UNIT-IV: Analytical Techniques

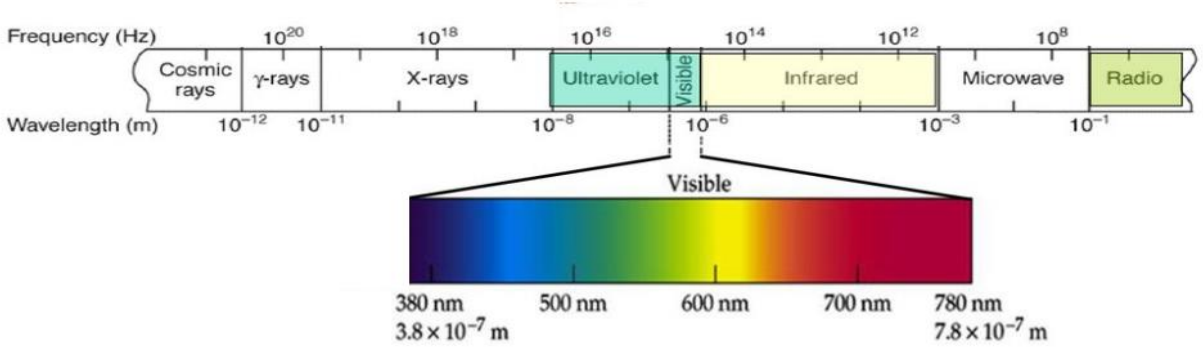
Absorption spectroscopy: Beer-Lambert's law and its limitations, transmittance, Absorbance, and molar absorptivity; Application of Beers-Lamberts law for simultaneous quantitative analysis of Cr in $K_2Cr_2O_7$, Mn in $KMnO_4$

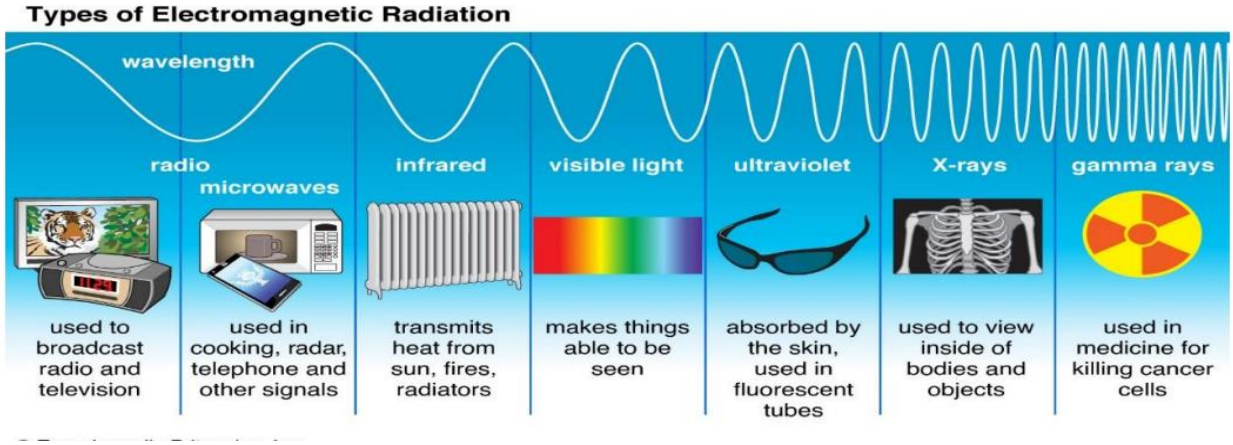
Separation techniques: Solvent extraction: Principle and process, Batch extraction, Continuous extraction and counter current extraction, Industrial Applications.

Absorption spectroscopy:

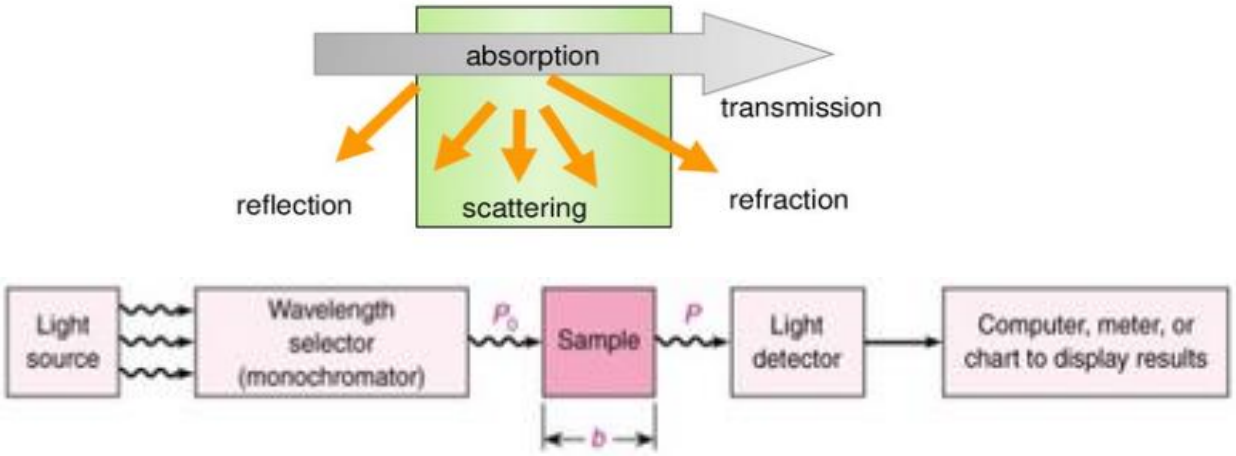
Introduction:

- Spectroscopy is the branch of science that deals with the study of interaction of electromagnetic radiation (EMR) with matter.



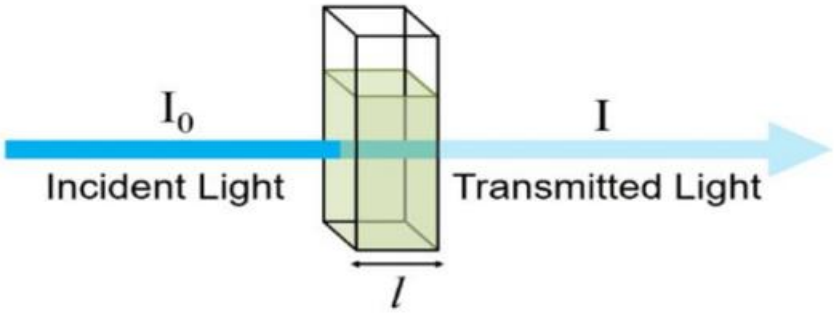


- Spectrophotometer: A device used to measure intensity (I) of light as a function of wavelength (λ) of a light.
- Types of interactions of EMR with matter are: Absorption, Emission, Reflection, Transmission, Scattering, Refraction etc.



- **Some definitions:**

Consider monochromatic light transmitted through a solution; with an incident intensity of I_0 and a transmitted intensity of I.



The **transmittance, T,** of the solution is defined as the ratio of the transmitted intensity, I, over the incident intensity, I_0,

$$T = \frac{I}{I_0}$$

However, it is more commonly expressed as a percentage transmittance: $T(\%) = 100\frac{I}{I_0}$

Absorbance (A) states how much of the light the sample absorbed. It is also referred to as "optical density." Absorbance is calculated as a logarithmic function of Transmittance, T.

$$A = \log_{10}(1/T) = \log_{10}(Io/I)$$

Molar absorptivity, also known as the molar extinction coefficient, is a measure of how well a chemical species absorbs a given wavelength of light.

$$\varepsilon = A/lc$$

The standard units for molar absorptivity are liters per mole centimeter (L mol^{-1} cm^{-1})

- *Absorption laws:*

  Lambert's law: When a beam of monochromatic radiation is passed through the absorbing medium, then the decrease in the intensity of radiation will be directly proportional to the thickness (path length) of the solution.

$$A \alpha l$$
$$A = \varepsilon l$$

- *Beer's law:* When a beam of monochromatic radiation is passed through the absorbing medium, then the decrease in the intensity of radiation will be directly proportional to the concentration of the solution.

$$A \alpha c$$
$$A = \varepsilon c$$

- **Beer-Lambert's law:** When a beam of monochromatic radiation is passed through the absorbing medium, then the decrease in the intensity of radiation will be directly proportional to the thickness (path length) as well as concentration of the solution.

$$A = \varepsilon l c$$

Q: At 249 nm, paracetamol gives 0.330 absorbance when using 0.5 cm thickness cuvette and $\varepsilon = 0.165 \times 10^3$ L/mol-cm. Determine the concentration of the solution.

Solution:

$$A = \varepsilon l c \qquad c = \frac{A}{\varepsilon l}$$

$$c = \frac{0.330}{0.165 \times 10^3 \frac{L}{mol-cm} \text{ X } 0.5 \text{ cm}} = 4 \times 10^{-3} \frac{mol}{Lit}$$

Limitations of Beer-Lambert's law:

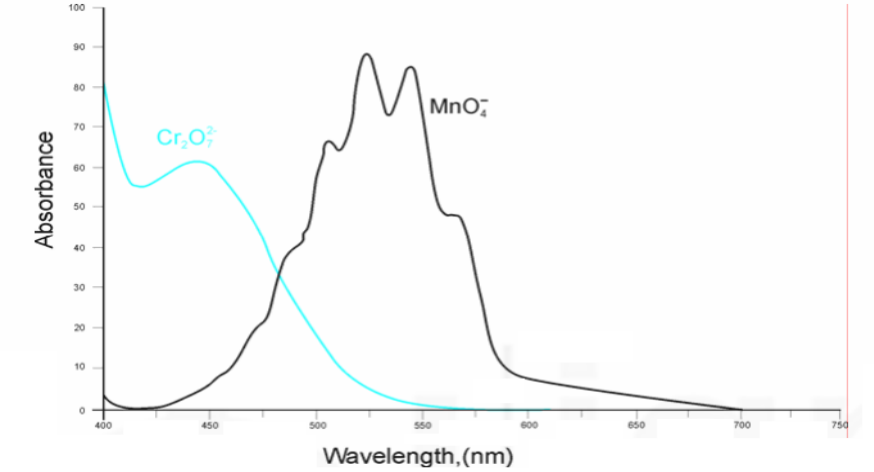
Beer-Lambert's law proves a direct correlation between the absorbance (A) of a molecule to the concentration (c) and the path length (l) of the sample. However, under certain circumstances the Beer-Lambert relationship breaks down and gives a non-linear relationship.

- If the concentration of the solution is more than 10^{-2} M (0.01 M) in that case the linear relation is not obtained. That means the law is deviated.
- Deviations occur due to chemical phenomenon involving the analyte molecules due to association, dissociation and interaction with the solvent to produce a product with different absorption characteristics.

- The law is also deviated if the monochromatic light is not used.
- Change of temperature also leads to deviation of Beer-Lambert's law.

Application of Beers-Lambert's law for simultaneous quantitative analysis of Cr in $K_2Cr_2O_7$, Mn in $KMnO_4$:

- In this experiment, the amounts of chromium and manganese are determined in a given mixture.
- In a given mixture, these are present as dichromate and manganate ions respectively. The spectra of these ions overlap to certain extent.



- The orange red colored dichromate shows maximum absorption (λ_{max}) at 440 nm while for the pink colored permanganate the λ_{max} is at 545 nm.
- However, permanganate also absorbs at 440 nm to a smaller extent. Similarly, dichromate ions also have small absorption at 545 nm. In simple words, both the species absorb at the wavelengths of maximum absorptions.
- The general expressions for the simultaneous equations are:

$$A_{\lambda_1} = C_1(\varepsilon_1)_{\lambda_1} + C_2(\varepsilon_2)_{\lambda_1}$$

$$A_{\lambda_2} = C_1(\varepsilon_1)_{\lambda_2} + C_2(\varepsilon_2)_{\lambda_2}$$

$$A_{440} = \varepsilon_{Cr,440}[Cr_2O_7^{2-}] + \varepsilon_{Mn,440}[MnO_4^-] \quad \text{.....(1)}$$

$$A_{545} = \varepsilon_{Cr,545}[Cr_2O_7^{2-}] + \varepsilon_{Mn,545}[MnO_4^-] \quad \text{.....(2)}$$

- The expressions for the concentrations of dichromate and permanganate ions are:

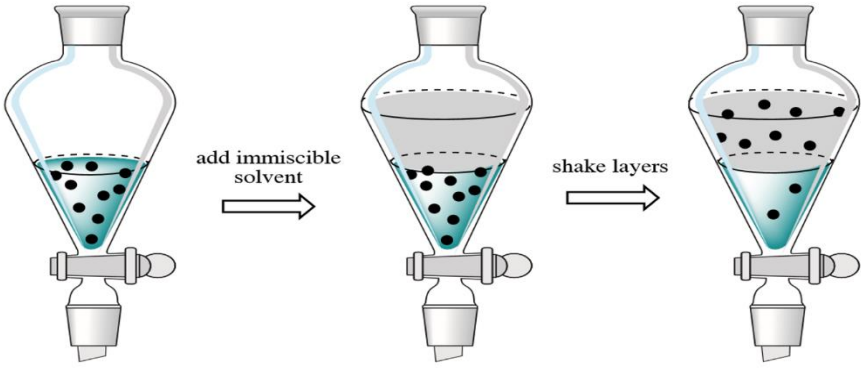
$$\left[Cr_2O_7^{2-}\right] = \frac{A_{440}(\varepsilon_{MnO_4^-})_{545} - A_{545}(\varepsilon_{MnO_4^-})_{440}}{(\varepsilon_{Cr_2O_7^{2-}})_{440}\ (\varepsilon_{MnO_4^-})_{545} - (\varepsilon_{MnO_4^-})_{440}(\varepsilon_{Cr_2O_7^{2-}})_{545}} \quad \ldots (3)$$

$$\left[MnO_4^-\right] = \frac{A_{545} - (\varepsilon_{Cr_2O_7^{2-}})_{545}\left[Cr_2O_7^{2-}\right]}{(\varepsilon_{MnO_4^-})_{545}} \quad \ldots (4)$$

