DR. MRS. SMITA SURESH GIRI

GOPAL KRUSHNA GOKHALE COLLEGE KOLHAPUR.

CHEMISTRY DEPARTMENT

26 AUG 2018

Gravimetric Analysis

Introduction

1.) **Gravimetric Analysis:**

(i) A technique in which the amount of an analyte in a sample is determined by converting the analyte to some product

- *Mass of product can be easily measured*

(ii) Analyte: the compound or species to be analyzed in a sample

(iii) Overall, gravimetry sounds simple.

- *Advantages* - when done correctly is highly accurate (most accurate of all time); requires minimal equipment

- *Disadvantage* - requires skilled operator, slow.

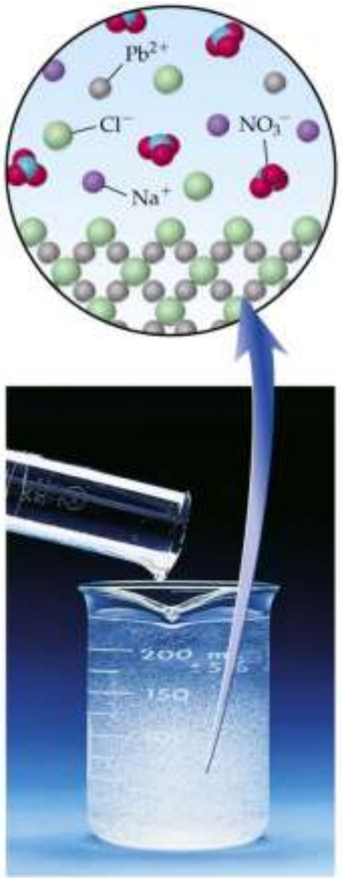
Convert analyte into a solid, filter, weigh, calculate via a mole map

Gravimetric Analysis

Introduction

1.) **Gravimetric Analysis:**

(iii) Example:



- Determination of lead (Pb^{+2}) in water

$$Pb^{+} \quad + \quad 2Cl^{-} \rightarrow \quad PbCl_2(s)$$

Analyte — Reagent — Solid Product

- By adding excess Cl^- to the sample, essentially all of the Pb^{+2} will precipitate as $PbCl_2$.

- Mass of $PbCl_2$ is then determined.
  - ***used to calculate the amount of Pb^{+2} in original solution***

Gravimetric Analysis

Introduction

1.) **Gravimetric Analysis:**

(v) Example:

- What is the %KCl in a solid if 5.1367 g of solid gives rise to 0.8246 g AgCl?

$$Cl^- \quad + \quad Ag^+ \quad \rightarrow \quad AgCl(s)$$

Gravimetric Analysis

Types of Gravimetric Analysis

1.) **Combustion Analysis**
2.) **Precipitation**

Combustion Analysis

- **Common method used to determine the amount of carbon and hydrogen**
- **One modified method (Dumas Method) can also determine the amount of nitrogen in a sample**
- **Technique is accurate and usable with a wide range of compounds.**
  - Often one of the first methods used to characterize a new compound

Gravimetric Analysis

Combustion Analysis

1.) **Principals:**

(i) Sample is heated in presence of Oxygen (O_2)

- Converts carbon in sample to CO_2
- Converts hydrogen in sample to H_2O

$$C_{(sample)} + O_2 \xrightarrow[Pt]{\Delta} CO_2$$

$$2H_{(sample)} + \frac{1}{2}O_2 \xrightarrow[Pt]{\Delta} H_2O$$

- Pt, CuO, PbO_2, or MnO_2 is used as a catalyst in this process

(ii) As CO_2 and H_2O form, leave the sample and flow through a series of chambers

- Chambers contain chemicals that bind one or both of these products
- Example:

