

## Gravimetric Methods of Analysis

Methods based on measurement of weight of an analyte or a compound containing the analyte.

**Precipitation methods.** Based on isolation of an insoluble precipitate of known composition.

**Volatilization methods.** Analyte is volatilized, weighed and the loss is determined.

## Gravimetric Methods of Analysis

Calculations associated with the methods are based on stoichiometry.

“The weight relationship between you analyte and the material actually weighed.”

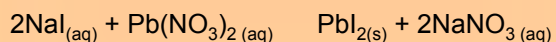
**Empirical formula** - simplest whole number ratio of atoms in a compound

**Chemical formula** - actual number of atoms in a compound

**Molecular formula** - gives connectivity.

## Stoichiometry of a reaction

A balanced chemical formula gives the ratios, in moles, of materials produced or consumed in a reaction.



If the weight of any one species used or produced is known, the others are readily calculated.

## Example

How much  $\text{Pb}(\text{NO}_3)_2$  is need to convert 1.0 grams of  $\text{NaI}$  to  $\text{PbI}_2$ ?

Formula weighs

$\text{Pb}(\text{NO}_3)_2$	331.2 g/mol
$\text{NaI}$	149.9 g/mol

## Example

quantity measured	conversion to moles	stoichiometric factor	convert to grams
1.0 g $\text{NaI}$	$\times \frac{1 \text{ mol NaI}}{149.9 \text{ g NaI}}$	$\times \frac{1 \text{ mol Pb}(\text{NO}_3)_2}{2 \text{ mol NaI}}$	$\times \frac{331.2 \text{ g Pb}(\text{NO}_3)_2}{\text{mol Pb}(\text{NO}_3)_2}$

= 1.1 grams  $\text{Pb}(\text{NO}_3)_2$

Final  
result

## Gravimetric calculations

Gravimetric calculations are simply an extension of stoichiometric calculations.

Our stoichiometric factor is most often based on the amount (in moles) of our analyte in the material actually weighed.

Gravimetric factor = GF

$$\text{GF} = \frac{\text{moles analyte in weighed form} \times \text{FW analyte}}{\text{formula weight of weighed form}}$$

## Gravimetric calculations

The best way to see what is going on is to give an overview of the approach.

We can then introduce the relative simple calculations with each step.

The first premise is that have a sample that contains an analyte of interest.

Your goal is to determine the % analyte in the sample

## Gravimetric calculations

Start by weighing out your sample.

Next, convert the sample to a measurable form like a 'pure' precipitate

If the measurable form is the analyte then  
 $\% \text{ analyte} = (\text{wt analyte} / \text{wt sample}) \times 100$

More often, the measured form contains the analyte along with other materials. The weight of analyte must first be determined using the gravimetric factor.

## Gravimetric calculations

**Example** Determination of phosphate in an organic sample.

Step one.

Weigh out a known amount of your sample. In this case, 0.352 grams.

Step two.

Convert to a pure, measurable form.

We'll dissolve the sample and then convert it to  $\text{Mg}_2\text{P}_2\text{O}_7$ .

## Gravimetric calculations

**Example**

Step two - conversion.



## Gravimetric calculations

**Example**

Step three.

Obtain accurate weight.

In this case, you would place the sample in a desiccator and allow it to cool.

Weight the sample, return it to the desiccator.

Repeat until you obtain a constant weight.

## Gravimetric calculations

Now, you're ready to do the calculations.

Formula weights

$$\text{P} = 30.97 \text{ g/mol}$$

$$\text{Mg}_2\text{P}_2\text{O}_7 = 222.6 \text{ g/mol}$$

Gravimetric factor

$$\begin{aligned} \text{GF} &= \frac{\text{mol P in Mg}_2\text{P}_2\text{O}_7 \times \text{FW P}}{\text{FW Mg}_2\text{P}_2\text{O}_7} \\ &= 0.2783 \end{aligned}$$

So P represents to 27.83 of the total weight.

## Gravimetric calculations

% Phosphate

$$\% P = \frac{\text{g Mg}_2\text{P}_2\text{O}_7 \times .2783 \text{ gP/gMg}_2\text{P}_2\text{O}_7}{\text{grams sample}} \times 100$$
$$= 17.1 \% P$$

## Properties of precipitates

To obtain good results, you must be able to produce a 'pure' precipitate that can be recovered with high efficiency.

### We want the precipitate to:

- Have low solubility
- Be easy to recover by filtration
- Be unreactive to air, water, . . .
- Be something where our analyte is only a small portion of the ppt.

