

**JSS College of Arts, Commerce and Science (Autonomous)**

**Ooty Road, Mysuru**

**MSc Chemistry: I Semester**

**Essentials of Analytical Chemistry**

**Study Material on**

**Unit-II**

**SOLVENT EXTRACTION**

Separation is a method that converts a mixture or solution of chemical substances into two or more distinct product mixtures

**Results**

- ✓ to retrieve at least one of the interested constituents
- ✓ may fully divide the mixture into pure constituents
- ✓ Purification/to remove interferences

**Basis:**

Differences in chemical or physical properties (such as size, shape, mass, density, or chemical affinity) between the constituents of a mixture

**Separation of compounds from different systems**

**I. SOLID IN LIQUID MIXTURES**

Homogenous mixtures:

1. Evaporation
2. Distillation
3. Centrifugation

Heterogenous mixtures:

1. Sedimentation / gravitation
2. Filtration
3. Magnetic separation
4. Fractional distillation

**II. Liquid in liquid mixtures**

Homogenous:

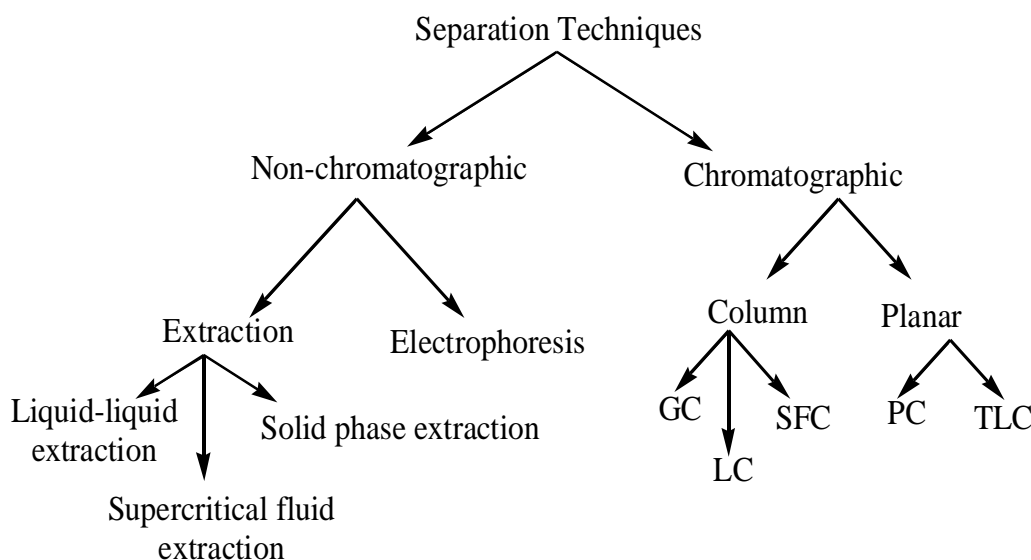
1. Simple or fractional distillation.
2. Chromatography
3. Electrophoresis

Heterogenous: Partition by separation using funnel

**QUALITY aspect of finished product is very significant in:**

1. Mining industry
2. Food processing laboratories/industries
3. Synthetic laboratories/in research

**Family tree of separation techniques**



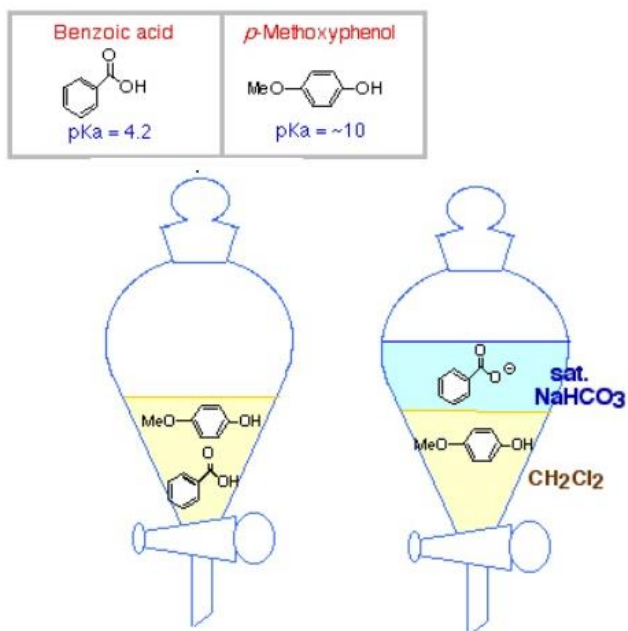
## SOLVENT EXTRACTION

Is a process in which compounds are separated based on their relative SOLUBILITIES.

**Ex: Separation of Benzoic acid and *p*-methoxy phenol**

**Requirements:** Solvents and separating funnel

- Mixture in CH<sub>2</sub>Cl<sub>2</sub> in Sep. funnel
- Add sat.NaHCO<sub>3</sub> solution
- Shake separating funnel
- Equillibrate



Therefore, solvent extraction is a process in which selective transfer of solute from one liquid phase to another liquid phase based on its relative solubility is involved.

### Aqueous Solvents

#### Factors to be considered:

- Purity
- Even modifiers too with adequate purity
- During dissolution, analyte has to be made less hydrophilic and more hydrophobic

#### Choices:

- Pure Water
- Acidic (pH 0 - 6) /basic (pH 8 - 14)
- High Ionic strength solutions
- Complexing agents
- Ion-pairing agents
- Chiral agents

## Organic phase

- Immiscibility
- Density
- Volatility
- Toxicity
- Polarity (matching with solute)
- Cost

## Choices:

- Chlorinated solvents



- Hydrocarbons

- ✓ Aliphatics: C<sub>5</sub> (pentane) and above
- ✓ Aromatics: Toluene & Xylene
- ✓ Alcohols: C<sub>6</sub> and above (immiscible with water)
- ✓ Esters
- ✓ Ketones: C<sub>6</sub> and above
- ✓ Ethers: Diethyl and above

## Theory of solvent extraction-Partition

Solvent extraction, sometimes called liquid-liquid extraction, involves **the selective transfer of a substance from one liquid phase to another**. Usually, an aqueous solution of the sample is extracted with an immiscible organic solvent. **For example**, if an aqueous solution of iodine and sodium chloride is shaken with carbon tetrachloride, and the liquids allowed to separate, most of the iodine will be transferred to the carbon tetrachloride layer, whilst the sodium chloride will remain in the aqueous layer. The extraction of a solute in this manner is governed by the *Nernst partition or distribution law* which states that “*at equilibrium, a given solute will always be distributed between two essentially immiscible liquids in the same proportions*”. Thus, for solute A distributing between an aqueous and an organic solvent,

$$[\text{A}]_{\text{o}}/[\text{A}]_{\text{aq}} = K_{\text{D}} \text{ ----- (1)}$$

where square brackets denote concentrations (strictly activities) and  $K_D$  is known as the equilibrium distribution or partition coefficient which is independent of total solute concentration.

It should be noted that constant temperature and pressure are assumed, and that A must exist in exactly the same form in both phases. Equilibrium is established when the chemical potentials (free energies) of the solute in the two phases are equal and is usually achieved within a few minutes by vigorous shaking. The value of  $K_D$  is a reflection of the relative solubilities of the solute in the two phases.

In many practical situations solute A may dissociate, polymerize or form complexes with some other component of the sample or interact with one of the solvents. In these circumstances the value of  $K_D$  does not reflect the overall distribution of the solute between the two phases as it refers only to the distributing species. Analytically, the total amount of solute present in each phase at equilibrium is of prime importance, and the extraction process is therefore better discussed in terms of the distribution ratio  $D$  where

$$D = (C_A)_o / (C_A)_{aq} \text{ ----- (2)}$$

and  $(C_A)$  represents the total concentration of all forms of solute A. If no interactions involving A occurred in either phase,  $D$  would be equal to  $K_D$ . Considerable variation in the experimental value of  $D$  can be achieved by altering solution conditions so that solvent extraction is a very versatile technique.

