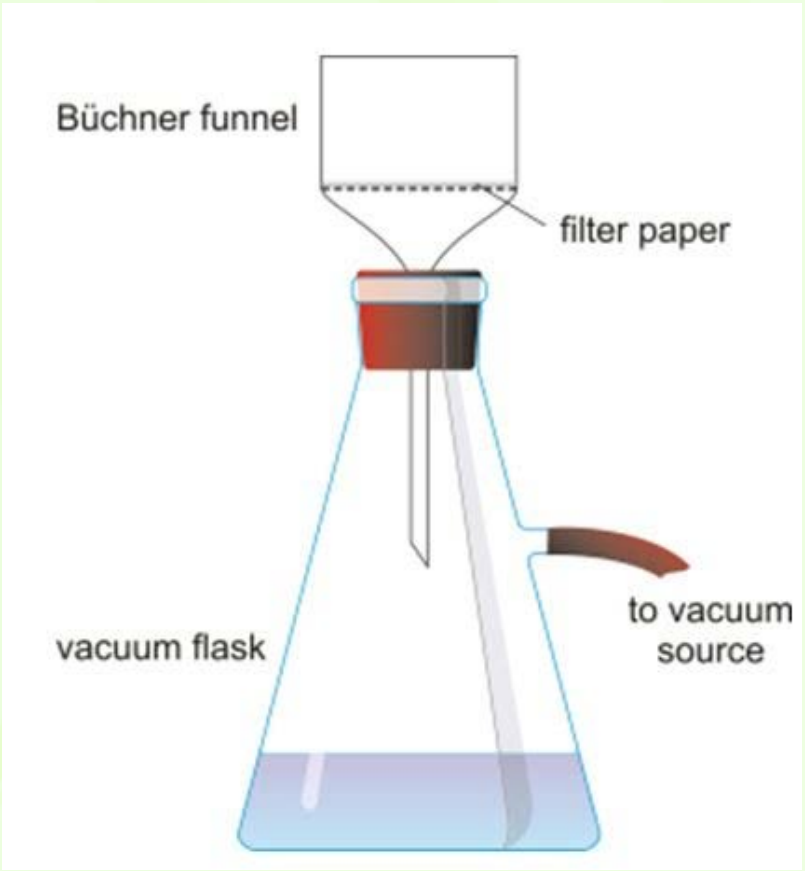
# Gravimetry

The analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.
Ideal: pure, insoluble, easily filterable, known composition, stoichiometry

It is based on mass measurements made with an analytical balance.



# Gravimetry

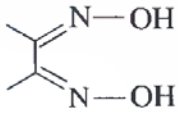
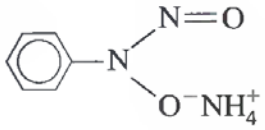
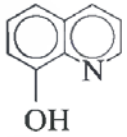
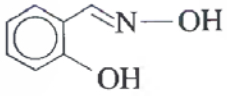
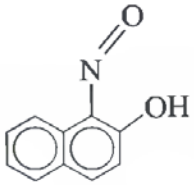
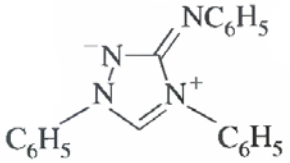
Steps:

- selective precipitation
- filtering
- washing
- drying/heat treatment
- mass measurement

