

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.

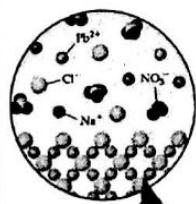
Convert analyte into a solid, filter, weigh, calculate via a mole map

Gravimetric Analysis

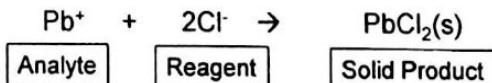
Introduction

1.) Gravimetric Analysis:

(iii) Example:



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



- 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

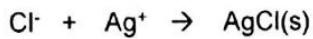
Gravimetric Analysis

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?



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

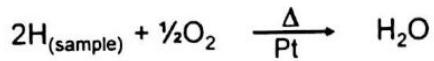
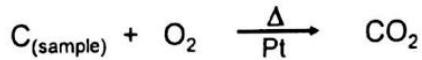
Gravimetric Analysis

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



> 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

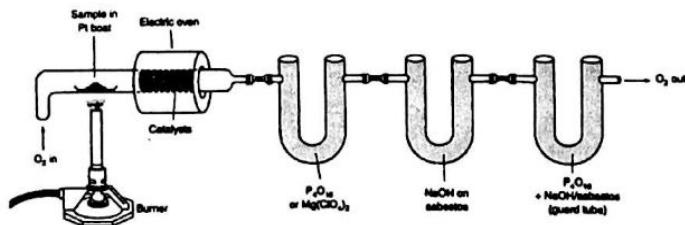


Ascarite

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, C₆H₁₂ (FM 84.159), and oxirane, C₂H₄O (FM 44.053). When the mixture was analyzed by combustion analysis, 21.999 mg of CO₂ (FM 44.010) was produced.

Find the weight percent of oxirane in the mixture.

Gravimetric Analysis

Precipitation Analysis

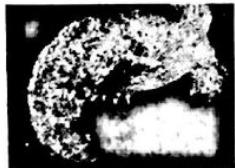
1.) Principals:

(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

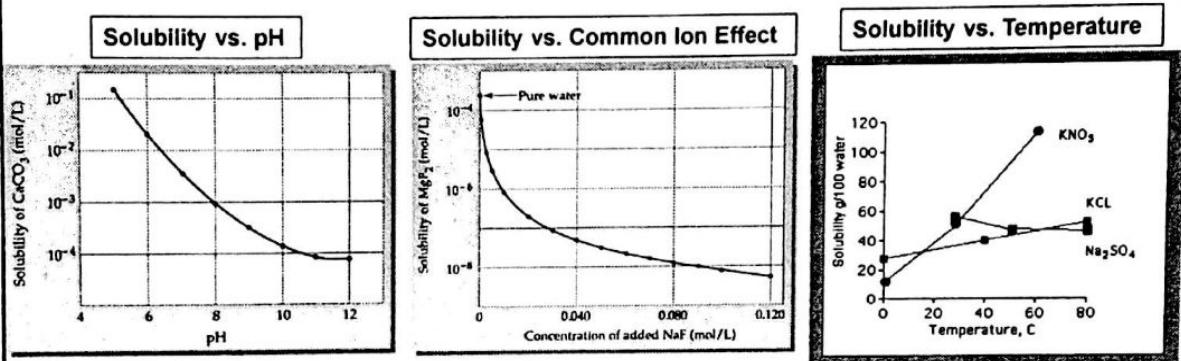
Gravimetric Analysis

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*)



Gravimetric Analysis

Precipitation Analysis

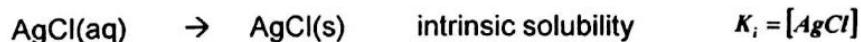
1.) Gravimetric Analysis:

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

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



$$K_o = \frac{[\text{AgCl}]}{[\text{Ag}^+][\text{Cl}^-]}$$



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

Gravimetric Analysis

Precipitation Analysis

3.) Filterability:

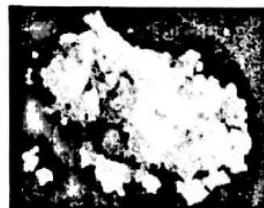
(i) Want product to be large enough to collect on filter:

