Spectroscopy

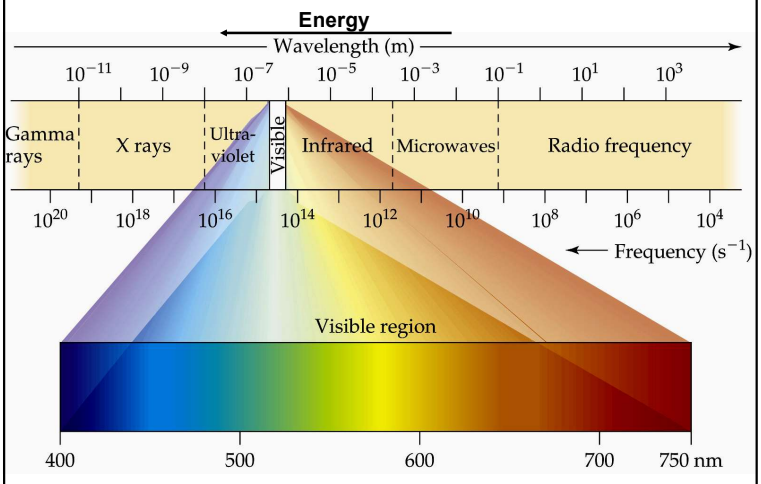
Spectroscopy

The study of the interaction between ELECTROMAGNETIC (EM) RADIATION and MATTER

The electromagnetic spectrum

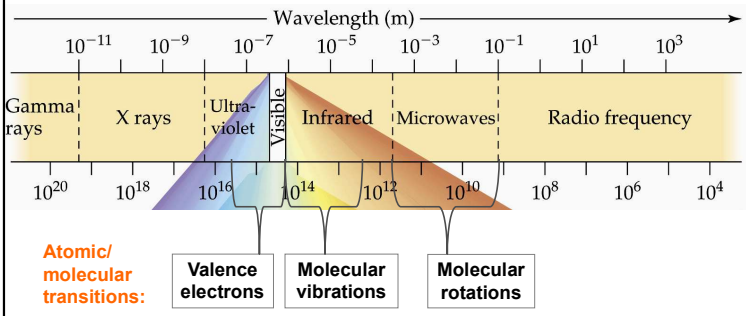
- All forms of spectroscopy use a part of the electromagnetic spectrum to give us information about the materials around us.
- Electromagnetic radiation interacts with atoms and molecules.
- The nature of this interaction depends upon the energy of the electromagnetic radiation.

- **Various spectroscopic techniques provide us with information about:**
  - The type of atom of molecule that is present
  - How much of a particular atom or molecule is present
  - The structure and bonding of the molecule.



All electromagnetic radiation travels at the same speed, *c*

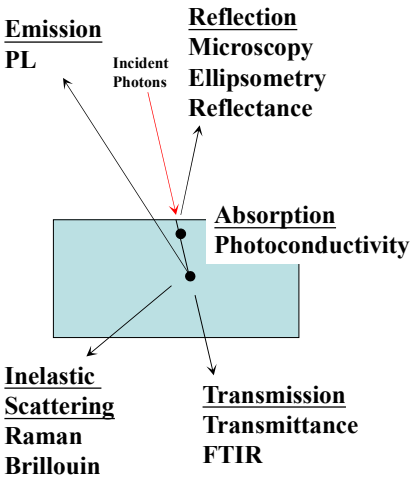
The interactions of radiations with chemical systems follow different mechanism and provide different kinds on information.



Basis of Spectroscopy

- Spectroscopy techniques utilise the fact that:
  - Atoms or molecules absorb and emit electromagnetic radiation of specific energies
  - Atoms and molecules undergo a change when they absorb electromagnetic radiation
  - Different parts of the electromagnetic spectrum affect different parts of the atom or molecule

Spectroscopic Techniques



INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the **energy levels** of the atoms or molecules.

- A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule is called **absorption**.
- A transition from a higher level to a lower level is called **emission** if energy is transferred to the radiation field, or nonradiative decay if no radiation is emitted.
- Redirection of light due to its interaction with matter is called **scattering**, and may or may not occur with transfer of energy, i.e., the scattered radiation has a slightly different or the same wavelength.

Absorption of Radiation

Electron-photon interaction.