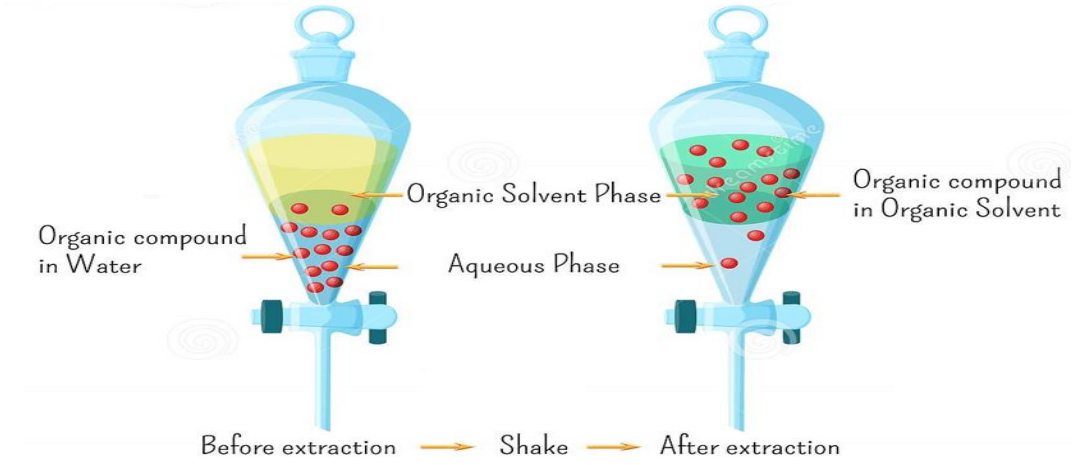
- Thus, the concentrations of the two ions can be obtained from the absorbance measurements at 440 and 545 nm, if we know the molar absorption coefficients for both the ions at these wavelengths.

Solvent extraction: Principle and process:

- Solvent extraction, also called liquid-liquid extraction (LLE), is a method to separate compounds based on their relative solubilities in two different immiscible liquids. These liquids are usually water and an organic solvent. LLE is an extraction of a substance from one liquid into another liquid phase.

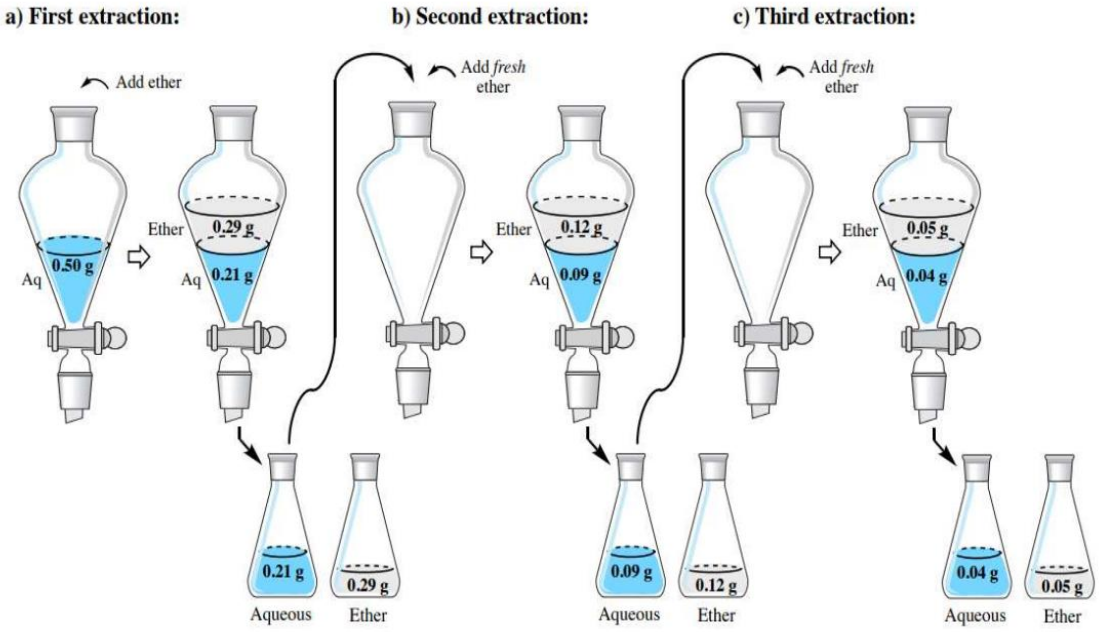


- Organic compounds are generally much more soluble in organic solvents, like benzene, chloroform, and ether, than in water and these solvents are immiscible with water.
- Organic compounds are then quite easily separated from the mixture with inorganic compounds in aqueous medium by adding benzene, chloroform, etc. Upon shaking, these separate into two layers.
- Since organic compounds have their distribution ratio largely in favour of the benzene phase, more of them would pass into a non-aqueous layer. Finally, this non-aqueous layer is removed and distilled to obtain the purified compound.