- > Doesn't clog filter
- > Doesn't pass through filter

(ii) Best Case: Pure Crystals



Brownian Motion



Worst Case: Colloidal suspension

- > 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

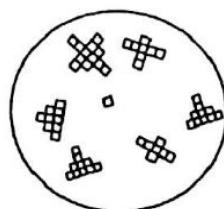
Gravimetric Analysis

Precipitation Analysis

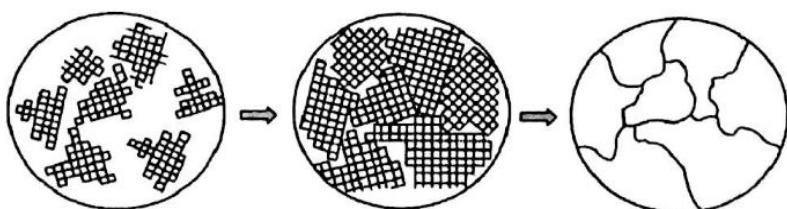
4.) Process of Crystal Growth:

(i) Two Phases in Crystal Growth

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

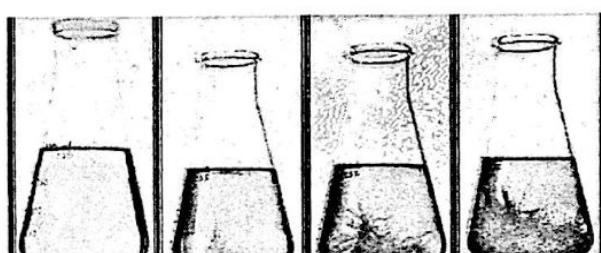
4.) Process of Crystal Growth:

(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



Want to
Convert to



Colloidal suspension

Crystal formation

Gravimetric Analysis

Precipitation Analysis

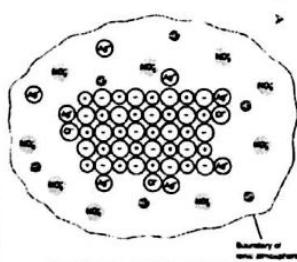
4.) Process of Crystal Growth:

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

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

$$R = (Q - S) / S$$

S = concentration of solute in solution at equilibrium
Q = actual concentration of solute added to solution



Colloidal Particle

(iv) If R is large,

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

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

Gravimetric Analysis

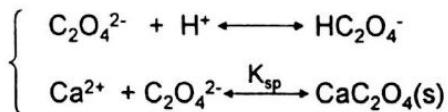
Precipitation Analysis

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 $\text{C}_2\text{O}_4^{2-}$

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



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)

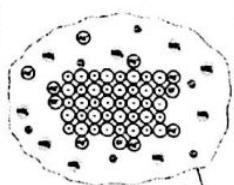
Gravimetric Analysis

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 HNO₃
- Allows the small nucleation aggregates to better overcome any charge repulsion and promotes particle growth

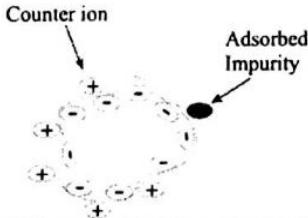


(ii) Impurities may also be present in the crystal

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

(iii) Types of Impurities

- Impurities adsorbed to crystal surface



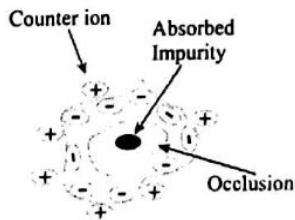
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Precipitation Analysis

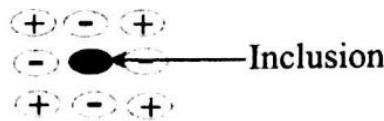
5.) Miscellaneous Notes on Precipitation:

(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 R small

- large pure crystals decrease occlusions and adsorbed impurities



Color → Impurity

2. Digestion allowing precipitate to stand in mother liquor (precipitating solution), usually while being heated

- promotes removal of impurities from crystal

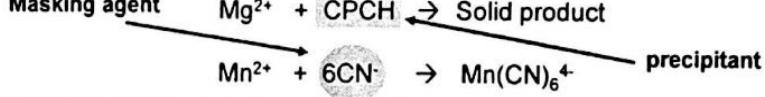
- increases size of crystals

3. Wash precipitate, redissolve the precipitate in fresh solvent and reprecipitate

- helps decrease all types of impurities

4. Add a masking agent to solution

- keeps impurities from precipitating, but not analyte



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

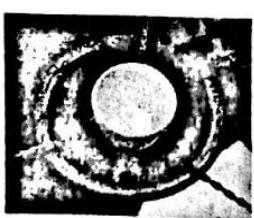
- removed by drying

- 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

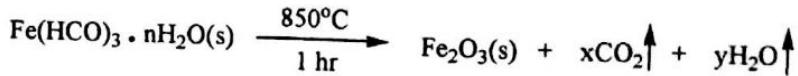


- > Many precipitates contain varying amounts of H_2O

- 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



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 ₆ H ₅) ₄	KB(C ₆ H ₅) ₄	NH ₄ ⁺ , Ag ⁺ , Hg ²⁺ , Ti ⁴⁺ , Rb ⁺ , Cs ⁺
Mg ²⁺	Mg(NH ₄)PO ₄ ·6H ₂ O	Mg ₂ P ₂ O ₇	Many metals except Na ⁺ and K ⁺
Ca ²⁺	CaC ₂ O ₄ ·H ₂ O	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⁺
Tl ⁴⁺	TlO(5,7-dibromo-8-hydroxyquinoline) ₂	Same	Fe ³⁺ , Zr ⁴⁺ , Cu ²⁺ , C ₂ O ₄ ²⁻ , citrate, HF
VO ₄ ³⁻	H ₈ VO ₄	V ₂ O 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 ·H ₂ O	Mn ₂ P ₂ O ₇	Many metals
Fe ²⁺	Fe(HCO ₃) ₂	Fe ₂ O ₃	Many metals
Co ²⁺	Co(1-nitroso-2-naphtholate) ₂	CoSO ₄ (by reaction with H ₂ SO 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 ·H ₂ O	Zn ₂ P ₂ O ₇	Many metals
Ce ⁴⁺	Ce(O ₂) ₃	CeO ₂	Tl ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺
Al ³⁺	Al(8-hydroxyquinolate) ₂	Same	Many metals
Sn ⁴⁺	Sn(cupferron) ₄	SnO ₂	Ca ²⁺ , Pb ²⁺ , As(III)
Pb ²⁺	PbSO ₄	PbSO ₄	Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Hg ²⁺ , Ag ⁺ , HCl, HNO ₃ , K ⁺ , Rb ⁺ , Cs ⁺
NH ₄ ⁺	NH ₄ B(C ₆ H ₅) ₄	NH ₄ B(C ₆ H ₅) ₄	Br ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
Cl ⁻	AgCl	AgCl	Cl ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
Br ⁻	AgBr	AgBr	Cl ⁻ , Br ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
I ⁻	AgI	AgI	Cl ⁻ , Br ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻ , CN ⁻
SCN ⁻	CuSCN	CuSCN	NH ₄ ⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺
CN ⁻	AgCN	AgCN	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻
F ⁻	(C ₆ H ₅) ₂ SnF	(C ₆ H ₅) ₂ SnF	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⁺
PO ₄ ³⁻	Mg(NH ₄)PO ₄ ·6H ₂ O	Mg ₂ P ₂ O 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 ₂ O 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 Al₂O₃ (FM 101.96) and Fe₂O₃ (FM 159.69) weighs 2.019 g. When heated under a stream of H₂, Al₂O₃ is unchanged, but Fe₂O₃ is converted into metallic Fe plus H₂O (g).

If the residue weighs 1.774 g, what is the weight percent of Fe₂O₃ in the original mixture?

