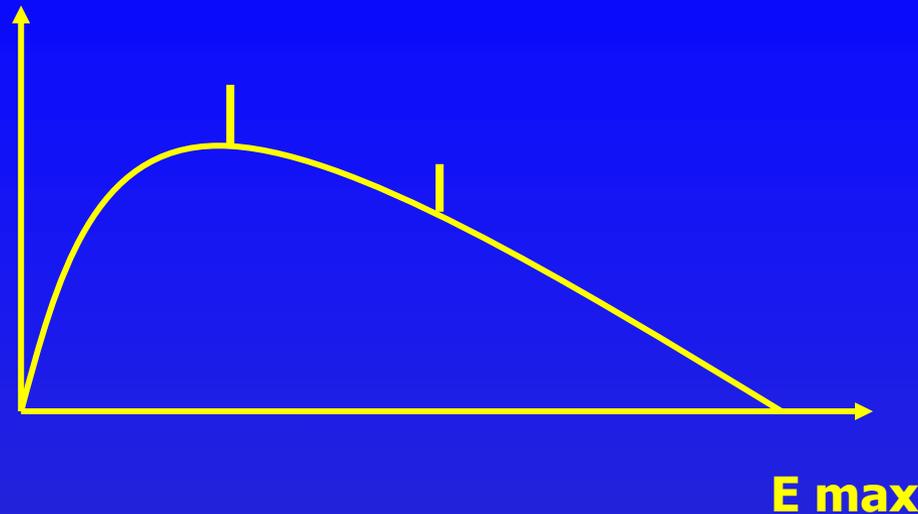
**The  $E_{max}$  or the maximum energy of the x-rays measured as (keV) is equal to voltage applied to the Xray tube (kilovolt peak or kVp).**

**For example:**

**An applied voltage of 70 kVp produces an x-ray spectra with  $E_{max}$  of 70 KeV and average energy of about 23 keV.**

# Characteristic X-ray Radiation

# Characteristic X rays

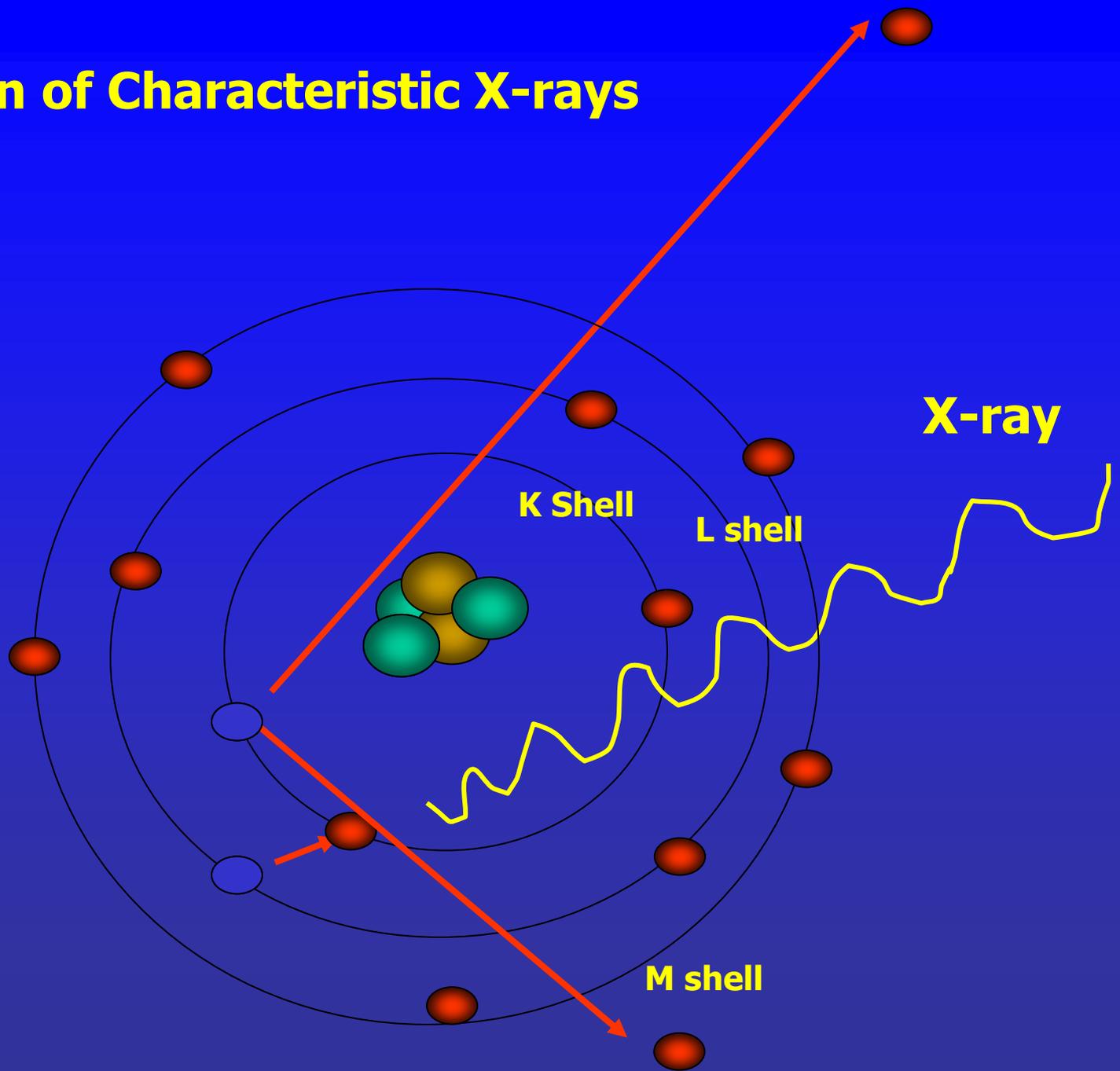


**To produce characteristic x-rays the projectile electrons must have sufficient energy to displace orbital electrons**

- **If the projectile electron has sufficient energy, it may cause the ejection of an orbital electron (usually in the K shell) from an atom in the anode.**
- **An outer shell electron (usually from the L or M shells) fills the vacancy in the inner orbital and sheds energy as an x-ray of characteristic energy.**

- **The most common transition is from L to K shell.**
- **Each shell transition has a characteristic energy and this energy is dependent on the atomic number of the atom.**
- **M-to-K transitions are less common and are of higher energy.**
- **For tungsten the characteristic Xray spectra are represented by peaks at 58 and 69 keV representing L-to-K and M-to-K shell transitions respectively.**

# Production of Characteristic X-rays

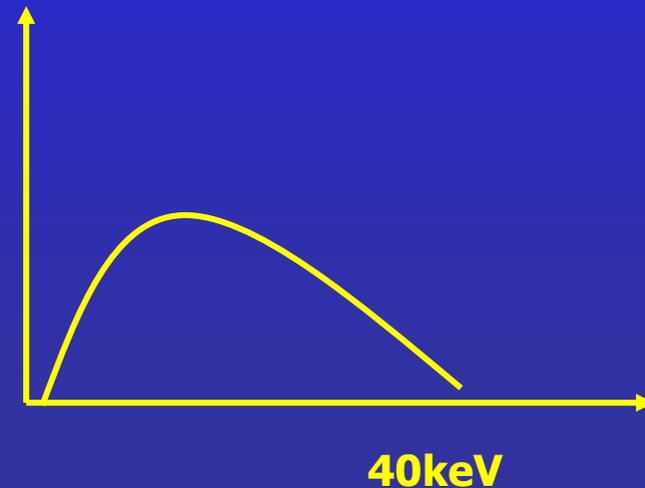
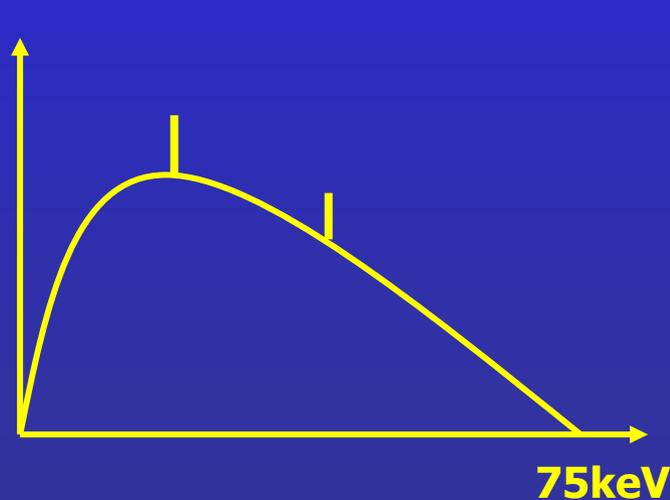


**Note that the impinging electron from the cathode must have sufficient energy to displace the K shell electron of the anode.**

**This energy is the excitation energy of the electron shells and the energy is characteristic for each and each element**

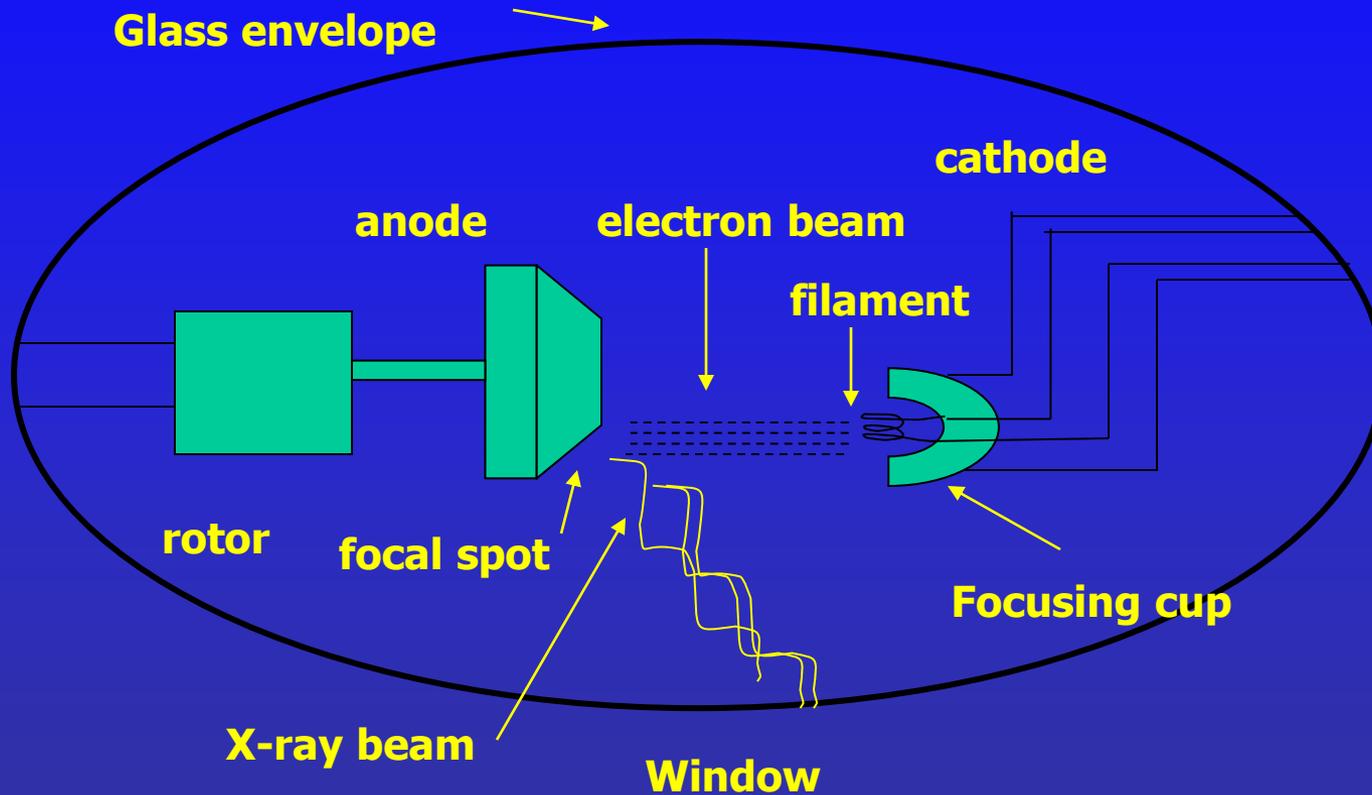
**For a tungsten anode the electrons from the cathode must have at least 69.5 keV to dislodge a K shell electron.**