- P_4O_{10} can be used to absorb H_2O

- Ascarite can be used to absorb CO_2

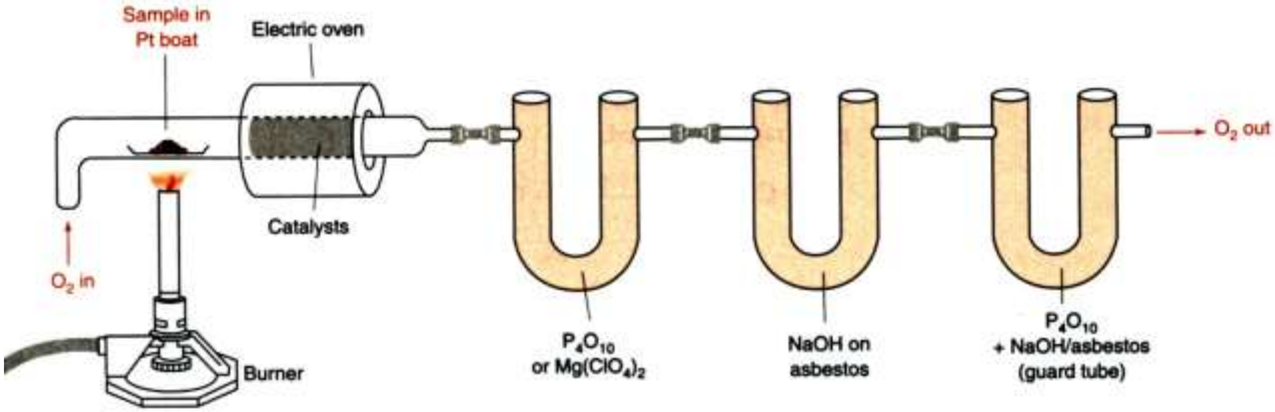
- Ascarite - Sodium Hydroxide Coated Non-Fibrous Silicate

Ascarite

Gravimetric Analysis

Combustion Analysis

2.) **Apparatus:**



(i) After the sample is completely burned:
- Remove P_4O_{10} and Ascarite cartridges and weigh
- If C and H are present in sample, both cartridges will increase in mass

(ii) Amount of C and H in the original sample is determined from:
- Knowing the amount of sample burned
- Change in weight in each cartridge

Gravimetric Analysis

Combustion Analysis

2.) **Example Calculation:**

A mixture weighing 7.290 mg contained only cyclohexane, C_6H_{12} (FM 84.159), and oxirane, C_2H_4O (FM 44.053). When the mixture was analyzed by combustion analysis, 21.999 mg of CO_2 (FM 44.010) was produced.

Find the weight percent of oxirane in the mixture.

Gravimetric Analysis

Precipitation Analysis

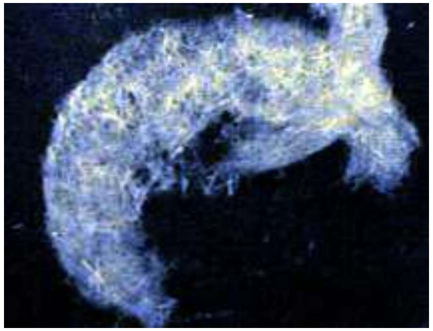
1.) **Principals:**

(i)

Reagent + Analyte ⟶ Solid Product (collect and measure mass)

(ii) Desired Properties of Solid Product

- Should be very insoluble
- Easily filterable (i.e., large crystals)
- Very Pure
- Known and constant composition



Few precipitates have all of these properties, but in most cases appropriate techniques can help optimize these qualities