- An electron that absorbs a photon will gain energy.
- An electron that loses energy must emit a photon.

For absorption to occur, the energy of the photon must exactly match the energy level in the atom (or molecule) it contacts.

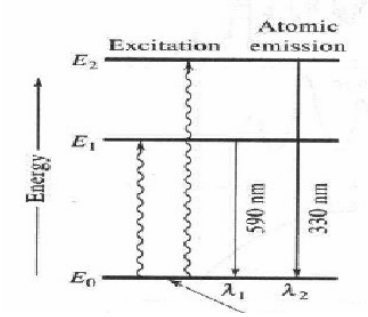
- $E_{photon} = E_{electronic\ transition}$

Two types of absorption

i) Atomic

ii) Molecular

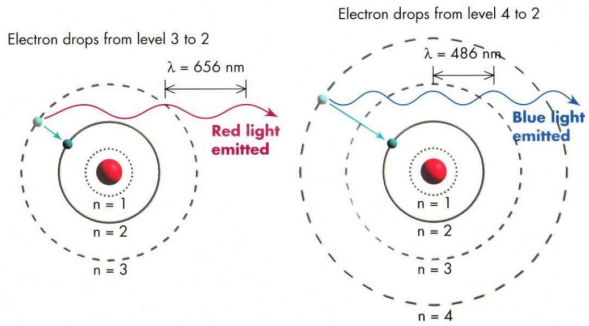
Atomic Transition



- E_0 – lowest energy electronic level or ground state
- E_1, E_2 – higher-energy electronic levels

Emission

The energy of photon that can promote electrons to excite/jump to a higher energy level depends on the energy difference between the electronic levels.



Molecular Absorption

In molecules the electronic states are subdivided into vibrational states.

The energy, E, associated with the molecular bands:

$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational}$

In general, a molecule may absorb energy in 3 ways:

1. By raising an electron (or electrons) to a higher energy level. (**electronic**)
2. By increasing the vibration of the constituent nuclei. (**vibrational**)
3. By increasing the rotation of the molecule about the axis. (**rotational**)

Various types of Spectroscopy

Table 7.1 Spectroscopic techniques make use of the way electromagnetic radiation interacts with atoms and molecules

Spectroscopic technique	Part of the electromagnetic spectrum	Wavelength range (cm) (approx)	Part of atom or molecule affected
Ultraviolet spectroscopy (UV)	Ultraviolet	4×10^{-5} to 10^{-7}	Electrons in molecules
Colorimetry	Visible	7×10^{-5} to 4×10^{-5}	Valence electrons in molecules
Atomic absorption (AAS) and atomic emission spectroscopy (AES); flame tests	Visible	7×10^{-5} to 4×10^{-5}	Valence electrons in atoms
Infrared spectroscopy (IR)	Infrared	0.01 to 7×10^{-5}	Bending and stretching of bonds in molecules
Nuclear magnetic resonance spectroscopy (NMR)	Radio	> 10	Nuclear spin states

Analysis of Atoms

- The following 3 techniques that use radiation from the visible region of the electromagnetic spectrum to give us information about the elements present in a sample.
  - Flame tests
  - Emission Spectroscopy
  - Absorption absorption spectroscopy

Flame Tests

- A simple form of qualitative analysis
- Identifies certain atoms in a compound.
- Atoms of different elements have different electron arrangements and hence different capacities to absorb and emit electromagnetic radiation

UV-Visible Spectroscopy

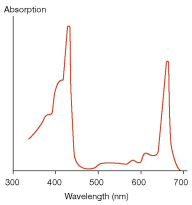
- Makes use of the fact that many substances absorb light of characteristic wavelengths
- The wavelengths of the light absorbed by compounds can be useful for their identification
- UV-visible spectroscopy involves the sample, in aqueous solution, being placed in a glass holder or as a film on glass substrate.
- Ultraviolet or visible light at a **wavelength strongly absorbed by the species** being analysed for, is passed through the solution and **the amount of light absorbed is directly related to the amount of that species present** in the sample

UV-Visible Spectroscopy

- When a substance absorbs visible light, it appears coloured.
- The colour observed is the compliment of the absorbed colour because this is what remains to reach our eyes.