Section 09

Gravimetric Analysis and Precipitation Equilibria

How to Perform a Successful Gravimetric Analysis

- **What steps are needed?**
 1. Sampled dried, triplicate portions weighed
 2. Preparation of the solution
 3. Precipitation
 4. Digestion
 5. Filtration
 6. Washing
 7. Drying or igniting
 8. Weighing
 9. Calculation

Gravimetric Analysis

- Gravimetric Analysis – one of the most accurate and precise methods of macro-quantitative analysis.
- Analyte selectively converted to an insoluble form.
- Measurement of mass of material
- Correlate with chemical composition
- Why?
- Simple
- Often required for high precision

Gravimetric Analysis

- How?
- Quantitative collection of material of known composition
 - Precipitation of analyte with selective agent
 - Volitization and collection of analyte
 - w/o loss of material in handling/processing
 - Free from solvent, impurities
- Determination of mass
 - Direct or
 - By difference

Gravimetric Analysis

- Precipitation Techniques
 - Add precipitating reagent to sample solution
 - Reacts with analyte to form insoluble material
 - Precipitate has known composition or can be converted to known composition
- Precipitate handling involves
 - Quantitative collection (no losses)
 - Isolation of pure product
- Measure mass of precipitate
- Calculation of original analyte content (concentration)

Gravimetric Analysis

- Desirable properties of analytical precipitates:
 - Readily filtered and purified
 - Low solubility, preventing losses during filtration and washing
 - Stable final form (unreactive)
 - Known composition after drying or ignition

Gravimetric Analysis

- Precipitating reagents:
- Selective
 - $\text{Ag}^+ + \text{Halides } (\text{X}^-) \rightarrow \text{AgX}_{(\text{s})}$
 - $\text{Ag}^+ + \text{CNS}^- \rightarrow \text{AgCNS}_{(\text{s})}$
- Specific
 - Dimethylglyoxime (DMG)
 - $2 \text{ DMG} + \text{Ni}^{2+} \rightarrow \text{Ni(DMG)}_{2(\text{s})} + 2 \text{ H}^+$

Gravimetric Analysis

- Filterability of Precipitates:
- Colloidal suspensions
 - 10^{-7} to 10^{-4} cm diameter
 - Normally remain suspended
 - Very difficult to filter
- Crystalline suspensions
 - > tenths of mm diameter
 - Normally settle out spontaneously
 - Readily filterable

Gravimetric Analysis

- Filterability of Precipitates:
 - Precipitate formation affected by
 - RELATIVE SUPERSATURATION(R.S.)
- $R.S. = (Q-S)/S$
 - S = Equilibrium Solubility of Precipitate
 - Q = Instantaneous Concentration
- Larger Q leads to colloidal precipitates.

Important Factors for Gravimetric Analysis

- **Nucleation**
 - Individual ions/atoms/molecules coalesce to form “nuclei”
- **Particle Growth**
 - Condensation of ions/atoms/molecules with existing “nuclei” forming larger particles which settle out
- **Colloidal Suspension**
 - Colloidal particles remain suspended due to adsorbed ions giving a net + or - charge

Important Factors for Gravimetric Analysis

- **Coagulation, agglomeration**

- Suspended colloidal particles coalesce to form larger filterable particles (inert electrolyte allows closer approach)

- **Peptization**

- Re-dissolution of coagulated colloids by washing and removing inert electrolyte

Important Factors for Gravimetric Analysis

- **Co-precipitation**

- Normally soluble compounds carried down with insoluble precipitate (surface adsorption, occlusion, mixed crystals, entrapment)

- **Digestion**

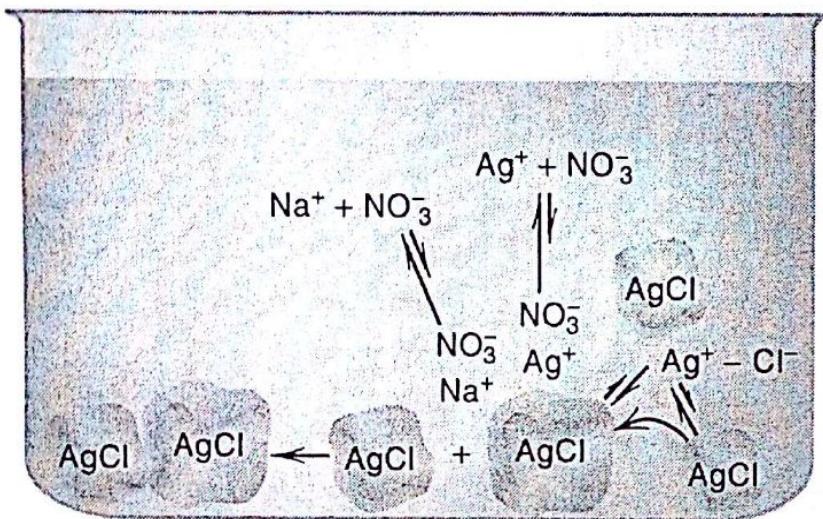
- Precipitation heated for hour(s) in contact with solution from which it was formed