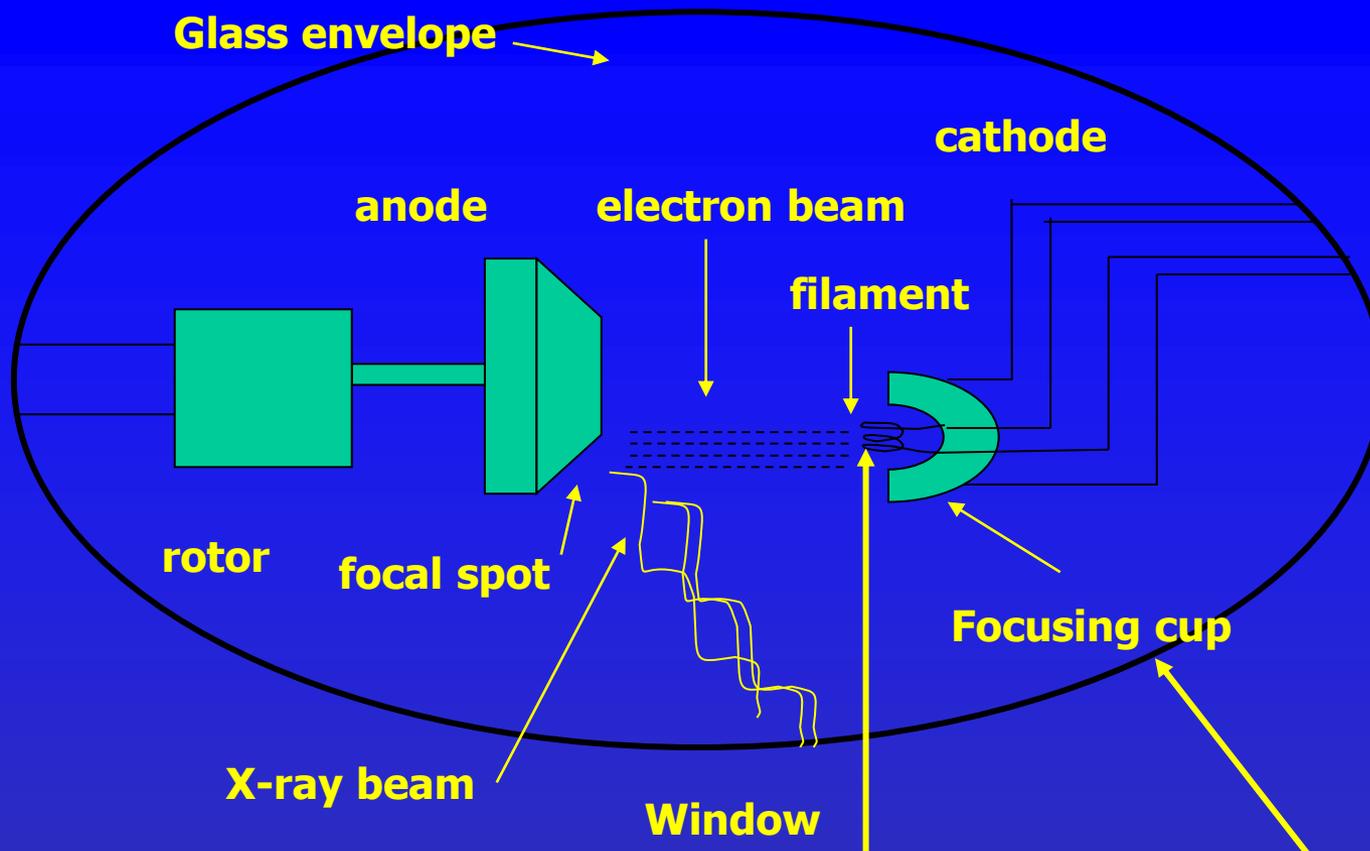
**Consequently no lines will appear if the x-ray tube with a tungsten anode is operated at 20 kVp or 40 kVp**



**Note that characteristic X ray spectra are independent of voltage once the threshold values have been reached**

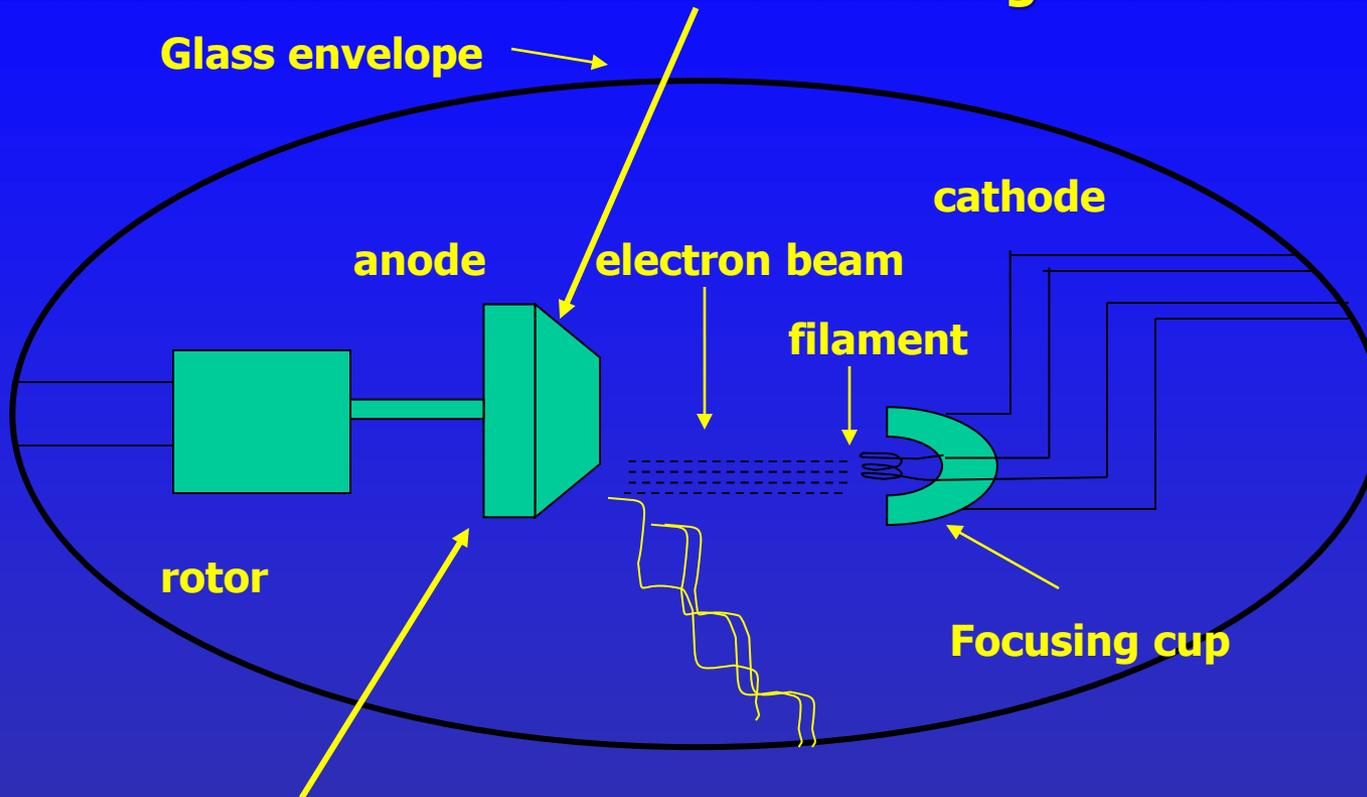
# A Schematic X ray Tube





- The filament is heated to boil off electrons which are then accelerated to the anode
- The filament is contained within the cathode which is cup shaped to focus the electrons onto the focus spot on the anode
- Tube currents of 50-800 mill amperes are used whereas filament currents are in the range of 2-5 amperes

- The anode is bevelled at an angle of 12 to 17 degrees in order to maximise the contact area while focussing the resultant beam



- The anode is usually composed of tungsten or molybdenum as it must withstand very high temperatures (>3000 degrees C)
- Correct warm up and stand by procedures are essential to maximise tube and filament life

**End of Section 1**

**Why not test your understanding  
using the quiz booklet**

## **Slide Show 2:**

**Factors affecting x-ray beam  
quality and quantity**

**This slide show will examine:**

**The factors that affect the quantity of x-rays  
and their characteristics**

- **The energy of the x-rays is determined by the voltage applied.**

- **The amount of x-rays is determined by the current.**

# **Factors affecting x-ray beam quality and quantity**

- **Anode material**
- **Voltage applied (kVp)**
- **Tube Current (mA)**
- **Filters used**

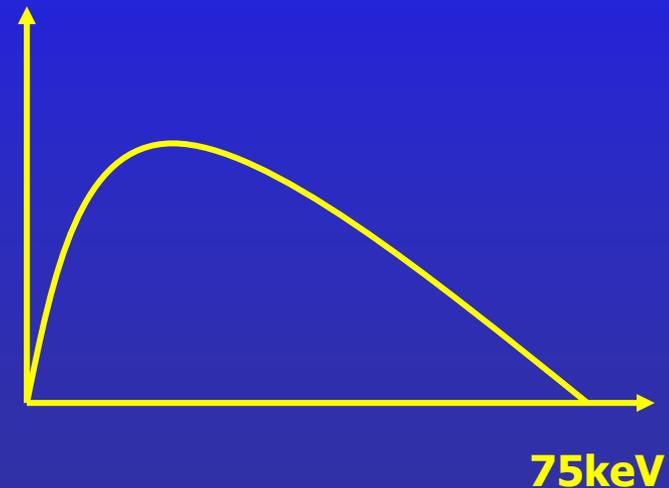
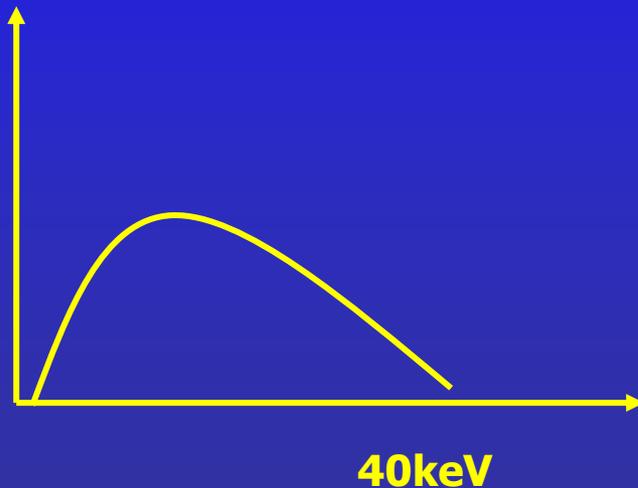
# **1. Anode material**

**Different anode materials will produce different characteristic x-ray spectra and different amounts of bremsstrahlung radiation.**

## 2. Voltage (kVp)

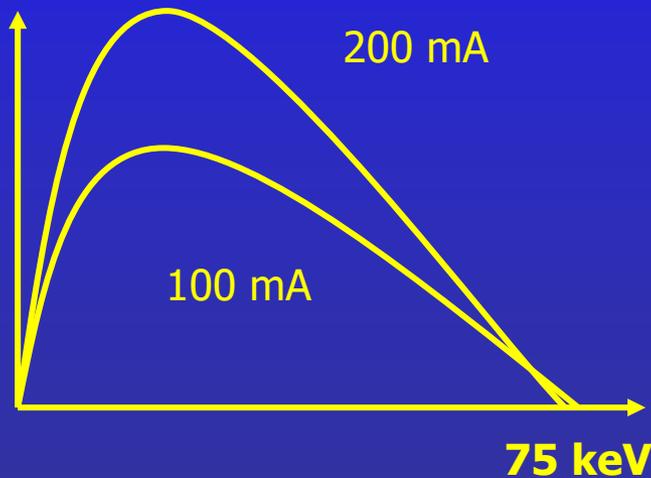
**Note that increasing the applied voltage or kVp will increase the maximal energy, the average energy and the intensity of the x-rays.**

**Characteristic x rays do not change with a change in kVp**



### 3. Tube current (mA)

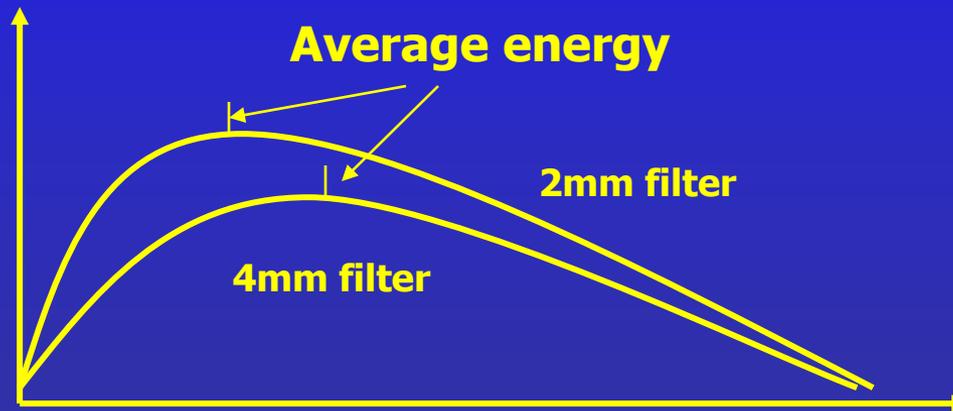
Increasing the current (ie mA) will not change energy of the beam only the intensity (i.e. the amount) of x-rays. The quantity of x-rays is directly proportional to the tube current.