Gravimetric Analysis

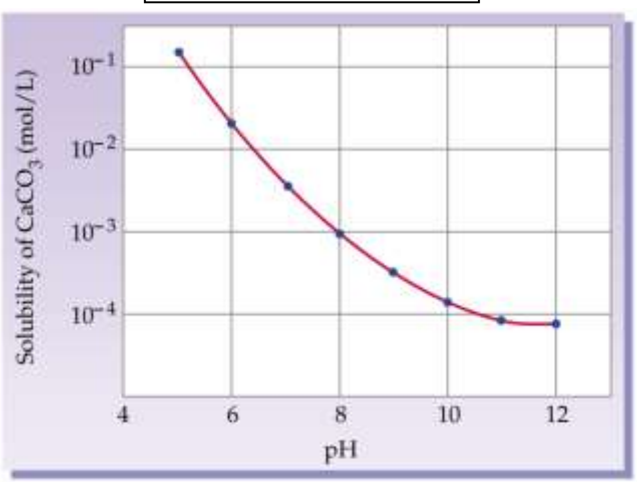
Precipitation Analysis

2.) **Solubility:**

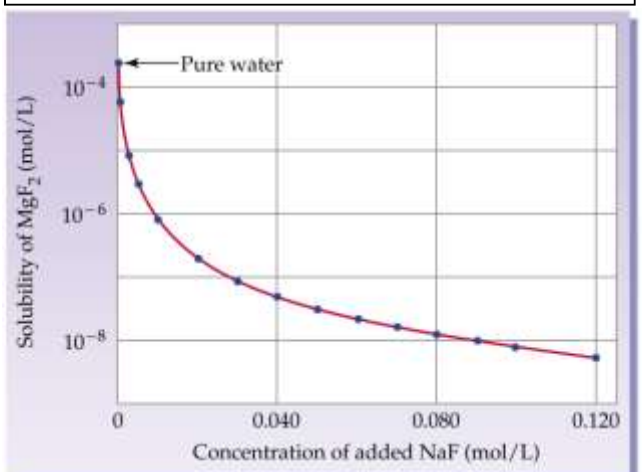
(i) The solubility of a precipitate can be decreased by:

- Decreasing temperature of solution
- Using a different solvent
  - usually a less polar or organic solvent (*like dissolves like*)

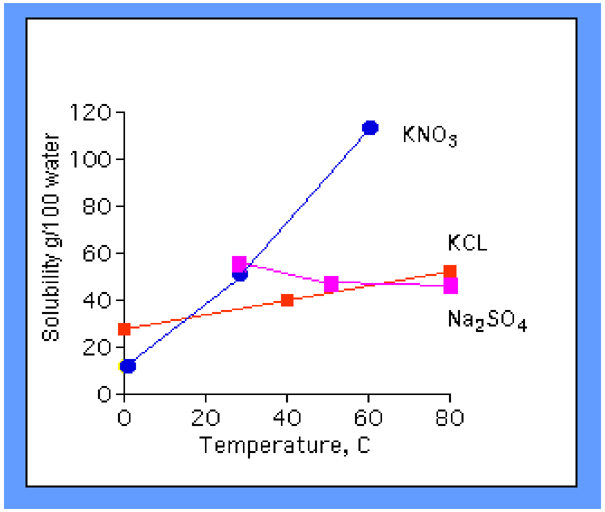
Solubility vs. pH



Solubility vs. Common Ion Effect



Solubility vs. Temperature



Gravimetric Analysis

Precipitation Analysis

1.) **Gravimetric Analysis:**

(vi) Governed by equilibrium: AgCl $K_{sp} = 1.8 \times 10^{-10}$

Solubility of AgCl = $[Ag^+] + [AgCl] + [AgCl^{2-}]$

$Cl^- + Ag^+ \rightarrow AgCl(ag)$ ion pair formation $K_o = \frac{[AgCl]}{[Ag^+][Cl^-]}$

$AgCl(aq) \rightarrow AgCl(s)$ intrinsic solubility $K_i = [AgCl]$

$AgCl + Cl^- \rightarrow AgCl^{2-}$ complex ion formation $K_f = \frac{[AgCl^{2-}]}{[AgCl][Cl^-]}$

$$S = \frac{[AgCl]}{[Cl^-]}K_o + K_i + \frac{[AgCl]}{[Cl^-]}K_f = \frac{K_o}{[Cl^-]K_o} + K_i + K_f K_o [Cl^-]$$

