12 Gravimetric Methods of Analysis

Gravimetric analysis: based upon <u>mass measurements</u>
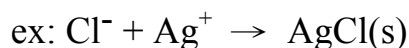**highly <u>accurate and precise</u>.**
--- **Isolation (pure known substance) & weighing**
*<u>Advantages</u>
  1. accuracy
  2. single fundamental chemical precipitation reaction

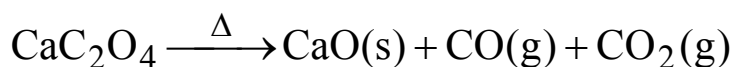   ex: $Cl^- + Ag^+ \rightarrow AgCl(s)$
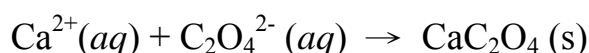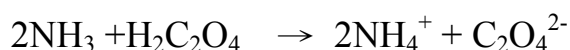
  3. require no accuracy known standard solution

12A Precipitation Gravimetry

  1. <u>**Precipitation methods**</u>
       ex: For Calcium in natural water
   AOAC (Association of Official Analytical Chemists)

       $2NH_3 + H_2C_2O_4 \rightarrow 2NH_4^+ + C_2O_4^{2-}$

       $Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$

   $$CaC_2O_4 \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2(g)$$

  2. <u>Volatilization methods</u>

   ex: For $NaHCO_3$ in antacid tablets
    $NaHCO_3(aq) + H_2SO_4(aq) \rightarrow CO_2(g) + H_2O(l) + NaHSO_4(aq)$
                                         $\downarrow$
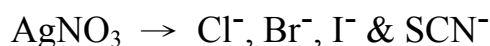   absorption tube
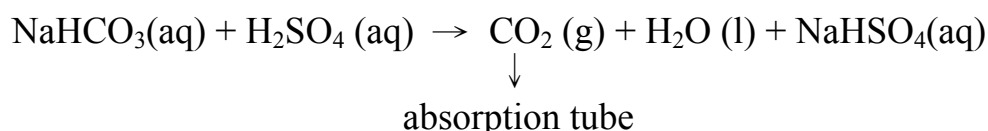
12A-1 Properties of Precipitates and Precipitating Agents

  specifically (rare): reactly only with a single chemical species.
                dimethylglyoxime $\rightarrow Ni^{2+}$
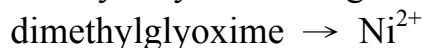
  selectively (common): react with a limited number of species.
                $AgNO_3 \rightarrow Cl^-, Br^-, I^- \& SCN^-$
  1. Readily filtered and washed free of contaminants.
  2. Of sufficiently low solubility so that no significant loss of the analyte occurs
     during filtration and washing.
  3. Unreactive with constituents of the atmosphere.
  4. Of known composition after it is dried or, if necessary, ignited.

12A-2 <u>Particle size and filterability of precipitates</u>

Particle size: • colloidal suspensions ($10^{-7} \sim 10^{-4}$ cm or $10^{-6} \sim 10^{-4}$ mm)

           ex: $Fe(OH)_3$ (gelatinous)

         • curdy : ex: $AgCl$

         • crystalline ($10^{-2} \sim 10$ mm): ex: $BaSO_4$

♦ **Factors that determine the particle size of precipitates**

    1. ppt solubility

    2. temperature

    3. reactant concentrations

    4. rate at which reactants are mixed

♦ *relative supersaturation(RS) or Von Weimarn ratio*

$$RS = \frac{Q - S}{S}$$

       Q: conc. of the solute at any instant

       S: equilibrium solubility

Particle size $\propto \dfrac{1}{RS}$

RS $\uparrow \rightarrow$ ppt size $\downarrow$ (colloidal)

RS $\downarrow \rightarrow$ ppt size $\uparrow$ (crystalline solid)

♦ **Mechanism of precipitate formation**

   1. supersaturated soln formed

   2. nucleation

   3. particle growth

♦ **Experimental Control of Particle Size**

   * RS$\downarrow$, Q$\downarrow$, S$\uparrow$ $\rightarrow$ particle size $\uparrow$