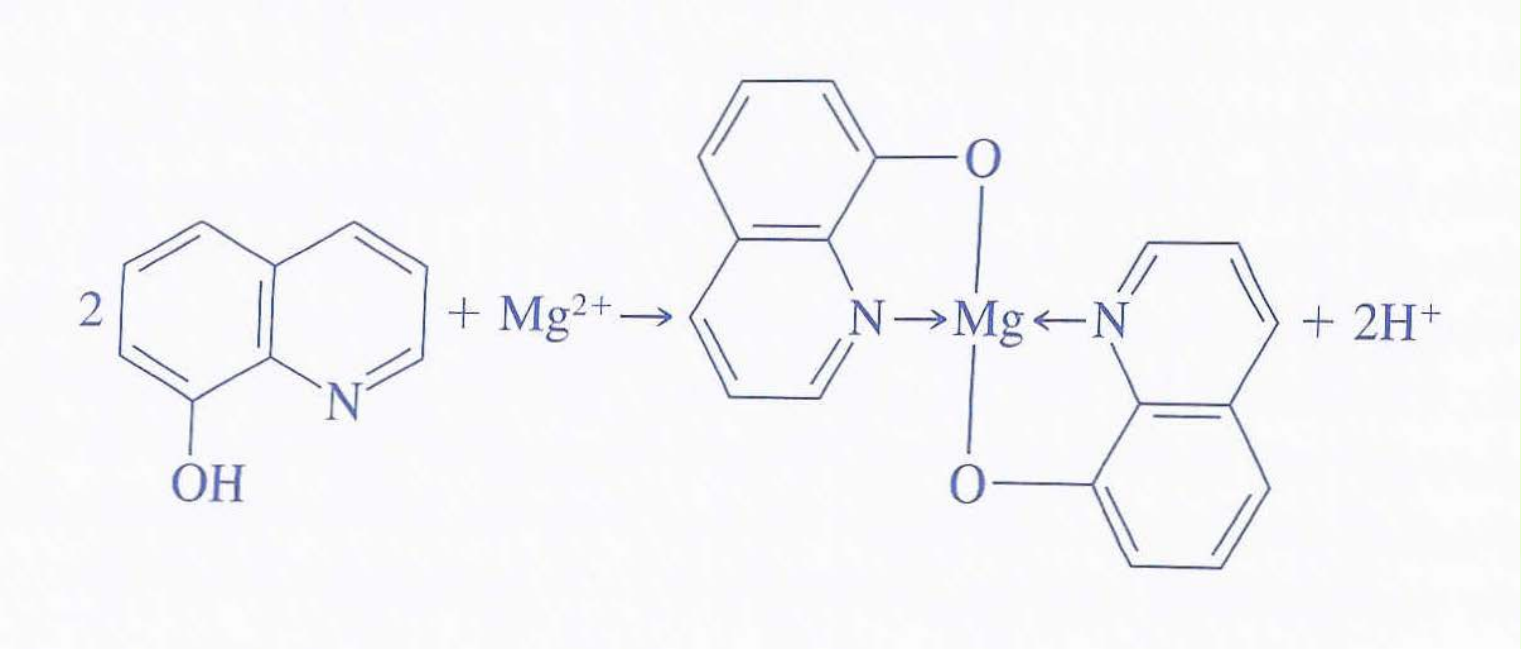
# Representative gravimetric analyses

| Species analyzed | Precipitated form | Form weighed | Interfering species |
|---|---|---|---|
| $K^+$ | $KB(C_6H_5)_4$ | $KB(C_6H_5)_4$ | $NH_4^+$, $Ag^+$, $Hg^{2+}$, $Tl^+$, $Rb^+$, $Cs^+$ |
| $Mg^{2+}$ | $Mg(NH_4)PO_4 \cdot 6H_2O$ | $Mg_2P_2O_7$ | Many metals except $Na^+$ and $K^+$ |
| $Ca^{2+}$ | $CaC_2O_4 \cdot H_2O$ | $CaCO_3$ or $CaO$ | Many metals except $Mg^{2+}$, $Na^+$, $K^+$ |
| $Ba^{2+}$ | $BaSO_4$ | $BaSO_4$ | $Na^+$, $K^+$, $Li^+$, $Ca^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Sr^{2+}$, $Pb^{2+}$, $NO_3^-$ |
| $Ti^{4+}$ | TiO(5,7-dibromo-8-hydroxyquinoline)$_2$ | Same | $Fe^{3+}$, $Zr^{4+}$, $Cu^{2+}$, $C_2O_4^{2-}$, citrate, HF |
| $VO_4^{3-}$ | $Hg_3VO_4$ | $V_2O_5$ | $Cl^-$, $Br^-$, $I^-$, $SO_4^{2-}$, $CrO_4^{2-}$, $AsO_4^{3-}$, $PO_4^{3-}$ |
| $Cr^{3+}$ | $PbCrO_4$ | $PbCrO_4$ | $Ag^+$, $NH_4^+$ |
| $Mn^{2+}$ | $Mn(NH_4)PO_4 \cdot H_2O$ | $Mn_2P_2O_7$ | Many metals |
| $Fe^{3+}$ | $Fe(HCO_2)_3$ | $Fe_2O_3$ | Many metals |
| $Co^{2+}$ | Co(1-nitroso-2-naphtholate)$_3$ | $CoSO_4$ (by reaction with $H_2SO_4$) | $Fe^{3+}$, $Pd^{2+}$, $Zr^{4+}$ |
| $Ni^{2+}$ | Ni(dimethylglyoximate)$_2$ | Same | $Pd^{2+}$, $Pt^{2+}$, $Bi^{3+}$, $Au^{3+}$ |
| $Cu^{2+}$ | CuSCN | CuSCN | $NH_4^+$, $Pb^{2+}$, $Hg^{2+}$, $Ag^+$ |
| $Zn^{2+}$ | $Zn(NH_4)PO_4 \cdot H_2O$ | $Zn_2P_2O_7$ | Many metals |
| $Ce^{4+}$ | $Ce(IO_3)_4$ | $CeO_2$ | $Th^{4+}$, $Ti^{4+}$, $Zr^{4+}$ |
| $Al^{3+}$ | Al(8-hydroxyquinolate)$_3$ | Same | Many metals |
| $Sn^{4+}$ | Sn(cupferron)$_4$ | $SnO_2$ | $Cu^{2+}$, $Pb^{2+}$, As(III) |
| $Pb^{2+}$ | $PbSO_4$ | $PbSO_4$ | $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Hg^{2+}$, $Ag^+$, HCl, $HNO_3$ |
| $NH_4^+$ | $NH_4B(C_6H_5)_4$ | $NH_4B(C_6H_5)_4$ | $K^+$, $Rb^+$, $Cs^+$ |
| $Cl^-$ | AgCl | AgCl | $Br^-$, $I^-$, $SCN^-$, $S^{2-}$, $S_2O_3^{2-}$, $CN^-$ |
| $Br^-$ | AgBr | AgBr | $Cl^-$, $I^-$, $SCN^-$, $S^{2-}$, $S_2O_3^{2-}$, $CN^-$ |
| $I^-$ | AgI | AgI | $Cl^-$, $Br^-$, $SCN^-$, $S^{2-}$, $S_2O_3^{2-}$, $CN^-$ |
| $SCN^-$ | CuSCN | CuSCN | $NH_4^+$, $Pb^{2+}$, $Hg^{2+}$, $Ag^+$ |
| $CN^-$ | AgCN | AgCN | $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $S^{2-}$, $S_2O_3^{2-}$ |
| $F^-$ | $(C_6H_5)_3SnF$ | $(C_6H_5)_3SnF$ | Many metals (except alkali metals), $SiO_4^{4-}$, $CO_3^{2-}$ |
| $ClO_4^-$ | $KClO_4$ | $KClO_4$ | |
| $SO_4^{2-}$ | $BaSO_4$ | $BaSO_4$ | $Na^+$, $K^+$, $Li^+$, $Ca^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Sr^{2+}$, $Pb^{2+}$, $NO_3^-$ |
| $PO_4^{3-}$ | $Mg(NH_4)PO_4 \cdot 6H_2O$ | $Mg_2P_2O_7$ | Many metals except $Na^+$, $K^+$ |
| $NO_3^-$ | Nitron nitrate | Nitron nitrate | $ClO_4^-$, $I^-$, $SCN^-$, $CrO_4^{2-}$, $ClO_3^-$, $NO_2^-$, $Br^-$, $C_2O_4^{2-}$ |
| $CO_3^{2-}$ | $CO_2$ (by acidification) | $CO_2$ | (The liberated $CO_2$ is trapped with Ascarite and weighed.) |