## 4. Filtration

Often filters of thin aluminium or other metals are used to filter out low energy x-rays.

Filters will increase the average x-ray energy but decreases the intensity. The maximum energy and the characteristic x-rays remain unchanged



# **End of Section 2**

**Why not test your understanding  
using the quiz booklet**

## **Slide Show 3.**

# **Interaction of X-ray Radiation with Matter**

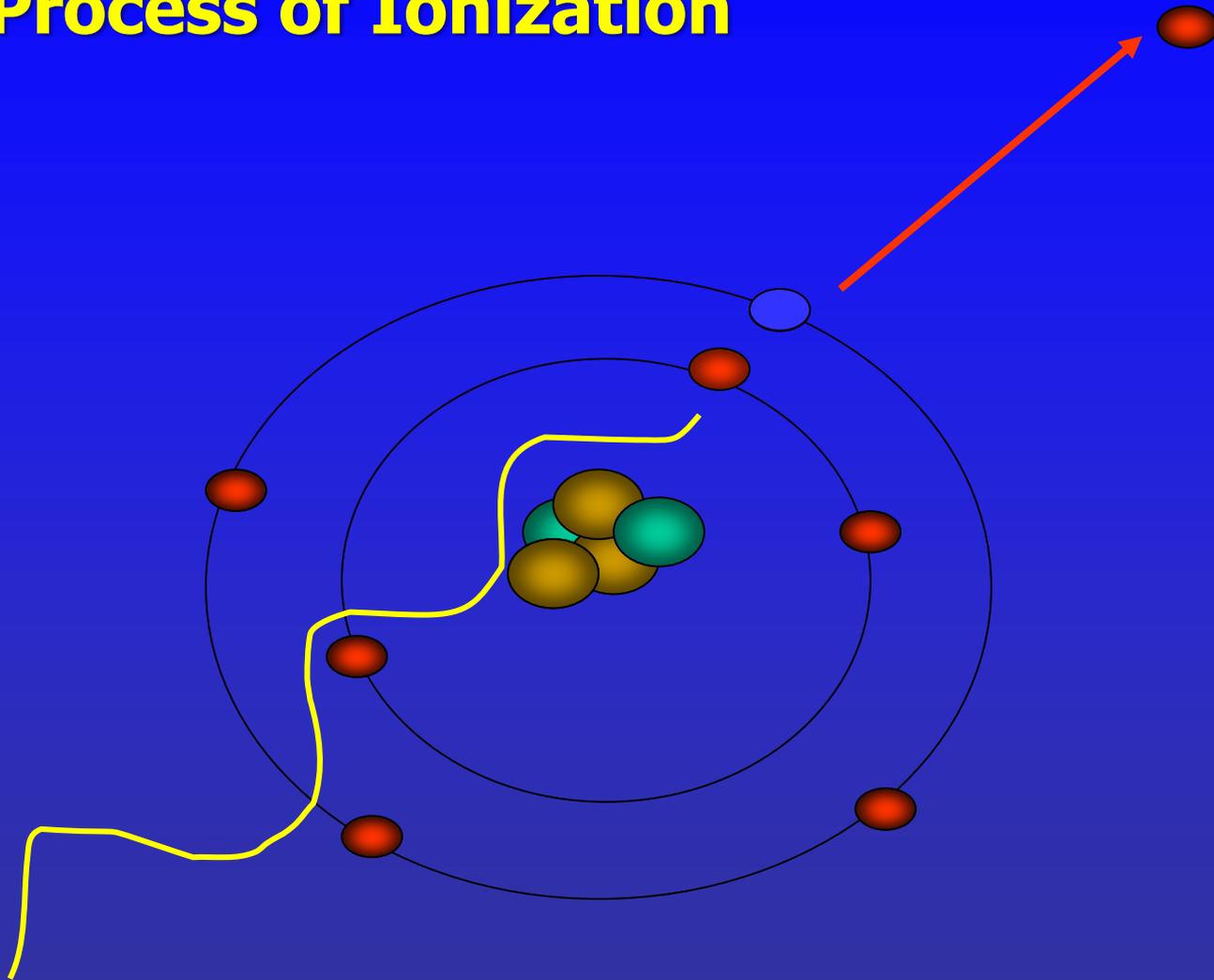
**This slide show will:**

- 1. Examine the energy transfer that accompanies interaction of radiation with matter**
- 2. Examine how x-rays interact with matter and the types of interaction**

# **Interaction of Radiation with Matter (Transfer of Energy)**

- If energy of particle or photon is absorbed - radiation will appear to have stopped**
- If energy not completely deposited in the matter - remaining energy will pass through.**
- If energy is absorbed – ionization is more likely**
- Ionization occurs when the energy transferred is sufficient to eject electron from the incident atom**

# The Process of Ionization



**An Ion Pair is created**

# **Slide Show 3:**

## **How X-rays Interact with Matter**

**This slide show will:**

**Examine the 5 types of interactions between  
x-rays and matter**

# **Interaction of X-rays with Matter**

**X-rays are classified as penetrative radiation**

**The penetration of x-rays (or conversely the amount of attenuation) is a function of:**

- energy of the photon**
- atomic number of irradiated matter**
- thickness of irradiated material**
- density of irradiated material**

## Attenuation of X-rays

**X-rays are attenuated as they pass through matter**

**The degree of that any given material is able to attenuate x-rays is a function of its atomic number and its density**

### Half Value Thickness

**It is conventional to refer to measure attenuation in terms of half value thickness**

**i.e. the thickness of material required to reduce an x-ray to half its original intensity**

# Interaction of X-rays with matter

There are five types of interactions:

- *Coherent Scattering*
- *Photoelectric effect* ←
- *Compton scattering* ←
- *Pair production* ←
- *Photodisintegration* ←

With the exception of coherent scattering, all can result in ionisation of tissue

# Interaction of X-rays with matter

Four interactions resulting in ionisation:

- *Photoelectric effect*

X-rays of low energy

X-ray transfers energy to an electron which then ejected

- *Compton scattering*

Dominant in biological materials

X-ray is scattered at angle depending on amount of energy transferred

- *Pair production*

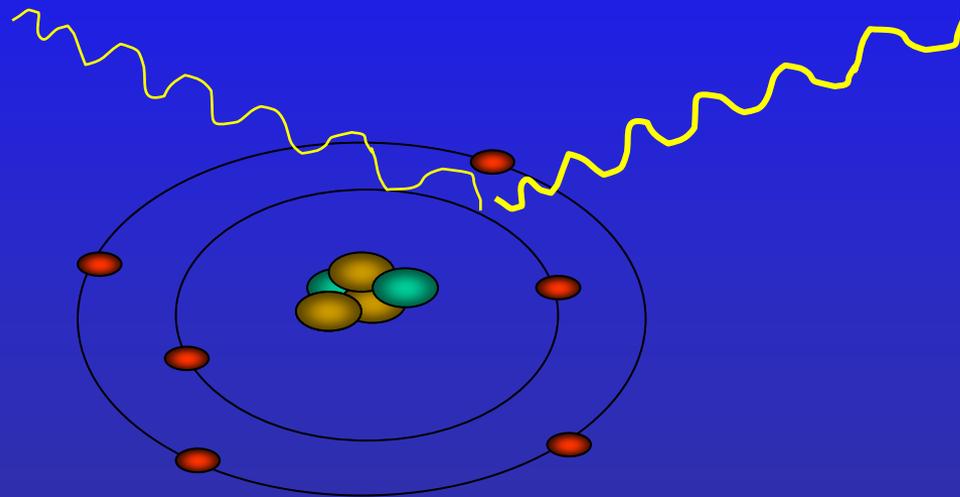
X-rays  $> 1.02\text{MeV}$

- *Photodisintegration*

X-rays  $> 10\text{MeV}$

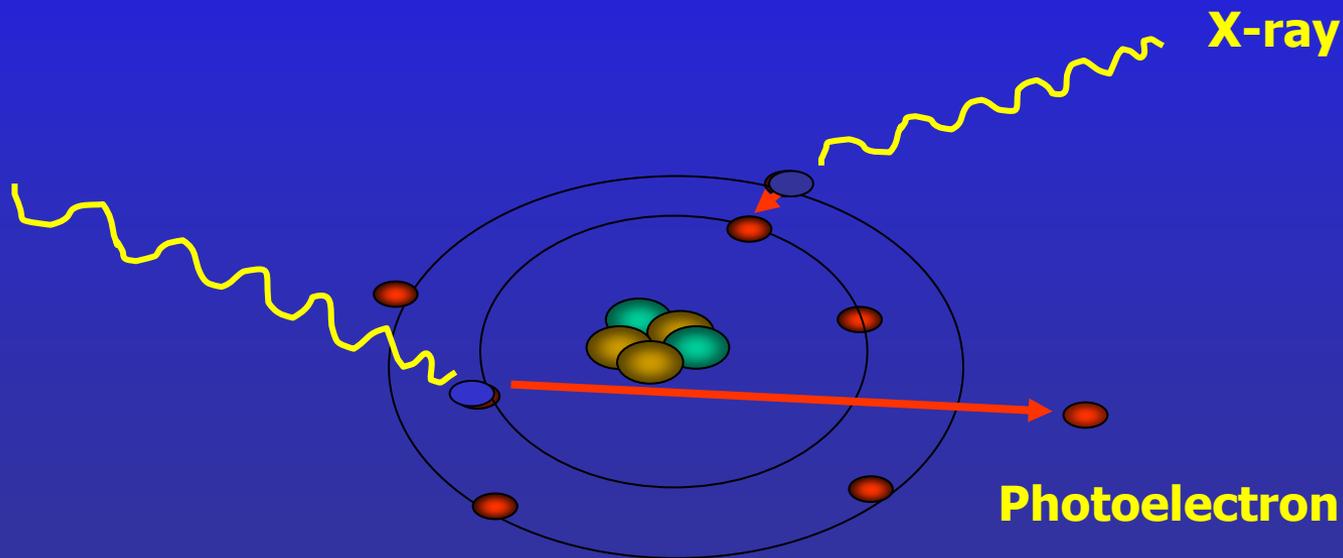
# Coherent scattering

- Also known as Classical or Thompson Scattering
- Change in x-ray direction with no ionisation
- Occurs at energies  $< 10$  keV



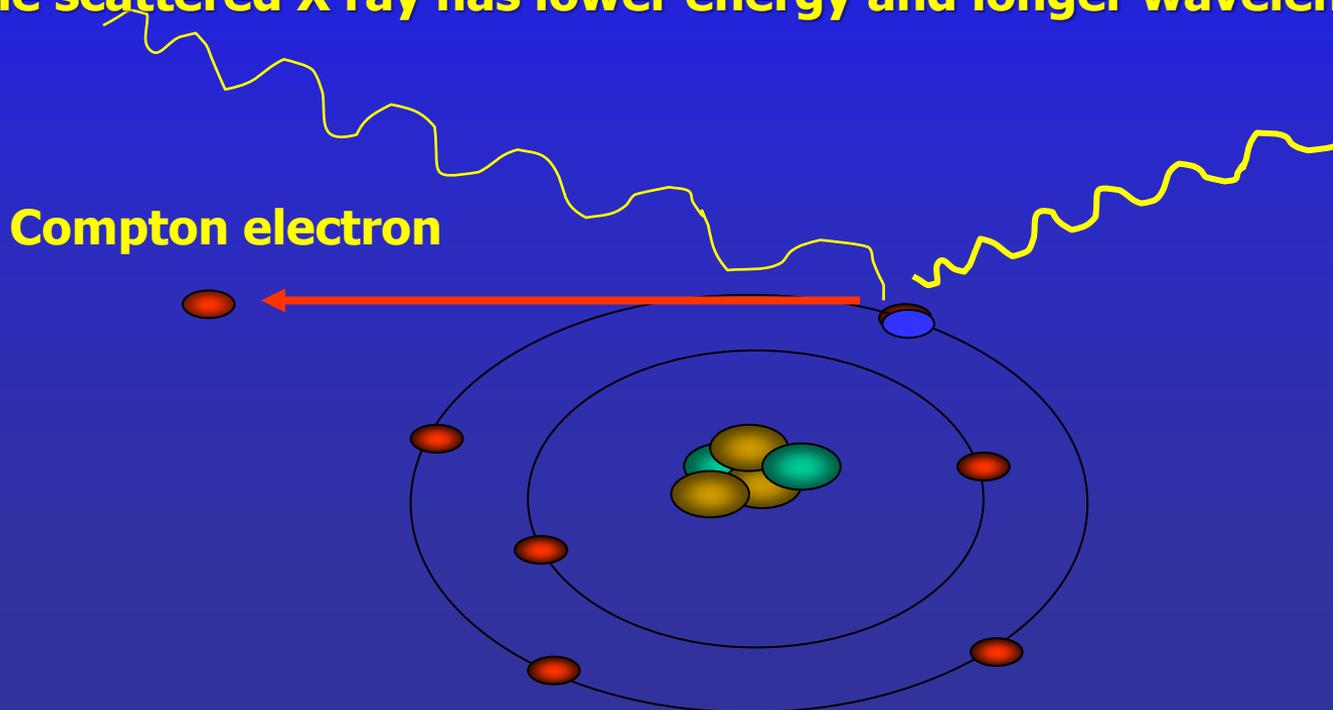
# Photoelectric effect

- X-ray transfers energy to an inner shell electron which then ejected.
- Filling the inner shell electron results in a characteristic x-ray.
- Characteristic x-rays from nitrogen, carbon and oxygen have very low energies.
- The final result is absorption of the x-ray (i.e. there is no exit radiation)