  1. dilute sample soln and dilute reagents (Q $\downarrow$)

  2. slow addition of precipitating agent with good stirring (Q $\downarrow$)

  3. in hot solution (S $\uparrow$)

  4. pH control, acidity solution (S $\uparrow$)

     ex: precipitation of calcium oxalate

       a. in mildly acidic, calcium oxalate $\rightarrow$ large, easily filtered crystals

                                         (moderately soluble)

       b. adding aqueous ammonia $\rightarrow$ pH $\uparrow$ $\rightarrow$ completed ppt

   *Precipitates with very low solubilities, such as many sulfides and hydrous
   oxides, generally form a colloids.

12A-3 Colloidal Precipitates

   Coagulation (or agglomeration) of colloids: converting a colloid suspension
       into a filterable solid.

Adsorption: a process in which a substance (gas, liquid or solid) is held on the surface of a solid. In contrast, absorption, involves retention of a substance within the pores of a solid.

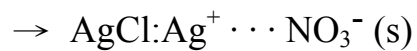**Electric double layer:**
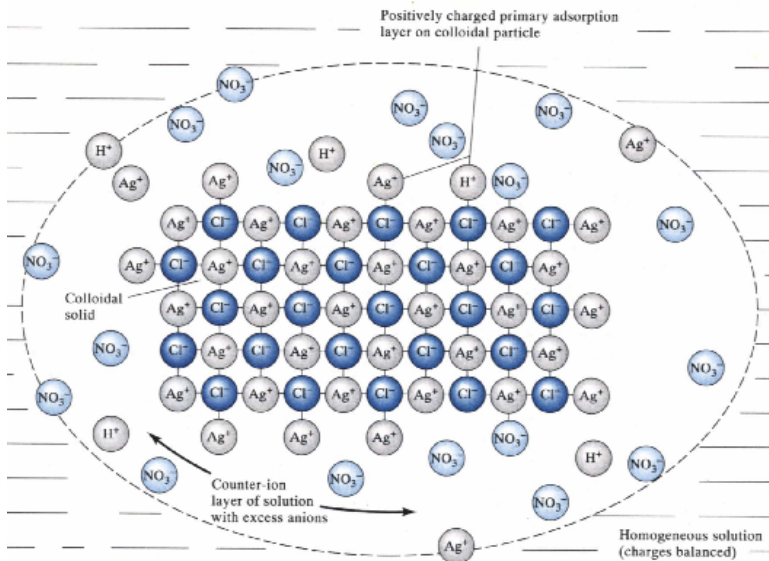
◆Primary adsorbed layer
primary adsorbed ion:
1. lattice ions which in excess.
2. held by chemical bound
3. fixed on ppt surface
ex: AgCl in excess Ag^+

$\rightarrow$ AgCl:Ag^+ (s)

◆Counter-ion layer

counter-ions
1. opposite charge of primary adsorbed ion
2. held by electrostatic attraction
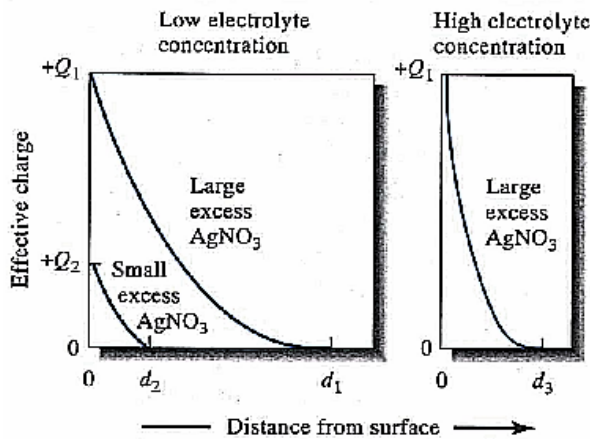3. loosely held in soln surrounding the ppt

