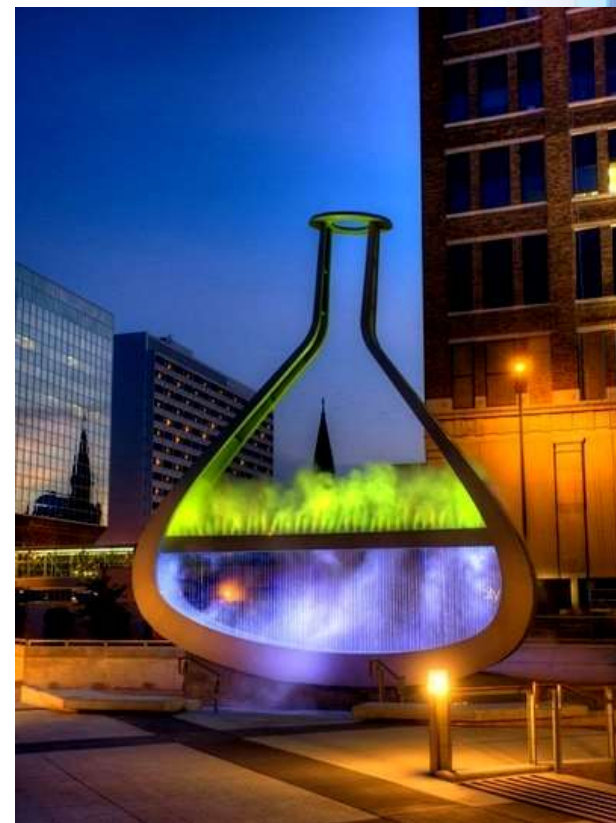


Analytical chemistry

Gravimetric analysis



“Some loads are light, some heavy. Some people prefer the light to the heavy . . .”

Mao Tse-tung



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Gravimetric methods are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

Gravimetric methods of analysis are based on mass measurements with an analytical balance, an instrument that yields highly accurate and precise data. In fact, if you perform a gravimetric determination in your laboratory, you may make some of the most accurate and precise measurements of your life.

In this process the analyte is selectively converted to an insoluble form. The separated precipitate is dried or ignited, possibly to another form, and is accurately weighed. From the weight of the precipitate and a knowledge of its chemical composition, we can calculate the weight of analyte in the desired form.

Theodore W. Richards at Harvard University developed highly precise and accurate gravimetric analysis of silver and chlorine. He used these methods to determine the atomic weights of 25 elements by preparing pure samples of the chlorides of the elements, decomposing known weights of the compounds, and determining the chloride content by gravimetric methods.



T. W. Richards used GA to determine atomic weights. He received the Nobel Prize in 1914 for his work.



Types of Gravimetric Methods

Based on the preparation of the sample before weighing the analyte compound, there are four fundamental types of gravimetric analysis:

1. Physical gravimetry, is the most common type used in environmental control engineering. It involves the physical separation and classification of matter based on volatility and particle size (e.g., total suspended solids).

2. Thermogravimetry, for the analysis of volatile solids. Changes in the sample mass when heated are recorded. When thermal or chemical energy is used to remove a volatile species, we call the method **volatilization gravimetry**. In determining the moisture content of food, thermal energy vaporizes the H_2O . The amount of carbon in an organic compound may be determined by using the chemical energy of combustion to convert C to CO_2 .

3. Electrogravimetry or *electro-deposition* which usually involves the electrochemical reduction and simultaneous deposition of metal ions at a cathode. **Electrogravimetry** - a gravimetric method in which the signal is the mass of an electrodeposit on the cathode or anode in an electrochemical cell. The oxidation of Pb^{2+} , and its deposition as PbO_2 on a Pt anode is one example of electrogravimetry. The electrodeposition of Cu on a Pt cathode, for example, provides a direct analysis for Cu^{2+} .

4. Chemical precipitation, the most common in a “classical” sense. It relies on a chemical reaction to transform the solved analyte in a very low soluble precipitate. Its most important application in the environmental field is with the analysis of sulfate or sulfite. **Precipitation gravimetry** - a gravimetric method in which the signal is the mass of a precipitate.



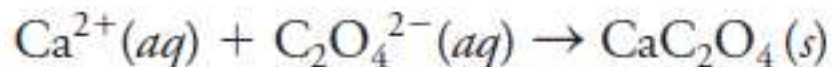
Type of gravimetry	Analyte	Procedure
1	2	3
<i>Physical</i>	Total Solids	Evaporation
	Suspended Solids	Filtration
	Dissolved Solids	Filtration + Evaporation
1	2	3
<i>Physical</i>	Oil & Grease	Extraction with $C_2Cl_3F_3$ + distillation of solvent
	Surfactants	Extraction into ethylacetate + evaporation
	Volatile Solids	Evaporation + 550°C for 15 min
<i>Thermal</i>	Volatile Solids	Evaporation + 550°C for 15 min
	Volatile Suspended Solids	Filtration + 550°C for 15 min
<i>Precipitative</i>	Mg^{2+}	With Diammonium hydrogen phosphate and final pyrolysis
	Na^+	With zinc uranyl acetate
	Silica	Precipitation/ ignition/ volatilization (with HF)
	SO_4^{2-}	With Ba^{2+}

Gravimetry - method in which the signal is a mass or change in mass.