During digestion at elevated temperature:

Small particles tend to dissolve and reprecipitate on larger ones.

Individual particles agglomerate.

Adsorbed impurities tend to go into solution.



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Fig. 10.1. Ostwald ripening.

Cl^- adsorbs on the particles when in excess (primary layer).

A counter layer of cations forms.

neutral double layer causes the colloidal particles to coagulate.

The

Washing with water will dilute the counter layer and the primary layer charge causes the particles to revert to the colloidal state (peptization).

So we wash with an electrolyte that can be volatilized on heating (HNO_3).

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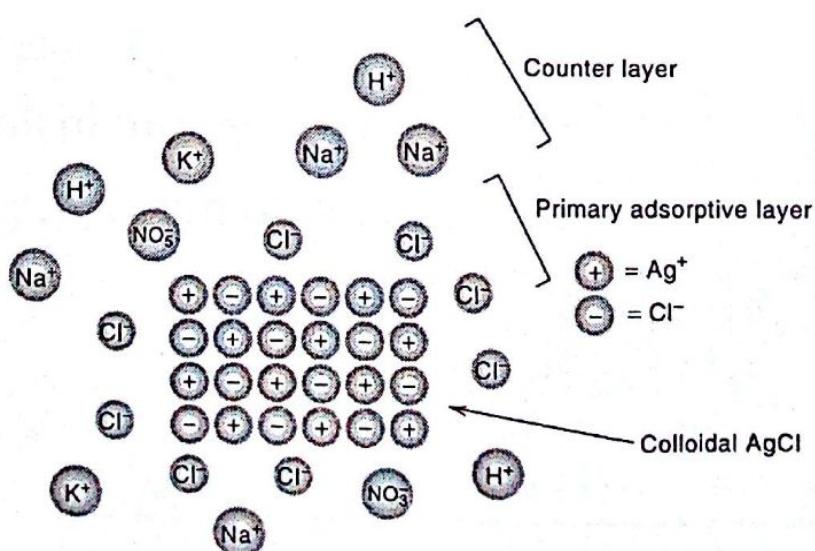


Fig. 10.2. Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.

Organic precipitating agents are chelating agents.
They form insoluble metal chelates.

Table 10.2
Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	$\text{CH}_3 - \text{C} = \text{NOH}$ $\text{CH}_3 - \text{C} = \text{NOH}$	Ni(II) in NH_3 , or buffered HOAc ; Pd(II) in HCl $(\text{M}^{2+} + 2\text{HR} \rightarrow \underline{\text{MR}}_2 + 2\text{H}^+)$
α -Benzoinoimine (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($\text{M}^{2+} + \text{H}_2\text{R} \rightarrow \underline{\text{MR}}_2 + 2\text{H}^+$; $\text{M}^{2+} = \text{Cu}^{2+}$, MoO_4^{2-} , WO_4^{2-}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III) , V(V) , Ti(IV) , Zr(IV) , Sn(IV) , U(IV) $(\text{M}^{2+} + n\text{NH}_2\text{R} \rightarrow \underline{\text{MR}}_n + n\text{NH}_4^+)$ Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) $(\text{M}^{2+} + n\text{HR} \rightarrow \underline{\text{MR}}_n + n\text{H}^+)$
Sodium diethyldithiocarbamate	S $(\text{C}_2\text{H}_5)_2\text{N}-\text{C}-\text{S}^-\text{Na}^+$	Many metals from acid solution $(\text{M}^{2+} + n\text{NaR} \rightarrow \underline{\text{MR}}_n + n\text{Na}^+)$
Sodium tetraphenylboron	$\text{NaB}(\text{C}_6\text{H}_5)_4$	K^+ , Rb^+ , Cs^+ , Tl^+ , Ag^+ , Hg(II) , Cu(I) , NH_4^+ , RNH_2^+ , R_2NH_2^+ , R_3NH^+ , R_4N^+ . Acidic solution $(\text{M}^+ + \text{NaR} \rightarrow \underline{\text{MR}} + \text{Na}^+)$
Tetraphenylarsonium chloride	$(\text{C}_6\text{H}_5)_4\text{AsCl}$	$\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , ReO_4^- , MoO_4^{2-} , WO_4^{2-} , ClO_4^- , I_3^- . Acidic solution ($\text{A}^+ + n\text{RCI} \rightarrow \text{R}_n\text{A} + n\text{Cl}^-$)