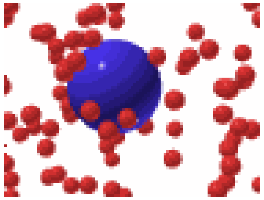
Gravimetric Analysis

Precipitation Analysis

3.) **Filterability:**

(i) Want product to be large enough to collect on filter:
- Doesn't clog filter
- Doesn't pass through filter

(ii) Best Case: <u>Pure Crystals</u>



Brownian Motion

Worst Case: <u>Colloidal suspension</u>
- Difficult to filter due to small size
- Tend to stay in solution indefinitely → suspended by Brownian motion

  - usually 1-100 nm in size

Whether crystals or colloids are obtained depends on conditions used in the precipitation

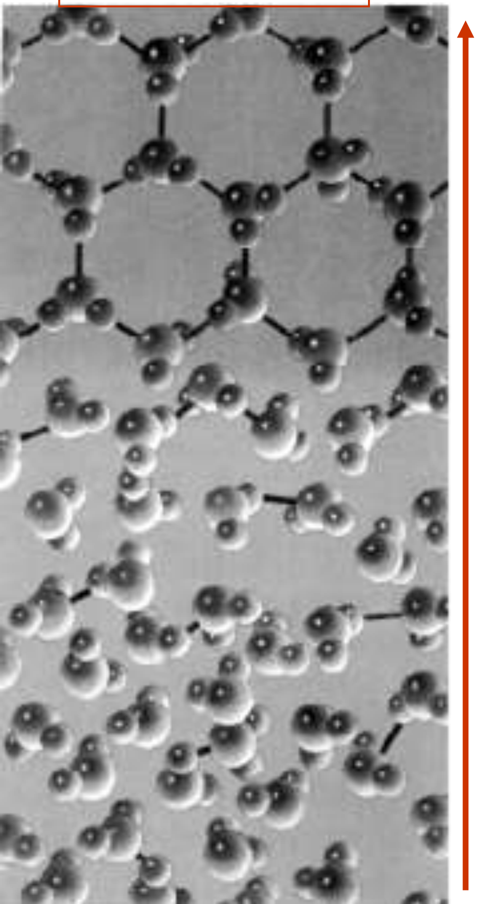
Gravimetric Analysis

Precipitation Analysis

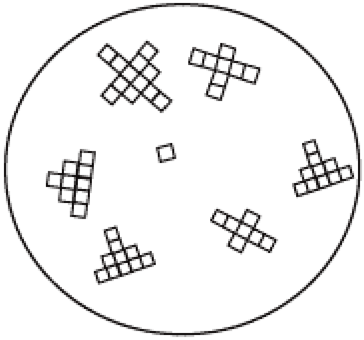
4.) **Process of Crystal Growth:**

(i) Two Phases in Crystal Growth

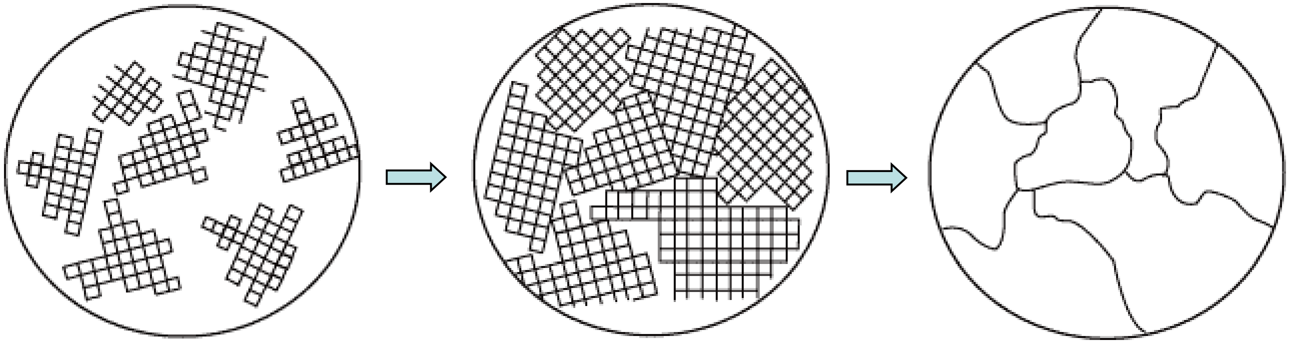
Crystal Growth



Nucleation – molecules in solution come together randomly and form small aggregates



Particle growth – addition of molecules to a nucleus to form a crystal



Gravimetric Analysis

Precipitation Analysis

4.) **Process of Crystal Growth:**

(ii) Nucleation and Particle growth always compete for molecules/ions being precipitated.