Table 7.4 Colours of visible light and complementary colours

Wavelength (nm)	Colour absorbed	Colour observed
380–420	Violet	Green–yellow
420–440	Violet–blue	Yellow
440–470	Blue	Orange
470–500	Blue–green	Red
500–520	Green	Purple
520–550	Yellow–green	Violet
550–580	Yellow	Violet–blue
580–620	Orange	Blue
620–680	Red	Blue–green
680–780	Purple	Green



Visible spectrum Of chlorophyll

UV-Visible Spectroscopy

- Although it can be useful for qualitative analysis. UV-visible spectroscopy is usually used for determining concentration of a substance in a sample or band-gap ditermination of a semiconductor.
- The procedure involves recording the spectrum of the pure substance and selecting a wavelength at which the substance absorbs strongly but other components of the sample do not.
- The absorbance of the sample is then measured at this wavelength and compared to the absorbance of a series of standard solutions.

Uses

- Clinical analysis, such as the haemoglobin content and sugar levels in blood
- Determining the amount of coloured dyes in plastics
- Detrmination of band gap of semiconducting samples
- In qualitative analysis of DNA and proteins in the field of molecular biology
- Determining the levels of nutrients, additives and contaminants in water and foods.

BASIC COMPONENTS OF SPECTROPHOTOMETER

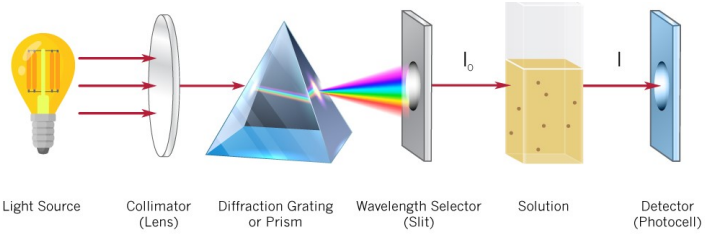
1)Source - A stable source of radiant energy at the desired wavelength (or λ range).

2)Wavelength Selector - A device that isolates a restricted region of the EM spectrum used for measurement (monochromators, prisms, & filters).

3)Photoelectric Transducer - (Detector) Converts the radiant energy into a useable signal (usually electrical).

4)Signal Processor & Readout - Amplifies or attenuates the transduced signal and sends it to a readout device such as a meter, digital readout, chart recorder, computer, etc.

UV-Visible Spectroscopy



- The substance to be analysed is place in a special vial.
- **A reference cell** must be used which contains pure solvent. This is used to compensate from any reflection, scattering or absorbance of the light by the solvent.

I. Sources of Radiation

- **Generate a beam of radiation that is stable and has sufficient power.**

A. Continuum Sources

- emit radiation over a broad wavelength range and the intensity of the radiation changes slowly as a function of wavelength.

This type of source is commonly used in UV, visible and IR instruments.

- **Deuterium lamp is the most common UV source.**
- **Tungsten lamp is the most common visible source.**
- **Glowing inert solids are common sources for IR instruments.**

B. Line Sources

- Emit a limited number *lines* or bands of radiation at specific wavelengths.

- **Used in atomic absorption spectroscopy**
- **Types of line sources:**

1) Hollow cathode lamps

2) Electrodeless discharge lamps

3) Lasers -Light -amplification by stimulated emission of radiation

II. Wavelength Selectors

- **Wavelength selectors output a limited, narrow, continuous group of wavelengths called a *band*.**
- **Two types of wavelength selectors:**

A) Filters

B) Monochromators

A. Filters

- **Two types of filters:**

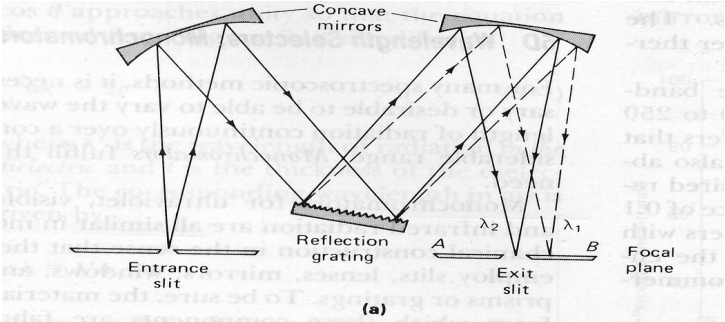
1) Interference filters: reflects some wavelengths (colors) of light and transmits others