## Particle size and filterability

### Colloidal Suspensions

- Size range:  $10^{-6}$  -  $10^{-4}$  mm
- No tendency to settle
- Difficult or impossible to filter

### Crystalline suspensions

- Size Range:  $10^{-1}$  - 10 mm
- Will settle spontaneously
- Readily filtered
- Typically of higher purity than colloids

## Particle size and filterability

We have some control on particle size based on how we add our reagents.

### Relative supersaturation (RSS)

$$\text{RSS} = \frac{Q - S}{Q}$$

Where

- Q = concentration of solute at any time
- S = equilibrium solubility of solute

RSS can be used estimate/control the type of precipitate that is formed.

## Particle size and filterability

$$\text{RSS} = \frac{Q - S}{Q}$$

- If RSS is large, we tend to form colloids.
- If RSS is small, we tend to form crystalline ppts.

### We can keep RSS small by:

- Using dilute solutions and reagents.
- Slowly adding our ppt reagent.
- Stirring the solution.
- Warming the solution.

## Mechanisms of precipitation

### Two competing processes

#### Nucleation

When a small number of ions, atoms, molecules initially unite.

- Spontaneous
- Induced

#### Particle growth

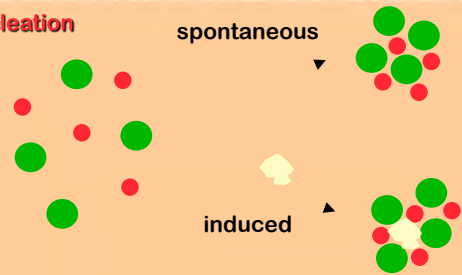
The three dimensional growth of a particle nucleus into a larger crystal.



## Mechanisms of precipitation

### Nucleation

spontaneous



induced

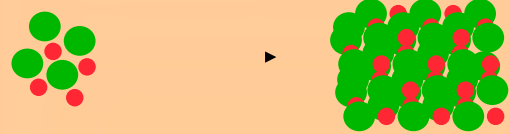


Spontaneous nucleation will occur on its own.

Induced nucleation requires a 'seed' particle to get things started (dust, another crystal, glass fragment, ...)

## Mechanisms of precipitation

### Particle growth

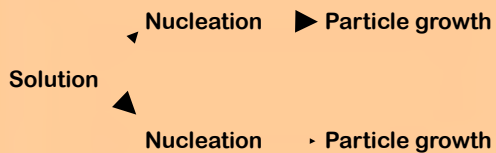


Once a nucleation site has formed, other ions are attracted to the site. This will result in the formation of large, filterable particles.

If done properly, it also reduces contaminants since they don't 'fit in' to the crystal structure.

## Mechanisms of precipitation

Nucleation and particle growth are competing processes although at least some nucleation must initially occur.



We want particle growth to be the predominate factor in precipitate formation.

## Mechanisms of precipitation

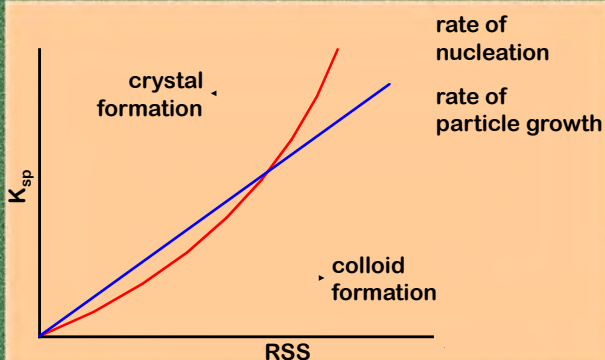
Rate of nucleation is  $R_{SS}$

Rate of particle formation is  $R_{SS}$

If  $R_{SS}$  is large, nucleation is favored and colloidal suspensions tend to be formed.

If  $R_{SS}$  is small, particle growth will predominate resulting in crystalline precipitates.

## Mechanisms of precipitation



## Mechanisms of precipitation

The goal is to form crystalline precipitates so  $R_{SS}$  must be minimized.

This can be done by:

### Increasing S

Elevate temperature, pH control

### Decrease Q

Use dilute solutions  
Slowly add reagents  
Stirring the solution

## Precipitates

OK, now we have some of the basics on precipitate formation.

It time to get up close and personal with the process to see what's going on and what we can do about it.

Colloidal and crystalline precipitates each have their own problems.