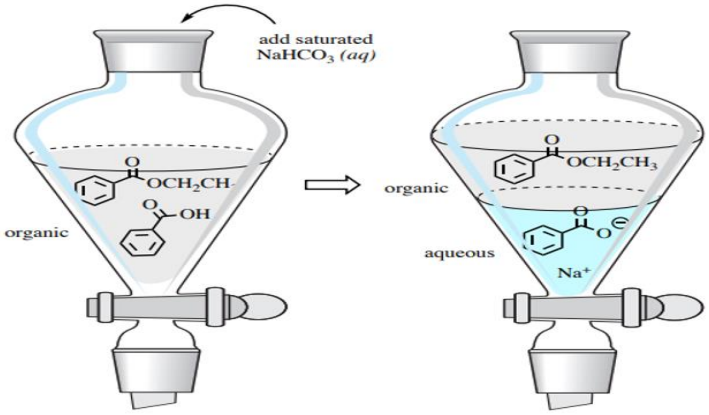
Batch Extraction:

- This is the simplest and most widely used method. In this method, the substance to be extracted is brought in contact with small volumes of the extracting solvent. Hence it is called batch extraction.
- In general, in batch extraction process, a given volume of solution containing solute is shaken with a given volume of the organic solvent (ether, $CHCl_3$ etc.) in a separatory funnel. When the equilibrium is reached, the two layers are then allowed to settle and the layer containing the desired constituent is removed.