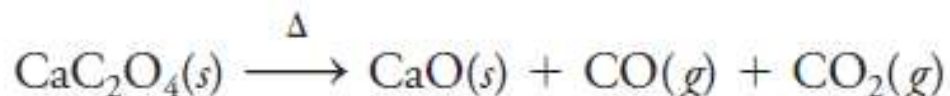


Precipitation method for determining calcium in water

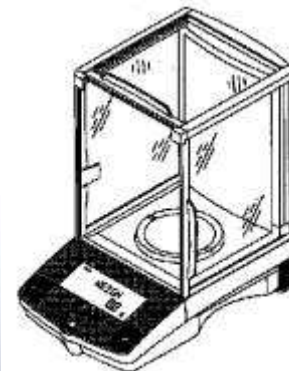
In this technique, an excess of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is added to an aqueous solution of the sample. Ammonia is then added, which neutralizes the acid and causes essentially all of the calcium in the sample to precipitate as calcium oxalate. The reactions are



The CaC_2O_4 precipitate is filtered using a weighed filtering crucible, then dried and ignited. This process converts the precipitate entirely to calcium oxide. The reaction is



After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible.



Precipitation Gravimetry

Precipitation gravimetry is based on the formation of an insoluble compound following the addition of a precipitating reagent, or **precipitant**, to a solution of the analyte. **Precipitant** - a reagent that causes the precipitation of a soluble species.

Ideally, a gravimetric precipitating agent should react *specifically or at least selectively* with the analyte. Specific reagents, which are rare, react only with a single chemical species. Selective reagents, which are more common, react with a limited number of species. In addition to specificity and selectivity, the ideal precipitating reagent would react with the analyte to give a product that is

1. easily filtered and washed free of contaminants;
2. of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing;
3. unreactive with constituents of the atmosphere;
4. of known chemical composition after it is dried or, if necessary, ignited

An example of a selective reagent is AgNO_3 . The only common ions that it precipitates from acidic solution are Cl^- , Br^- , I^- , and SCN^- . Dimethylglyoxime is a specific reagent that precipitates only Ni^{2+} from alkaline solutions.

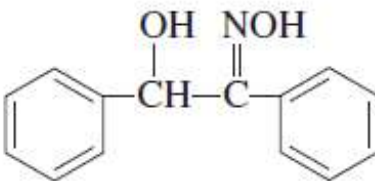
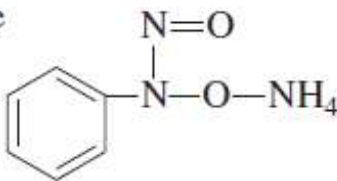
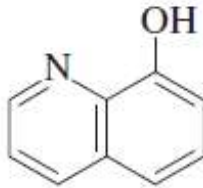


Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated*
$\text{NH}_3(aq)$	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 (<u>As_2O_3</u> or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (<u>Sb_2O_3</u>), or Sb_2O_5 , Bi (Bi_2S_3)
$(\text{NH}_4)_2\text{S}$	Hg (<u>HgS</u>), Co (Co_3O_4)
$(\text{NH}_4)_2\text{HPO}_4$	Mg ($\text{Mg}_2\text{P}_2\text{O}_7$), Al (AlPO_4), Mn ($\text{Mn}_2\text{P}_2\text{O}_7$), Zn ($\text{Zn}_2\text{P}_2\text{O}_7$), Zr ($\text{Zr}_2\text{P}_2\text{O}_7$), Cd ($\text{Cd}_2\text{P}_2\text{O}_7$), 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 (<u>Rb_2PtCl_6</u>), Cs (<u>Cs_2PtCl_6</u>)
$\text{H}_2\text{C}_2\text{O}_4$	Ca (CaO), Sr (SrO), Th (ThO_2)
$(\text{NH}_4)_2\text{MoO}_4$	Cd (CdMoO_4)†, Pb (<u>PbMoO_4</u>)
HCl	Ag (AgCl), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
AgNO_3	Cl (AgCl), Br (<u>AgBr</u>), I (<u>AgI</u>)
$(\text{NH}_4)_2\text{CO}_3$	Bi (Bi_2O_3)
NH_4SCN	Cu [$\text{Cu}_2(\text{SCN})_2$]
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 [$\text{Hg}_5(\text{IO}_6)_2$]
NaCl , $\text{Pb}(\text{NO}_3)_2$	F (PbClF)
BaCl_2	SO_4^{2-} (BaSO_4)
MgCl_2 , NH_4Cl	PO_4^{3-} ($\text{Mg}_2\text{P}_2\text{O}_7$)



Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	$\begin{array}{c} \text{CH}_3 - \text{C} = \text{NOH} \\ \\ \text{CH}_3 - \text{C} = \text{NOH} \end{array}$	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 -Benzoinoxime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ $(\text{M}^{2+} + \text{H}_2\text{R} \rightarrow \underline{\text{MR}} + 2\text{H}^+; \text{M}^{2+} = \text{Cu}^{2+}, \text{MoO}_2^+, \text{WO}_2^{2+})$ Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) $(\text{M}^{n+} + n\text{NH}_4\text{R} \rightarrow \underline{\text{MR}}_n + n\text{NH}_4^+)$ Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) $(\text{M}^{n+} + n\text{HR} \rightarrow \underline{\text{MR}}_n + n\text{H}^+)$
Sodium diethyldithiocarbamate	$(\text{C}_2\text{H}_5)_2\text{N} - \text{C} \begin{array}{c} \text{S} \\ \\ \text{S}^- \text{Na}^+ \end{array}$	Many metals from acid solution $(\text{M}^{n+} + n\text{NaR} \rightarrow \underline{\text{MR}}_n + n\text{Na}^+)$



Precipitation Gravimetry

The steps required in a gravimetric analysis, after the sample has been dissolved:

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

1. Prepare the solution

- preliminary separation (eliminate interfering materials)
- adjust the solution conditions to maintain low solubility of the precipitate
- obtain it in a form suitable for filtration.

Factors that must be considered include the volume of the solution during precipitation, the concentration range of the test substance, the presence and concentrations of other constituents, the temperature, and the pH.

II 2. Precipitation

- easily filtered and washed free of contaminants;
- of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing;
- unreactive with constituents of the atmosphere;
- of known chemical composition after it is dried or, if necessary, ignited
- should react *specifically or at least selectively* with the analyte.



Mechanism of Precipitation

1. induction period (supersaturation)

A **supersaturated solution** is an unstable solution that contains a higher solute concentration than a saturated solution.

2. nucleation

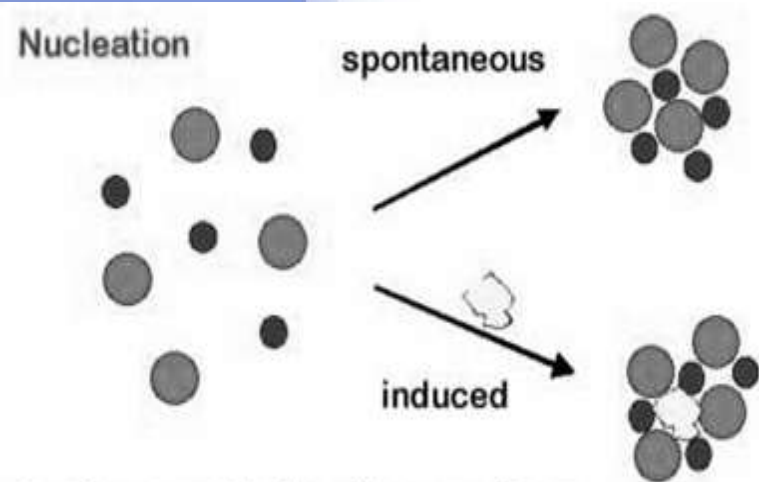
Nucleation is a process in which a minimum number of atoms, ions, or molecules join together to give a stable solid.

The higher the degree of supersaturation, the greater the rate of nucleation. The formation of a greater number of nuclei per unit time will ultimately produce more total crystals of smaller size. The total crystal surface area will be larger, and there will be more danger that impurities will be adsorbed.

Precipitates form by nucleation and by particle growth. If nucleation predominates, a large number of very fine particles is produced. If particle growth predominates, a smaller number of larger particles is obtained.

Although nucleation should theoretically occur spontaneously, it is usually induced, for example, on dust particles, scratches on the vessel surface.

3. The initial nucleus will grow by depositing other precipitate particles to form a crystal of a certain geometric shape. Again, the greater the supersaturation, the more rapid the crystal growth rate. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.



Spontaneous nucleation will occur on its own.

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



Von Weimarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process:

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

where Q is the concentration of the mixed reagents before precipitation occurs, S is the solubility of the precipitate at equilibrium, and $Q - S$ is the degree of supersaturation.

This ratio, $(Q - S)/S$, relative supersaturation, is also called the **von Weimarn ratio**.

High relative supersaturation → many small crystals
(high surface area)

Low relative supersaturation → fewer, larger crystals
(low surface area)

When a solution is supersaturated, it is in a state of metastable equilibrium, and this favors rapid nucleation to form a large number of small particles. we want to keep Q low and S high during precipitation. Several steps are commonly taken to maintain favorable conditions for precipitation:



How to minimize supersaturation and obtain larger crystals?

1. Precipitate from *dilute solution*. *This keeps Q low.*
2. Add dilute precipitating reagents *slowly, with effective stirring*.
This also keeps Q low. *Stirring prevents local excesses of the reagent.*
3. Precipitate from *hot solution*. *This increases S .*

The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.

4. Precipitate at as *low a pH as is possible to maintain quantitative precipitation*.

As we have seen, many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate (which comes from a weak acid) combines with protons in the solution.