### Efficiency of Extraction

The efficiency of an extraction depends on the magnitude of  $D$  and on the relative volumes of the liquid phases. The percentage extraction is given by

$$E = 100D / [D + (V_{aq}/V_o)] \text{ ----- (3)}$$

where  $V_{aq}$  and  $V_o$  are the volumes of the aqueous and organic phases respectively, or

$$E = 100D / (D + 1) \text{ ----- (4)}$$

when the phases are of equal volume.

If  $D$  is large, i.e.  $> 10^2$ , a single extraction may effect virtually quantitative transfer of the solute, whereas with smaller values of  $D$  several extractions will be required. The amount of solute remaining in the aqueous phase is readily calculated for any number of extractions with equal volumes of organic solvent from the equation

$$(C_{\text{aq}})_n = C_{\text{aq}} [V_{\text{aq}} / (DV_o + V_{\text{aq}})]^n \text{ ----- (5)}$$

where  $(C_{\text{aq}})_n$  is the amount of solute remaining in the aqueous phase, volume  $V_{\text{aq}}$ , after  $n$  extractions with volumes  $V_o$  of organic phase, and  $C_{\text{aq}}$  is the amount of solute originally present in the aqueous phase.

If the value of  $D$  is known, equation (5) is useful for determining the optimum conditions for quantitative transfer.

**Suppose, for example,** that the complete removal of 0.1 g of iodine from 50 cm<sup>3</sup> of an aqueous solution of iodine ( $I_2$ ) and sodium chloride is required. Assuming the value of  $D$  for carbon tetrachloride/water is 85, then for a single extraction with 25 cm<sup>3</sup> of  $\text{CCl}_4$ ,

$$\begin{aligned} (C_{\text{aq}})_1 &= 0.1 [50 / (85 \times 25 + 50)]^1 \\ &= 0.0023 \text{ g in } 50 \text{ cm}^3 \end{aligned}$$

i.e. 97.7% of the  $I_2$  is extracted.

For three extractions ( $n = 3$ ) with 8.33 cm<sup>3</sup> of  $\text{CCl}_4$ ,

$$\begin{aligned} (C_{\text{aq}})_3 &= 0.1 [50 / (85 \times 8.33 + 50)]^3 \\ &= 0.000029 \text{ g in } 50 \text{ cm}^3 \end{aligned}$$

i.e. 99.97% of the  $I_2$  is extracted which for most purposes can be considered quantitative.

It is clear therefore that extracting several times with small volumes of organic solvent is more efficient than one extraction with a large volume. This is of particular significance when the value of  $D$  is less than  $10^2$ .

### Selectivity of Extraction

Often, it is not possible to extract one solute quantitatively without partial extraction of another. The ability to separate two solutes depends on the relative magnitudes of their distribution ratios. For solutes A and B, whose distribution ratios are  $D_A$  and  $D_B$ , the separation factor  $\beta$  is defined as the ratio  $D_A/D_B$  where  $D_A > D_B$ . **Table 1** shows the degrees of separation achievable with one extraction, assuming that  $D_A = 10^2$ , for different values of  $D_B$  and  $\beta$ . For an essentially quantitative separation  $\beta$  should be at least  $10^5$ .

**Table 1** Separation of two solutes with one extraction, assuming equal volumes of each phase

$D_A$	$D_B$	$\beta$	%A Extracted	%B Extracted
	10	10	99.0	90.9
	1	$10^2$	99.0	50.0
$10^2$	$10^{-1}$	$10^3$	99.0	9.1
	$10^{-2}$	$10^4$	99.0	1.0
	$10^{-3}$	$10^5$	99.0	0.1

Successive extractions, whilst increasing the efficiency of extraction of both solutes, may lead to a poorer separation. For example, if  $D_A = 10^2$  and  $D_B = 10^{-1}$ , one extraction will remove 99.0% of A and 9.1% of B whereas two extractions will remove 99.99% of A but 17% of B. In practice, a compromise must frequently be sought between completeness of extraction and efficiency of separation. It is often possible to enhance or suppress the extraction of a particular solute by adjustment of pH or by complexation. This introduces the added complication of several interrelated chemical equilibria which makes a complete theoretical treatment more difficult.

A separation can be made more efficient by adjustment of the proportions of organic and aqueous phases. The optimum ratio for the best separation is given by the Bush-Densen equation

$$V_o/V_{aq} = (1/D_A D_B)^{1/2} \quad \text{----- (6)}$$

## Extraction Systems

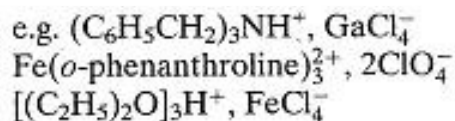
The basic requirement for a solute to be extractable from an aqueous solution is that it should be uncharged or can form part of an uncharged ionic aggregate. Charge neutrality reduces electrostatic interactions between the solute and water and hence lowers its aqueous solubility. Extraction into a less polar organic solvent is facilitated if the species is not hydrated, or if the coordinated water is easily displaced by hydrophobic coordinating groups such as bulky organic molecules. There are three types of chemical compound which can fulfil one or more of these requirements:

(1) essentially covalent, neutral molecules

e.g.  $I_2$ ,  $GeCl_4$ ,  $C_6H_5COOH$

(2) uncharged metal chelates e.g. metal complexes of acetylacetone, 8-hydroxyquinoline, dithizone, etc.

## (3) ion-association complexes



The partition of all three types should obey the Nernst law, but in most cases the concentrations of extractable species are affected by chemical equilibria involving them and other components of the system. These must be taken into account when calculating the optimum conditions for quantitative extraction or separation.

- **Extraction of Covalent, Neutral Molecules**

In the absence of competing reactions in either phase and under controlled conditions, the extraction of a simple molecule can be predicted using equations (3) to (5). However, the value of the distribution ratio  $D$  may be **pH dependent** or **it may alter in the presence of a complexing agent**. It may also be affected by association of the extracting species in either phase. These effects are considered in turn.

**pH Effect**

Consider the extraction of a carboxylic acid from water into ether. The partition coefficient is given by

$$K_D = \frac{[RCOOH]_{et}}{[RCOOH]_{aq}} \quad \text{----- (7)}$$

In water, dissociation occurs



and the acid dissociation constant is given by

$$K_a = \frac{[RCOO^-]_{aq}[H^+]_{aq}}{[RCOOH]_{aq}} \quad \text{----- (8)}$$

The distribution ratio, which involves the total concentration of solute in each phase, is

$$D = \frac{[RCOOH]_{et}}{[RCOOH]_{aq} + [RCOO^-]_{aq}} \quad \text{----- (9)}$$

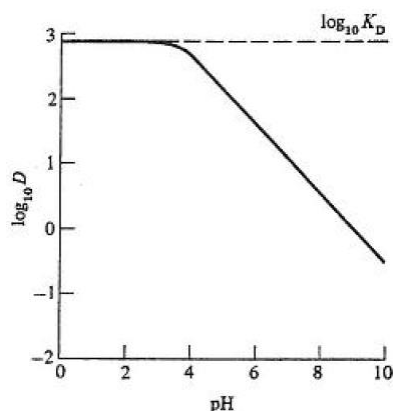
Substituting for  $[RCOO^-]_{aq}$  in (9) and rearranging

$$D = \frac{[RCOOH]_{et}}{[RCOOH]_{aq}(1 + K_a/[H^+]_{aq})} \quad \text{----- (10)}$$

$$\therefore D = \frac{K_D}{1 + K_a/[H^+]_{aq}} \quad \text{----- (11)}$$



At low pH, where the acid is undissociated,  $D \approx K_D$  and the acid is extracted with greatest efficiency. At high pH, where dissociation of the acid is virtually complete,  $D$  approaches zero and extraction of the acid is negligible. Graphical representation of equation (11) for benzoic acid shows the optimum range for extraction, **Figure 1(a)**. Curves of this type are useful in assessing the separability of acids of differing  $K_a$  values. A similar set of equations and extraction curve can be derived for bases, e.g. amines.