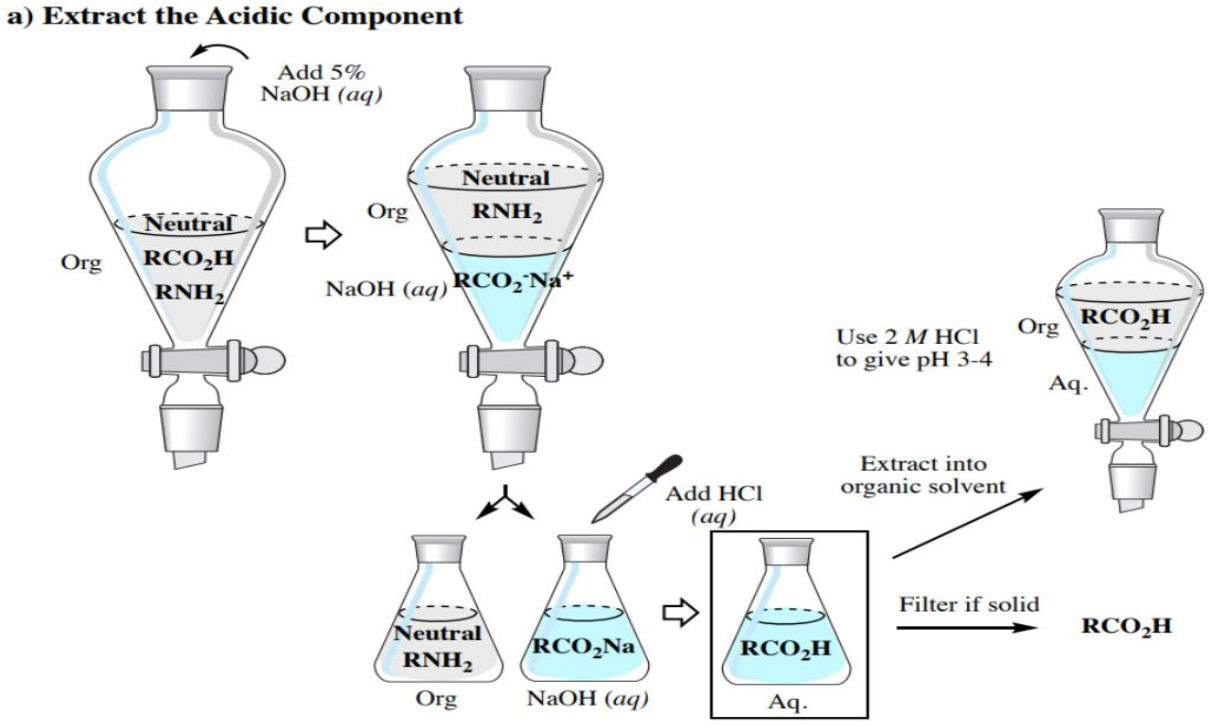


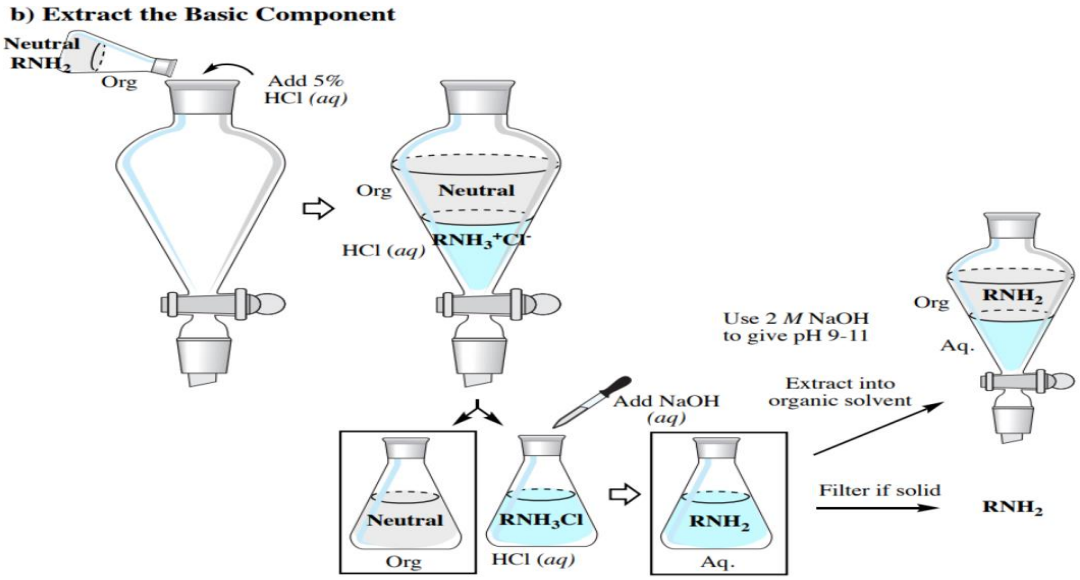
- The extraction process repeated by adding fresh organic solvent to the aqueous solution which is in funnel. Until the completion of the extraction, process was repeated as many times as required.
- The solution which contains the desired constituent collected in each step is mixed together in a flask and distilled to obtain the purified compound.

  Ex: Separation of an ester and a carboxylic acid.



Ex: Separation of a mixture containing acidic (RCO_2H), basic (RNH_2), and neutral components.



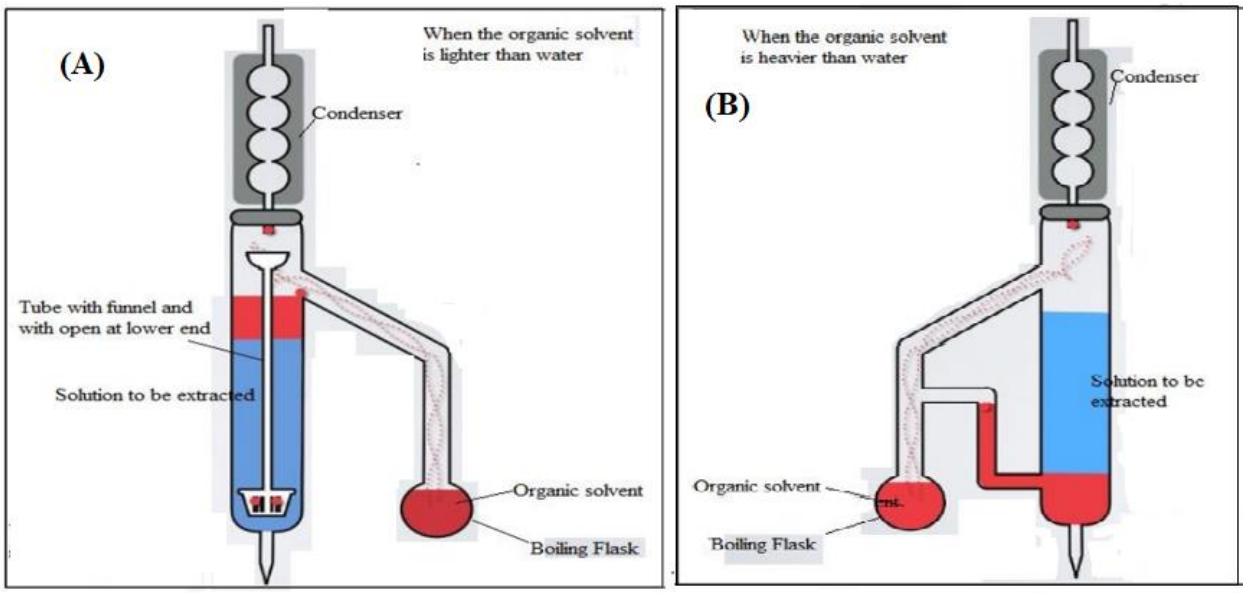


Continuous extraction:

- This method involves the continuous flow of immiscible solvent through the solution to be extracted. The solute should be non-volatile and thermally stable.
- Extraction equipment have been devised for continuous extraction using organic solvents which are lighter than water or heavier than water.

  (A) Solvents lighter than water: ether, toluene etc.

  (B) Solvents heavier than water: dichloromethane or CCl_4, or CS_2 etc.