- If nucleation is faster than particle growth:

  - a large number of small aggregates occur giving colloidal suspensions

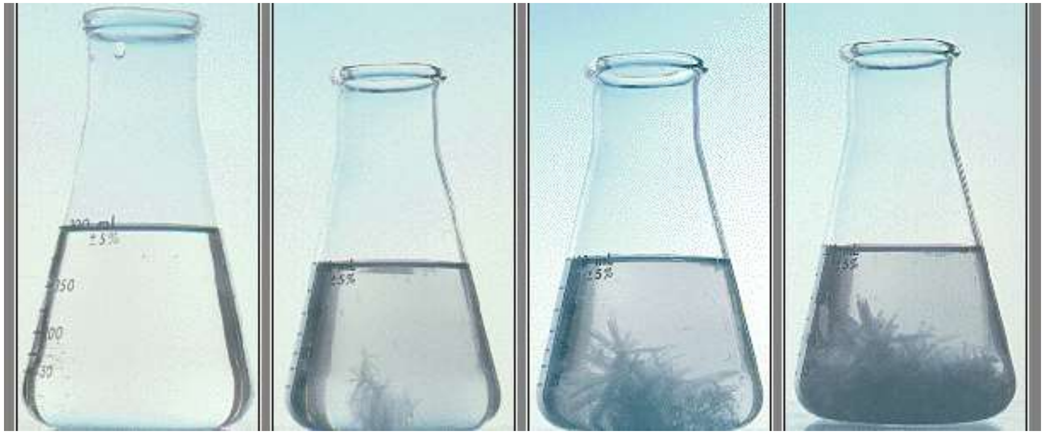
- If particle growth is faster than nucleation:

  - only a few, large particles form giving pure crystals

Colloidal suspension

Want to

Convert to



Crystal formation

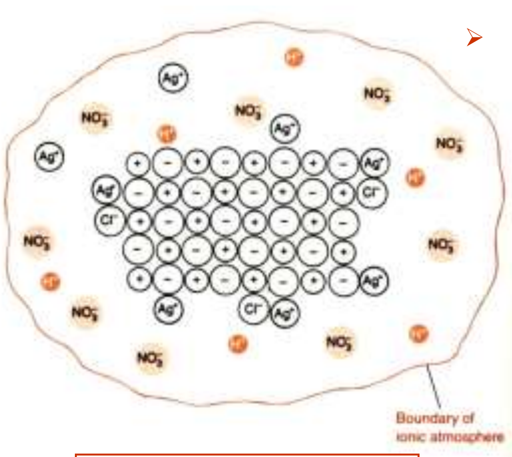
Gravimetric Analysis

Precipitation Analysis

4.) **Process of Crystal Growth:**

(iii) Rates of nucleation vs. particle growth depends on:

- Amount of precipitation solute present
- Described by a quantity known as the <u>Relative Supersaturation</u> (R)



Colloidal Particle

$$R = \frac{(Q - S)}{S}$$

S = concentration of solute in solution <u>at equilibrium</u>
Q = actual concentration of solute added to solution

(iv) If *R* is large,

- Large relative amount of solute in solution
- Favors nucleation and colloid formation

(v) In gravimmetry based on precipitations, a small value of *R* (~1.0) is desired in order to favor large crystal growth