ex: AgCl in excess $AgNO_3$
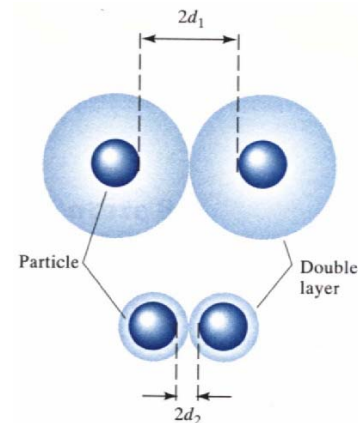
$\rightarrow$ AgCl:$Ag^+ \cdots NO_3^-$ (s)

Fig. 12-2 (a)   (b)

Fig. 12-3

*__Coagulation__ of a colloidal suspension

1. **heating**: a. $\downarrow$ no. of adsorbed ions and the thickness d_1 of the double layer.

b. gain enough kinetic energy to overcome the barrier to close approach posed by the double layer.

2. **stirring**

3. **adding an electrolyte**: conc. of counter ions $\uparrow$ $\rightarrow$ shrinkage of the counter-ion layer (Fig. 12-2b) $\rightarrow$ particle can then approach one another more closely and agglomerate.

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*Peptization of Colloids

Peptization : a process by which a coagulated colloid returns to its dispersed state.

washing coagulated colloid $\rightarrow$ removal of electrolyte

$\rightarrow$ volume of the counter-ion layer $\uparrow$

Peptization is prevented by washing ppt with a soln of a volatile electrolyte. ex: AgCl, washed with a d-HNO_3.

*Treatment of Colloidal Precipitates

Digestion : a process in which a ppt is heated for an hour or more in the soln from which it was formed (the mother liquor)

$\rightarrow$ $\uparrow$ purity and filterability

1. colloidal suspension $\rightarrow$ coagulated to curdy ppt

2. small crystalline particles $\rightarrow$ reprecipitated on the large crystalline particles

3. impurities tend to dissolve $\rightarrow$ pure crystalline particles

12A-4 Crystalline Precipitates

Methods of Improving Particle Size and Filterability: Q $\downarrow$, S $\uparrow$, digestion

12A-5 Coprecipitation:

a process in which normally <u>soluble</u> compounds are carrier out of solution by a precipitate.
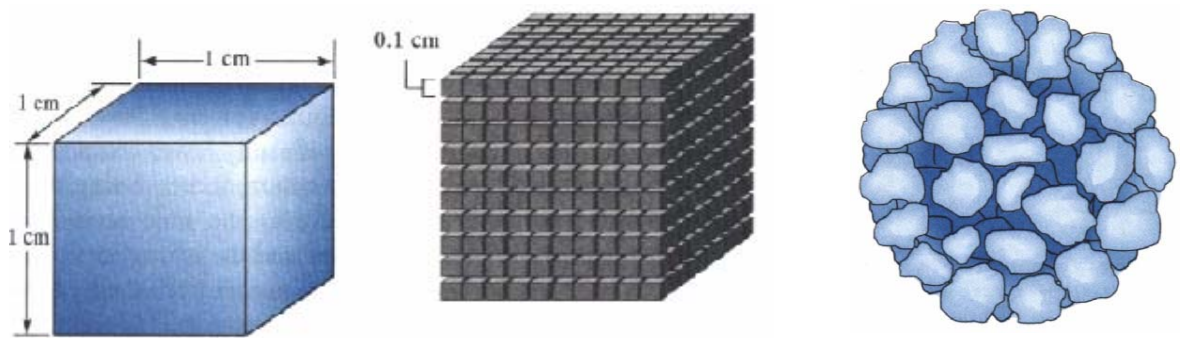
<u>**Four types of coprecipitation:**</u>

1. surface adsorption

2. mixed-crystal formation

3. occlusion

4. mechanical entrapment

1, 2 $\rightarrow$ equilibrium processes

3, 4 $\rightarrow$ arise from the kinetics of crystal growth

1. Surface adsorption

specific <u>surface areas(SA)</u> $\uparrow \rightarrow$ adsorption $\uparrow$ SA = (cm^2)/mass(g)