Gravimetric Analysis

- Calculations of analyte content requires knowledge of :
- Chemistry
- Stoichiometry
- Composition of precipitate

Gravimetry and Solution Equiliria

- Thermal Conversion to Measurable Form
- Removal of volatile reagents & solvent
- Extended heating at 110 to 115 °C
- Chemical conversion to known stable form
 - $\text{CaC}_2\text{O}_{4(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{(g)} + \text{CO}_{2(g)}$
 - Volatilization & trapping of component
 - $\text{NaHCO}_{3(aq)} + \text{H}_2\text{SO}_{4(aq)} \rightarrow \text{CO}_{2(g)} + \text{H}_2\text{O} + \text{NaHSO}_{4(aq)}$

Gravimetric Calculations

- Gravimetric Factor (GF):
- $\text{GF} = (\text{fwt analyte (g/mol})/\text{fwt precipitate(g/mol)}) \times (a(\text{moles analyte})/b(\text{moles precipitate}))$
- $\text{GF} = \text{g analyte/g precipitate}$
- $\% \text{ analyte} = (\text{weight analyte (g)}/\text{weight sample (g)}) \times 100\%$
- $\% (\text{w/w}) \text{ analyte (g)} = ((\text{wt ppt (g)} \times \text{GF})/\text{wt sample}) \times 100\%$

Gravimetric Errors

- Unknown Stoichiometry:
- Consider Cl^- determination with AgNO_3
- $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$
- $\text{Ag}^+ + 2 \text{Cl}^- \rightarrow \text{AgCl}_2$
- Gravimetric Factor:
- $\text{GF} = \frac{\text{fwt analyte}}{\text{fwt precipitate}} \times \frac{\text{moles analyte}}{\text{moles precipitate}}$
- Calculation for Cl^- = wt. Ppt * GF

Gravimetric Errors

Fwt analyte grams	Fwt ppt grams	Moles analyte	Moles ppt	Grav factor	Weigh ppt grams	Weigh analyte grams
35.453	143.32	1	1	.2474	.606	0.149, ~0.150
35.453	178.77	2	1	0.3966	.606	0.240, ~0.240

Gravimetric Errors

Co-precipitation: (w/AgCl)

<u>Co-precipitant</u>	<u>Error</u>	<u>Rationale</u>
NaF	Positive	All NaF is excess
NaCl	Negative	Fwt Na < Ag
AgI	Positive	All AgI is excess
PbCl ₂ (fwt 278.1)	Negative	Gravimetric Factors decreases

Alternative Gravimetry Technique

- Homogeneous Precipitation
- What?
 - Precipitating agent generated slowly by chemical reaction in analyte solution
- Why?
 - Precipitant appears gradually throughout
 - Keeps relative supersaturation low
 - Larger, less-contaminated particles
- How?
 - (OH⁻) by urea decomposition
 - (NH₂)₂CO → 2 OH⁻ + CO₂ + 2 NH₄⁺
 - (S⁼) by thioacetamide decomposition
 - CH₃CSNH₂ → H₂S + CH₃CONH₂
 - (DMG) from biacetyl + hydroxylamine
 - CH₃C(=O)-C(=O)CH₃ + 2 H₂NOH → DMG + 2 H₂O