# Common organic precipitating agents for gravimetry

| Name | Structure | Ions precipitated |
|---|---|---|
| Dimethylglyoxime |  | $Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$ |
| Cupferron |  | $Fe^{3+}$, $VO_2^+$, $Ti^{4+}$, $Zr^{4+}$, $Ce^{4+}$, $Ga^{3+}$, $Sn^{4+}$ |
| 8-Hydroxyquinoline (oxine) |  | $Mg^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Fe^{3+}$, $Bi^{3+}$, $Ga^{3+}$, $Th^{4+}$, $Zr^{4+}$, $UO_2^{2+}$, $TiO^{2+}$ |
| Salicylaldoxime |  | $Cu^{2+}$, $Pb^{2+}$, $Bi^{3+}$, $Zn^{2+}$, $Ni^{2+}$, $Pd^{2+}$ |
| 1-Nitroso-2-naphthol |  | $Co^{2+}$, $Fe^{3+}$, $Pd^{2+}$, $Zr^{4+}$ |
| Nitron |  | $NO_3^-$, $ClO_4^-$, $BF_4^-$, $WO_4^{2-}$ |
| Sodium tetraphenylborate | $Na^+B(C_6H_5)_4^-$ | $K^+$, $Rb^+$, $Cs^+$, $NH_4^+$, $Ag^+$, organic ammonium ions |
| Tetraphenylarsonium chloride | $(C_6H_5)_4As^+Cl^-$ | $Cr_2O_7^{2-}$, $MnO_4^-$, $ReO_4^-$, $MoO_4^{2-}$, $WO_4^{2-}$, $ClO_4^-$, $I_3^-$ |

# 8-hydroxyquinoline (oxine)



# Gravimetry

***Precipitation***: precipitation with easily filtered particles (macrocrystals)

$$V_{\text{nucleation}} < V_{\text{particle growth}}$$

Goal: Maintaining the relative supersaturation at low level

$$\textit{Relative supersaturation} = \frac{Q - S}{S}$$

*S*: solubility

*Q*: supersaturation concentration of the analyte

*increase of S*: increase of temperature

*decrease of Q*: dilution

slow addition of the precipitating agent

proper mixing

Practical execution: precipitation from very diluted solution

precipitation from very concentrated solution followed by standing (digestion)