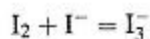


**Figure 1:** The effect of pH and complex formation on extracting species.

(a)  $\log_{10} D$  against pH for the extraction of benzoic acid,  $K_a = 6.3 \times 10^{-5} \text{ mol dm}^{-3}$ .

### Effect of Complex Formation

Returning to the extraction of iodine from an aqueous solution of iodine and sodium chloride, the effect of adding iodide to the system is to involve the iodine in formation of the triiodide ion



and

$$K_f = \frac{[I_3^-]_{\text{aq}}}{[I_2]_{\text{aq}}[I^-]_{\text{aq}}} \quad \text{----- (12)}$$

where  $K_f$  is the formation constant of the triiodide ion.

The partition coefficient is given by

$$K_D = \frac{[I_2]_o}{[I_2]_{\text{aq}}} \quad \text{----- (13)}$$

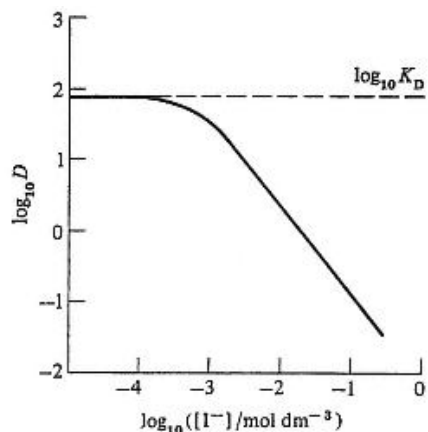
and the distribution ratio by

$$D = \frac{[I_2]_o}{[I_2]_{\text{aq}} + [I_3^-]_{\text{aq}}} \quad \text{----- (14)}$$

Substituting for  $[I_3^-]_{\text{aq}}$  in (14) and rearranging,

$$D = \frac{K_D}{1 + K_f[I^-]_{\text{aq}}} \quad \text{----- (15)}$$

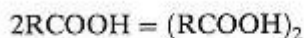
Thus, the presence of iodide affects  $D$  in such a way that at very low concentrations and iodine is extracted with greatest efficiency. At high iodide concentrations,  $K_f[I^-]_{\text{aq}} \gg 1$ , and  $D$  is reduced with a consequent reduction in the extraction of iodine (**Figure 1(b)**).



**Figure 1:** The effect of pH and complex formation on extracting species.  
(b)  $\log_{10} D$  against  $\log_{10} ([I^-]/\text{mol dm}^{-3})$  for the extraction of  $I_2$ .

### Effect of Association

The distribution ratio is increased if association occurs in the organic phase. Carboxylic acids form dimers in solvents of low polarity such as benzene and carbon tetrachloride,



$$K_{\text{dimer}} = \frac{[(\text{RCOOH})_2]_o}{[\text{RCOOH}]_o^2} \quad \text{----- (16)}$$

and

$$D = \frac{[\text{RCOOH}]_o + 2[(\text{RCOOH})_2]_o}{[\text{RCOOH}]_{\text{aq}}} \quad \text{----- (17)}$$

Substituting for  $[(\text{RCOOH})_2]_o$  in (17) and rearranging,

$$D = \frac{[\text{RCOOH}]_o + 2K_{\text{dimer}}[\text{RCOOH}]_o^2}{[\text{RCOOH}]_{\text{aq}}} \quad \text{----- (18)}$$

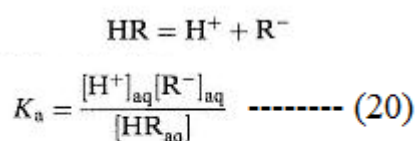
$$\therefore D = K_D(1 + 2K_{\text{dimer}}[\text{RCOOH}]_o) \quad \text{----- (19)}$$

If  $K_{\text{dimer}}$  is large  $D$  becomes larger than  $K_D$  at low pH, resulting in a more efficient extraction of the acid. Dimerization is only slight in oxygenated solvents and extraction into them is therefore less efficient than into benzene or carbon tetrachloride.

- **Extraction of Uncharged Metal Chelates**

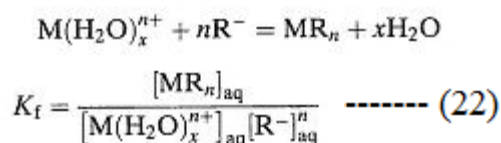
To form uncharged chelates which can readily be extracted into organic solvents the reagent must behave as a weak acid whose anion can participate in charge neutralization and contain hydrophobic groups to reduce the aqueous solubility of the complex. The formation and extraction of the neutral chelate is best considered stepwise as several equilibria are involved.

For example, a monobasic reagent HR dissociates in aqueous solution (dissociation constant  $K_a$ ) and is distributed between the organic and aqueous phases (distribution coefficient  $K_{DR}$ ). Thus



$$K_{DR} = \frac{[\text{HR}]_{\text{o}}}{[\text{HR}]_{\text{aq}}} \text{----- (21)}$$

The hydrated metal ion  $\text{M}(\text{H}_2\text{O})_x^{n+}$  reacts with the reagent anion  $\text{R}^-$  to form the neutral chelate  $\text{MR}_n$  (formation constant  $K_f$ ), i.e.



The metal chelate distributes itself between the aqueous and organic phases according to the Nernst law

$$K_{DC} = \frac{[\text{MR}_n]_{\text{o}}}{[\text{MR}_n]_{\text{aq}}} \text{----- (23)}$$

and the corresponding distribution ratio is

$$D = \frac{[\text{MR}_n]_{\text{o}}}{([\text{MR}_n]_{\text{aq}} + [\text{M}(\text{H}_2\text{O})_x^{n+}]_{\text{aq}})} \text{----- (24)}$$

If several simplifying assumptions are made, e.g.

- (1) the concentrations of chelated species other than  $\text{MR}_n$  are negligible
- (2) the concentrations of hydroxy or other anion coordination complexes are negligible
- (3) the reagent HR and the chelate  $\text{MR}_n$  exist as simple undissociated molecules in the organic phase, and  $[\text{MR}_n]_{\text{aq}}$  is negligible then it can be shown that

$$D = \frac{K_f K_{Dc} K_a^n [\text{HR}]_o^n}{K_{Dr}^n [\text{H}^+]_{\text{aq}}^n} \text{----- (25)}$$

or

$$D = K^* [\text{HR}_o^n] [\text{H}^+]_{\text{aq}}^{-n} \text{----- (26)}$$

(Substituting for each equilibrium constant in (25) gives equation (24)).

Thus, for a given reagent and solvent, the extraction of the metal chelate is dependent only upon pH and the concentration of reagent in the organic phase and is *independent* of the initial metal concentration. In practice, a constant and large excess of reagent is used to ensure that all the complexed metal exists as  $\text{MR}_n$  and  $D$  is then dependent only on pH, i.e.