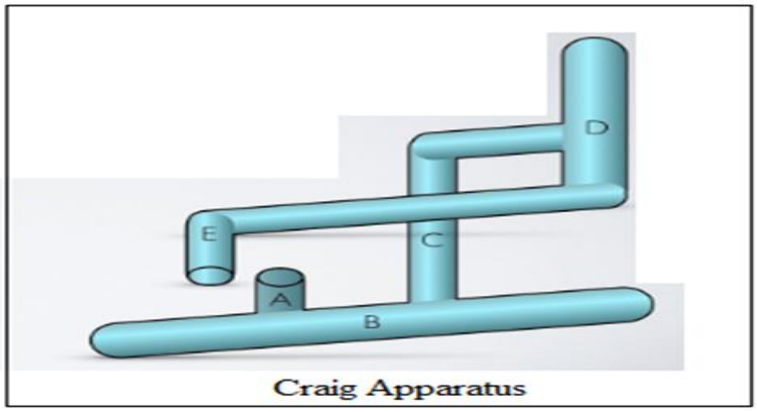


- (A): It consists of a long vertical tube, boiling flask, condenser and a long tube with a funnel at top and open at lower end.

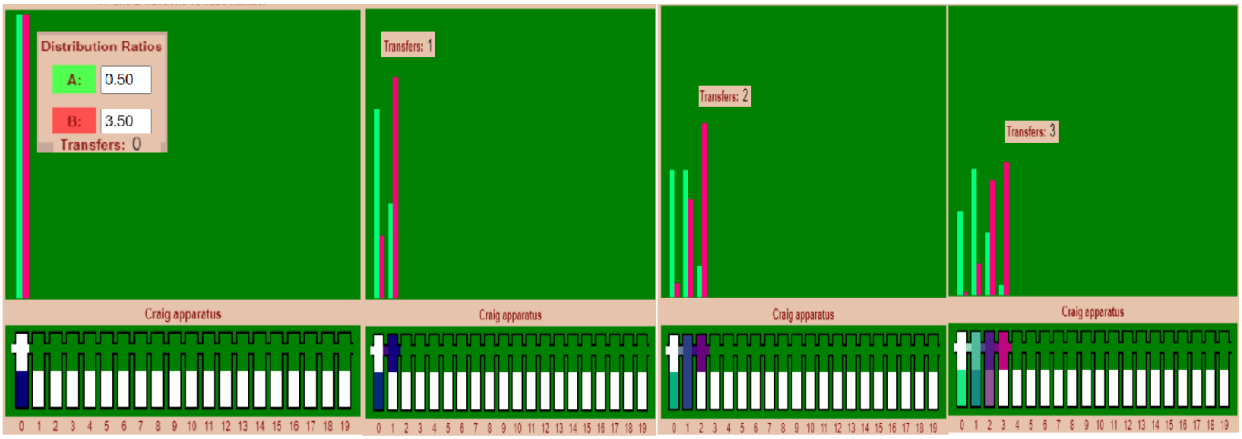
- The solution to be extracted is taken in a long vertical tube. The funnel tube is inserted in it and condenser at the top and the boiling flask with solvent is connected at the bottom of the tube through side arm.
- The solvent distils from a boiling flask and condenses in a condenser. The condensed liquid passes through the funnel downward in a narrow tube which is opened at lower end and enters to the aqueous solution held in a long vertical tube.
- This liquid goes to the bottom but as it is light, it rises to the surface and returns to the boiling flask. During its passage extracted some portion of the dissolved solute from it.
- By repeated separations, all of the desired solute is extracted and caused to accumulate in the boiling flask.
- In this, the level of the solution in the tube is below the side arm hole otherwise some of the aqueous solution being carried over in to the solvent flask.
- (B): It consists of a long vertical tube, boiling flask, condenser. The reservoir contains the some organic solvent.
- The solvent in reservoir is heated slowly which is converted into vapours, which move up and are condensed and the organic solvent is converted into liquid which is heavy and descent.
- While moving through aqueous solution, the solute gets transferred from aqueous to organic and at the bottom we get organic solution. So, the level increases and the corresponding solution will fall in reservoir.
- This continues till maximum amount of solute is transferred from aqueous to organic.
- Then by opening the stopper at the bottom, we can separate organic and aqueous layer, then solute can be extracted from organic solution.

Counter-Current Extraction:

- The multistage separation in LLE is called as counter-current extraction. It is discovered by L.C. Craig, so the process is known as Craig counter-current extraction process.
- The Craig apparatus consists of a large number of connected glass tubes. Five Craig type tubes are sealed together in a single unit. Complete multistage extraction apparatus consists of any number of these five-tube units.
- This is a solvent extraction technique in which two immiscible solvents move in opposite directions in continuous contact with each other with a resultant separation of solutes.