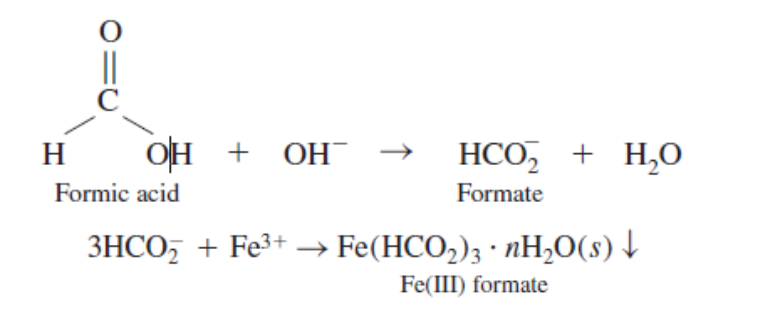
slow precipitation from hot, diluted solution

homogeneous precipitation

# Gravimetry

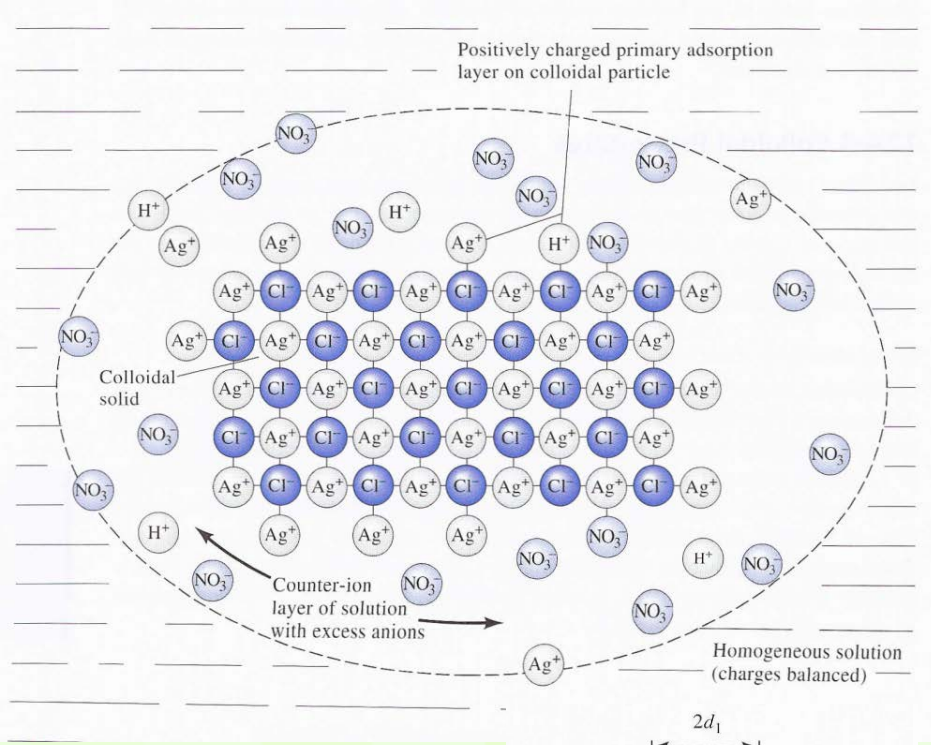
## Common reagents used for homogeneous precipitation

| Precipitant | Reagent | Reaction | Some elements precipitated |
|---|---|---|---|
| $OH^-$ | Urea | $(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$ | Al, Ga, Th. Bi. Fe, Sn |
| $OH^-$ | Potassium cyanate | $HOCN + 2H_2O \rightarrow NH_4^+ + CO_2 + OH^-$ (Hydrogen cyanate) | Cr. Fe |
| $S^{2-}$ | Thioacetamide[a] | $CH_3\overset{\overset{S}{\|}}{C}NH_2 + H_2O \rightarrow CH_3\overset{\overset{O}{\|}}{C}NH_2 + H_2S$ | Sb, Mo, Cu, Cd |



# Gravimetry

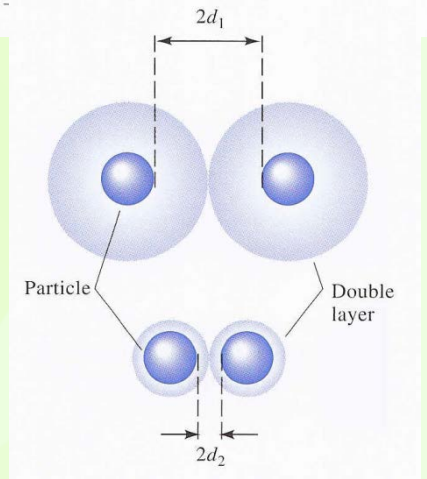
Formation of colloidal suspension (AgCl formed in excess AgNO3 solution)




Coagulation can be hastened by heating, strirring or adding electrolyte

Crystal structure may change on standing

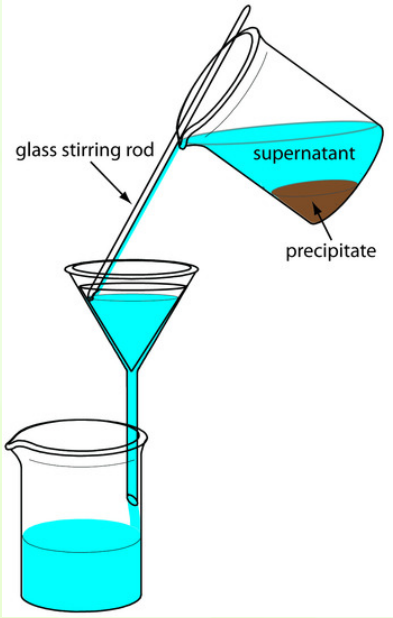
With increasing diameter the solubility decreases




*coprecipitation*: „normally” soluble compounds are precipitated (adsorbed or included impurities)

*reprecipitation*: improves the purity of the precipitate (filtered solid is redissolved and precipitated again.