$SA = 1 \times 1 \times 6 = 6 \text{ cm}^2$ $SA = 1000 \times 0.1^2 \times 6 = 60 \text{ cm}^2$ A coagulated colloid

Adsorption, a normally soluble compound is carried out of soln on the surface of a coagulated colloid. This compound consists of the primarily adsorbed ion and an ion of opposite charge from the counter-ion layer.

ex: in chloride analysis

primary adsorbed ion : Ag^+

counter-ion layer : NO_3^- or other anions

→ $AgNO_3$ (normally soluble) is coprecipitated with the AgCl.

*Methods for Minimizing Adsorbed Impurities on Colloids

a. Digestion:

particle size ↑ → specific surface area ↓ → adsorption ↓

b. Washing with volatile electrolyte soln

ex: in Ag^+ analysis, primary adsorbed ion : Cl^-

washing with an acidic soln → counter-ion layer : H^+

→ HCl volatilized when ppt is dried

c. Reprecipitation, double precipitation

2. Mixed-crystal formation

a contaminant ion replaces an ion in the lattice of a crystal

a. the same charge

b. the size differ < 5 %

c. salt : the same crystal class

ex: (a). $PbSO_4$ in $BaSO_4$

$BaCl_2$ + soln containing sulfate, lead & acetate

→ $BaSO_4 + PbSO_4$ (Pb + acetate → lead acetate)

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(b). $MgKPO_4$ in $MgNH_4PO_4$

(c). $SrSO_4$ in $BaSO_4$

(d). MnS in CdS

3. Occlusion

A compound is trapped within a pocket formed during rapid crystal growth.

4. Mechanical entrapment

Several crystals grow together & in so doing trap a portion of the solution in a tiny pocket.

3 & 4 : rate of ppt formation ↓ (low supersaturation)

→ occlusion & mechanical entrapment at a minimum

Digestion decrease these coprecipitation.

*Coprecipitation error: negative or positive errors

Ex: (a). in Cl analysis, colloidal $AgCl + AgNO_3$ → (+) error

(b). in Ba^{2+} → $BaSO_4$ analysis

if $Ba(NO_3)_2$ (larger FW than $BaSO_4$) → (+) error

if $BaCl_2$ (FW: $BaCl_2 < BaSO_4$) → (-) error

12A-6 Precipitation from Homogeneous Solution (Table 12-1)

Homogeneous precipitation:

a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

Solid formed by homogeneous precipitation are generally purer and more easily filtered than precipitate generated by direct addition of a reagent to the analyte solution.
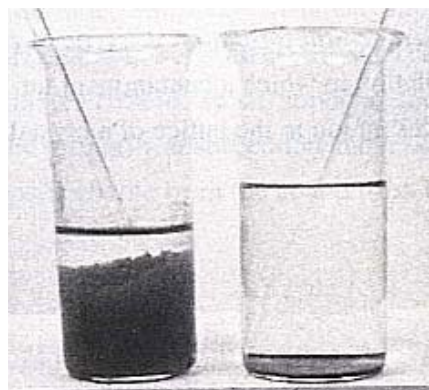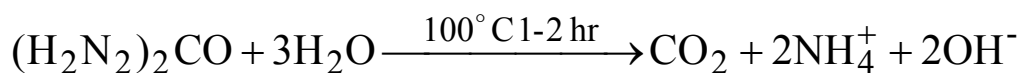

Fig. 12-5 $Al(OH)_3$ formed by the direct addition of NH_3(left) and the homogeneous production of hydroxide(right).

ex: urea → OH⁻ for Fe(III) & Al

$$(H_2N_2)_2CO + 3H_2O \xrightarrow{100°C\,1\text{-}2\,hr} CO_2 + 2NH_4^+ + 2OH^-$$