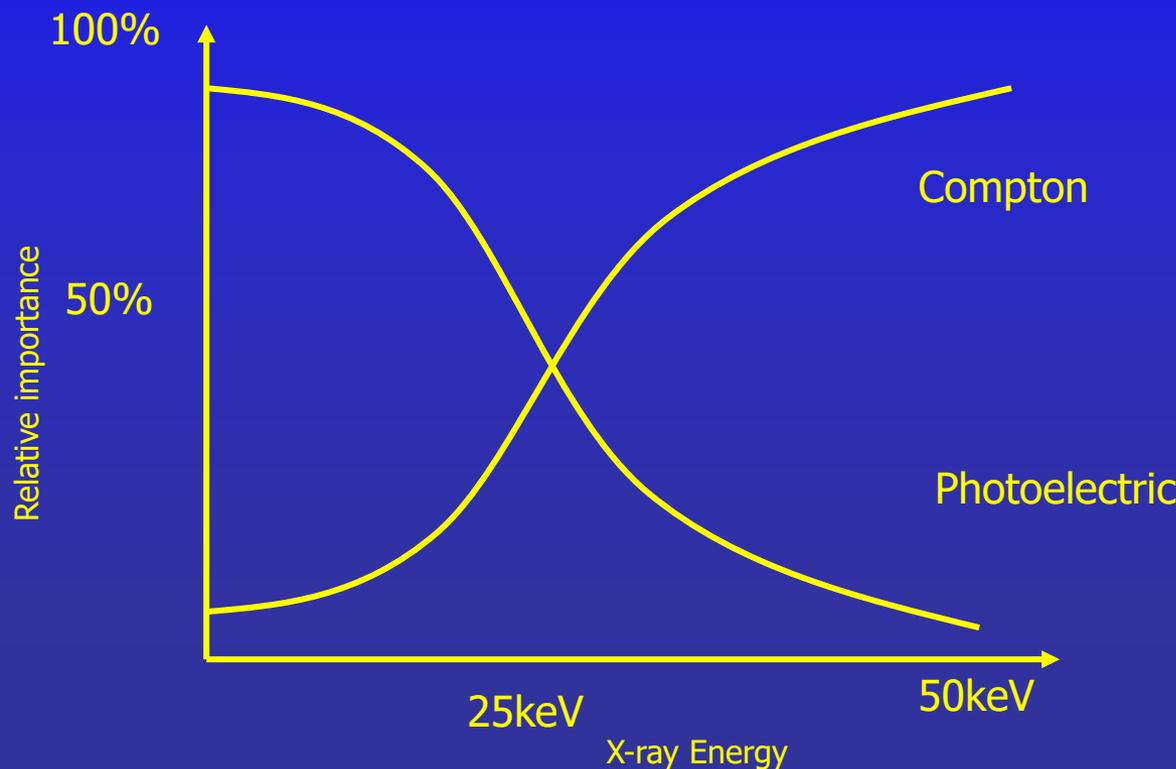
# Compton Scattering

- The incident x-ray is scattered by an outer shell electron which is also ejected (Compton electron)
- The X-ray is scattered at angle depending on amount of energy transferred
- The energy of the incident x-ray is shared between the scattered x-ray and the Compton electron
- The scattered X ray has lower energy and longer wavelength



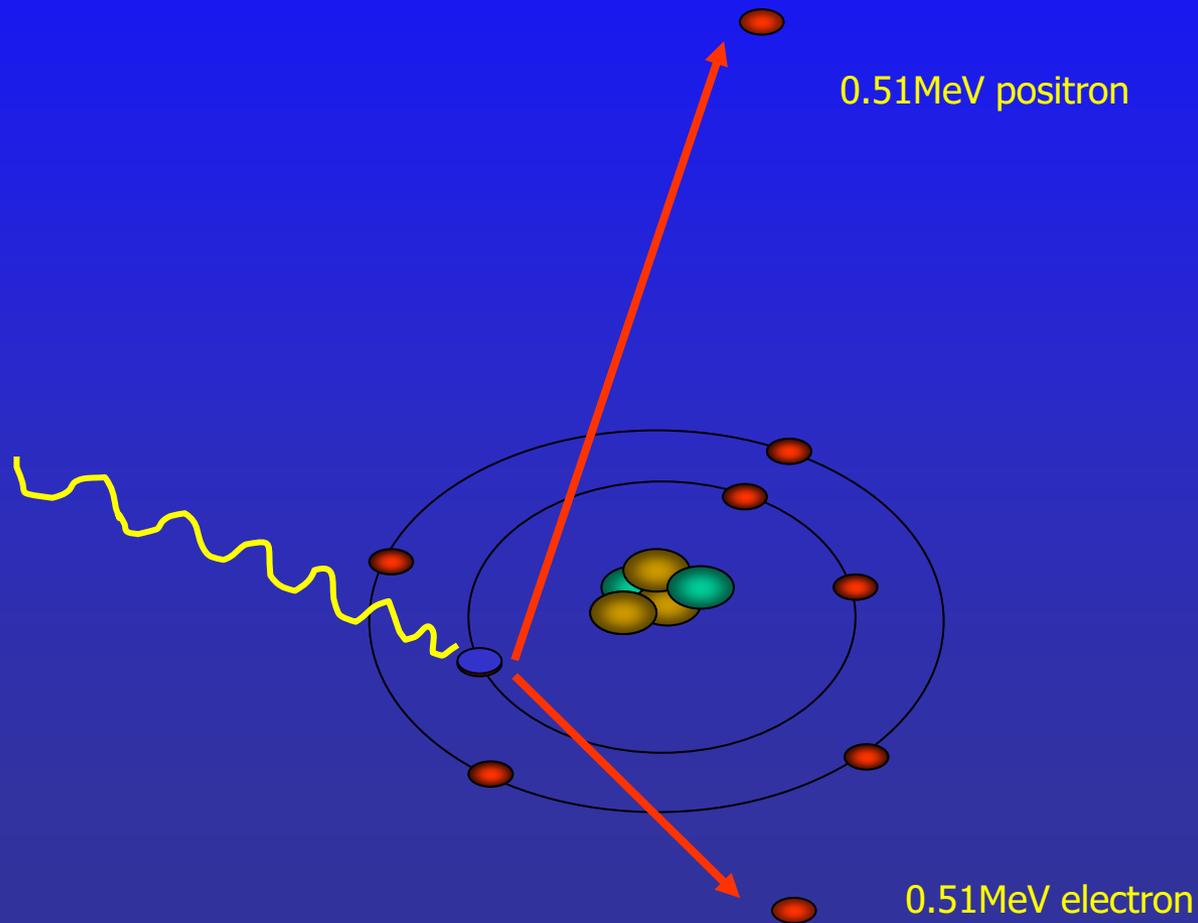
# The Medical Application of the Photoelectric Effect

The photoelectric effect is responsible for most x-ray attenuation in tissue  
Photoelectric attenuation increases with increasing atomic number.  
Bone absorbs 4x the x-ray than tissue at lower x-ray energies  
Photoelectric attenuation also decreases with increasing energy of the x-ray  
Above 26 keV Compton Scattering becomes more dominant



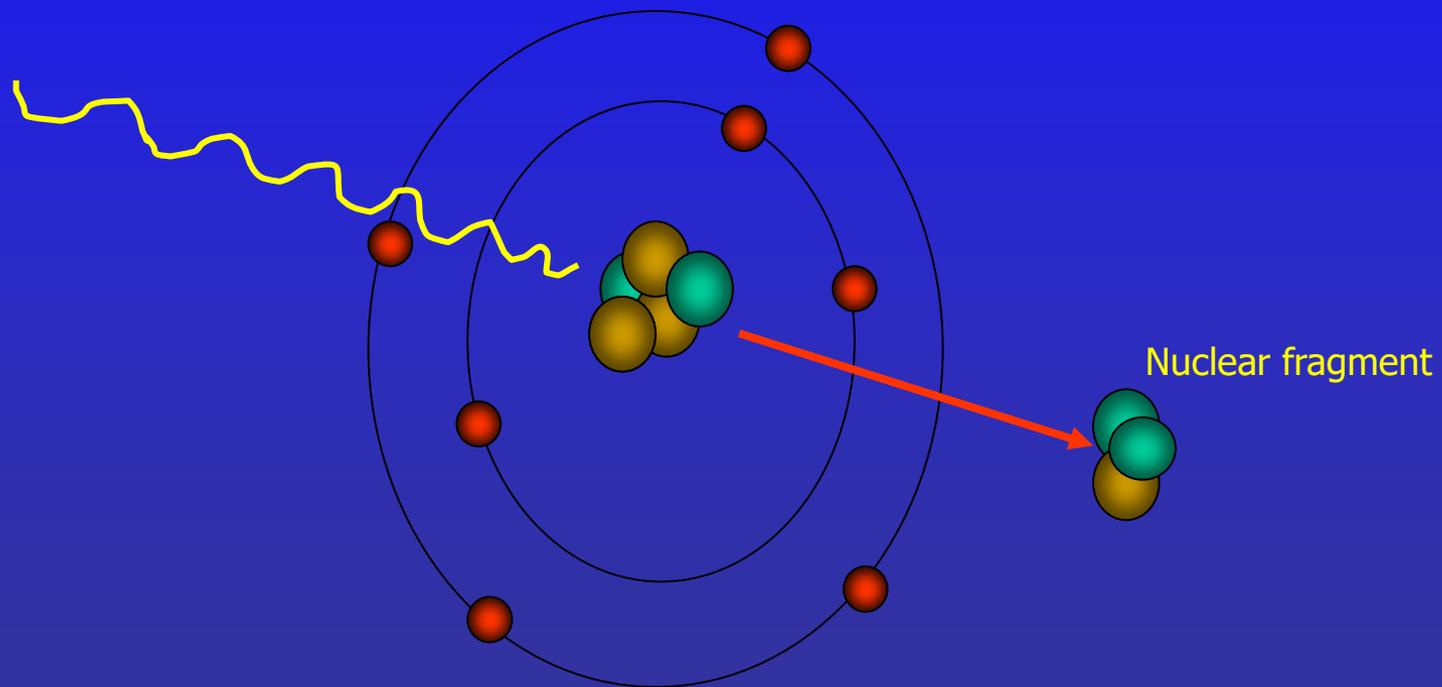
# Pair Production

Occurs with high energy x-ray ( $> 1.02\text{MeV}$ )



# Photonuclear Disintegration

Only occurs with very high energy x-ray ( $> 10$  MeV)



# Linear Energy Transfer (LET)

**Rate of energy transfer - ionizations per mm or keV/mm**

**High LET radiation is not penetrative (i.e. energy is deposited in a small distance)**

**Low LET radiation is penetrative (i.e. much less chance energy is deposited in a small distance)**

**X-rays are lower LET radiation**

# Linear Energy Transfer (LET)

Rate of energy transfer - ionizations per mm or keV/mm

<b>Alpha</b>	<b>Not penetrative Higher LET than beta</b>	<b>20</b>
<b>Beta</b>		<b>1</b>
<b>X-rays</b>	<b>More penetrative Slightly lower LET than beta</b>	<b>1</b>

# **End of Section 4**

**Why not test your understanding using  
the quiz booklet**

## **Slide Show 4:**

# **The Effect of Radiation on Living Organisms**

## **This slide show will:**

- 1. Examine the effect of ionising radiation on living organisms**
- 2. Describe units of exposure and dose**

# Effect of Radiation on Living Organisms

## **Molecular Effect of Ionizing Radiation**

- **Disruption of bonds - reduced molecular weight**
- **Alteration of the tertiary and quaternary structure**
- **Cross-linking**

# Molecular Effect of Ionising Radiation

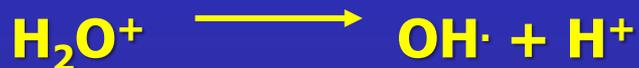
## Direct Effect

Radiolysis of DNA

Primary feature of high LET radiation

## Indirect Effect

Free radicals by radiolysis of water.