Gravimetric Analysis

Precipitation Analysis

4.) **Process of Crystal Growth:**

(vi) Methods for Minimizing *R*

1. Increase temperature of solution
   - **- increases *S***
   - **- increase amount of solute that can be in solution at equilibrium**
2. Add precipitating reagent (precipitant) slowly while vigorously mixing solution
   - **- avoids local high concentrations of solution**
   - **- avoid nucleation and colloid formation**
3. Keep volume of solution large
   - **- keep concentration of analyte and precipitating reagent low**
4. Control *S* through chemical means
   - **- by adjusting pH**
   - **- adding complexing agents**
   - **- example: precipitation of Ca^{2+} with $C_2O_4^{2-}$**

Note: As pH ($[H^+]$) changes, the solubility of CaC_2O_4 changes

$$\begin{cases} C_2O_4^{2-} + H^+ \leftrightarrow HC_2O_4^- \\ Ca^{2+} + C_2O_4^{2-} \overset{K_{sp}}{\leftrightarrow} CaC_2O_4(s) \end{cases}$$

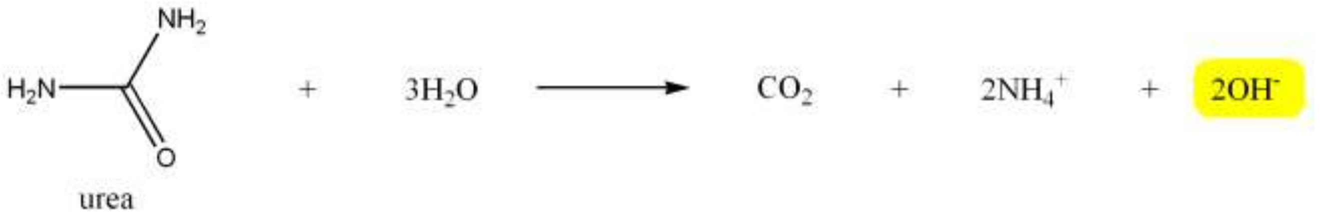
Gravimetric Analysis

Precipitation Analysis

5.) **Homogeneous Precipitation:**

(i) Precipitating agent is generated directly in solution by means of a chemical reaction.

- Ideal case for precipitations
  - **- agent is generated uniformly throughout the solution**
  - **- excess are avoided**
- Example:

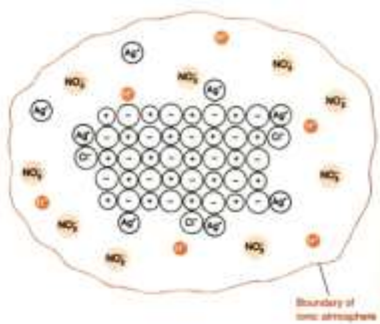


As OH^- is produced, pH gradually increases → precipitates a number of compounds (CaC_2O_4)

Gravimetric Analysis

Precipitation Analysis

5.) **Miscellaneous Notes on Precipitation:**



(i) Most ionic compounds are precipitated in the presence of some added electrolyte

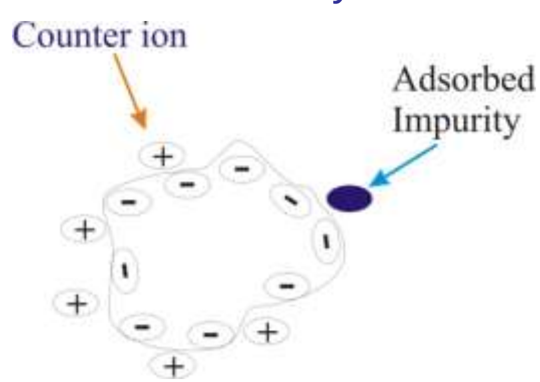
- e.g. 0.1 M HNO_3
- Allows the small nucleation aggregates to better overcome any charge repulsion and promotes particle growth