*Filtration

   1.Sintered-glass filtering crucible: 110 ℃～250 ℃

       crystalline or granular type ppt
         pore: coarse, medium, fine

   2. Gooch crucible with an asbestos mat: 800 ℃～1000 ℃

   3. Filter paper
      ashless filter paper : residue **< 0.1 mg**.

 *Washing the Precipitate

   wash soln

   1. Wash out all impurity but leave it unchanged in composition.

   2. Not introduce insoluble product into ppt

   3. completely volatile at drying temp of ppt

   • pure water → peptization

   • electrolyte soln

12A-7 Drying and ignition of Precipitates
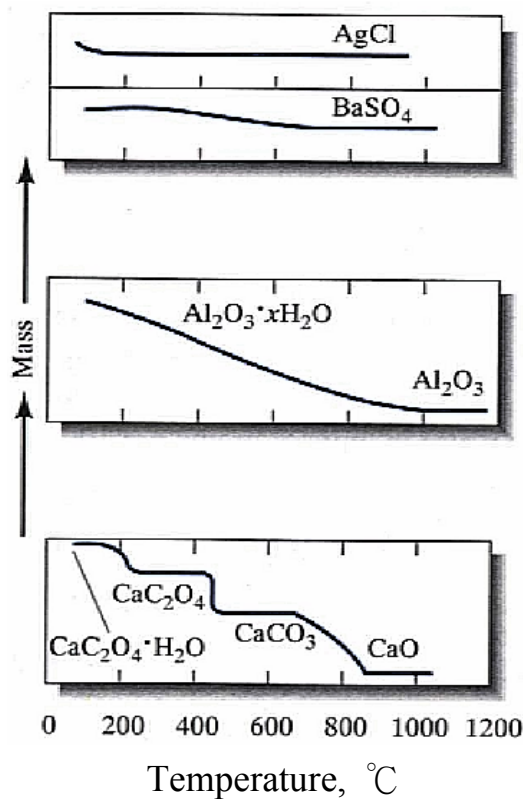
← Fig. 12-6 Effect of temperature on
          precipitate mass.

1. oven 110℃～ 250℃→desiccator, cool →
    weight

2. ignite (ashless filter paper)
    $Fe^{3+} + OH^- →Fe(OH)_3 → Fe_2O_3$
                          weighing form

3.desiccator or vacuum desiccator

*Constant weight (恆量)
  ◆依照中華藥典第四版 (CHP IV)：檢品按
    照規定經乾燥稱量後，再乾燥一小時，或
    熾灼稱量後，再熾灼十五分鐘，直至前後
    稱量之差，以檢品每 g 不得超過 _0.5 mg_
    而言。
  ◆二次連續稱重不大於 0.2 mg。

12B Calculation of Results from Gravimetric Data

$$\boxed{\frac{R \times FW_{species}}{FW_{ppt}}}$$

Gravimetric factor (GF)

$$\boxed{\frac{g\ ppt \times GF}{g\ impure\ sample} = \%\ species\ sought}$$

Ex. 12-1. **The Ca in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4. The ppt was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the con. of Ca (40.078 g/mol) in the water in units of grams per 100 mL.**

mass of CaO = 26.7134 - 26.6002 = 0.1132 g

moles Ca = moles CaO

$$amount\ of\ Ca = \frac{0.1132\ g}{56.077\ g/mol} = 2.0186\ mmol$$

$$\frac{mass\ Ca}{100\ mL} = \frac{2.0186\ mmol \times 40.078 g/mol}{200\ mL} \times 100\ mL = 0.04045\ g/100\ mL$$