Hydroxyl radicals react with other molecules (such as DNA) damaging them.

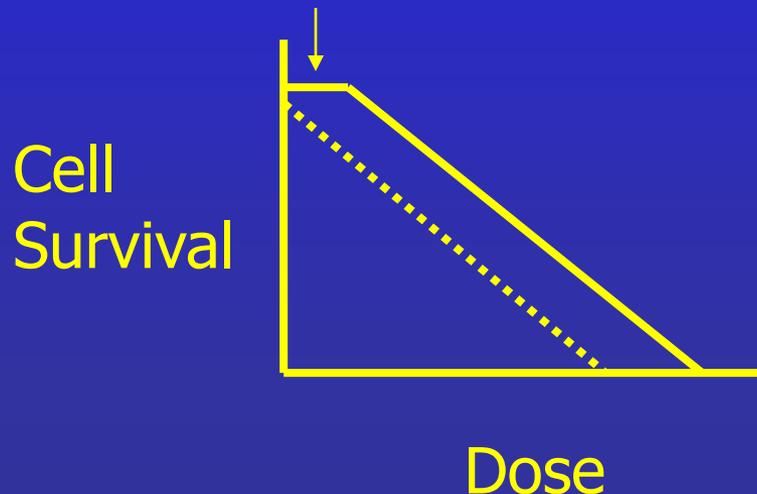
# Effect of Radiation on Cells

- **Relationship to dose rate (cell survival curve)**

At lower doses cells are able to repair damage without cell death (shoulder region)

Higher doses cell death occurs directly proportional to dose

Higher LET there is no shoulder region (i.e. cell repair mechanism overwhelmed by radiation)



# Effect of Radiation on Tissues and Cells

## •Tissue Type (Law of Bergonne and Tribondeau)

1. Rapidly dividing tissue is more radiosensitive
2. Rapidly growing cells are more radiosensitive
3. Younger and more immature cells are more radiosensitive
4. Mature cells are less radiosensitive  
(cf. tissue weighting factor)

**NB: Dividing cells are more sensitive in G2 and G1 parts of the cell cycle**

## •Organ toxicity

**Eye lens is particularly sensitive**

# Effect of Radiation on Humans

## **Stochastic effects**

Threshold after which there is an all or nothing effect  
e.g. Cancer or genetic effects

## **Deterministic Effects**

Vary with Dose

e.g. lens opacification, blood changes

## **Total body irradiation**

Highly unlikely that an individual would survive a total exposure of more than 3 Gray without intensive medical treatment

## **Partial body irradiation**

Cataracts are formed if eyes are exposed to more than 2 Gray  
Hair loss occurs at exposures over 3 Gray

# **Units of Radiation Exposure and Dose**

# Units of Radiation Exposure and Dose

- Exposure (Roentgens)
- Absorbed dose (Gray)
- Dose Equivalence (Sievert)  
Relative biological effectiveness of different types of ionizing radiation
- The Effective Dose Rate (Sievert)

# **Exposure**

- **Unit is Roentgen**
- **Amount of x-rays that will cause 1 gram of air to absorb 86.9 ergs**
- **Useful for gamma and x-rays only**

## **Absorbed dose**

- **SI Unit is Gray (Gy); old unit is rad**
- **Dose absorbed by the irradiated material accompanied by 1 joule (100 ergs) of energy.**
- **The quantity of energy absorbed per gram per Roentgen is dependent on the material**
- **Therefore the absorbed dose is a useful measure and is applicable to any type or energy of ionising radiation**

# *Dose Equivalence*

- Unit is Sievert (Sv); old unit is rem
- Dose is multiplied by a radiation weighting factor ( $W_R$ ) similar to LET
- Dose Equivalence =  $D \times W_R$

Radiation Weighting factors of emissions are approximately:

Alpha particles = 20

Protons, neutrons = 10

Beta particles = 1

Gamma rays and x-rays = 1

**The Sievert takes into account the Biological Effectiveness of the radiation**

**It can be thought of the absorbed dose of any radiation that produces the same biological effect as 1 Gray of therapeutic x-rays**

**For example:**

**If 2.5 Sieverts of radiation are required for a given biological effect – then this could be delivered by 2.5 Gray of therapeutic x-rays or 0.25 Gray of neutrons**

**Explanation:**

**neutrons are 10 x more effective at producing the same biological effect (ie: have a Quality Factor of 10) and hence 1/10 effective dose of neutrons is required for the same biological effect.**

# *The Effective Dose*

- Unit = Sievert (Sv)
- Takes into account how different parts of the body react to ionizing radiation

$$\text{Effective Dose Rate} = D \times Q \times w_T$$

$w_T$  is a tissue weighting factor for organs and tissues

e.g.  $w_T$  gonads = 0.2 while  $w_T$  Skin is 0.01

# Prescribed Limits for Dose

# Dose

## ICRP Prescribed Limits per annum

- **Members of public**

  - 1 mSv per annum above background**

  - 5 mSv to eye**

  - 20 mSv to hands**

- **Radiation workers**

  - 20 mSv per annum above background**

  - 150 mSv to eye**

  - 500 mSv to hands**

- **Pregnant women must receive no more than 2mSv per annum**

**Note that:**

- **Exposure limits are set for all 'members of the public' including pregnant women, babies etc.**
- **University staff members and students should consider themselves members of the public for the purposes of setting exposure limits**

# Background Dose in NZ

- **Is approx 1.8 mSv per annum**
- **Background depends on activity (e.g. number of medical x-rays received in a year)**

**Note- that airline crew on international flights are the most occupationally exposed group in NZ - 6-8 mSv per annum received as a result of increased cosmic radiation received at higher altitudes**

# Measurement of dose

## Dosimeters

Measurement of dose can only really be obtained with dosimeters. These range from film badges, to thermoluminescent detectors to hand-held monitors.

Hand held dosimeters are available in the University

## Geiger Muller meters

Geiger Muller meters only measure ionisation events impinging on the tube. These meters are useful for detecting point leakage from x-ray apparatus.

Any readings obtained should be used with care as the high x-ray intensity can give alarming results Always verify any reading with a dosimeter

# **End of Section 4**

**Why not test your  
understanding using the quiz  
booklet**

# Lecture no.9

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# Inductively Coupled Plasma (ICP)

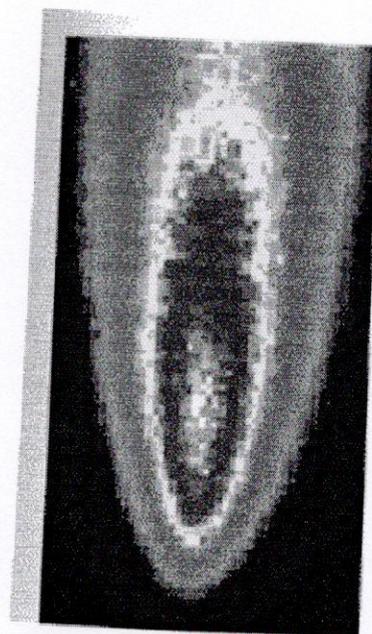
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by Traci Bradford and M. Nicole Cook

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  - Applications**
- **Combining ICP with Atomic Emission Spectroscopy**
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## Introduction

Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic wavelength specific light which can then be measured. The technology for the ICP method was first employed in the early 1960's with the intention of improving upon crystal growing techniques.

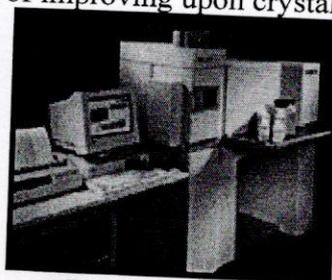


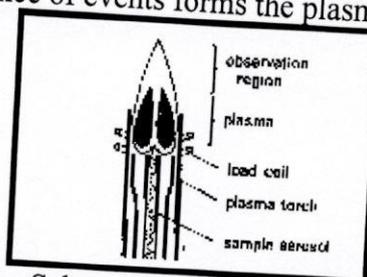
Photo of an ICP

Since then, ICP has been refined and used in conjunction with other procedures for quantitative analysis. Following is a cursory look at the driving forces behind this analytical tool, its use in series with other analytical tools, and environmental applications of ICP.

## The Workings of an ICP

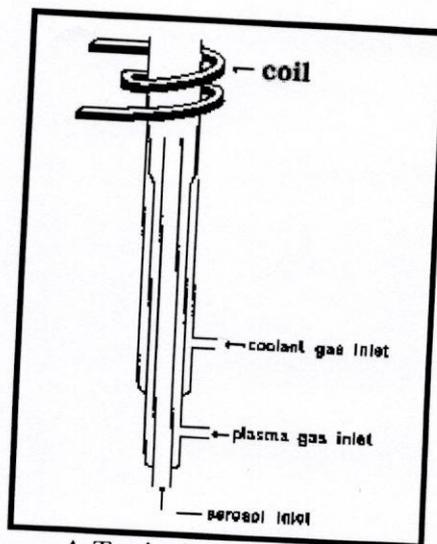
ICP hardware is designed to generate plasma, which is a gas in which atoms are present in an ionized state. The basic set up of an ICP consists of three concentric tubes, most often made of silica. These tubes, termed outer loop, intermediate loop, and inner loop, collectively make up the torch of the ICP. The torch is situated within a water-cooled coil of a radio frequency (r.f.) generator. As flowing gases are introduced into the torch, the r.f. field is activated and the gas in the coil region is made electrically conductive. This sequence of events forms the plasma.

Observation  
region



Schematic of ICP flame.

The formation of the plasma is dependent upon an adequate magnetic field strength and the pattern of the gas streams follows a particular rotationally symmetric pattern. The plasma is maintained by inductive heating of the flowing gases. The induction of a magnetic field generates a high frequency annular electric current within the conductor. The conductor, in turn, is heated as the result of its ohmic resistance.

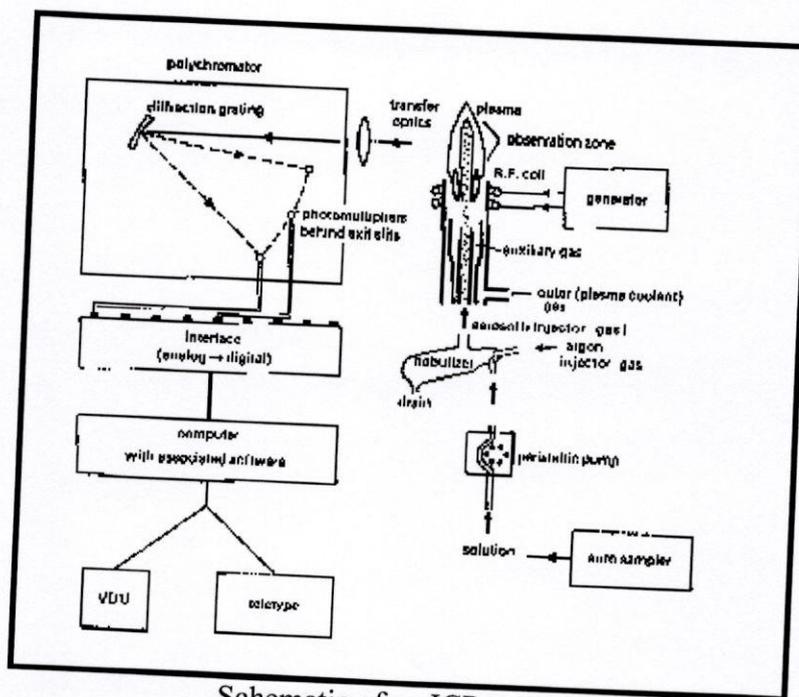


A Typical plasma torch.