Precipitation Equilibria: The Solubility Product

- Solubility of Slightly Soluble Salts:
- $\text{AgCl}_{(\text{s})} \rightleftharpoons (\text{AgCl})_{(\text{aq})} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- Solubility Product $K_{\text{SP}} = \text{ion product}$
- $K_{\text{SP}} = [\text{Ag}^+][\text{Cl}^-]$
- $\text{Ag}_2\text{CrO}_4_{(\text{s})} \rightleftharpoons 2 \text{Ag}^+ + \text{CrO}_4^{2-}$
- $K_{\text{SP}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$

The molar solubility depends on the stoichiometry of the salt.
A 1:1 salt is less soluble than a nonsymmetric salt with the same K_{sp} .

Table 10.3
Solubility Product Constants of Selected Slightly Soluble Salts

Salt	K_{sp}	Solubility, s (mol/L)
PbSO ₄	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
Al(OH) ₃	2×10^{-32}	5×10^{-9}
Fe(OH) ₃	4×10^{-38}	2×10^{-10}
Ag ₂ S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

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Precipitation Equilibria: The Common Ion Effect

- Common Ion Effect
- Will decrease the solubility of a slightly soluble salt.

The common ion effect is used to decrease the solubility.

Sulfate concentration is the amount in equilibrium and is equal to the BaSO_4 solubility.

In absence of excess barium ion, solubility is 10^{-5} M .

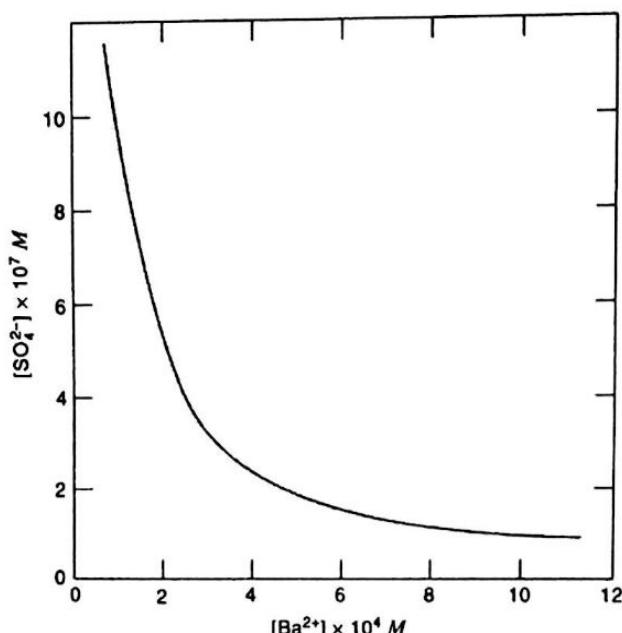


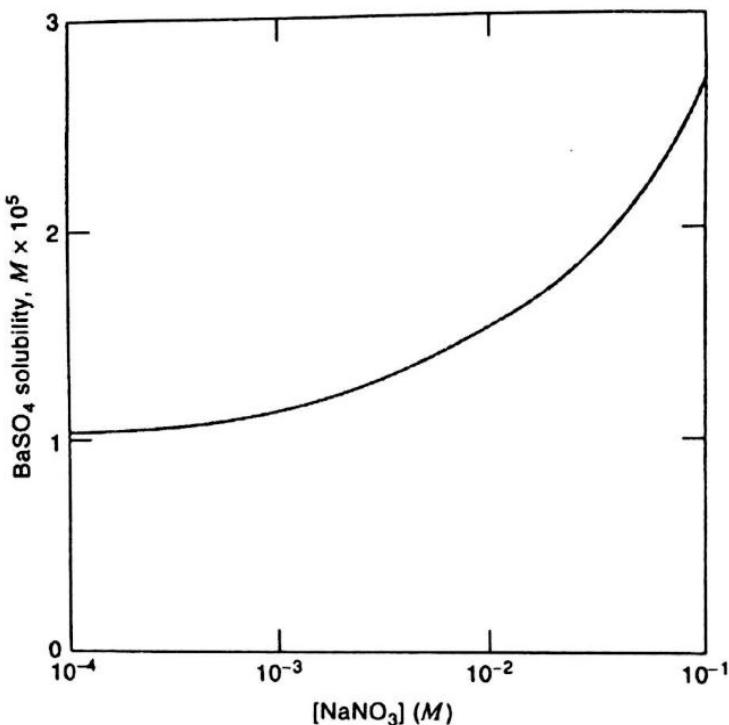
Fig. 10.3. Predicted effect of excess barium ion on solubility of BaSO_4 .