Ex. 12-2. **An iron ore was analyzed by dissolving a 1.1324-g sample in c-HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temp. to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.**

$$amount\ Fe_2O_3 = \frac{0.5394\ g}{159.69\ g/mol} = 3.3778\ mmol$$

(a) mass Fe = 3.3778×10^{-3} mol × 2 × 55.847 g/mol = 0.37728 g

$$\%\ Fe = \frac{0.37728 g}{1.1324 g} \times 100\% = 33.317 \approx 33.32\ \%$$

(b) $3\ Fe_2O_3 \quad \rightarrow \quad 2\ Fe_3O_4 + \frac{1}{2}\ O_2$
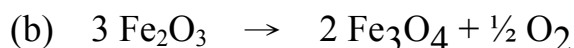
mass Fe_3O_4 = 3.3778 mmol × ⅔ × 231.54 g/mol = 0.52140 g

$$\%\ Fe_3O_4 = \frac{0.52140 g}{1.1324 g} \times 100\% = 46.044 \approx 46.04\ \%$$

Ex. 12-3. A 0.2356-g sample containing only NaCl (58.44 g/mol) and BaCl$_2$ (208.25 g/mol) yielded 0.4637 g of dried AgCl(143.32 g/mol). Calculate the percent of each halogen compound in the sample.

let x = mass of NaCl, y = mass of BaCl$_2$ $\rightarrow$ $x + y = 0.2356$ g

mass AgCl from NaCl $= \dfrac{x \text{ g} \times 143.32 \text{ g/mol}}{58.44 \text{g/mol}} = 2.4524x$ g

mass AgCl from BaCl$_2$ $= \dfrac{y \text{ g} \times 2 \times 143.32 \text{ g/mol}}{208.23 \text{ g/mol}} = 1.3766y$ g

$2.4524x$ g $+ 1.3766y$ g $= 2.4524x$ g $+ 1.3766 (0.2356 - x)$ g $= 0.4637$ g

$$1.0758x = 0.13942$$

$$x = \text{mass NaCl} = 0.12960 \text{ g NaCl}$$

% NaCl $= \dfrac{0.12956 \text{ g NaCl}}{0.2356 \text{ g}} \times 100\% = 55.01\%$

% BaCl$_2$ = 100 % – 55.01% = 44.99 %

Ex. 12-4. **Sample: <u>NaCl + NaBr + inert</u> = 1.000 g**

Ag: 107.87,
Cl: 35.45
Na: 22.99
Br: 79.90

excess AgNO$_3$ $\Downarrow$

<u>AgCl(s) + AgBr(s)</u> = 0.5260 g

Cl$_2$ treatment $\Downarrow$

<u>AgCl(s) + AgCl(s)</u> = 0.4260 g

NaCl = ? % ; NaBr = ? %

Ans: if NaCl = x g, NaBr = y g

g of AgCl(s) $= \dfrac{x \times 143.32}{58.44}$; g of AgBr(s) $= \dfrac{y \times 187.77}{102.89}$

$\dfrac{x \times 143.32}{58.44} + \dfrac{y \times 187.77}{102.89} = 0.5260$ g	% NaCl $= \dfrac{x \times 100}{1.000}$
$\dfrac{x \times 143.32}{58.44} + \dfrac{y \times 143.32}{102.89} = 0.4260$ g	% NaBr $= \dfrac{y \times 100}{1.000}$

12C Applications of Gravimetric Methods

(a). most inorganic anions and cations

(b). neutral species: water, SO_2, CO_2, I_2.

(c). organic substances: lactose in milk products, salicylates in drug preparations, nicotine in pesticides, cholesterol in cereals, benzaldehyde in almond extracts