$$D = K^{*'} [\text{H}^+]_{\text{aq}}^{-n} \text{----- (27)}$$

or

$$\log D = \log K^{*'} = npH \text{----- (28)}$$

where

$$K^{*'} = (K_f K_{Dc} K_a^n [\text{HR}]_o^n) / K_{Dr}^n \text{----- (29)}$$

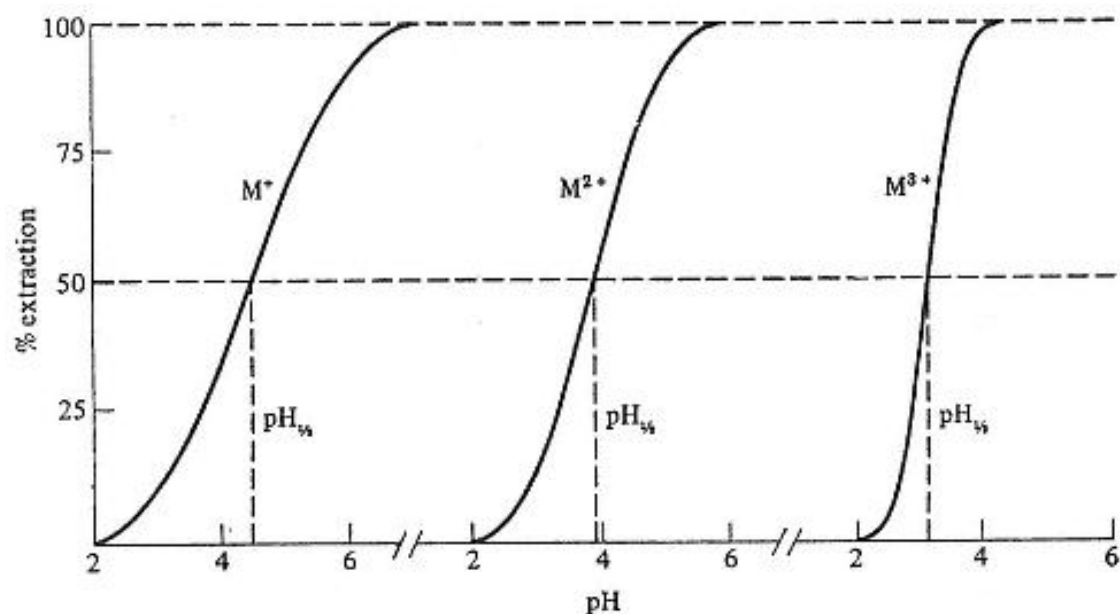
The relation between  $D$  and  $E$ , the percentage extracted, is

$$D = E / (100 - E) \text{----- (30)}$$

for equal volumes of the two phases

$$\therefore \log D = \log E - \log (100 - E) = \log K^{*'} + npH \text{----- (31)}$$

Equation (31), which defines the extraction characteristics for any chelate system, is represented graphically in **Figure 2** for a mono-, di- and trivalent metal, i.e.  $n = 1, 2$  and  $3$  respectively, and shows the pH range over which a metal will be extracted. No significance should be attached to the positioning of the curves relative to the pH scales as these are determined by the value of  $K^{*'}$ . Thus the more acidic the reagent or the stronger the metal complex, the lower the pH range over which the metal will be extracted. Increased reagent concentration has a similar effect.



**Figure 2:** Extraction as a function of pH for metals of different formal valencies.  
(Note: the position of each curve along the pH abscissa is not significant).

The pH at which 50% of the metal is extracted,  $pH_{1/2}$ , can be used to assess the degree of separability of two or more metals. At  $E = 50$ , equation (31) reduces to

$$\log K^{*'} = -npH_{\frac{1}{2}} \quad \text{----- (32)}$$

Substituting this value for  $\log K^{*'}$  in equation (28)

$$\log D = n(pH - pH_{\frac{1}{2}}) \quad \text{----- (33)}$$

For two metals, the separation factor  $\beta$  is defined as  $D'/D''$ , where  $D' > D''$ , or

$$\log \beta = \log D' - \log D'' \quad \text{----- (34)}$$

Therefore, for extraction at a specified pH,

$$\log \beta = n'(pH - pH_{\frac{1}{2}}') - n''(pH - pH_{\frac{1}{2}}'') \quad \text{----- (35)}$$

If  $n' = n''$ , i.e. the metals have the same formal valency,

$$\log \beta = n\Delta pH_{\frac{1}{2}} \quad \text{----- (36)}$$

Assuming that  $\log \beta$  should be at least 5 for an essentially quantitative separation by a single extraction  $\Delta pH_{1/2}$  should be 5, 2.5 and 1.7 respectively for pairs of mono-, di- and trivalent metals. Selectivity by pH control is greatest, therefore, for trivalent metals and least for monovalent. This is reflected in the slopes of the curves which are determined by  $n$  and decrease in the order  $M^{3+} > M^{2+} > M^{+}$ .

It can be seen from equation (25) that the value of  $\beta$  is determined by the formation constants and distribution coefficients of the two chelates, i.e.

$$\beta = D'/D'' = (K'_f K'_{D_c}) / (K''_f K''_{D_c}) \text{ ----- (37)}$$

If  $\beta$  is insufficiently large to enable a quantitative separation to be made by pH control alone, the addition of a *masking agent* which forms a water-soluble complex more strongly with one metal than the other will shift the extraction curve for the former to a higher pH range with a consequent increase in  $\beta$ , which is now given by

$$\beta = (K'_f K'_{D_c} K''_{f_m}) / (K''_f K''_{D_c} K'_{f_m}) \text{ ----- (38)}$$

where  $K'_{f_m}$  and  $K''_{f_m}$  are the formation constants of the metal complexes with the masking agent and  $K''_{f_m} > K'_{f_m}$ . Some examples of neutral chelate extraction systems are given in **Table 2**.

**Table 2** Typical chelate extraction systems

Chelating agent	Metals extracted
$\beta$ -diketones e.g. acetylacetone, thenoyltrifluoro-acetylacetone	react with over 50 metals; especially useful for alkali metals, Be, Sn, Cr, Mn, Mo
8-hydroxyquinoline (oxine) and its derivatives	react with over 50 metals, especially useful for Al, Mg, Sr, V, W
$\alpha$ -dioximes e.g. dimethylglyoxime, $\alpha$ -furildioxime	Ni, Pd
di-alkyldithiocarbamates	react with many metals including Bi, Tl(III), Sb(III), Te(IV), As(III), Se(IV), Sn(IV), V(V)
dithizone (diphenyldithiocarbazone)	Pb, Hg, Cu, Pd, Pt, Ag, Bi, Zn and others
cupferron (ammonium salt of <i>N</i> -nitrosophenylhydroxylamine)	reacts with many metals, including Fe(III), Ga, Sb(III), Ti(IV), Sn(IV), Hf, Zr, V(V), U(IV), Mo(VI)
PAN (1-(2-pyridylazo)-2-naphthol)	reacts with over 50 metals, including U(VI), In, V(V), Pd, Zn, Cd, Mn, Y
1-nitroso-2-naphthol	Co(III) (Cu, Ni)

- **Extraction of Ion-association Complexes**

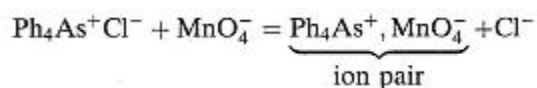
The extraction of charged species from an aqueous solution is not possible unless the charge can be neutralized by chelation, as described in the previous section, or by association with other ionic species of opposite charge to form a complex that is electrically neutral. A further requirement to aid extraction is that at least one of the ions involved should contain bulky hydrophobic groups. Metals and mineral acids can both be extracted as cationic or anionic complexes, chelated or otherwise, and often solvated by the organic solvent. The Nernst partition law is obeyed by ion-association systems but the number of equilibria involved is greater than for neutral chelates and the mathematical treatment, which is correspondingly more involved.

**Salting-out agents** are often used to increase the distribution ratio. These are electrolytes, such as di- and trivalent metal nitrates, with a pronounced tendency to hydration. They bind large numbers of water molecules thereby lowering the dielectric of the solution and favouring ion-association.

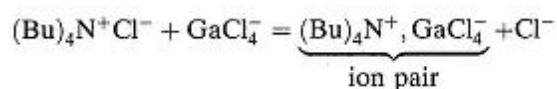
Ion-association complexes may be classified into three types: *non-chelated complexes*; *chelated complexes*; *oxonium systems*.

### *Non-chelated Complexes*

These include the simplest ion-association systems in which bulky cations and anions are extracted as pairs or aggregates without further coordination by solvent molecules. An example of this type of system is the extraction of manganese or rhenium as permanganate or perrhenate into chloroform by association with the tetraphenylarsonium cation derived from a halide salt



Anionic metal complexes such as  $\text{ZnCl}_4^{2-}$ ,  $\text{GaCl}_4^-$  and  $\text{Co}(\text{CN})_6^{3-}$  can be extracted with tetraalkylammonium salts, e.g.