Diverse Ion Effect on Solubility:

- Presence of diverse ions will increase the solubility of precipitates due to shielding of dissociated ion species.
- K_{SP}° and Activity Coefficients
- $\text{AgCl}_{(\text{s})} \rightleftharpoons (\text{AgCl})_{(\text{aq})} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- Thermodynamic solubility product K_{SP}°
- $K_{\text{SP}}^{\circ} = a_{\text{Ag}^+} \cdot a_{\text{Cl}^-} = [\text{Ag}^+]f_{\text{Ag}^+} \cdot [\text{Cl}^-]f_{\text{Cl}^-}$
- $K_{\text{SP}}^{\circ} = K_{\text{SP}} f_{\text{Ag}^+} \cdot f_{\text{Cl}^-}$
- $K_{\text{SP}} = K_{\text{SP}}^{\circ} / (f_{\text{Ag}^+} \cdot f_{\text{Cl}^-})$

$$K_{sp} = K_{sp}^0 / f_{Ag+} f_{SO4^2-}$$

Solubility increases with increasing ionic strength as activity coefficients decrease.



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Predicted effect of increased ionic strength on solubility of BaSO₄. Solubility at zero ionic strength is 1.0 × 10⁻⁵ M.

Gravimetric calculation using spreadsheet.

Cell B3 calculates %Fe from g. Fe₂O₃ (Cell D2) and g. sample (Cell B2).

	A	B	C	D	E	F	G	H
1	Calculation of % Fe.							
2	g. sample:	2.287	g. Fe ₂ O ₃ :	0.8792				
3	% Fe:	26.88797						
4								
5	%Fe = {[g Fe ₂ O ₃ × 2Fe/Fe ₂ O ₃ (g Fe/g Fe ₂ O ₃)]/g sample} × 100%							
6	=							
7	B3 =							
8								
9	The answer is 26.89% Fe.							

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Using Excel Solver to calculate solubility.

Enter the formula ($=s^2/K_{sp}$) in Cell E4 (don't enter =1; that goes in Solver).

The value of s (Cell C4) is changed iteratively until the formula equals 1.

	A	B	C	D	E	F
1						
2	K _{sp} :	1.00E-10		formula = $s^2/K_{sp} = 1$		
3						
4		s =	1E-05	formula:	1.000001	
5						
6				formula Cell E4: = C4^2/B2		
7				Solver:		
8				E4 = Target Cell		
9				Set value to 1		
10				Changing Cell = C4		
11	The solubility is 1.0×10^{-5} M.					

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Calculating Results from Gravimetric Data

- The calcium in a 200.0 mL sample of a natural water was determined by precipitating the cation as CaC₂O₄. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (fwt 56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (fwt 40.078 g/mol) in the water in units of grams per 100 mL.

Calculating Results from Gravimetric Data

- An iron ore was analyzed by dissolving a 1.1324 g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ by addition of NH₃. After filtration and washing, the residue was ignited at high temperature to give 0.5394 g pure Fe₂O₃ (fwt 159.69 g/mol). Calculate (a) the % Fe (fwt 55.847 g/mol) and (b) % Fe₃O₄ (fwt 231.54 g/mol) in the sample.

Calculating Results from Gravimetric Data

- A 0.2356 g sample containing only NaCl (fwt 58.44 g/mol) and BaCl₂ (fwt 208.23 g/mol) yielded 0.4637 g of dried AgCl (fwt 143.32 g/mol). Calculate the percent of each halogen compound in the sample.