Colloids are worse so lets start there.

## Colloidal precipitates

As an example, we'll use the following precipitate formation through out:

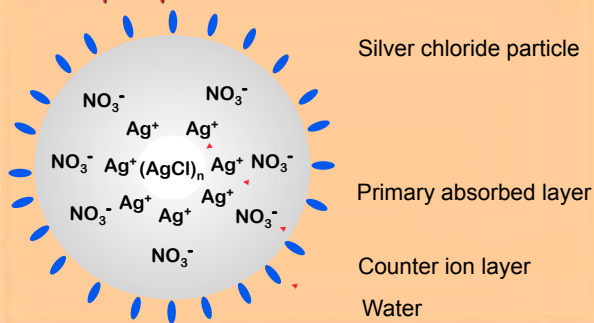


NaCl will be our precipitating reagent.

AgCl tends to form colloidal (amorphous) precipitates.

## Colloidal precipitates

### Start of precipitation

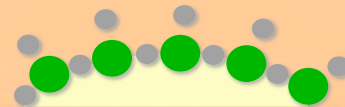


## Colloidal precipitates

### Start of precipitation

Initially, there is very little free chloride in the solution due to the excess of Ag<sup>+</sup>.

The outer layer of the precipitate contains both Ag<sup>+</sup> and Cl<sup>-</sup> which tends to attract additional Ag<sup>+</sup> to the surface- **primary absorbed layer**.



## Colloidal precipitates

### Start of precipitation

This primary layer is simply an extension of the precipitate but we've run out of Cl<sup>-</sup>

The counter ion in excess (nitrate) is attracted to this layer by electrostatic forces - maintains electrical neutrality.

Since the overall structure tends to appear negative to the solution, it attracts water molecules that move with the particle.

## Colloidal precipitates



High [Ag<sup>+</sup>]



Low [Ag<sup>+</sup>]

At high silver concentrations, we have a higher charge on the precipitate. This results in a larger particle.

The problem is even worse when the counter ion is large.

## Colloidal precipitates

### Net result

At high silver concentrations and with large counter ions we tend to form stable colloids.

The charged structures have difficulty approaching each other since they are similarly charged.

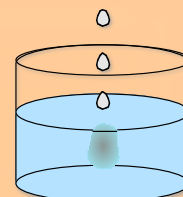
**Note:** The same type of problem will occur when chloride is in excess  
- towards end of precipitation.

## Colloidal precipitates

It would seem that the solution is to keep the concentration of  $\text{Ag}^+$  low at all times.

This is impossible to do!

As  $\text{Ag}^+$  is added, we create locally high concentrations even when using dilute solutions.



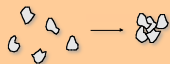
Since we can't eliminate the problem, we need ways to minimize its effect.

## Obtaining a good precipitate

Several steps can be taken to help precipitate a colloid and reduce impurities.

Any steps taken must address two competing processes.

**Coagulation** - The process where colloidal particles 'lump' together into larger particles.



**Peptization** - when a coagulated colloid reverts to its dispersed state.

## Coagulation of Colloids

Two common approaches for causing a colloid to coagulate are heating and adding an electrolyte to the solution.

### Heating the colloid while stirring

This significantly decreases the number of adsorbed ions per particle.

This reduces the size of the counter ion layer, making it easier for the particles to approach each other.

## Coagulation of Colloids

### Increasing the electrolyte concentration of the solution.

An unrelated, non-interfering ionic compound can be added to the solution.

This reduces the volume of solution that contains sufficient ions of opposite charge to neutralize the particle.

The result is that a smaller structure is formed.

## Addressing peptization

If we've gone to the trouble of making a coagulated colloid, we don't want to lose it in our attempt to clean it up.

Washing a colloid to remove excess counter ion or trapped impurities can result in peptization.

There are several common approaches that can be used to address this problem.



## Treatment of colloidal precipitates

### Use a volatile electrolyte

A relative volatile salt can be used to wash the precipitate.

This displaces the less volatile, excess counter ion.

Heating the precipitate (during drying) will remove the volatile electrolyte.

**Example.** For AgCl, wash with HCl. Drying ppt at 110°C will remove HCl.

## Treatment of colloidal precipitates

### Digestion and aging

**Digestion.** Heating the solution for about an hour after precipitate formation. This helps to remove weakly bound water.

**Aging.** Storing the solution, unheated, overnight. This allows trapped contaminants time to 'work their way out.'

Both can result in a denser precipitate that is easier to filter.