# Gravimetry




***Filtration***:

Filtering medium: filter paper (pore size, ash content)

glass filter (pore size)

Selection of filtering medium depends on the way of drying.

Speeding up: decantation, filtration while hot, use of vacuum

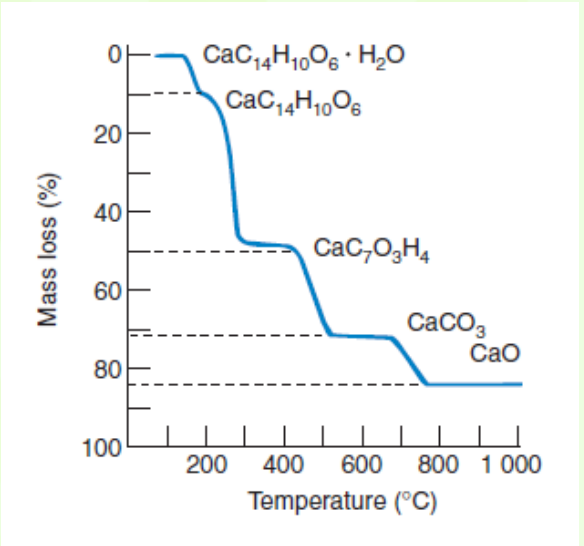
***Washing***:

Peptization: colloidal redissolution of the precipitate

The ionic precipitate is washed with volatile electrolite

eg: metal hydroxide: $NH_3$ – $NH_4Cl$ solution

metal sulphides: $H_2S$ water




***Drying, heat treatment***:

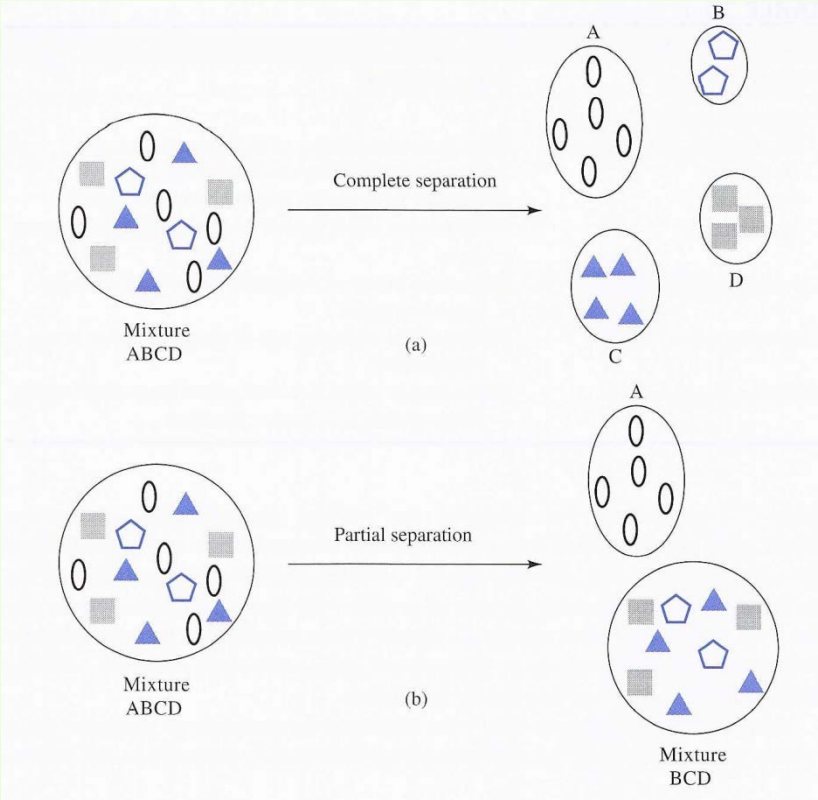
Conversion into a compound with known stoichiometry: drying, heating (ignition)

Thermogravimetry can help to find a known and a (mass) stable composition

# Separation menthods

Mechanical phase separation:

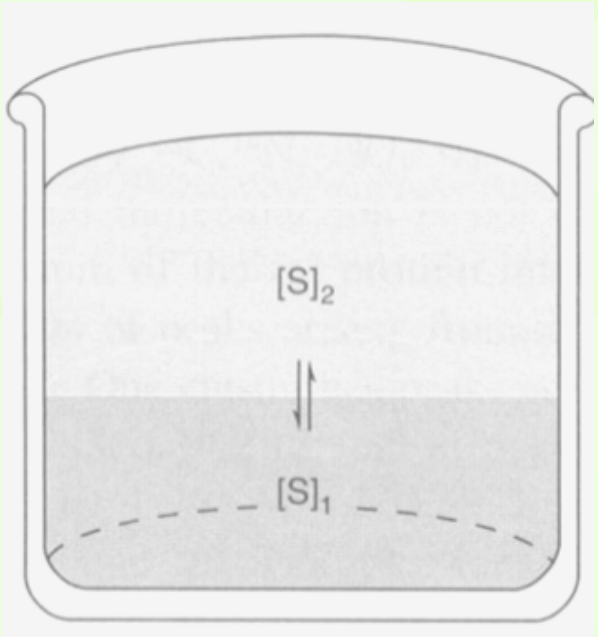
- precipitation and filtration
- distillation
- extraction




Goals:

- identify and quantify the separated constituent
- eliminate or
  reduce interferences
- enrichment

# Liquid – liquid extraction




Partition coefficient

$$d = \frac{[S]_2}{[S]_1}$$

sometimes abbreviated by *K* instead of *d*

Fraction remaining in phase 1 after one extraction: *q*

$$d = \frac{[S]_2}{[S]_1} = \frac{(1-q)m/V_2}{qm/V_1} \Rightarrow q = \frac{V_1}{V_1 + dV_2}$$

$V_1$: volume of phase 1

$V_2$: volume of phase 2

*m*: mole

After *n* extractions the fraction remaining in the water: $q^n$

$$q^n = \left(\frac{V_1}{V_1 + dV_2}\right)^n$$

# Liquid – liquid extraction

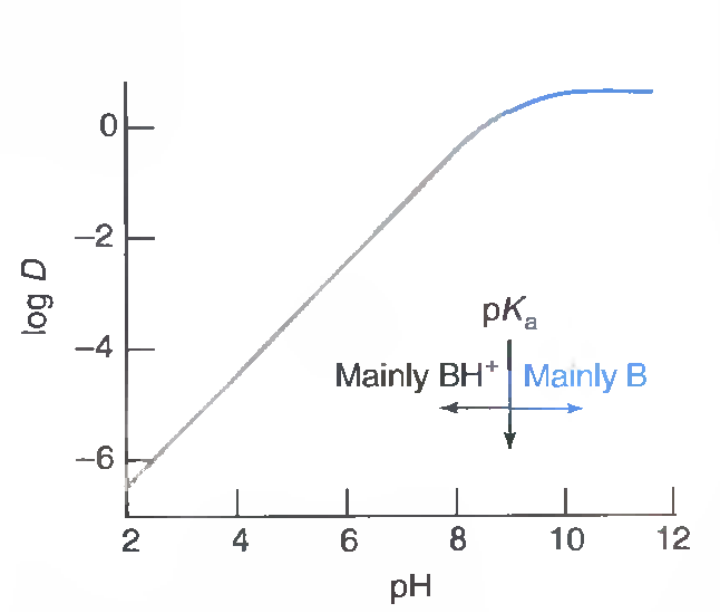
Distribution coefficient: $D = \dfrac{\text{total concentration in phase 2}}{\text{total concentration in phase 1}}$

Effect of pH: B neutral, water soluble molecule capable of protonation

$K_a = [H^+][B]_{aq}/[BH^+]_{aq}$

in phase 2 (organic) only the neutral form (B) is soluble

$$D = \frac{[B]_{org}}{[B]_{aq} + [BH^+]_{aq}} \Rightarrow D = \frac{d\,K_a}{K_a + [H^+]} \qquad \left( d = \frac{[B]_{org}}{[B]_{aq}} \right)$$