## 12C-1 Inorganic precipitating agents (Table 12-2)

PrecipitatingAgent	Element Precipitated
$NH_3(aq)$	Be(BeO), Al(Al_2O_3), Sc(Sc_2O_3),Cr(Cr_2O_3), Fe(Fe_2O_3), Ga(Ga_2O_3), Zr(ZrO_2), In(In_2O_3), Sn(SnO_2), U(U_3O_8)
H_2S	Cu(CuO), Zn(ZnO or $ZnSO_4$), Ge(GeO_2), As(As_2O_3 or As_2O_5), Mo(MoO_3), Sn(SnO_2), Sb(Sb_2O_3 or Sb_2O_5), Bi(Bi_2S_3)
$(NH_4)_2S$	Hg(HgS), Co(Co_3O_4)
$(NH_4)_2HPO_4$	Mg(MgP_2O_7), Al($AlPO_4$), Mn($Mn_2P_2O_7$), Zn($Zn_2P_2O_7$), Zr($Zr_2P_2O_7$), Cd($Cd_2P_2O_7$), Bi($BiPO_4$)
H_2SO_4	Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)
H_2PtCl_6	K(K_2PtCl_6 or Pt), Rb(Rb_2PtCl_6), Cs(Cs_2PtCl_6)
$H_2C_2O_4$	Ca(CaO), Sr(SrO), Th(ThO_2)
$(NH_4)_2MoO_4$	Cd($CdMoO_4$), Pb ($PbMoO_4$)
HCl	Ag(AgCl), Hg(Hg_2Cl_2), Na(as NaCl from butyl alcohol), Si(SiO_2)
$AgNO_3$	Cl(AgCl), Br(AgBr), I(AgI)
$(NH_4)_2CO_3$	Bi(Bi_2O_3)
NH_4SCN	Cu[$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir(precipitated as hydrous oxides; reduced with H_2 to metallic state)
HNO_3	Sn(SnO_2)
H_5IO_6	Hg[$Hg_5(IO_6)_2$]
NaCl, $Pb(NO_3)_2$	F(PbClF)
$BaCl_2$	SO_4^{2-}($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-}(MgP_2O_7)

12C-2 Reducing agents (Table 12-3)

Reducing agents	Analyte	Reducing agents	Analyte
SO_2	Se, Au	HCOOH	Pt
SO_2 + H_2NOH	Te	$NaNO_2$	Au
H_2NOH	Se	$SnCl_2$	Hg
$H_2C_2O_4$	Au	Electrolytic	Co, Ni, Cu, Zn, Ag,
H_2	Re, Ir	reduction	In, Sn, Sb, Cd, Re, Bi

12C-3 Organic precipitating agents

1. Chelating agents: form slightly soluble, nonionic products coordination compound (chelates).
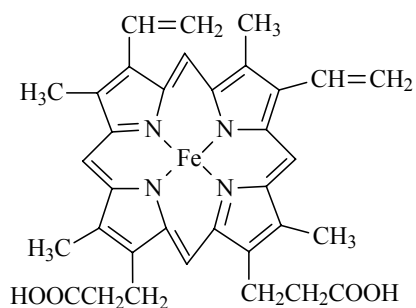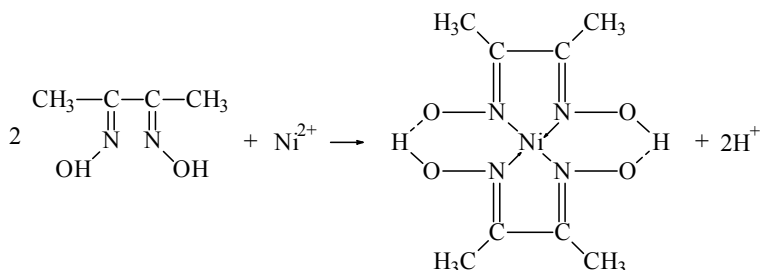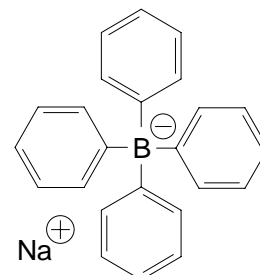
   (a). Hydroxyquinoline(oxine): 24 cations
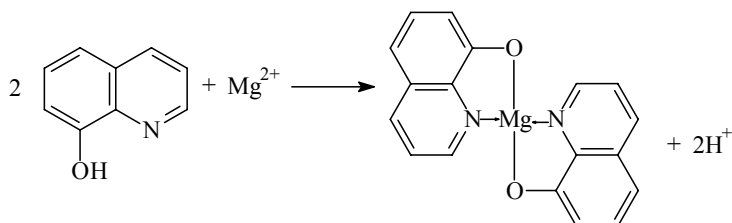
   8-Hydroxyquinoline   Mg 8-hydroxyquinolate