## Crystalline precipitates

This type of precipitate is much easier to work with.

They are easier to filter and purified.

You have greater control over the precipitation process.

In general, the best approach is to slowly form your precipitate using warm, dilute solutions. Allow it to then digest without stirring.

## Coprecipitation

When an otherwise soluble compound is precipitated along with your analyte.

This does not include materials that would normally be insoluble.

### Sources of coprecipitation

- Surface absorption
- Occlusion
- Mixed crystal formation
- Mechanical entrapment

## Surface adsorption

The surface of our precipitate will contain some primary absorbed ions. As a result, counter ions will also be present.

**Example.** In our AgCl example, the precipitate will commonly contain some nitrate.

Occurs with colloidal and crystalline ppts.

Worse for colloids because the surface area is significantly larger.

## Surface adsorption

### AgCl example

If nitrate is co-precipitated, our results will be too high - nitrate weights more than chloride.

Further, the results will be variable since the surface area may differ from sample to sample.

A lower weight counter ion will result in our results being too low.

## Surface adsorption

### Dealing with surface absorption

#### Washing

This may help but not much. The attraction of the counter ion is usually too strong so you only get a limited exchange.

#### Washing with a volatile electrolyte

This is a better approach since the excess can be removed during drying. For AgCl, washing with HCl is a reasonable approach.

## Surface adsorption

### Dealing with surface absorption

#### Reprecipitation

The filtered precipitate is dissolved and then precipitated a second time.

Only a small portion of the contaminant makes it into the second solution.

The second precipitate will be purer.

This approach is one of last resort since it significantly adds to the analysis time.

## Mixed crystal formation

If similar ions are present, they can replace our analyte ion in the crystal lattice during precipitation.

Similar ions have the same charge and have sizes within 5% of our ion.

**Example.** Determination of  $\text{SO}_4^{2-}$  as  $\text{BaSO}_4$

The presence of Pb or Sr will cause a mixed crystal containing either  $\text{PbSO}_4$  or  $\text{SrSO}_4$

## Mixed crystal formation

This is a problem with both colloidal and crystalline precipitates.

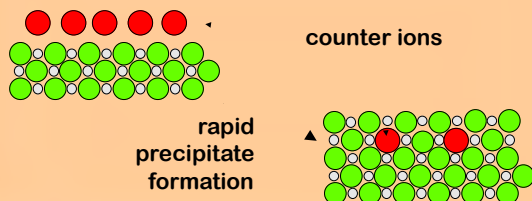
There is no easy solution to minimize the problem.

When encountered, your only choices are to remove the interferences prior to precipitation or to select a different reagent.

## Occlusion and entrapment

### Occlusion

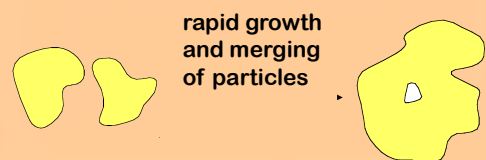
If crystal growth is too rapid, some counter ions don't have time to escape from the surface.



## Occlusion and entrapment

### Mechanical entrapment

When rapid growth traps a pocket of solution. While the solvent can be removed, the trapped ions will remain after drying.





### Occlusion and entrapment

The best way to deal with these problems is to slow things down.

Using dilute, warm solutions during precipitation gives counter ions time to leave and helps break up pockets.

Digestion and aging the precipitate provides additional times for this to occur as well.

### Precipitation from homogeneous solution

When a precipitation reagent is added as a solution to our analyte there will always be locally high concentrations.

This is responsible for many of our problems regardless of how slowly we add the reagent or how fast we stir.

Precipitation from homogeneous solution is an approach that can avoid this problem.

### Precipitation from homogeneous solution

#### Basis

Our reagent is added in an unreactive form to our sample solution.

This permits a complete mixing of all materials.

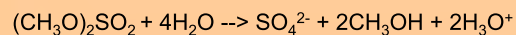
Some property of the solution is changed to slowly convert the reagent to a reactive form.

The solution slowly and uniformly changes - no locally high concentrations.

### Precipitation from homogeneous solution

#### Example

Dimethyl sulfate -  $(\text{CH}_3\text{O})_2\text{SO}_2$

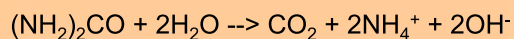


Useful for the determination of Ba, Ca, Sr and Pb as sulfates.