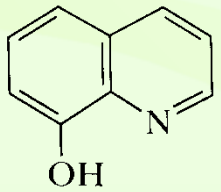



$d$ = 3.0

p$K_a$ (BH$^+$) = 9.0

# Liquid – liquid extraction

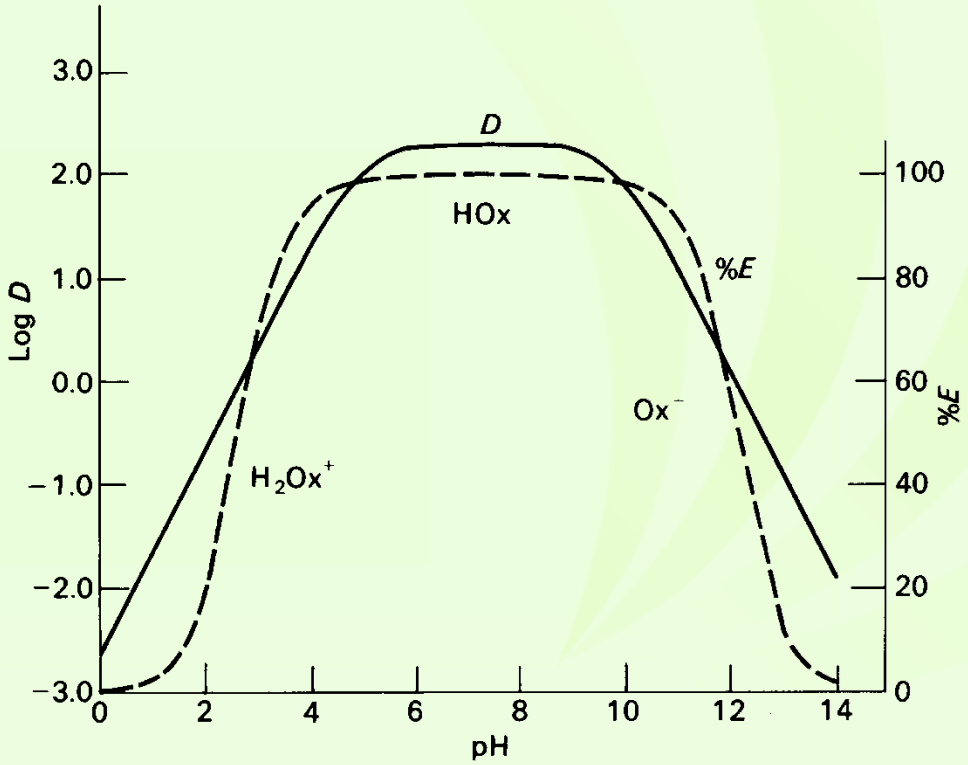
Example: oxine



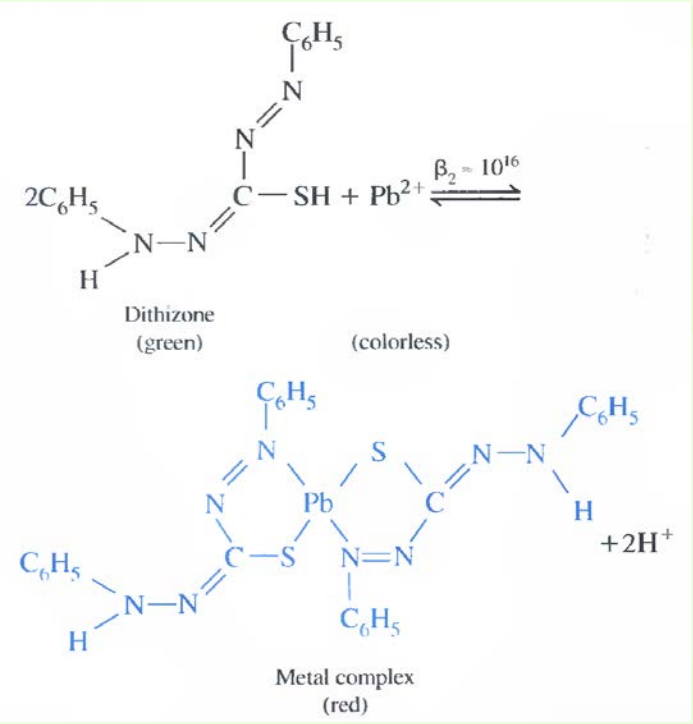

8-hydroxy-quinoline (oxine: HOx)

$H_2Ox^+ \rightleftharpoons HOx \rightleftharpoons Ox^-$

$$D = \frac{[HOx]_{org}}{[H_2Ox^+]_{aq} + [HOx]_{aq} + [Ox^-]_{aq}}$$



# Extraction with metal chelators




## Equilibria in aqueous phase

$HL_{aq} \rightleftharpoons H^+_{aq} + L^-_{aq} \quad K_a = [H^+]_{aq}[L^-]_{aq}/[HL]_{aq}$

$nL^-_{aq} + M^{n+}_{aq} \rightleftharpoons ML_{n\,aq} \quad \beta = [ML_n]_{aq}/[M^{n+}]_{aq}/[L^-]^n_{aq}$

## Distribution equilibria

$HL_{aq} \rightleftharpoons HL_{org} \qquad d_L = [HL]_{org}/[HL]_{aq}$

$ML_{n\,aq} \rightleftharpoons ML_{n\,org} \quad d_{ML} = [ML_n]_{org}/[ML_n]_{aq}$

$$D = \frac{[\text{total metal ion}]_{org}}{[\text{total metal ion}]_{aq}} \approx \frac{[ML_n]_{org}}{[M^{n+}]_{aq}}$$

$$[ML_n]_{org} = d_M[ML_n]_{aq} = d_M\beta[M^{n+}]_{aq}[L^-]^n_{aq}$$

$$[ML_n]_{org} = \frac{d_M\beta[M^{n+}]_{aq}K_a{}^n[HL]^n_{aq}}{[H^+]^n_{aq}} \Rightarrow D = \frac{d_M\beta K_a{}^n[HL]^n_{aq}}{[H^+]^n_{aq}} \qquad \text{and} \quad [HL]_{aq} = [HL]_{org}/d_L$$