(ii) Impurities may also be present in the crystal

- Known as co-precipitation
- Creates errors in gravimetric analysis

(iii) Types of Impurities

- Impurities adsorbed to crystal surface



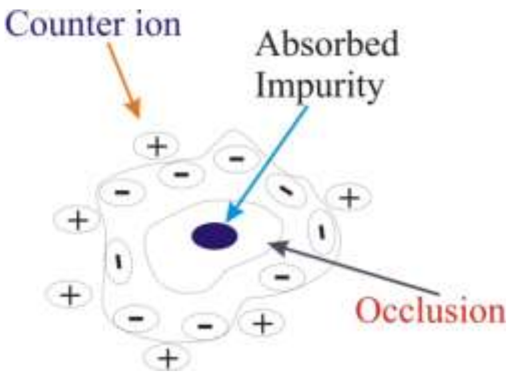
Gravimetric Analysis

Precipitation Analysis

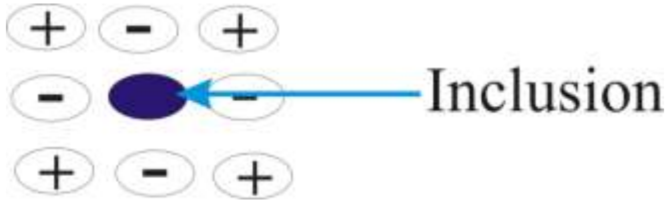
5.) **Miscellaneous Notes on Precipitation:**

(iii) Types of Impurities

- Impurities absorbed or trapped within pockets in the crystal
- Occlusion



- Impurities similar to the analyte or reagent
- Impurities placed in the crystal instead of analyte



Gravimetric Analysis

Precipitation Analysis

5.) **Miscellaneous Notes on Precipitation:**

(iv) Impurities are undesirable

- Change the chemical composition of the precipitate
- Causes errors in the analysis

(v) Ways to Minimize Impurities

1. Keep <u>*R*</u> small
   - large pure crystals decrease occlusions and adsorbed impurities
2. <u>Digestion</u> allowing precipitate to stand in mother liquor (precipitating solution), usually while being heated
   - promotes removal of impurities from crystal
   - increases size of crystals
3. Wash precipitate, redissolve the precipitate in fresh solvent and reprecipitate
   - helps decrease all types of impurities
4. Add a <u>masking agent</u> to solution
   - keeps impurities from precipitating, but not analyte

Color → Impurity

Masking agent

$$Mg^{2+} + CPCH \rightarrow \text{Solid product}$$

$$Mn^{2+} + 6CN^{-} \rightarrow Mn(CN)_6^{4-}$$

precipitant

Gravimetric Analysis

Precipitation Analysis

5.) **Miscellaneous Notes on Precipitation:**

(vi) Washing Precipitates

- Precipitates from ionic compounds
  - **- need electrolyte in wash solution**
  - **- keep precipitate from breaking up and redissolving (*peptization*)**
- Electrolyte should be volatile
  - **- removed by drying**
  - **- HNO_3, HCl, NH_4, NO_3, etc.**
- Example:

  AgCl(s) should not be washed with H_2O, instead wash with dilute HNO_3

(vii) Drying/Igniting Precipitates

- Many precipitates contain varying amounts of H_2O
  - **- adsorbed from the air (i.e. hygroscopic)**
- Precipitates are dried for accurate, stable mass measurements
- Precipitates are also ignited to convert to a given chemical form

$$Fe(HCO)_3 \bullet nH_2O(s) \xrightarrow[1\ hr]{850^oC} Fe_2O_3(s) + xCO_2\uparrow + yH_2O\uparrow$$

Gravimetric Analysis

Scope of Gravimetric Analysis

1.) **Accurate**

2.) **Inexpensive**

- Only major equipment is balance

3.) **Method is more tedious than other approaches**

- must carefully consider how to minimize potential interferences

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)

Gravimetric Analysis

Calculations in Gravimetric Analysis

Example

A mixture containing only Al_2O_3 (FM 101.96) and Fe_2O_3 (FM 159.69) weighs 2.019 g. When heated under a stream of H_2, Al_2O_3 is unchanged, but Fe_2O_3 is converted into metallic Fe plus H_2O (g).

If the residue weighs 1.774 g, what is the weight percent of Fe_2O_3 in the original mixture?