When the precipitation is performed, a slight excess of precipitating reagent is added to decrease the solubility by mass action (common ion effect) and to assure complete precipitation.

If the approximate amount of analyte is known, a 10% excess of reagent is generally added.

Completeness of precipitation is checked by waiting until has settled and then adding a few drops of precipitating reagent to the precipitation! clear solution above it. If no new precipitate forms, precipitation is complete.

Very insoluble precipitates are not the best candidates for gravimetric analysis! They supersaturate too easily.

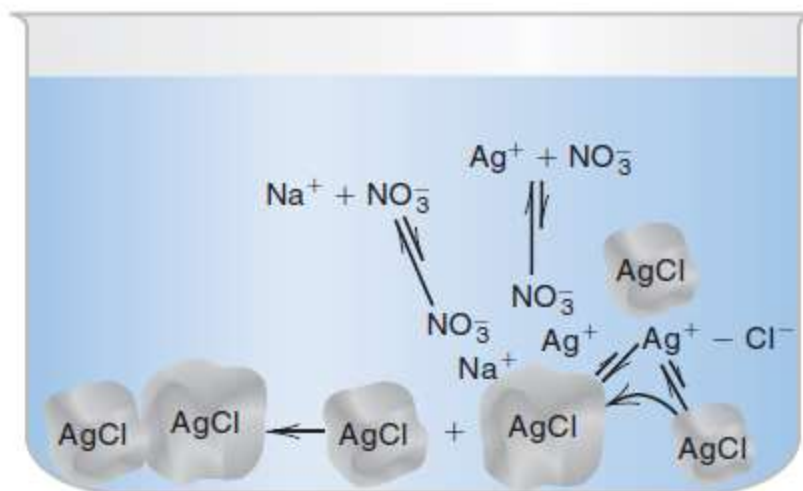


1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration

5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

III 3. Digest the precipitate to make larger and more pure crystals

When a precipitate is allowed to stand in the presence of the **mother liquor (the solution from which it was precipitated)**, the large crystals grow at the expense of the small ones. This process is called **digestion**, or **Ostwald ripening**.



Ostwald ripening improves the purity and crystallinity of the precipitate.

In addition, individual particles **agglomerate** to effectively share a common counterion layer, and the agglomerated particles finally *cement together by forming connecting bridges*. This noticeably decreases surface area.



Unfortunately, many precipitates cannot be formed as crystals under practical laboratory conditions. A colloidal solid is generally formed when a precipitate has such a low solubility that S *always remains negligible relative to Q* . *The relative supersaturation thus remains enormous throughout precipitate formation*, and a colloidal suspension results. For example, under conditions feasible for an analysis, the hydrous oxides of iron(III), aluminum, and chromium(III) and the sulfides of most heavy-metal ions form only as colloids because of their very low solubilities.

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

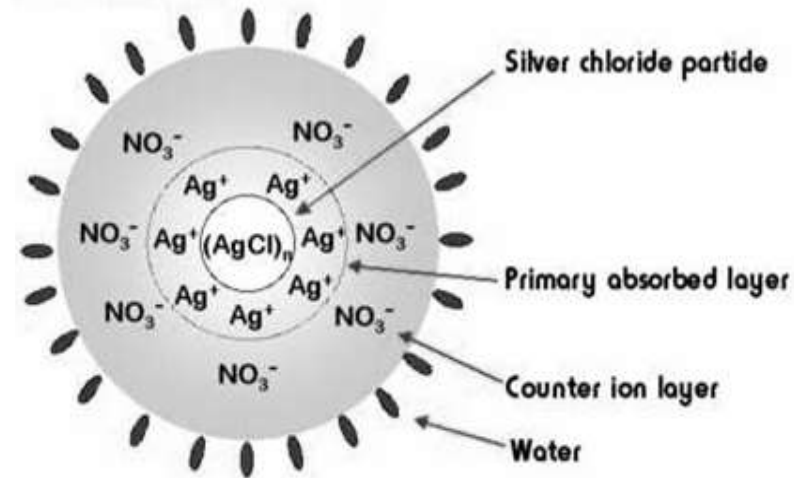
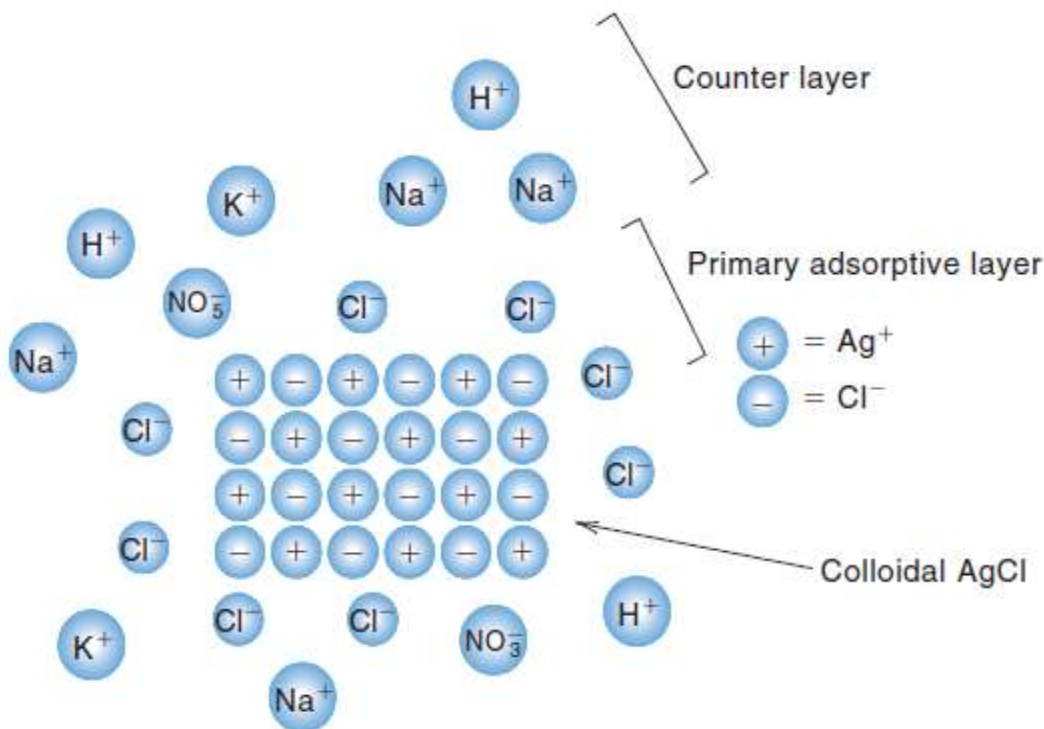
Individual colloidal particles are so small that they are not retained by ordinary filters. Moreover, Brownian motion prevents their settling out of solution under the influence of gravity. Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.