In order to prevent possible short-circuiting as well as meltdown, the plasma must be insulated from the rest of the instrument. Insulation is achieved by the concurrent flow of gasses through the system. Three gases flow through the system--the outer gas, intermediate gas, and inner or carrier gas. The outer gas is typically Argon or Nitrogen. The outer gas has been demonstrated to serve several purposes including maintaining the plasma, stabilizing the position of the plasma, and thermally isolating the plasma from the outer tube. Argon is commonly used for both the intermediate gas and inner or carrier gas. The purpose of the carrier gas is to convey the sample to the plasma.

**An ICP typically includes the following components:**

- sample introduction system (nebulizer)
- ICP torch
- High frequency generator
- Transfer optics and spectrometer
- Computer interface



Schematic of an ICP system

An ICP requires that the elements which are to be analyzed be in solution. An aqueous solution is preferred over an organic solution, as organic solutions require special manipulation prior to injection into the ICP. Solid samples are also discouraged, as clogging of the instrumentation can occur. The nebulizer transforms the aqueous solution into an aerosol. The light emitted by the atoms of an element in the ICP must be converted to an electrical signal that can be measured quantitatively. This is accomplished by resolving the light into its component radiation (nearly always by means of a diffraction grating) and then measuring the light intensity with a photomultiplier tube at the specific wavelength for each element line. The light emitted by the atoms or ions in the ICP is converted to electrical signals by the photomultiplier in the spectrometer. The intensity of the electron signal is compared to previous measured intensities of known concentration of the element and a concentration is computed. Each element will have many specific wavelengths in the spectrum which could be used for analysis. Thus, the selection of the best line the analytical application in hand requires considerable experience of ICP wavelengths.

## Advantages and Disadvantages

Advantages of using an ICP include its ability to identify and quantify all elements with the exception of Argon; since many wavelengths of varied sensitivity are available for determination of any one element, the ICP is suitable for all concentrations from ultratrace levels to major components; detection limits are generally low for most elements with a typical range of 1 - 100 g / L. Probably the largest advantage of employing an ICP when performing quantitative analysis is the fact that multielemental analysis can be accomplished, and quite rapidly. A complete multielement analysis can be undertaken in a period as short as 30 seconds, consuming only 0.5 ml of sample solution. Although in theory, all elements except Argon can be determined using an ICP, certain

unstable elements require special facilities for handling the radioactive fume of the plasma. Also, an ICP has difficulty handling halogens--special optics for the transmission of the very short wavelengths become necessary.

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## Applications

An ICP can be used in the quantitative analysis in the following areas:

natural materials such as rocks, minerals, soil, sediment air, water, and plant and animal tissue; pure and applied geochemistry, mineralogy, agriculture, forestry, animal husbandry, chemical ecology, and environmental sciences food industry, including purification and distribution of water the analysis of elements not readily identified by AAS such as Sulfur, Boron, Phosphorus, Titanium, and Zirconium

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## Combining ICP with Atomic Emission Spectroscopy

Often, ICP is used in conjunction with other analytical instruments, such as the Atomic Emission Spectroscopy (AES) and the Mass Spectroscopy (MS). This is an advantageous practice, as both the AES and MS require that sample to be in an aerosol or gaseous form prior to injection into the instrument. Thus, using an ICP in conjunction with either of these instruments eliminates any sample preparation time which would be required in the absence of an ICP.

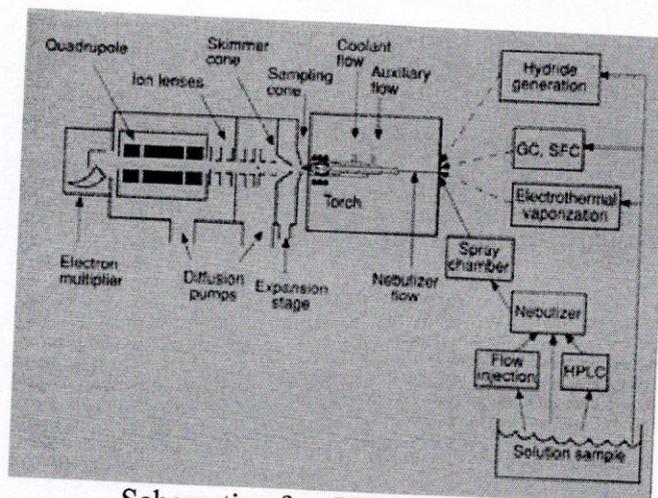
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## Combining ICP with Mass Spectrometry

The efficiency of the Inductively Coupled Plasma in producing singly-charged positive ions for most elements makes it an effective ionization source for mass spectrometry. Inductively coupled plasma-mass spectrometry is unique among the flame and plasma spectroscopy techniques in the ability to discriminate between the mass of the various isotopes of an element where more than one stable isotope occurs. Isotope dilution, in which the change in isotope ratio for two selected isotopes of an element of interest is measured in a solution after the addition of a known quantity of a spike that contains enrichment of one of the isotopes, permits calculation of the concentration of the element. Isotope dilution is the most reliable method of accurate determination of elemental concentration. The conventional method of sample introduction for inductively coupled plasma-mass spectroscopy is by aspiration, via a nebulizer, into a spray chamber. A small fraction of the resulting aerosol is swept by argon into the torch. Approximately 1 mL of sample is required per analytical run, about 99% of which is wasted.

Recently, low cost, low uptake rate, high efficiency nebulizers have been employed to combat this problem. The high efficiency nebulizer operates more efficiently at 10-200 L/min. The detection limits and precision obtained with the high efficiency nebulizer are superior to conventional nebulizers.



Schematic of an ICP-MS system

The schematic diagram depicted above detail a two- or three- stage differentially pumped interface used to extract ions from the atmospheric pressure plasma into the low pressure mass spectrometer. Ions pass through a cold sampling cone (typically Ni) with an orifice approximately 1mm in diameter. The gas expands behind the first orifice, and a portion passes through a second orifice in the skimmer cone. A series of ion lenses, maintained at appropriate voltages, are used to direct the ions into the quadrupole mass analyzer. The ions are transmitted through the quadrupole on the basis of their mass to charge ratios and then detected by an electron multiplier.

The use of a quadrupole mass analyzer gives better than unit mass resolution over a mass range up to  $m/z=300$ . The inductively coupled plasma-mass spectrometry system is considered a sequential multielement analyzer that has scan times less than 20 ms for one sweep. The signal intensity is a function of the number of analyte ions in the plasma and the mass-dependent transport through the mass spectrometer.

The most important advantages of ICP-MS include multi-element capability, high sensitivity, and the possibility to obtain isotopic information on the elements determined. Disadvantages inherent to the ICP-MS system include the isobaric interferences produced by polyatomic species arising from the plasma gas and the atmosphere. The isotopes of argon, oxygen, nitrogen, and hydrogen can combine with themselves or with other elements to produce isobaric interferences. ICP-MS is not useful in the detection of nonmetals.

## Applications in Environmental Analysis

Environmental matrices, which may contain low concentrations and contain interfering elements, have historically presented difficulties in determining sample analysis. ICP-MS was developed in the 1980's and has been used increasingly in the environmental field due to its high sensitivity and multi-element capabilities. ICP-MS offers the possibility of simple and direct determination of some of the elements in soils, such as boron, phosphorus, and molybdenum, at levels not accessible by other methods.

ICP-AES has been widely used since the 1970's for the simultaneous multi-element analysis of environmental and biological samples after dissolution. The excellent sensitivity and wide working range for many elements- together with the low level of interferences, make ICP-AES a nearly ideal method so long as sample throughput is high enough to justify the initial capital outlay. Laser sampling, in conjunction with ICP is a way to avoid dissolution procedures of solid samples prior to the determination of the elements.

ICP-AES has been approved for the determination of metals by the EPA under Method 6010. Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP-AES. This method is approved for a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. The following table lists the elements for which Method 6010 is applicable. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in the following table provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

**Table 1. Recommended wavelengths and estimated instrumental detection limits**

Element	Wavelength (nm)	Estimated Detection Limit (?g/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See note c
Selenium	196.026	75
Silicon	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. In time, other elements may be added as more information becomes available and as required. The estimated instrumental detection limits shown are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

# Inductively coupled plasma mass spectrometry for trace analysis using flow injection on-line preconcentration and time-of-flight mass analyser

Karima Benkhedda, Heidi Goenaga Infante, Freddy C. Adams\*

<sup>a</sup>Micro and Trace Analysis Centre (MiTAC), Department of Chemistry, University of Antwerp (UIA), Universiteitsplein 1, B-2610 Antwerp, Belgium

Elisaveta Ivanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Flow injection (FI) methodologies extend the performance of atomic spectroscopic techniques particularly when on-line preconcentration and separation procedures are involved. This article reviews some of the most relevant aspects of the coupling of FI procedures with inductively coupled plasma-mass spectrometry (ICP-MS), as an attractive approach to perform ultra-trace metal determinations in samples containing a high proportion of total dissolved solids. The capabilities of ICP-time-of-flight (TOF) MS as a fast transient detector for simultaneous determination of a large number of isotopes in a FI peak are also reviewed. © 2002 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Flow injection analysis; Inductively coupled plasma-mass spectrometry; Preconcentration; Time-of-flight mass analyser; Trace elements

## 1. Introduction

Attempts to extend modern analytical methods to significantly lower detection limits are often fraught with problems of sampling and storage as well as contamination. Hence,

\*Corresponding author: Tel.: +32 (03) 820 20 10; Fax: +32 (03) 820 23 76. E-mail: adams@uia.ua.ac.be

advances in instrumental detection capabilities should go hand-in-hand with improvements in sample-pre-treatment methodology. This trend has essentially encouraged the growth of FI methodologies. Miniaturization of sample-handling and pre-treatment utensils and their on-line coupling to detection instruments allow complex chemical processing to be accomplished without the need for extensive, costly clean room facilities while also permitting information to be gathered for small-size samples and reducing the consumption and the waste of chemical reagents.

Flow injection analysis (FIA) is now well-established in modern chemical analysis. Gradually it was recognized that FIA could serve as an interface between solution chemistry and various analytical instruments [1]. This is evident from the numerous papers currently published in the scientific and technical literature (estimated to be approaching 10,000 including numerous monographs [2,3]). Many reports show the inclusion of flow methods in standard analytical procedures. There is also a growing market of commercial instruments.

The important role of FI techniques for the automation, acceleration and miniaturization of solution handling in sample pre-treatment has been well documented in the past 20 years [4-12]. Such determinations can be performed with

practically all methods of detection that are used in contemporary chemical analysis [13]. The achievements and benefits of FI methodologies were treated in two recent dedicated monographs "Flow injection atomic absorption spectrometry" [14] and "Flow analysis with atomic spectrometric detectors" [15].

The combination of FI-based preconcentration and separation methodologies with atomic spectrometry has great potential for enhancing the selectivity and sensitivity of atomic spectrometric techniques, such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS). Sample-introduction flow rates of FI systems are usually compatible with the continuous working mode of these techniques and permit on-line operation using relatively simple interfaces. The coupling of FI systems to ICP-MS, for example, is relatively simple and is normally achieved by connecting the outlet of the FI manifold with the liquid flow inlet of the ICP-MS nebuliser via a short length of narrow-bore tubing of polytetrafluoroethylene (PTFE) or another inert material.

In the case of plasma-based atomic sources, by far the most common is ICP, which was first used for OES and, more recently, for MS. ICP-MS is undoubtedly the technique that is most in vogue today for trace-element analysis. Developments of ICP-MS applications for environmental, biological and clinical analysis have been very active areas of research. The major attraction of ICP-MS is its exceptional multi-elemental sensitivity combined with high speed of analysis. In addition, the possibility of performing isotope and isotope-ratioing analysis offers a unique field of application that is unique to MS. However, no method is without shortcomings and ICP-MS is hampered by various limitations, such as several different sample-matrix problems, spectral and non-spectral interferences, and limited precision in the isotope-ratio mode. Transient signal mass analysis is another weak point of ICP-MS when employing conventional sequential mass analysers interfaced to analytical

systems that deliver discrete short-time sample volumes, such as FI, chromatography, electrothermal vaporisation (ETV) or laser ablation (LA) [16]. Overcoming these limitations requires some modifications of the strategies of analysis to improve the detection system. In what follows, FI on-line preconcentration procedures and a TOF mass analyser in combination with the ICP source are reviewed as possible ways to extend the capabilities of ICP-MS.

## 2. Coupling of FIA with ICP-MS

ICP-MS methods suffer non-spectral and spectral interferences from any sample component, including high concentrations of easily ionised elements, salts, mineral acids and organic solvents [17]. The non-spectral interferences include cones, nebuliser and torch clogging; change of nebulisation efficiency and transport, ionisation in the plasma, and ion extraction, and the spectral include formation of polyatomic species and isobaric interferences. As a consequence, direct analysis of samples with complex matrix composition is difficult or even impossible. Through injection of a discrete sample volume, FI offers an effective way of dealing with the above-mentioned interferences in ICP-MS analysis of, for example, environmental samples [18], since the problems of orifice clogging of the sampler and skimmer caused by the matrix are effectively minimised.