2) Absorption Filters: work by absorbing the unwanted wavelengths of light

B. Monochromators

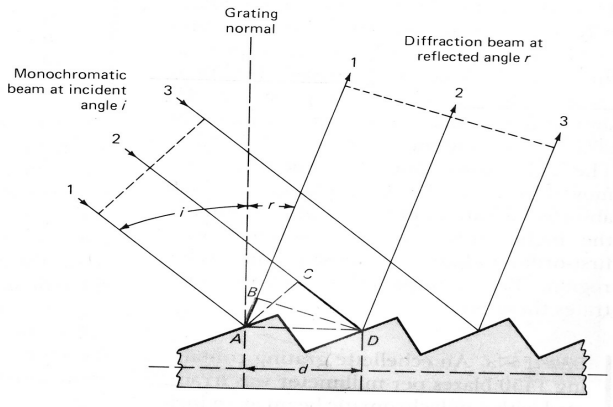
- Separates **polychromatic** light (such as sunlight or light coming from a lamp) into a **range of individual wavelengths**
- Used in most scanning spectrometers including UV, visible, and IR instruments.

Monochromator: Czerny-Turner design



The parallel light rays reach a **diffraction grating, which then bends different wavelengths** of light at different angles (Figure 1D). The light then reaches a second concave mirror that focuses different wavelengths of light at different points (Figure 1E). Rotating the grating (Figure 1D) controls the range of light wavelengths that will then subsequently pass to the CCD detector.

Grating



III. Radiation Transducers (Detectors)

Early detectors in spectroscopic instruments were the human eye, photographic plates or films. Modern instruments contain devices that convert the radiation to an electrical signal.

Two general types of radiation transducers:

a. **Photon detectors**
b. **Thermal detectors**

A. Photon Detectors

Commonly useful in ultraviolet, visible, and near infrared instruments.

Several types of photon detectors are available:

1. **Photovoltaic cells**
2. **Photomultiplier tubes**
3. **Vacuum phototubes**
4. **Silicon photodiodes**
5. **Diode array transducers**
6. **Photoconductivity transducers**

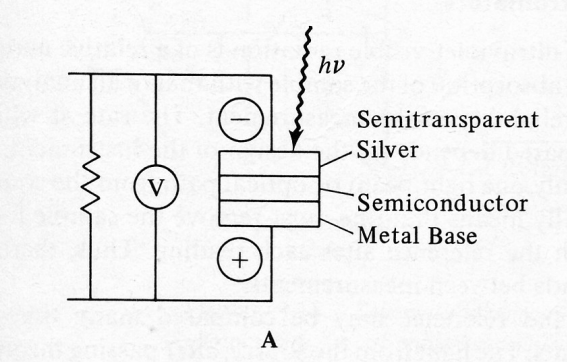
B. Thermal Detectors

- **Used for infrared spectroscopy because photons in the IR region lack the energy to cause photoemission of electrons.**

- **Three types of thermal detectors :**

1. **Thermocouples**
2. **Bolometers**
3. **Pyroelectric transducers**

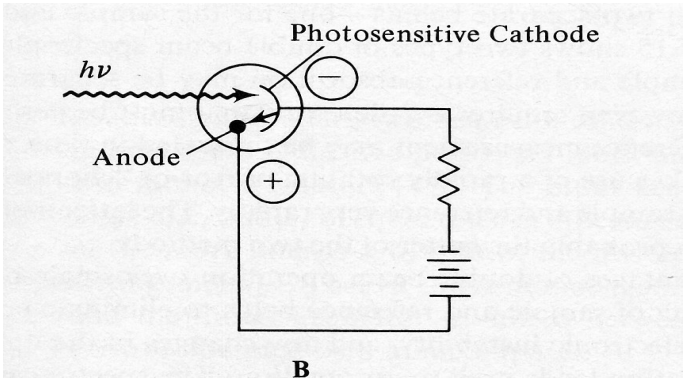
Detector: Barrier Layer/Photovoltaic



Principle of Barrier Layer/Photovoltaic Detector

- This device measures the intensity of photons by means of the voltage developed across the semiconductor layer.
- Electrons, ejected by photons from the semiconductor, are collected by the silver layer.
- The potential depends on the number of photons hitting the detector.