Colloidal particles

Colloidal particles are very small (1 to 100 nm) and have a very large surface to-mass ratio, which promotes surface adsorption. They are formed by virtue of the precipitation mechanism.

In addition to the **primary adsorbed silver ion**, there are some nitrate ions aggregating further from the AgCl **nucleus**. These are counter ions and tend to aggregate around the $[\text{AgCl}:\text{Ag}]^+$ centre because these centres have a net positive charge (excess Ag^+) and additional negative charge is required to maintain electrical neutrality.

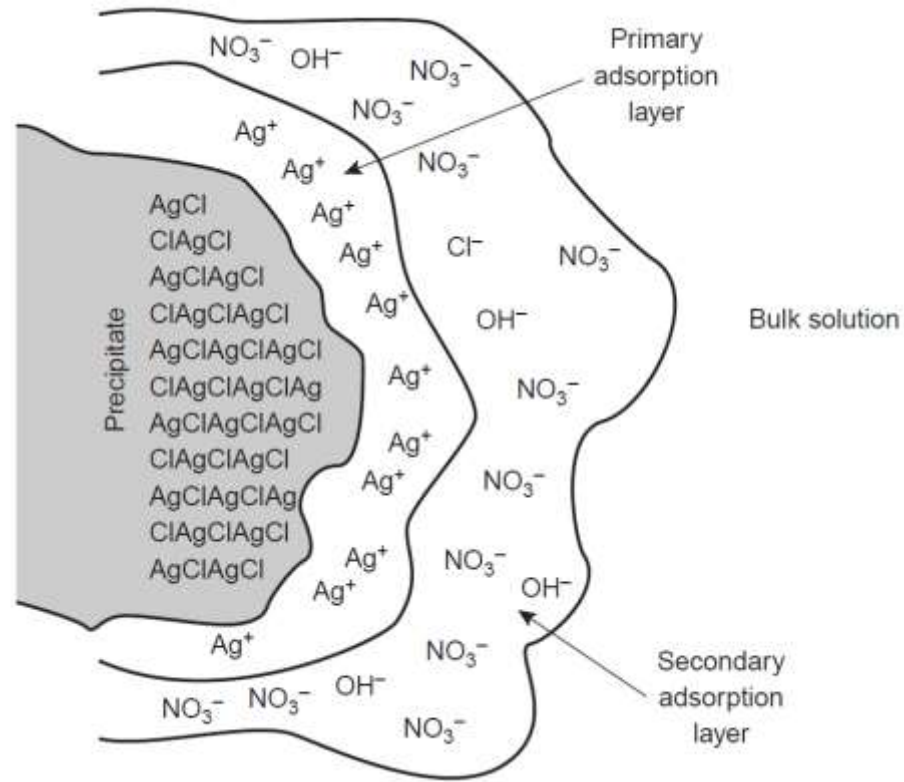
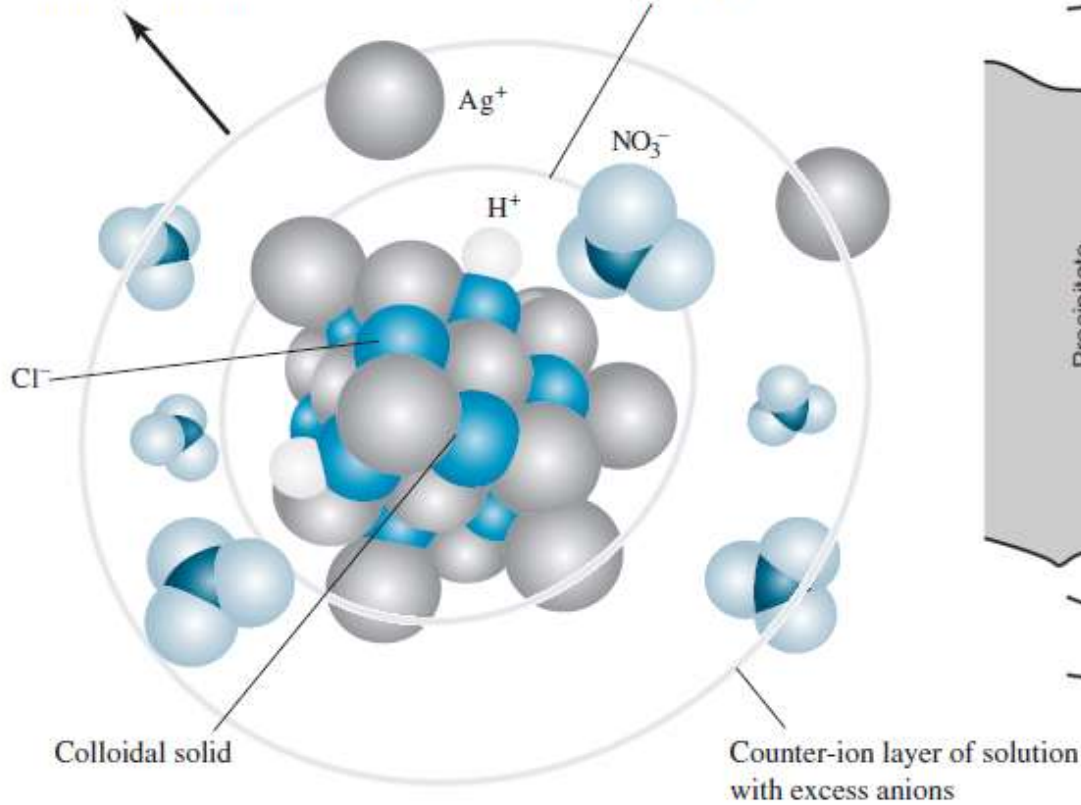