### Precipitation from homogeneous solution

#### Example

Urea -  $(\text{NH}_2)_2\text{CO}$



Process is controlled by heating the solution just below boiling

Used for the precipitation of Al, Ga, Th, Bi, Fe and Sn as hydroxides.

### Precipitate drying

After filtration, the precipitate must be dried to constant weight.

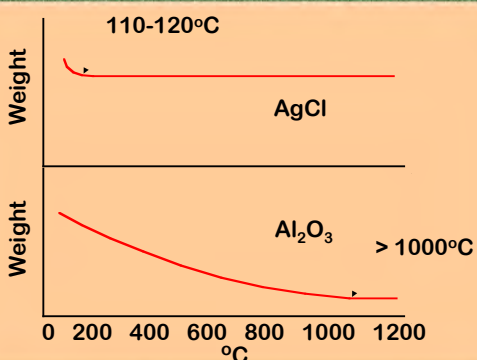
Removes excess solvent

Drives off any volatile species.

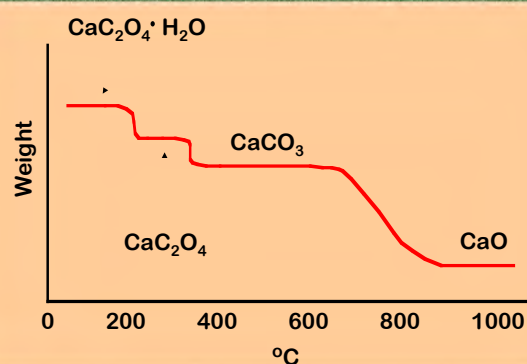
In some cases, the precipitate is heated to a point where it decomposes to a stable form for weighing.

Thermobalances can be used to determine optimum drying time and temperatures.

## Precipitate drying



## Precipitate drying



## Summary of method

### A relative slow method of analysis

However, most time is spent waiting with little effort for user.

### Minimal requirements

Major equipment is a good balance and an oven.

### No calibration is required

Results are based on formula weight

## Summary of method

### Accuracy

1-2 parts per thousand

### Sensitivity

Analyte concentration should be over 1%.  
Below that, you may encounter problems to solubility.

### Selectivity

Not very specific but can be made reasonably selective.

## Example applications

### Inorganic precipitating agents

Think back to when you were forced to do a qual scheme in freshman chemistry.

Many cations and anions can be precipitated as groups.

With a proper design, you can use this to precipitate a single species.

## Example applications

### A few inorganic precipitating agents

Agent	Analyte (form)
HCl	Ag (AgCl), Hg (Hg <sub>2</sub> Cl <sub>2</sub> )
(NH <sub>4</sub> ) <sub>2</sub> S	Hg (HgS), Co (Co <sub>3</sub> O <sub>4</sub> )
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Ca (CaO), Sr (SrO), Th (ThO <sub>2</sub> )
HNO <sub>3</sub>	Sn (SnO <sub>2</sub> )
BaCl	SO <sub>4</sub> <sup>2-</sup> (BaSO <sub>4</sub> )

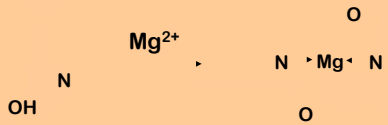
Your book contains a more complete table.

### Example applications

#### Organic reagents

Tend to be more selective

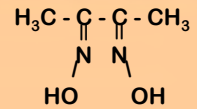
8-hydroxyquinoline - reacts with over 20 different metallic cations



pH can be used to control selectivity.

### Example applications

#### Dimethylglyoxime - DMG



Will only form complexes with

Pd - yellow, weak complex

Ni - bright red, very stable complex

Since Pd is not very common, DMG is considered specific for Ni.

### Example applications

#### Volatilization procedures

Methods where a volatile component is driven off, trapped and the weight increase of the trap measured.

#### Example

Water - collect on a desiccant.

Used for determination of % moisture in various materials.

### Example applications

#### Indirect volatilization procedures

A sample is still heated and the volatile component collected. The weight loss of the analyte is also measured.

A second method of analysis is used to determine the amount of the material.

This is not as good an approach - it assumes that only our compound of interest is volatilized.

### Example applications

#### Indirect volatilization procedures

Example

Determination of carbonates.

A sample is heated to constant weight, driving off CO<sub>2</sub>.

CO<sub>2</sub> is collected in a known NaOH solution, forming Na<sub>2</sub>CO<sub>3</sub>. You can then do a titration.