$$D = \frac{d_M\beta K_a{}^n}{d_L^n}\frac{[HL]^n_{org}}{[H^+]^n_{aq}}$$

# Extraction with metal chelators

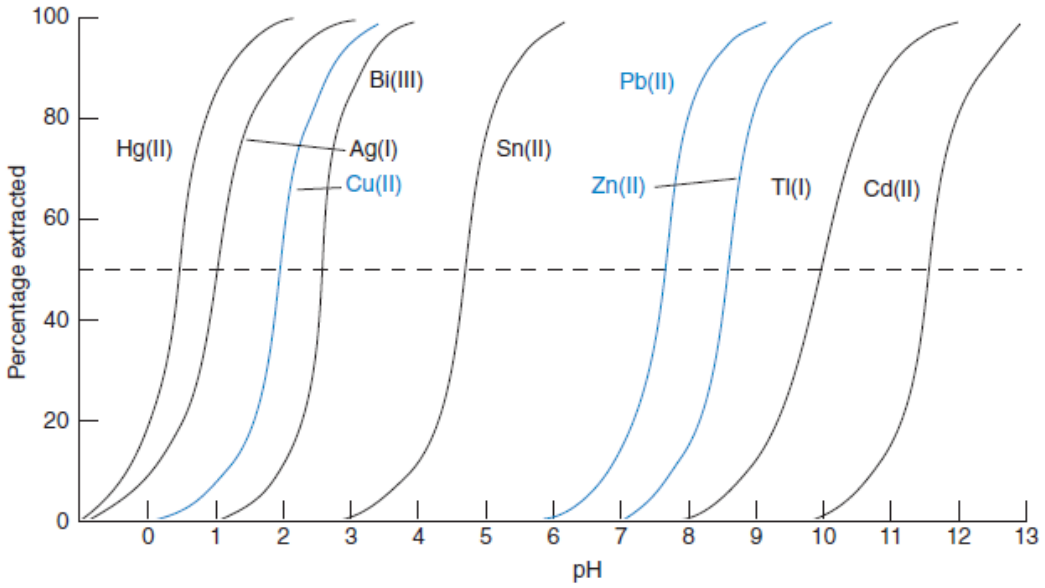


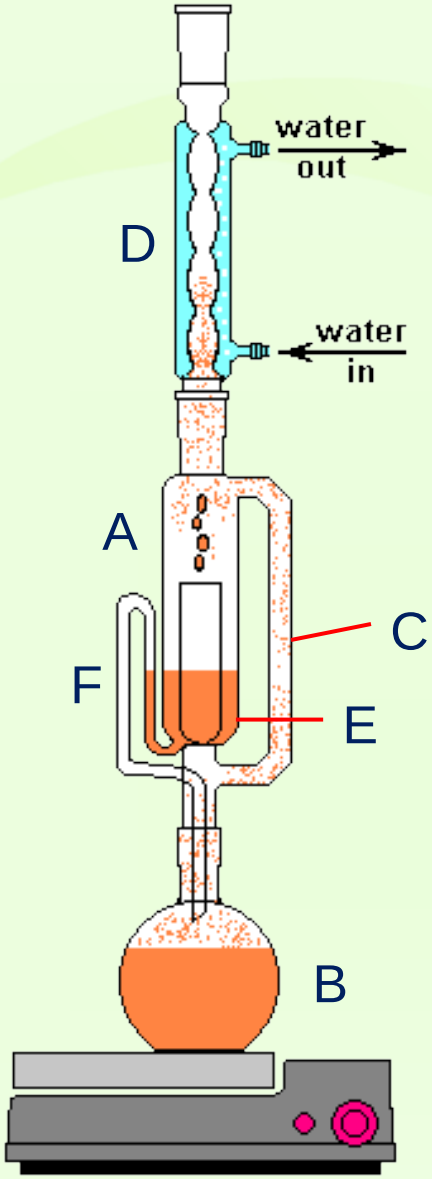

*Figure 23-4* Extraction of metal ions by dithizone into $CCl_4$. At pH 5, $Cu^{2+}$ is completely extracted into $CCl_4$, whereas $Pb^{2+}$ and $Zn^{2+}$ remain in the aqueous phase. *[Adapted from G. H. Morrison and H. Freiser in C. L. Wilson and D. Wilson, eds., Comprehensive Analytical Chemistry, Vol. IA (New York: Elsevier, 1959).]*

$$D = \frac{d_M \beta K_a^{\,n}}{d_L^n} \frac{[HL]_{org}^n}{[H^+]_{aq}^n}$$

Selectivity coefficient $$\alpha_{A,B} = \frac{D_A}{D_B}$$

# Solid – liquid extraction

Soxhlet extractor: continuous extraction of components from solid material




A: extraction chamber
B: boiling flask with extraction solvent
C: solvent vapour
D: condenser
E: container with the mixture to be extracted
F: siphon arm

After many cycles the component is concentrated in the distillation flask.