The counter ions are less tightly held than the primary adsorbed ions and the counter ion layer is somewhat diffuse and contains ions other than those of the counter ions. These layers of charges are known as the **electric double layer**

Colloidal particles

Homogeneous neutral aqueous solution (H_2O not shown)

Positively charged primary adsorption layer on colloidal particle



Colloids are characterized accordingly to the state (solid, liquid, or gas) of the dispersed phase and the state continuous phase: aerosol, foam, emulsion, sol, gel:

- fog and smoke are aerosols, which are liquid droplets or solid particles dispersed throughout a gas;
- an emulsion consist of liquid droplets dispersed throughout another liquid;
- a sol consist of solid particles dispersed in liquid.

Colloids with water continuous phase are divided on two major classes:

I. **Hydrophilic colloid** is a colloid in which there is a strong attraction between the dispersed phase and the continuous phase (water) – for example, H_2SiO_3 , $\text{Fe}(\text{OH})_3$. Many such colloids consist of macromolecules (very large molecules) dispersed in water. Except for the large size of the dispersed molecules, these are like normal solution.

II. **Hydrophobic colloid** is a colloid in which there is a lack of attraction between the dispersed phase and the continuous phase (water) – for example, AgI , As_2S_3 . Hydrophobic colloids are basically unstable. After different time, the dispersed phase comes out of solution by aggregation into larger particles. In this behaviour, they are quite unlike true solutions and hydrophilic colloids.

AgCl forms a hydrophobic colloid (a sol), which readily coagulates.

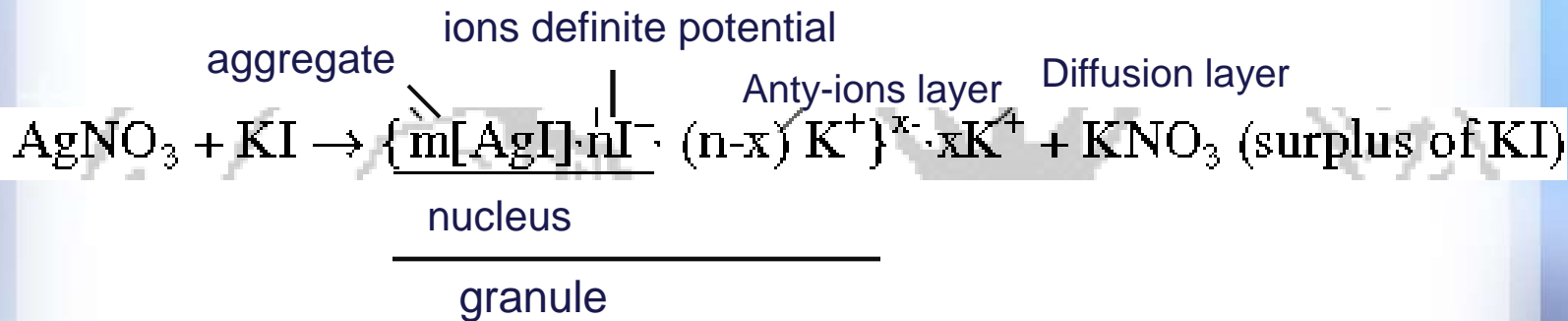
$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ forms a hydrophilic colloid (a gel) with large surface area.