Certain long-chain alkylammonium salts, notably tricaprylmethyl-ammonium chloride (Aliquat 336-S) and tri-*iso*-octylamine hydrochloride (TIOA) are liquids, sometimes referred to as liquid anion exchangers, which can form extractable ion pairs or aggregates with anionic metal complexes in the same way, e.g. in sulphuric acid solution uranium is extracted as  $2(\text{TIOA}-\text{H}^+), \text{UO}_2(\text{SO}_4^{2-})_2$ .

Alkyl esters of phosphoric acid and phosphine oxides will extract metals and mineral acids by direct solvation. Tri-*n*-butyl phosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO)

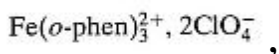


are both used for this purpose and will extract uranium, actinides and lanthanides as well as many other metals. The extractable species, such as  $\text{UO}_2^{2+}(\text{TBP})_2$ ,  $2(\text{NO}_3^-)$  and  $\text{H}^+(\text{TBP})_2$ ,  $\text{UO}_2(\text{NO}_3^-)_3$  in the case of uranium, vary in composition depending on acidity and total electrolyte concentration, but direct solvation of the metal ion or protons always plays an important role. TOPO is a better extractant than TBP,

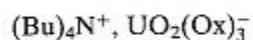
particularly for mineral acids, forming more definite solvates. Table 3 includes some of the more important non-chelated systems.

### *Chelated Complexes*

Many cationic and anionic chelates which are not extractable by the usual organic solvents due to residual charge can be extracted in the presence of a suitable counter-ion. Two examples of charged chelates extractable by chloroform are the Fe(II)-*o*-phenanthroline cation using perchlorate as a counter-ion,

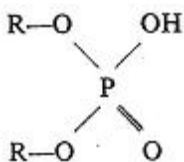


and the UO<sub>2</sub>(II)-8-hydroxyquinoline anion using a tetraalkylammonium cation as the counter ion,



EDTA complexes of trivalent metals can be extracted successively with liquid anion exchangers such as Aliquat 336-S by careful pH control. Mixtures of lanthanides can be separated by exploiting differences in their EDTA complex formation constants.

Acidic alkyl esters of phosphoric acid, of which dibutyl-phosphoric acid (HDBP) and di(2-ethylhexyl) phosphoric acid (HDEHP) are typical,



form extractable complexes by chelation and solvation, the acidic hydrogen being replaced by a metal, e.g. La(DBP, HDBP)<sub>3</sub>. Metals in high valency states, such as tetravalent actinides are the most readily extracted. The dialkyl phosphoric esters are liquids and are sometimes known as liquid cation exchangers.

**Table 3** includes some of the more important chelated systems.

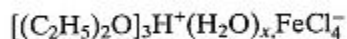


**Table 3** Typical ion-association extraction systems

System	Metals extracted
<i>Non-chelated ion-association systems</i> tetraphenylarsonium and tetraalkyl-ammonium salts	$\text{ReO}_4^-$ , $\text{MnO}_4^-$ , chloro, cyano and thiocyanato complexes of Bi, Ga, Zn, Cd, Ir(IV), Zn, Co(II)
Rhodamine-B— $\text{H}^+$ liquid anion exchangers e.g. Aliquat 336-S, TIOA	$\text{SbCl}_6^-$ , $\text{GaCl}_4^-$ , $\text{AuCl}_4^-$ , $\text{TlCl}_4^-$ , $\text{FeCl}_4^-$ extract many metals including U(VI), Co, Fe(III), Mo(VI), Ta, Ti(III), Zn as halide, sulphate or nitrate complexes
alkyl esters of phosphoric acid and phosphine oxides e.g. TBP and TOPO	U(VI), Pu(IV), Th(IV), Sc, Y, Zr, Nb, Mo, Sb, actinides, lanthanides, mineral acids
<i>Chelated ion-association systems</i>	
<i>o</i> -phenanthroline, $\text{ClO}_4^-$	Fe(II)
biquinoly, $\text{Cl}^-$	Cu(I)
EDTA, liquid anion exchangers	many metals can be extracted
oxine, tetraalkylammonium salts	U(VI)
acidic alkylphosphoric esters (liquid cation exchangers) e.g. HDBP, HDEHP	metals in higher valency states, i.e. actinides, U(VI), Pu(VI)
<i>Oxonium systems</i>	
$(\text{C}_2\text{H}_5)_2\text{O}$ , HCl	$\text{FeCl}_4^-$ , $\text{SbCl}_6^-$ , $\text{GaCl}_4^-$ , $\text{TlCl}_4^-$ , $\text{AuCl}_4^-$ and others
$\text{C}_2\text{H}_5\text{COCH}_3$ , HF	$\text{NbF}_6^-$ , $\text{TaF}_6^-$
$(\text{C}_2\text{H}_5)_2\text{O}$ , HI	Sb(III), Hg(II), Cd, Au(III), Sn(II)
$(\text{C}_2\text{H}_5)_2\text{O}$ , $\text{NH}_4\text{SCN}$	Sn(IV), Zn, Ga, Co, Fe(III)
$(\text{C}_2\text{H}_5)_2\text{O}$ , $\text{HNO}_3$	Au(III), Ce(IV), U(VI), Th(IV)

**Oxonium Systems**

Oxygen-containing solvents with a strong coordinating ability, such as diethyl ether, methyl *iso*-butyl ketone and *iso*-amyl acetate, form oxonium cations with protons under strongly acidic conditions, e.g.  $(\text{R}_2\text{O})_n\text{H}^+$ . Metals which form anionic complexes in strong acid can be extracted as ion pairs into such solvents. For example, Fe(III) is extracted from 7 M hydrochloric acid into diethyl ether as the ion pair



The efficiency of the extraction depends on the coordinating ability of the solvent, and on the acidity of the aqueous solution which determines the concentration of the metal complex. Coordinating ability follows the sequence ketones > esters > alcohols > ethers. Many metals can

be extracted as fluoride, chloride, bromide, iodide or thiocyanate complexes. **Table 4** shows how the extraction of some metals as their chloro complexes into diethyl ether varies with acid concentration. By controlling acidity and oxidation-state and choosing the appropriate solvent, useful separations can be achieved. As, for example, the number of readily formed fluoride complexes is small compared with those involving chloride, it is evident that a measure of selectivity is introduced by proper choice of the complexing ion. The order of selectivity is  $F^- > Br^- > I^- > Cl^- > SCN^-$ . Examples of oxonium systems are included in Table 3.

**Table 4** Extraction of metal chloro complexes into diethyl ether

Metal	0.3 M	1.4 M	HCl (M)		
			2.9 M	4.4 M	6 M
% extracted					
Au(III)	84	98	98		95
Fe(III)	trace	0.1	8	92	99
Tl(III)		~98		~99	~98
Sb(III)	0.3	8	22	13	6
Ge					~50
As(III)	0.2	0.7	7	37	68
Te(IV)	trace	0.2	3	12	34
Ga					~97
Sn(IV)	0.8	10	23	28	17
Hg(II)	13		0.4		0.2
Cu(II)	trace		0.05		0.05
Zn	trace		0.03		0.2
Ir(IV)	trace		0.02		5

The following metals are not extracted: Al, Be, Bi, Cd, Cr, Co, Fe(II), Pb, Mn, Ni, Pd, Os, Pt, rare earths, Ag, Ti, Th, W, U, Zr.

The use of oxonium and other non-chelated systems can be advantageous where relatively high concentrations of metals are to be extracted as solubility in the organic phase is not likely to be a limiting factor. Metal chelates, on the other hand, have a more limited solubility and are more suited to trace-level work.

## Methods of Extraction

### *Batch extraction*

It is the simplest and most useful method, the two phases being shaken together in a separatory funnel until equilibrium is reached and then allowed to separate into two layers. If the distribution ratio is large, a solute may be transferred essentially quantitatively in one extraction, otherwise several may be necessary. If several extractions are required, it is advantageous to use a solvent more dense than water, e.g. carbon tetrachloride or chloroform, so that the aqueous phase can be left in the separatory funnel until the procedure is complete.