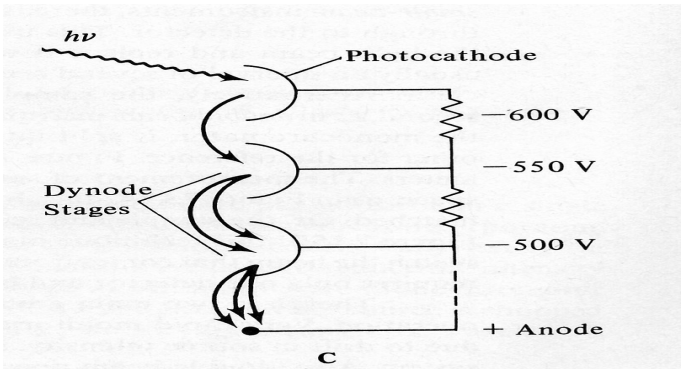
Detector: Phototube



Principle of Phototube Detector

- This detector is a vacuum tube with a cesium-coated photocathode.
- Photons of sufficiently high energy hitting the cathode can dislodge electrons, which are collected at the anode.
- Photon flux is measured by the current flow in the system.

Detector: Photomultiplier



Principle of Photomultiplier Detector

- The type is commonly used.
- The detector consists of a photoemissive cathode coupled with a series of electron-multiplying dynode stages, and usually called a photomultiplier.
- The primary electrons ejected from the photo-cathode are accelerated by an electric field so as to strike a small area on the first dynode.

Principle of Photomultiplier Detector

- The impinging electrons strike with enough energy to eject two to five secondary electrons, which are accelerated to the second dynode to eject still more electrons.
- A photomultiplier may have 9 to 16 stages, and overall gain of 10^6~10^9 electrons per incident photon.

IV. Sample Holder (Container)

- Sample containers, usually called ***cells*** or ***cuvettes*** must have windows that are transparent in the spectral region of interest.
- There are few types of cuvettes:
  - quartz or fused silica
  - silicate glass
  - crystalline sodium chloride

cuvette

QUARTZ OR FUSED SILICA
- REQUIRED FOR UV AND MAY BE USED IN VISIBLE REGION

SILICATE GLASS
- CHEAPER COMPARED TO QUARTZ. USED IN UV

CRYSTALLINE SODIUM CHLORIDE
- USED IN IR

Measuring Absorption of Light

- Detector measures P
- Amount of light transmitted through sample is what is measured
- **Transmittance (T):** fraction of original light that passes through sample
  - Absorbance is measured **INDIRECTLY**

$$T = \frac{P}{P_0} = \frac{\textbf{radiant power not absorbed by sample}}{\textbf{incident radiant power}}$$

$$\%T = 100\ T$$

Absorbance

Beer's Law:

$$A = \varepsilon bc$$

$\varepsilon \equiv$ Molar absorptivity (or extinction coefficient)

$b \equiv$ pathlength light travels through cuvet

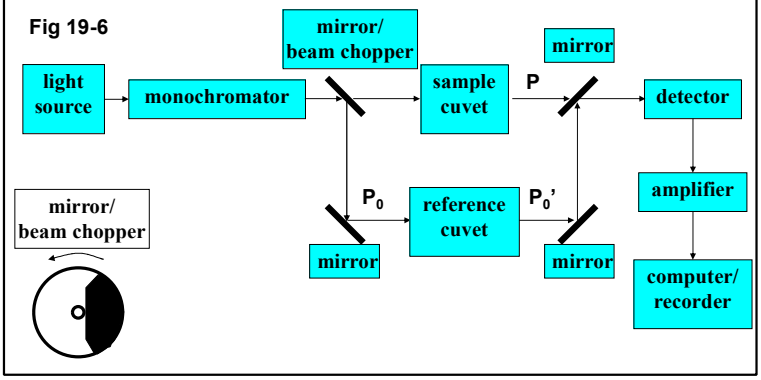
$c \equiv$ concentration of analyte

- Absorbance is directly proportional to concentration

Double-beam Scanning Spectrophotometer

- Alternately measuring P_0 and P by diverting light beam through reference cuvet