FI methodologies are particularly advantageous when separation and preconcentration methods are involved. For example, precise and accurate FI-ICP-MS methods have been developed for trace-metal determination in biological materials and environmental samples [19–21]. In a number of methods, however, the analytes are eluted from the preconcentration device using organic solvents. The latter are known to enhance sensitivity in atomic absorption spectrometry (AAS) but they may cause drift in the sensitivity of ICP-MS using conventional nebulisation as a result of the formation of new complex compounds or by causing changes in plasma conditions, often to the point of

extinction of the plasma. Small sample-injection volumes (down to microlitre-size), by means of FIA, are commonly used to minimize the effects of organic solvents, thus allowing the use of ICP-MS in methods involving nebulisation of organic solvents. In addition, other interfaces are used in ICP work for organic solvent nebulisation: a cooled spray chamber [22]; a solvent permeable membrane interface between the sample introduction and the ICP [23]; cryogenic desolvation [24]; a thermostated condenser between the spray chamber and plasma torch [25]; and, an ultrasonic nebuliser with membrane desolvation [26].

### 3. Preconcentration and separation procedures for ICP-MS

As mentioned above, it is often still necessary to use separation and preconcentration steps prior to detection and subsequent quantification using ICP-MS. The preconcentration step is aimed at lowering the limits of detection, by both removal of interferences and increasing the concentration of the species of interest. The drawbacks of batch-mode preconcentration procedures (large sample volumes, low sample throughput, high contamination risks, and irreproducible results due to manual manipulation) are avoided by performing them with FI. The most important FI preconcentration/separation techniques used in combination with ICP-MS are liquid-liquid and liquid-solid extractions, which will be briefly reviewed in the following sections.

#### 3.1. Liquid-liquid separation and preconcentration

The use of FI liquid-liquid extraction for analyte preconcentration has seen a slow development when compared to other on-line preconcentration techniques, such as liquid-solid extraction. This is probably because enrichment factors are limited to typically about 10–20. Most of these systems are coupled to FAAS and graphite furnace atomic absorption spectro-

metry (GFAAS) more easily than to ICP-MS. This is because relatively large amounts of sample and organic solvents are needed in comparison with other preconcentration methods based, for example, on sorption in knotted reactors (see below).

As pointed out above, the effects of organic solvents on the plasma conditions can be minimised by the use of adequate interfaces and/or minimal volumes of solvents, but cannot be avoided completely. Although liquid-liquid extraction is an established technique for the separation and preconcentration of heavy metals from a variety of samples, few studies based on off-line solvent extraction in ICP-MS work have been published [27]. To the best of our knowledge, no work is reported for the on-line coupling of solvent extraction preconcentration methods to ICP-MS.

#### 3.2. Liquid-solid separation and preconcentration

Liquid-solid separation and preconcentration are the most widely used procedures in FIA. The enormous number of papers published during the last few years reflects the developments in this area. For most of the procedures, the sample-loading sequence is always associated with retention of chemical species, often containing the analyte itself, on a solid surface. The enrichment factor (concentration factor) is directly related to the amount of sample loaded on the collection media, and the loading flow rate is usually the main factor which determines the sample throughput, that is, the efficiency of the procedure. Fang [14] summarized the advantages of FI on-line sorbent extraction compared to the corresponding off-line techniques as follows: higher efficiency with respect to sample throughput; lower consumption of sample and reagents; better precision; low risk of contamination (since a closed system made of inert materials is used); and, ease of automation.

##### 3.2.1. Column sorption

Compared to on-line liquid-liquid extraction, the advantages of on-line column sorption

systems are relative ease of operation and robustness. Enrichment factors up to 40 are achievable [14] using a well-designed preconcentration system. However, some flow instability can occur as a result of flow-impedance of packed columns (particularly with fine particle packings). This problem can be overcome by using high-quality pumps in the FI manifold and by optimising operational parameters. A column must be stable enough to be used for at least 100 sorption/elution cycles. Column packing with adequate chemical and physical stability, as well as fast kinetics in a relatively selective sorption of the analyte and its release in a suitable eluent, are extremely important for achieving optimal performance. Ion-exchangers without chelating functional groups are usually not selective enough for on-line preconcentration. Chelex-100 with iminodiacetic functional groups has found numerous applications in FIA, despite its strong swelling/shrinking properties and relatively slow kinetics. Muromac A-1, which has the same functional groups as Chelex-100, exhibits significantly better properties in on-line preconcentration with both AAS and ICP detectors [27]. Chelating ion-exchangers with quinolin-8-ol (HQ) functional groups azo-immobilised on porous glass have excellent mechanical and kinetic properties but suffer from a relatively low exchange capacity [15], which limits their application.

Sorption of metal complexes of low polarity from the aqueous phase by a reversed-phase mechanism using non-polar sorbents, such as C<sub>18</sub>-bonded silica, in on-line preconcentration atomic spectrometric systems has demonstrated advantages over sorption ion-exchangers, as regards selectivity, kinetics and stability of packing material. The C<sub>18</sub> sorbent is used to retain organic metal complexes with dithiocarbamates (Sodium diethyldithiocarbamate (NaDDC) [28] and ammonium pyrrolidinedithiocarbamate (APDC) [29]) and ammonium diethyldithiophosphate (DDPA) [30]. Different types of manifold designs for FI solid-liquid extraction have been proposed in the literature and are summarised in the monograph of Sanz-Medel [15].

### 3.2.2. Precipitation and coprecipitation

High enrichment factors and effective separations from interfering matrices can be achieved by precipitation, and particularly coprecipitation. When operated in the manual batch mode, they are tedious and require large sample volumes, and the precipitates are easily contaminated. Recently, with the development of FI techniques, there has been a revival in the use of these procedures. Precipitates are formed in a reaction coil, retained on a filter, which replaces the column, and subsequently dissolved by an appropriate agent. These on-line systems, however, have a relatively low efficiency, probably as a result of the low liquid-solid phase transfer associated with the solubility of the precipitate and the slow kinetics of the precipitation reaction [15]. In this respect, coprecipitation is more suitable for general use with fewer matrix interferences because it is less demanding on the solubility of the precipitate formed. Few studies have been reported on the coupling of FI on-line precipitation/coprecipitation methods to ICP-MS. This is probably because of the difficulties encountered with an increase in the amount of precipitate formed through the build-up of back pressure, and limited enrichment factors and sampling frequencies, as reported by Fang and Tao [15]. This problem can be avoided by the implementation of on-line precipitation-dissolution systems, for example, the work of Yan et al. [31], who have effectively coupled on-line, filterless precipitation-dissolution with ICP-MS. The precipitates were dissolved in a small amount of dilute nitric acid thus achieving high enrichment factors (55–75) for the determination of rare earth elements (REEs) in environmental and geological samples.

### 3.2.3. Knotted reactors

Knotted reactors (KRs) made of open PTFE tubing are now becoming interesting because of their potential to enhance the sensitivity and the selectivity of on-line preconcentration methods. Knotted reactors have mainly been used as precipitate collectors and as the sorption surface of some soluble metallo-organic complexes. The

main advantage of such systems is the relatively low flow impedance in the KR compared to that in packed columns (thus high flow rates can be used with KR to achieve higher pre-concentration efficiencies), the absence of stability problems of column packings and their practically unlimited lifetime. With knotted reactors, enrichment factors of up to 75 were achieved [31]

These systems were first coupled with FAAS, and more recently they have been extended to GFAAS applications by adding some improvements to the manifold: the addition of a washing step to the preconcentration procedure just after sample loading in the knotted reactor, which is aimed at removing residual matrices; and, the use of an air flow for both removal of the washing solution and driving the eluate into the graphite tube.

The large collection capacity with low impedance of the KR was exploited in ICP-MS determination of low levels of REEs in environmental samples using FI-on-line precipitate collection without filtration [31]. More recent developments involving KR for the FI on-line sorption preconcentration of metal complexes have been their coupling to ICP-TOFMS to determine ultratrace metals and sub-parts per trillion levels of REEs in natural waters and biological samples [26,32].

We have developed a FI method for the simultaneous on-line preconcentration of ultratrace of Cu, Ni, Sb, Co, Ag, Cd, Mo, In and Pb in a KR with a view to their determination in biological materials and natural waters [26]. This system was coupled to ICP-TOFMS using an ultrasonic nebuliser (USN) with a membrane desolvation (MEMSEP) interface. APDC was used as a chelating reagent to form complexes with the analytes. These complexes were retained in the knotted reactor and subsequently eluted with methanol before nebulisation and detection. The manifold used in this work (Fig. 1) was designed to be compatible with ICP-MS requirements. Some specific steps were essential for the preconcentration procedure; for example, the effluents from the preconcentration and KR-rinsing stages had to be sent

directly to waste to avoid admitting into the ICP substantial amounts of dissolved solids contained in the matrix. In parallel to the preconcentration step, a flow of  $1 \text{ mol l}^{-1} \text{ HNO}_3$  rinsed the USN, the MEMSEP and the sampling cone of ICP-MS in order to minimize memory effects. The use of a relatively small volume of eluent ( $100 \mu\text{l}$  of methanol), introduced via an eluent loop, along with the employment of the USN-MEMSEP interface, substantially minimized the problems related to the introduction of organic solvents into the plasma. The methanol was transported from the eluent loop through the KR to the USN by air. The use of air as a carrier overcomes the problems of dispersion that are mainly observed when small volumes of eluent are transported. The resultant higher transport efficiency of the analytes gives an enhancement in sensitivity. On the other hand, the air flow entering the plasma is negligible when compared to the nebuliser argon flow, so no important changes in plasma conditions occur.

#### 4. TOF as a detector of transient signals in ICP-MS

The sequential mass analysers commonly employed in plasma source MS are: ion trap; sector-field; and, quadrupole filter (QMS). Details of the principles of operation of each analyser can be found elsewhere [33]. QMS is, by far, the most commonly used because it combines excellent sensitivity with relatively low cost. With this sequential instrumentation, only one  $m/z$  value can be monitored at any given time, resulting in a necessary trade-off between the mass range that can be covered in any given period of time and the limits of detection. This compromise is especially pronounced in the analysis of the transient signals typically produced by FI systems, LA, chromatography, and ETV, particularly in the case of multi-elemental/multi-isotopic determinations. The limitation of measuring one isotopic peak at a time also constrains the precision that can be achieved in a ratioing mode.

It is generally known that the dominant sources of signal fluctuation in plasma-source spectrometry are the variation in nebuliser or spray chamber performance, and flutter in the plasma tail flame. These fluctuations are multiplicative, which means that all signals are affected in the same way. As a result, precision can be improved by a ratioing method such as internal standardization or isotope dilution. However, although QMS is rapid enough to achieve effective ratioing based compensation of the signal fluctuations, only few elements or isotope peaks can be measured at a time [33].

A number of researchers have investigated other types of mass analysers as alternatives to overcome the above mentioned shortcomings. There are considerable advantages in the use of a faster mass spectrometer coupled to the ICP source, for example, a TOFMS as outlined by

Hieftje et al. [33] and discussed below. In such instrumentation, the TOF can be placed either orthogonal or axial to the plasma. The on-axis geometry for ion extraction is intrinsically the more advantageous design because the ion segments are extracted in the direction of the movement of the plasma ion beam, avoiding mass bias inherent to the orthogonal geometry [34]. The first on-axis ICP-TOFMS instrument was commercialised by LECO Corporation (St. Joseph, MI, USA) in 1998. A detailed description of the instrument is given elsewhere [35] and a schematic illustration is shown in Fig. 2.