### *Continuous extraction*

It consists of distilling the organic solvent from a reservoir flask, condensing it and allowing it to pass through the aqueous phase before returning to the reservoir flask to be recycled. **Figure 3** illustrates two types of apparatus used for this purpose. The method is particularly useful when the distribution ratio is small, i.e.  $D < 1$ , and where the number of batch extractions required for quantitative transfer would be inconveniently large. *Discontinuous countercurrent distribution* is a method devised by Craig, **1** which enables substances with similar distribution ratios to be separated. The method involves a series of individual extractions performed automatically in a specially designed apparatus. This consists of a large number (50 or more) of identical interlocking glass extraction units (**Figure 4**) mounted in a frame which is rocked and tilted mechanically to mix and separate the phases during each extraction step. Initially, equal volumes of the extracting solvent, which should be the more dense phase, are placed in each of the extraction units. This can be termed the *stationary phase* as each portion remains in the same unit throughout the procedure.

A solution of the mixture to be separated, dissolved in the less dense phase, is placed in the first unit and the phases mixed and allowed to separate. The upper layer is transferred automatically to the second unit whilst a fresh portion, not containing any sample, is introduced into the first unit from a reservoir. By repeating the extraction and transfer sequence as many times as there are units, the portions of lighter phase, which may be termed the *mobile phase*, move through the apparatus until the initial portion is in the last unit, and all units contain portions of both phases. A schematic representation of the first four extractions for a single solute is shown in **Figure 5** where it is assumed that  $D = 1$  and equal volumes of the two phases are used throughout. It can be seen that the solute is distributed between the units in a manner which follows the coefficients of the binomial expansion of  $(x + y)^n$  (**Table 5**) where  $x$  and  $y$

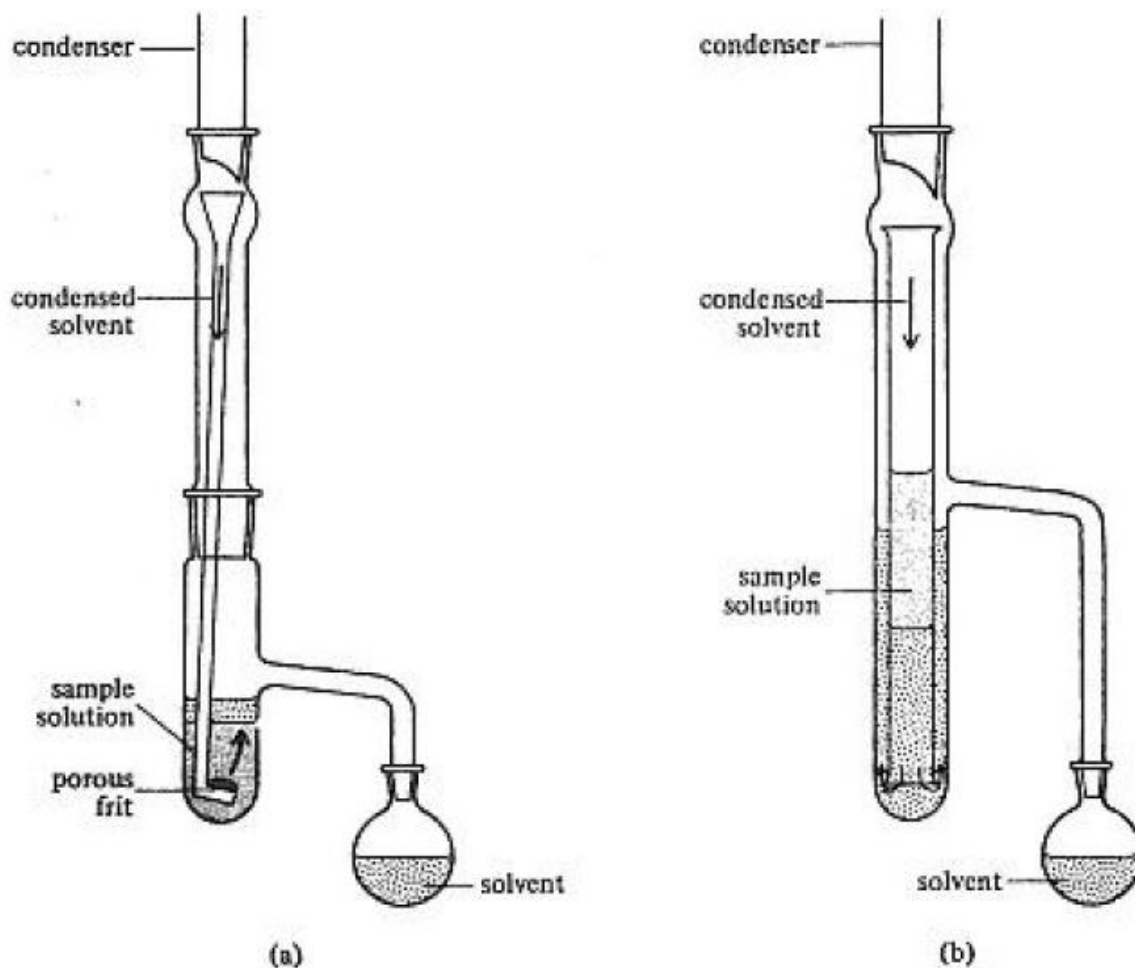
represent the fractions of solute present in the mobile and stationary phases and  $n$  is the number of extractions. The values of  $x$  and  $y$  are determined by  $D$  and the proportions of mobile and stationary phases used. For large values of  $n$  the distribution approximates to the normal error or Gaussian curve, and the effects of  $n$  and  $D$  are shown in **Figures 6** and **7** respectively. Thus, as the number of extractions  $n$  is increased, the solute moves through the system at a rate which is proportional to the value of  $D$ .

*Table 5 Proportional distribution of a solute between extraction units for Craig counter-current distribution*

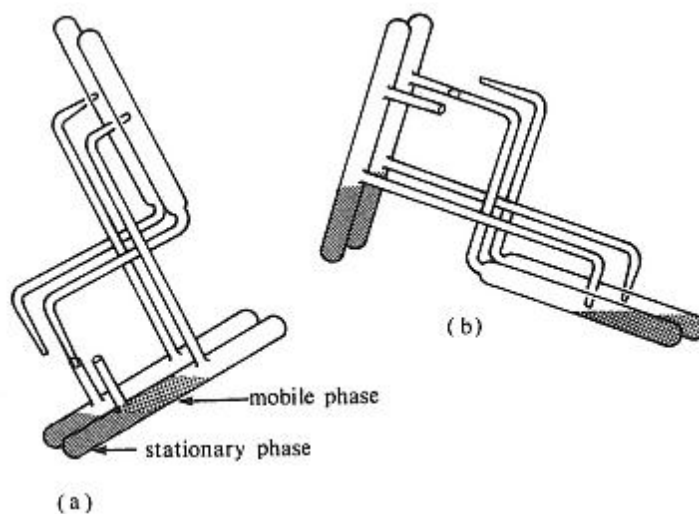
Extraction	Unit number						
	1	2	3	4	5	6	7
1st	1						
2nd	1	1					
3rd	1	2	1				
4th	1	3	3	1			
5th	1	4	6	4	1		
6th	1	5	10	10	5	1	
7th	1	6	15	20	15	6	1

With increasing  $n$  the solute is spread over a greater number of units, but separation of two or more components in a mixture will be improved. It should be noted that a 100% separation can never be achieved as the extremities of a Gaussian curve approach a baseline asymptotically. However, many separations are essentially quantitative within the context of a particular problem, e.g. 95, 99 or 99.9%.