Hydrophobic sol (solid phase dispersed in water) are often formed when a solid crystallises rapidly from a chemical reaction or a supersaturated solution. When crystallisation occurs rapidly, many centres of crystallisation (called nuclei) are formed at once. Ions are attracted to these nuclei and very small crystals are formed.

When molecules that have both a hydrophobic and a hydrophilic end are dispersed in water, they associate or aggregate to form colloidal-size particles, or micelles.

A **micelle** is a colloidal-size particle formed in water by the association of **molecules** that each has a hydrophobic end and hydrophilic end. The hydrophobic ends point inward toward one another, while the hydrophilic ends are on the outside of the micelle facing the water. A colloid in which the dispersed phase consists of micelle is called an association colloid.

Scheme of Micelle Structure



Coagulation is the process by which a colloid is made to come out solution by aggregation.



Prevention of Colloids Formation

For prevention of colloids formation on analytical reactions is necessary:

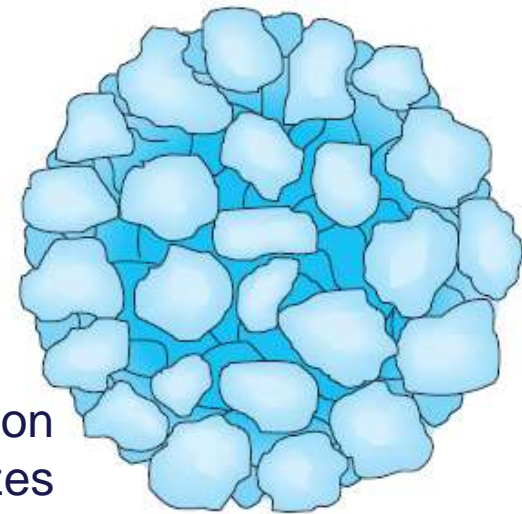
- 1) to add a small surplus of precipitant. It promotes the little solubility of precipitant and prevents to colloid formation;
- 2) to carry out precipitation process at heating;
- 3) for precipitation and washing of precipitates add electrolytes;
- 4) do not dilute the water solutions over precipitate (sediment).

Rules for amorphous precipitates coagulation:

1. Use warm solutions of analysed species and precipitant.
2. Use concentrated solution of precipitant.
3. Precipitant adds quickly.
4. Add strong electrolytes.

Peptization is the process by which a coagulated colloid reverts to its original dispersed state.

washing the precipitate with a solution containing an electrolyte that volatilizes when the precipitate is dried or ignited. For example, silver chloride is usually washed with a dilute solution of nitric acid.



A coagulated colloid.



IMPURITIES IN PRECIPITATES

Precipitation gravimetry is based on a known stoichiometry between the analyte's mass and the mass of a precipitate. It follows, therefore, that the precipitate must be free from impurities. Since precipitation typically occurs in a solution rich in dissolved solids, the initial precipitate is often impure. Any impurities present in the precipitate's matrix must be removed before obtaining its weight.

Coprecipitation is a process in which *normally soluble compounds are carried out of solution by a precipitate.*

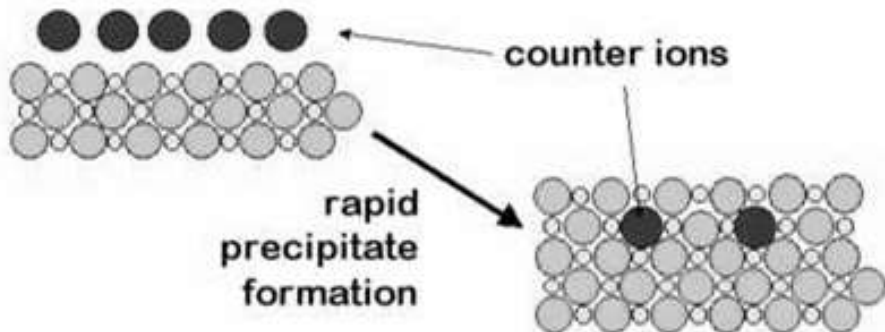
1. Occlusion and Inclusion.

In the process of **occlusion**, material that is not Occlusion is the trapping of part of the crystal structure is trapped within a crystal.