#### 4.1. Features and performance

Applying separation techniques engenders time-dependent signals. When measuring such transient signals, changes in time result in significant

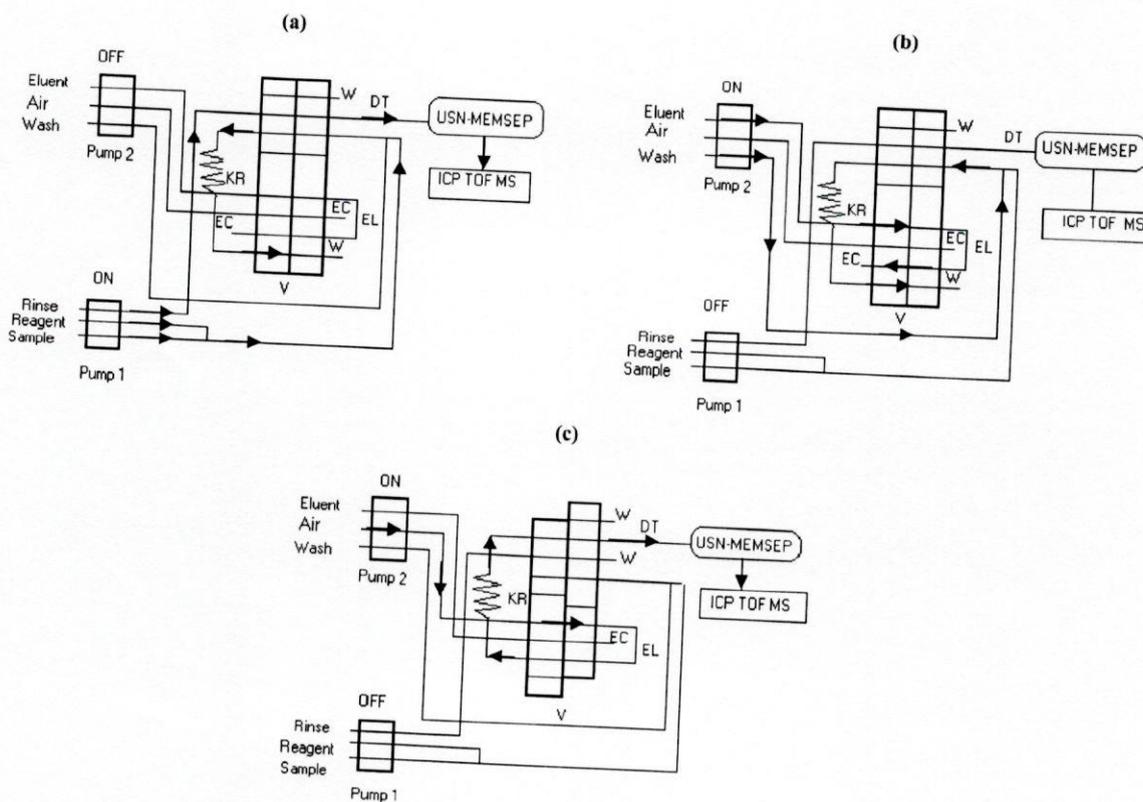


Fig. 1. FI on-line preconcentration manifold. V, valve; EL, eluent loop; W, waste; KR, knotted reactor; USN-MEMSEP, ultrasonic nebuliser-membrane desolvation interface; DT, delivery tube; EC, eluent container (adapted from [26]).  
 (a) preconcentration (b) KR rinsing (c) elution.

# Lecture no.10

# CHN analyzer

## Introduction

Carbon, hydrogen, nitrogen, and sulfur (CHNS) are fundamental elemental components that are analyzed on the ship during IODP expeditions. Fluctuations in the concentration and/or content ratio of carbon, nitrogen, and sulfur define the origin, depositional environment, and diagenetic alteration of source materials.

A few options for sample preparation method, instrument settings, and measurement methodology exist. In addition to the pregenerated methods, specific analytical methodology may be required based on the nature of certain sample materials. In this case, new methods will be created by the laboratory technicians working in conjunction with the scientists. Each instrument method is recorded by the USIO and will be associated with the measurements performed under that method.

Elemental analysis on **carbon, hydrogen,** and **nitrogen** is the oldest investigation performed to characterize and/or prove the elemental composition of an organic or inorganic sample. In fact, it used to be the only available routine method before modern spectroscopy was established in the 50s. The majority of organic compounds only contain the elements C, H, N, and O and the latter is seldom determined separately.

Our departmental analyser gives weight percentages of C, H, N done by combustion in O<sub>2</sub> and gas chromatographic analysis of CO<sub>2</sub>, H<sub>2</sub>O and NO<sub>2</sub>.

As an option S can be measured as SO<sub>2</sub> and oxygen as CO.

Other elements such as Cl, Br, and I must be determined by other means.

## **Carbon Analysis**

Most marine sediments and sedimentary rocks contain both carbonate (“inorganic”) carbon and organic carbon. The CHNS procedure measures total carbon (inorganic plus organic) when following the standard method. Organic carbon content is then determined by using the inorganic carbon value from coulometric analysis and calculating the difference between total carbon from CHNS analysis and inorganic carbon analyzed by coulometer. Alternative methodologies can be employed to measure organic and inorganic carbon.

## **Nitrogen Analysis**

Nitrogen is one of the important limiting nutrients in the ocean. The global carbon cycle and, consequently, atmospheric CO<sub>2</sub> might be tightly coupled to the nitrogen cycle, and therefore changes in the magnitude of the sinks and sources of fixed nitrogen in the oceans can significantly influence global climate. Biological nitrogen fixation, denitrification, and consumption of nitrate by phytoplankton are the major biological processes of the global nitrogen cycle. Changes in ocean circulation and nutrient supply, which occur in response to changes in environmental conditions, affect the relative importance and spatial extent of the major pathways of the nitrogen cycle.

# Chemicals and Reagents

## Gases

- Helium** (carrier gas): chromatography grade
- Oxygen** (sample oxidation gas): 99.995% minimum purity

## Reagents

Note that many of these materials are hazardous and before any work is done with them, the user must be familiar with the appropriate Material Safety Data Sheets (MSDS). )

Material Name	Description	Purpose
Aspartic acid	$C_4H_7NO_4$ : white fine crystals	Standard reference material
2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BBOT)	$C_{26}H_{26}N_2O_2S$ : pale green crystals	Standard reference material
Copper oxide	Pre-packed	Filling material
Electrolytic copper	Pre-packed	Filling material
Ethanol	$C_2H_5OH$	Solvent for sample preparation
Quartz wool	$SiO_2$	Filling material

## **Sample Preparation**

Bulk samples are freeze-dried, crushed and homogenized using a mortar and pestle or electric mill, and weighed into a tin sample cup (crucible) with vanadium pentoxide catalyst. The crucibles are then closed (referred to as “wrapping” the sample) and placed in the autosampler for instrumental analysis.

## **Drying and Homogenizing the Sample**

1. Break clumpy sample into pieces.
2. Fill a freeze-drying chamber with sample pieces and place into freeze dryer.
3. Freeze-dry sample for at least 12 hr until sample is completely dry (may require additional freeze-drying time, up to 3 hr). The sample is dry when there is no more condensate in the cold part of the tube.
4. Wipe an agate mortar and pestle with ethanol and allow to dry completely before grinding each sample. Be sure the mortar and pestle are *completely* dry; ethanol reagent residue can cause false C and H results.
5. Grind and homogenize sediment using the cleaned *and dry* agate mortar and pestle.
6. Fill a sample bottle with powdered homogenized sediment.
7. Place sample bottle into the desiccator. Many mineral species are hygroscopic (tend to absorb water), so the sample bottles containing the dried samples should be kept in the desiccator until used.

## Measuring Principle

The sample under test is weighed in using a tin capsule. The required amount is **2 to 3 mg of organic material** and can hardly exceed 10 mg, if inorganic matter with little carbon content is investigated. After folding the capsule (looking rather like wrapped tin foil) the sample is placed in the autosampler.

The tin capsule enclosing the sample falls into the reactor chamber where excess oxygen is introduced before. At about **990 °C the material is "mineralized"**. Formation of carbonmonoxide is probable at this temperature even under these conditions of excess oxygen.

The **complete oxidation is reached at a tungsten trioxide catalyst** which is passed by the gaseous reaction products. The resulting mixture should thus consist of **CO<sub>2</sub>, H<sub>2</sub>O** und **NO<sub>x</sub>**. But also some excess **O<sub>2</sub>** passes the catalyst.

The product gas mixture flows through a silica tube packed with copper granules. In this zone, held at about 500 °C, remaining oxygen is bound and nitric/nitrous oxides are reduced. The leaving gas stream includes the analytically important species **CO<sub>2</sub>, H<sub>2</sub>O** und **N<sub>2</sub>**. Eventually included **SO<sub>2</sub>** or hydrohalogenides are absorbed at appropriate traps.

High purity helium (Quality 5.0) is used as carrier gas. Finally the gas mixture is brought to a defined pressure/volume state and is passed to a gas chromatographic system. Separation of the species is done by so called zone chromatography. In this technique a staircase type signal is obtained and the step height is proportional to the substance amount in the mixture.

**Blank values** are taken from empty tin capsules

**Calibration** is done by elemental analysis of standard substances supplied by the instrument's manufacturer for this purpose.

## Working Range

Mineralization and detection covers every species of the analyte elements in the sample. Beside purely organic samples various metal organic compounds and even inorganic samples as carbides and nitrides have successfully been characterized.

The ***detection limit*** for carbon and nitrogen at sample amounts of 2 to 3 mg was found to be at about **0,05 w-% (500 ppm)** in what case the uncertainty stays at about 0,02 w-%.

According to the apparatus's supplier the instrument's uncertainty in the medium range stays below 0,3 w-% as required by journals to prove the expected composition. With very carbon rich samples we found this tolerance was slightly exceeded (still within 0,5 w-%).

## Problems and Interferences

The weighing of ***oily*** or ***fluid substances*** is impossible using the thin walled tin capsules. For this purpose alumina pans with a lid are available. These pans are tightly closed by cold welding to prevent loss of sample by spillage and evaporation. As the blank value for nitrogen is dramatically increased by the enclosed volume of air the determination limit for **N** in liquid samples is increased to 0,1 to 0,2 w-%.

With ***highly viscous*** or even ***glassy materials*** elemental analysis is even impossible with the above method.

It has long been known that *phosphorus* can interfere in the mineralization of organic material. In literature the formation of glassy  $P_2O_5 \cdot xH_2O \cdot yC$  has been described. Elemental analysis of phosphorus containing compounds can thus suffer from systematic deviations in the determined carbon content exceeding the tolerance limit of 0,3 w-%. This effect can be controlled by the addition of vanadium pentoxide ( $V_2O_5$ ).

*Fluorine* is mineralized to form HF which reacts at the wall of the silica tubes which form the main part of the reaction zone. The gaseous products, such as  $SiF_4$  and relatives, can cause systematic errors which rarely become significant with respect to the 0,3 w-% tolerance.

The mineralization of *metal containing samples* can also be affected by interferences. By modification of the method most of these can be compensated for.

## **Percentage Composition**

$C_xH_yO_z$  (9.83 mg) + excess  $O_2$  x  $CO_2$  (23.26 mg) +  $y/2 H_2O$  (9.52 mg)

millimoles of  $CO_2 = 23.26 \text{ mg} / 44.01 \text{ mg/mmol} = 0.5285 \text{ mmoles of } CO_2$

mmoles of  $CO_2 = \text{mmoles of C in original sample}$

$(0.5285 \text{ mmoles of C})(12.01 \text{ mg/mmol C}) = 6.35 \text{ mg of C in original sample}$

$C_xH_yO_z$  (9.83 mg) + excess  $O_2$  x  $CO_2$  (23.26 mg) +  $y/2 H_2O$  (9.52 mg)

mmoles of  $H_2O = 9.52 \text{ mg} / 18.02 \text{ mg/mmol} = 0.528 \text{ mmoles of } H_2O$

mmoles of  $H_2O = 1/2 \text{ mmoles of H in original sample}$

$(0.528 \text{ mmoles of H})(2)(1.008 \text{ mg/mmol H}) = 1.06 \text{ mg of H in original sample}$

## Weight Percentage Composition

$C_xH_yO_z$  (9.83 mg) + excess  $O_2$  x  $CO_2$  (23.26 mg) +  $y/2 H_2O$  (9.52 mg)

$$\%C = 6.35 \text{ mg} / 9.83 \text{ mg} \times 100 = 64.6\%$$

$$\%H = 1.06 \text{ mg} / 9.83 \text{ mg} \times 100 = 10.8\%$$

$$\%O = 100 - (64.6 + 10.8) = 24.6\%$$

## Calculation of Empirical Formula

assume for example a 100g sample

64.6% of C:  $64.6 \text{ g} / 12.01 \text{ g/mol} = 5.38$  moles of C

10.8% of H:  $10.8 \text{ g} / 1.008 \text{ g/mol} = 10.7$  moles of H

24.6% of O:  $24.6 \text{ g} / 16.0 \text{ g/mol} = 1.54$  moles of O

Thus:  $C_{5.38} H_{10.7} O_{1.54}$

converting to simplest ratio:

$C_{5.38/1.54}$ ;  $H_{10.7/1.54}$ ;  $O_{1.54/1.54}$

$C_{3.50} H_{7.00} O_{1.00} = C_7H_{14}O_2$