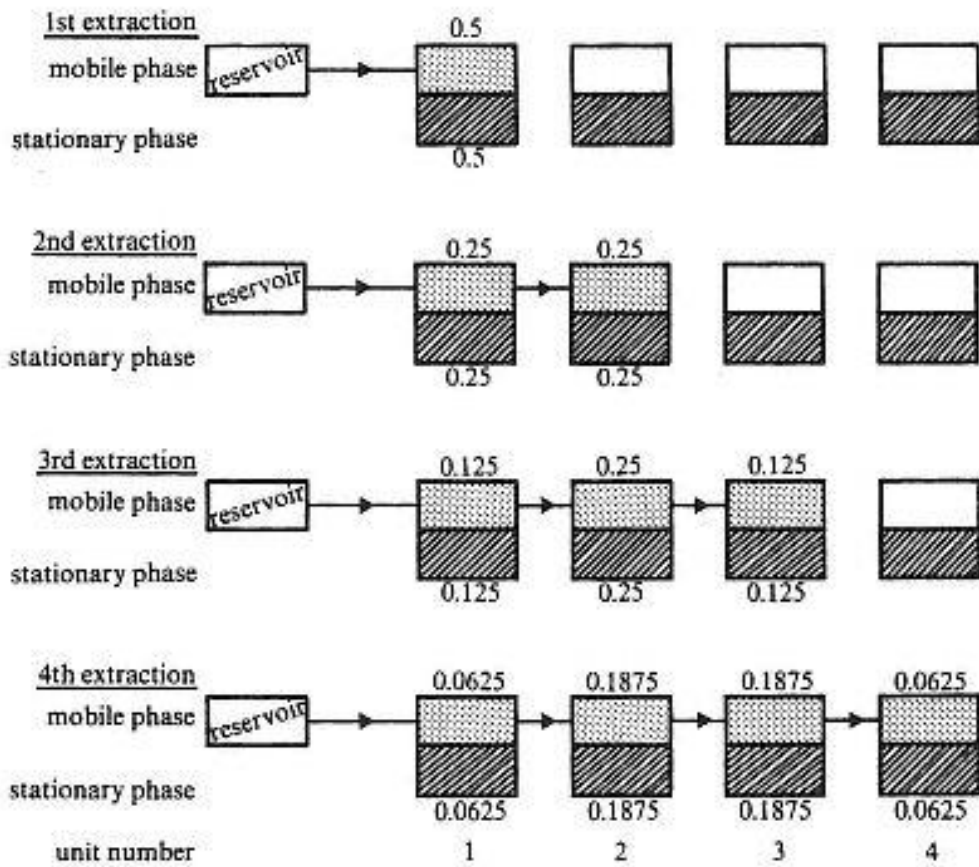
Theoretically, any number of solutes can be separated in this manner and the method has been applied, for example, to the separation of fatty acids, amino acids, polypeptides and other biological materials with distribution ratios in some cases differing by less than 0.1. However, the procedure can be lengthy and consumes large volumes of solvents. It is frequently more convenient to use one of the chromatographic techniques described later in this chapter. These can be considered as a development of the principle of counter-current distribution.



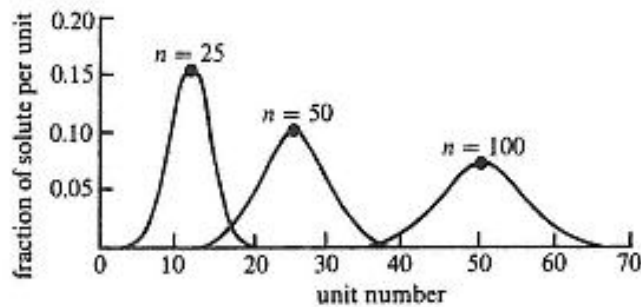
**Figure 3** Continuous extraction apparatus.  
 (a) Extraction with a solvent lighter than water.  
 (b) Extraction with a solvent heavier than water.



**Figure 4** Two interlocking glass units for Craig counter-current distribution.  
 (a) Position during extraction. (b) Position during transfer. (Note: By returning the apparatus from (b) to (a) the transfer is completed. The mobile phase moves on to the next unit and is replaced by a fresh portion).



**Figure 5** Extraction scheme for a single solute by Craig counter-current distribution. (Figures represent the proportions in each phase for  $D = 1$  and equal volumes. Only the first four extractions are shown).



**Figure 6** Effect of the number  $n$  of equilibrations on solute distributions for a distribution ratio  $D = 1$ .

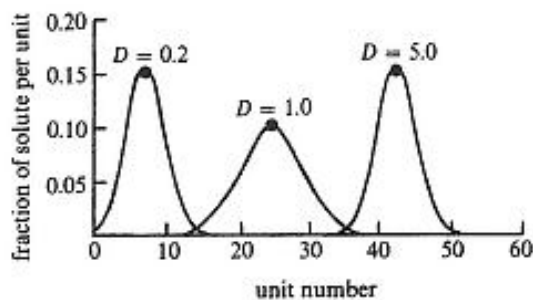


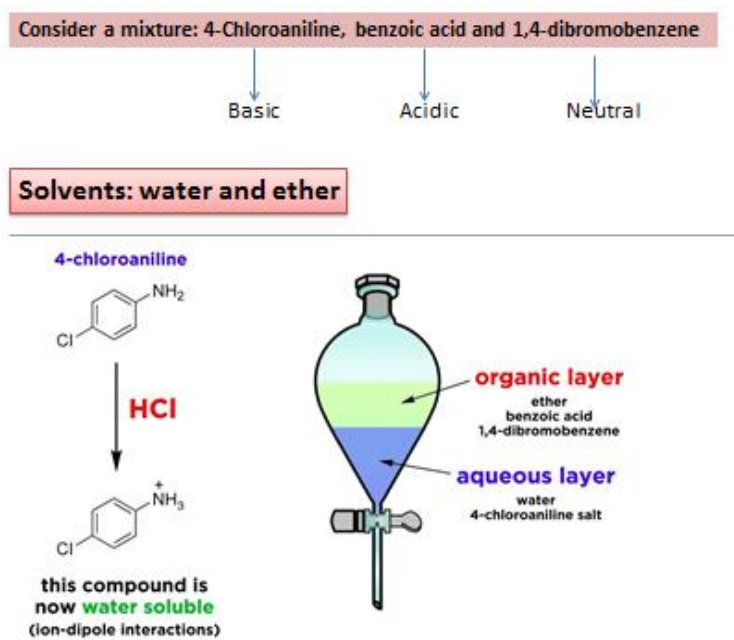
Figure 7 Effect of the distribution ratio  $D$  on solute distribution after 50 equilibrations.