Craig Apparatus

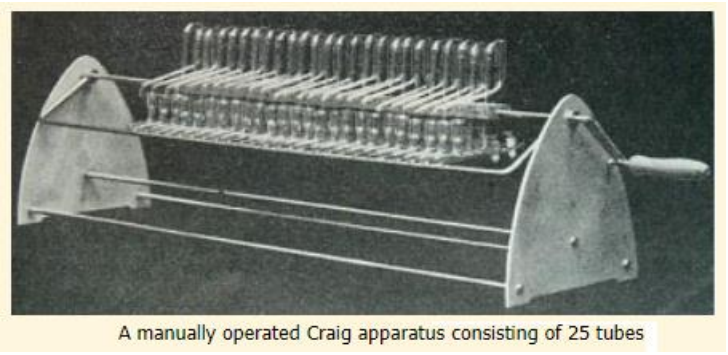


- Craig apparatus consists of a series of glass tubes (r = 0, 1, 2, 3, 4…) that are designed and arranged such that the lighter liquid phase is transferred from one tube to the next.
- The liquid-liquid extractions are taking place simultaneously in all tubes of the apparatus which is usually driven electromechanically.
- In the beginning, tube # 0 contains the mixture of substances to be separated in the heavier solvent and all the other tubes contain equal volumes of the same solvent.
- The lighter solvent is added to tube # 0 (transfers 0), extraction (equilibration) takes place and the phases are allowed to separate.
- The upper phase of tube # 0 is then transferred to tube #1 and fresh solvent is added to tube #0 (transfers 1), and the phases are equilibrated again.
- The upper layers of tubes #0 and #1 are simultaneously transferred to tubes #1 and #2 respectively (transfers 2), and the phases are equilibrated again.
- This cycle is repeated to carry on the process through the other tubes of the apparatus. In this way in a sequence the solute is transferred to different tubes. Obviously, substances with higher distribution ratio move faster than those with a lower distribution ratio.

- Compounds that are more soluble in the upper phase than lower phase faster and farther down the series of tubes while those compounds which are more soluble in the lower phase than the upper phase tend to lag behind.
- The greater the difference of the distribution ratio of various substances, the better the separation between each other. A much larger number of tubes is required to separate mixtures of substances with almost similar distribution ratios.
- The Craig apparatus is only rarely used because modern chromatographic techniques are by far more efficient and convenient.
- It is possible to calculate the relative fraction of the solute present in any tube 'r' after 'n' equilibrations using the expression:

$$f_{n,\,r} = \frac{n!}{r!(n-r)!}\frac{K^r}{(K+1)^n}$$

where n is number of equilibrations, r is tube number and K is distribution coefficient of solute.



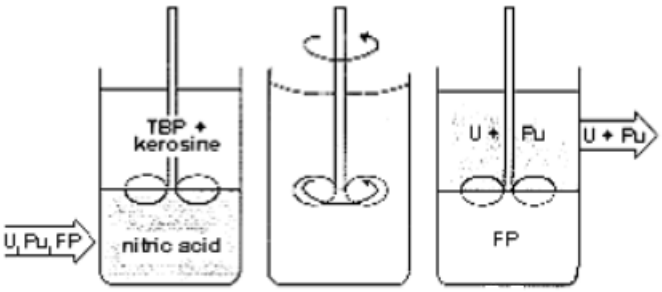
A manually operated Craig apparatus consisting of 25 tubes

Industrial applications of solvent extraction:

- In solvent extraction process, apparatus required are very simple. Time required for analysis is very small. The method is very well used for the detection of trace quantities of substances.
- The method can be used in the extraction of metal as metal chelate where chelate has solubility in an immiscible solvent such as $CHCl_3$ and C_6H_6.

  Ex: As metal-chelates are more soluble in non-polar solvents, Ni (II) in the tetra co-ordinate complex with dimethylglyoxime can be extracted into $CHCl_3$.
- The phenomenon is widely applied in drug analysis and clinical laboratory.
- *Nuclear industry (PUREX Process):*
  - The Plutonium Uranium Redox Extraction (PUREX) is a chemical method used to recovery U and Pu from used nuclear fuel.

- Following the dissolution of the irradiated fuel in aqueous nitric acid, uranium and plutonium are transferred to an organic phase by intensive mixing with an organic solvent (30% tributyl phosphate (TBP) in kerosene), while the fission products (Kr-85, Sr-90, Cs-137) remain in the aqueous nitric phase. Further process steps enable the subsequent separation of uranium and plutonium from one another.



- Solvent extraction is primarily used in waste water treatment for the removal of phenols, creosols, phenolic acids, formaldehyde, nitrobenzene etc.
- Separation of medicinally active portions of plant (and animal) tissues using selective solvents through standard procedures.
- *Extraction of bio-fuel:*
- Biodiesel is produced from vegetable oils or animal fats. The fuel is produced by transesterification—a process that converts fats and oils into biodiesel and glycerin (a co-product).
- Oil or fat is reacted with a short-chain alcohol (usually methanol) in the presence of a catalyst (usually NaOH or KOH) to form biodiesel and glycerin (or glycerol).
- The bio-diesel can be separated by using solvent extraction method.