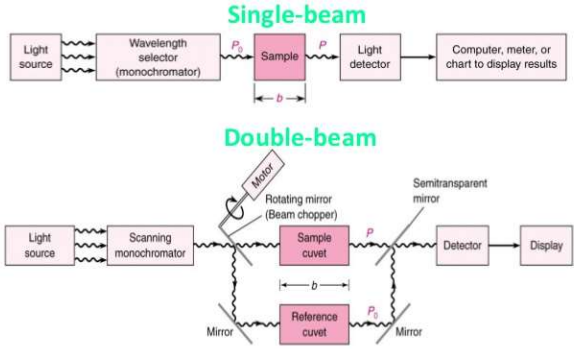
Fig 19-6



Spectrophotometers

- Single-beam spectrophotometer
  - insert reference blank once at beginning of exp't
  - only measure absorbance of EITHER sample OR reference blank at a time
- Double-beam spectrophotometer
  - continuously checks reference blank to account for changes in
    - source intensity (P_0)
    - detector response
  - if absorbance measurement from reference blank changes, spectrophotometer corrects for that change to find true absorbance of analyte

The Spectrophotometer



Quantitative Analysis: Beer's Law

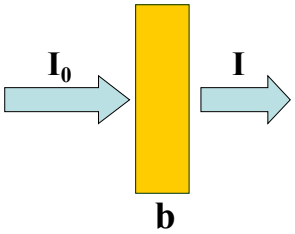
$A=\varepsilon bc$

ε: the molar absorptivity (L mol^{-1} cm^{-1})

b: the path length of the sample

c :the concentration of the compound in solution, expressed in mol L^{-1}

Transmittance



$$T = \frac{I}{I_0} \Rightarrow \frac{dI}{I_0} = kcdb$$

$$\int_{I_0}^{I} \frac{dI}{I_0} = -kc\int_0^b db$$

$$\Rightarrow \ln\left(\frac{I}{I_0}\right) = -kbc = 2.303\log\left(\frac{I}{I_0}\right)$$

$$\Rightarrow -\log\left(\frac{I}{I_0}\right) = -\log T = A = \varepsilon bc$$

$$\varepsilon = \frac{k}{2.303}$$

SUMMARY

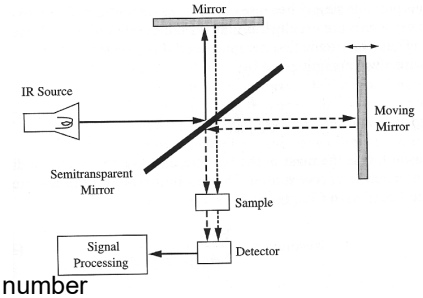
Types of source, sample holder and detector for various EM region

REGION	SOURCE	SAMPLE HOLDER	DETECTOR
Ultraviolet	Deuterium lamp	Quartz/fused silica	Phototube, PM tube, diode array
Visible	Tungsten lamp	Glass/quartz	Phototube, PM tube, diode array
Infrared	Nernst glower (rare earth oxides or silicon carbide glowers)	Salt crystals e.g. crystalline sodium chloride	Thermocouples, bolometers

FTIR: Fourier Transform Infrared Spectroscopy

Molecules absorb energy at characteristic wavelengths

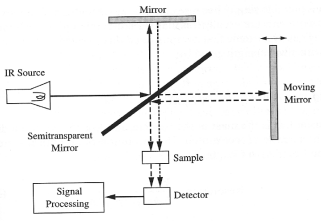
E = hν = hc/λ



Si-O-Si absorbs at wave number 1106/cm

C absorbs at wave number 607/cm

1. IR beam split & follows two separate paths to sample and detector
2. Moving mirror causes two beams to interfere constructively or destructively in a sinusoidal manner.
3. The Fourier transform of the signal will be a delta function proportional to incident beam intensity
4. If the frequency of the source is, swept the FT of the resulting transform will produce an intensity spectrum
5. If we insert a sample, the intensity spectrum will change because of absorption of specific wavelengths
6. Scan of sample is compared to a baseline scan to identify absorbed frequencies



Electrical Characterization: 4-point probe

Used to measure sheet resistivity

$\rho = 1/q(\mu_n n+\mu_p p)\ \Omega\text{-cm}$

us. n>>p or p>>n, so only one term is of interest

$\rho = 2\pi s\ V/I$

Typically,
0.5-mm< s <1.5-mm

Outer probe forces current through wafer; inner probes measure voltage drop