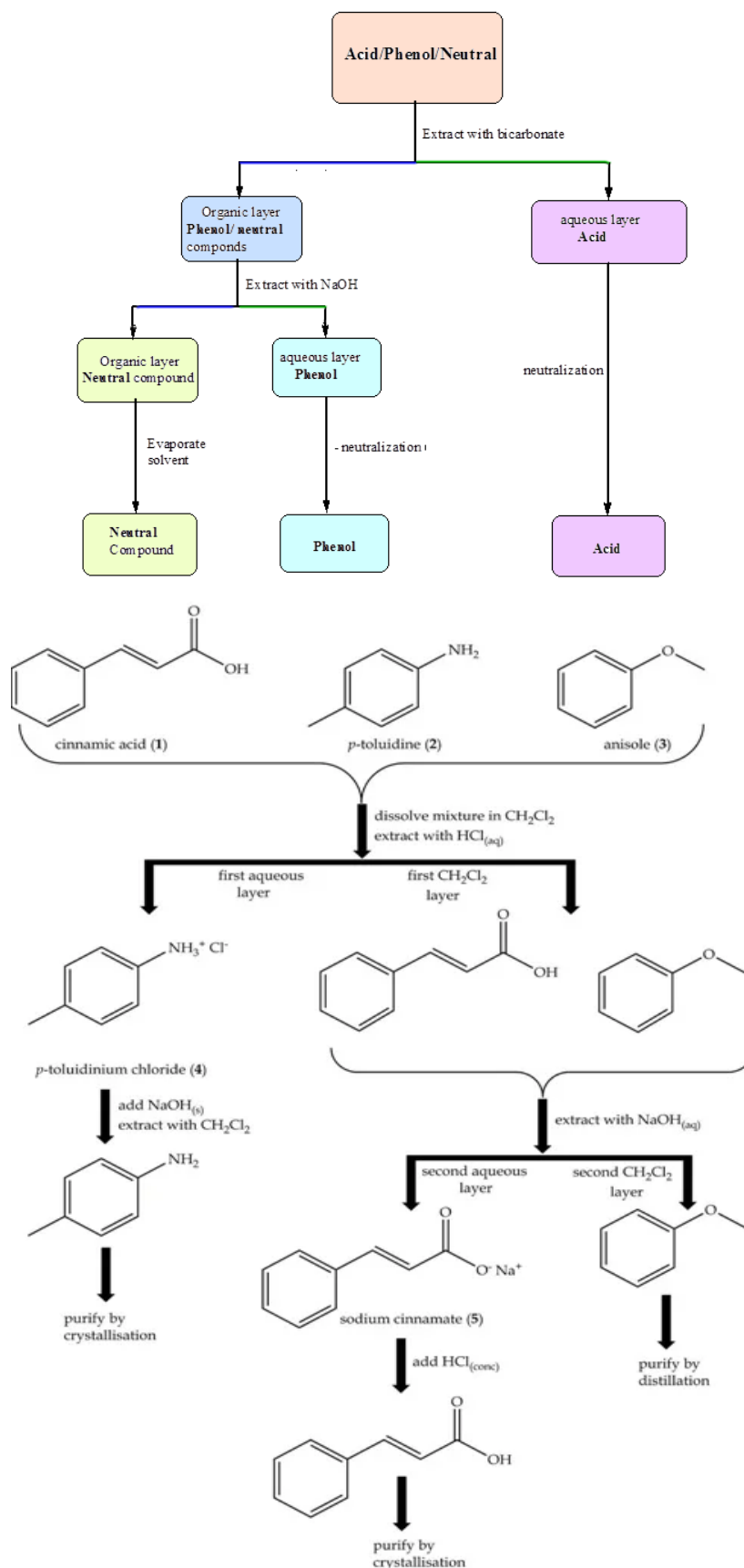
## Applications of Solvent Extraction

The technique is used predominantly for the isolation of a single chemical species prior to a determination and to a lesser extent as a method of concentrating trace quantities. The most widespread application is in the determination of metals as minor and trace constituents in a variety of inorganic and organic materials, e.g. the selective extraction and spectrometric determination of metals as coloured complexes in the analysis of metallurgical and geological samples as well as for petroleum products, foodstuffs, plant and animal tissue and body fluids.

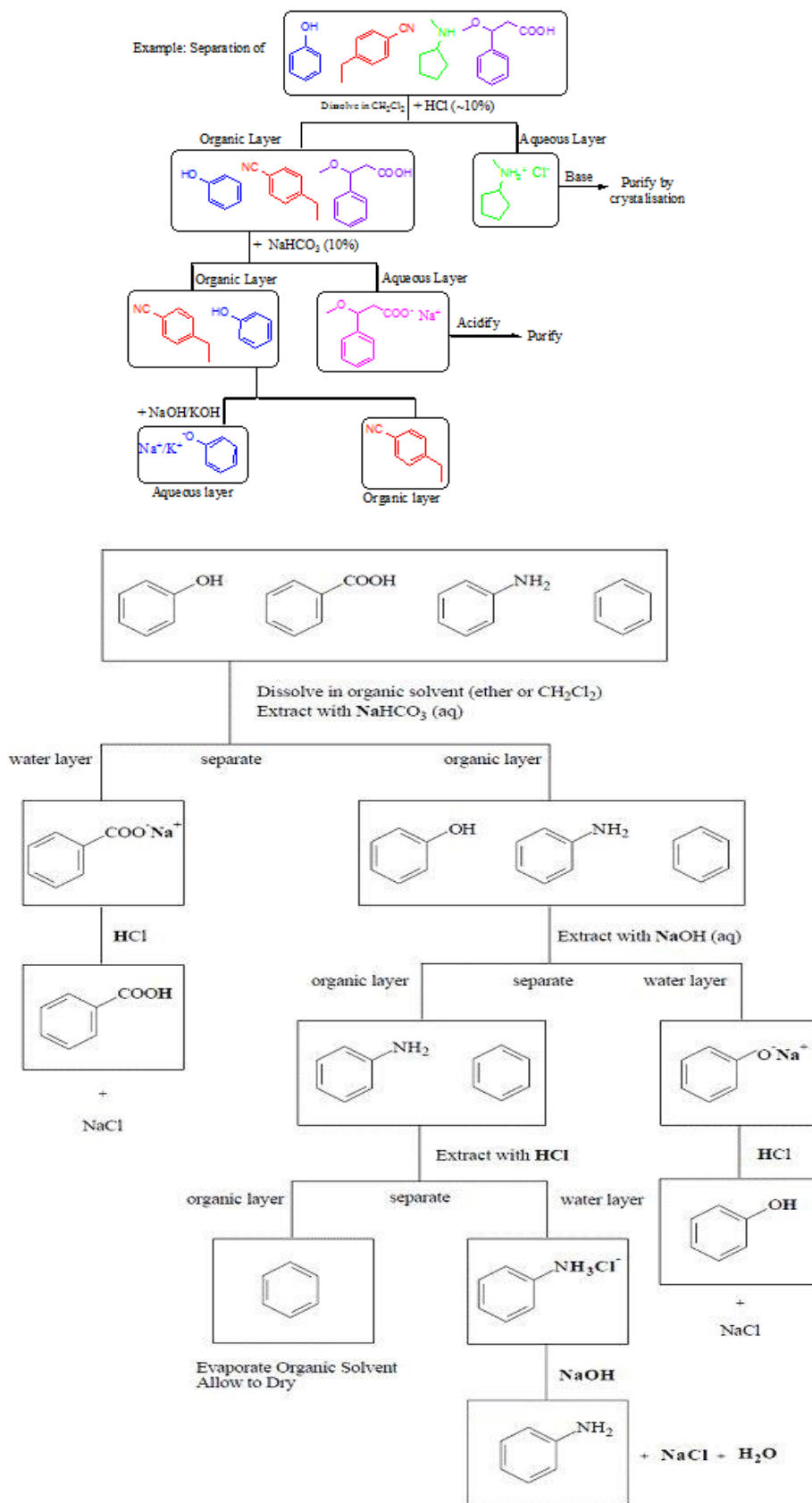
Separation procedures for purely organic species do not possess the same degree of selectivity as systems involving metals because of a general lack of suitable complexing and masking reactions. Nevertheless, classes of compounds such as hydrocarbons, acids, fats, waxes, etc., can often be isolated prior to analysis by other techniques.

### Some examples for analytical applications of solvent extraction

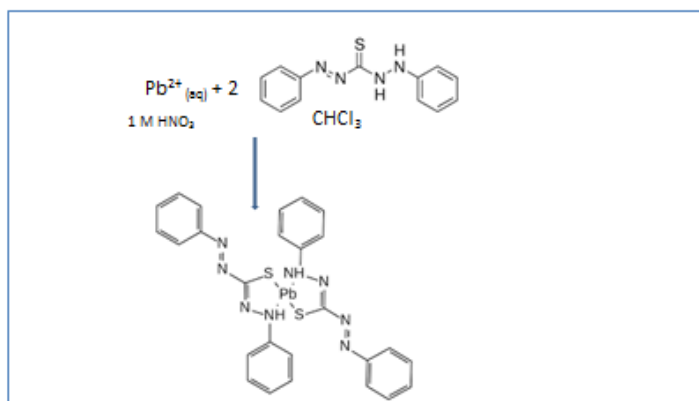
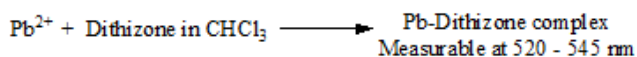








Determination of Pb in water or any real samples



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