   (b) Dimethylglyoxime:

   specific for Ni^{2+}

2. Sodium tetraphenylboron, $(C_6H_5)B^-Na$: for K^+ & NH_4^+
   → form ionic, saltlike ppts
   ppt : dry at 105 ℃ ∼ 120 ℃ → constant weight
   interference: mercury(II), rubidium & cesium

12C-4 Organic Functional Group Analysis (Table 12-4)

Functional Group	Basis for Method	Reaction and product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow$ $\boxed{R\text{-}CH=NNHC_6H_3(NO_2)_2}(s) + H_2O$ (RCOR' reacts similarly)
Aromatic Carbonyl	Mass of CO_2 formed at 230℃ in quinoline; CO_2 distilled, absorbed and weighed	$ArCHO \xrightarrow[CuCO_3]{230\ ℃} Ar + \boxed{CO_2}(g)$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH_3I or C_2H_5I	$ROCH_3 + HI \rightarrow ROH +$ $RCOOCH_3 + HI \rightarrow RCOOH + CH_3I$ $ROC_2H_5 + HI \rightarrow ROH + C_2H_5I$ $CH_3I + Ag^+ + H_2O \rightarrow \boxed{AgI}(s) + CH_3OH$

Aromatic nitro	Mass loss of Sn	$RNO_2 + 1.5 \boxed{Sn}(s) + 6H^+ \rightarrow$ $RNH_2 + 1.5Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN{=}NR' + 2\boxed{Cu}(s) + 4H^+ \rightarrow$ $RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$ROPO(OH)_2 + Ba^{2+} \rightarrow \boxed{ROPOO_2Ba}(s) + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with HNO_2	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow$ $ROH + \boxed{BaSO_4}(s) + N_2 + 2H^+$
Sulfinic acid	Mass of Fe_2O_3 after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$ $(ROSO)_3Fe \xrightarrow{O_2} CO_2 + H_2O + SO_2 + \boxed{Fe_2O_3}(s)$

12C-5 Volatilization Gravimetry

1. For water

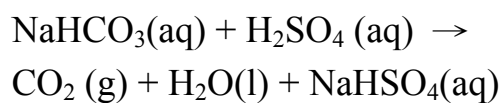 (a). Direct method: solid desiccant collection

  (b). Indirect method: heating $\rightarrow$ loss of weight

    • water is not the only compound volatilized)
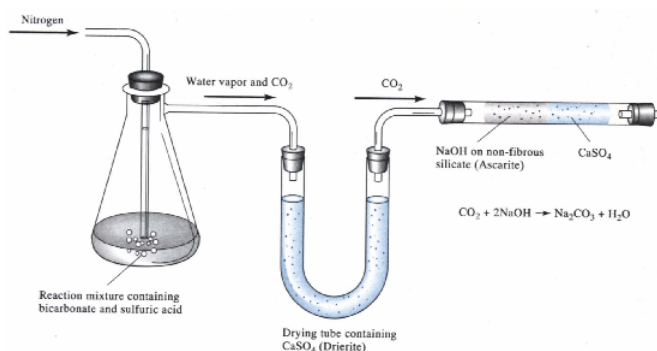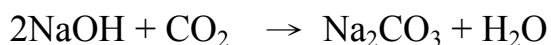
    • decomposition & change in water

2. For carbonate: carbon dioxide

   Solid adsorbent: Ascarite II - NaOH on a nonfibrous silicate

  ex: For $NaHCO_3$ in antacid tablets

   $NaHCO_3(aq) + H_2SO_4 (aq) \rightarrow$
   $CO_2 (g) + H_2O(l) + NaHSO_4(aq)$
   $\downarrow$
   absorption tube

 $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

3. For sulfides & sulfites: H_2S or SO_2

4. For carbon & hydrogen in organic compound
    $\rightarrow$ combustion product : H_2O & CO_2