Inclusion occurs when ions, generally of similar size and charge, are trapped within the crystal lattice (isomorphous inclusion, as with K^+ in NH_4MgPO_4 precipitation).

Occlusion

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



Occluded or included impurities are difficult to remove. Digestion may help some but is not completely effective. The impurities cannot be removed by washing. Purification by dissolving and reprecipitating is helpful.

Reprecipitation - process, when the filtered solid is redissolved and reprecipitated.

2. Surface Adsorption.

In adsorption, a normally soluble compound is carried out of solution 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.

Surface adsorption of impurities is the most common source of error in gravimetry. It is reduced by proper precipitation technique, digestion, and washing.

3. Isomorphous Replacement.

Two compounds are said to be isomorphous if they have the same type of formula and crystallize in similar geometric forms. When their lattice dimensions are about the same, one ion can replace another in a crystal, resulting in a **mixed crystal**. This process is called **isomorphous replacement** or isomorphous substitution.

4. Postprecipitation.

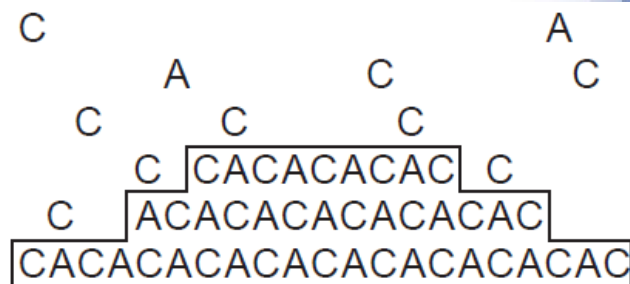
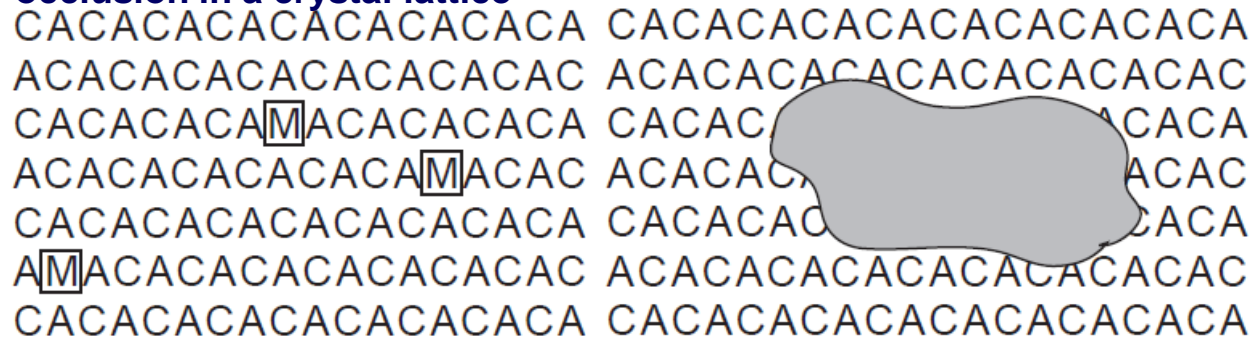
Sometimes, when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent. This is called **postprecipitation**.

C and A represent the cation–anion pair comprising the analyte and the precipitant, and is the impurity

**chemically adsorbed inclusion
or a physically adsorbed
occlusion in a crystal lattice**

**schematic of an occlusion by
entrapment of supernatant solution**

Surface adsorption of excess C



(a)

(b)

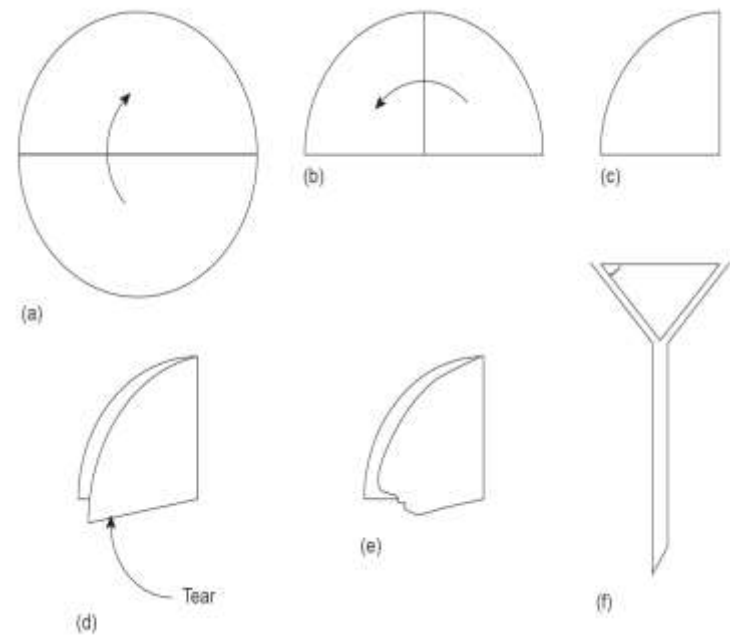
(c)

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration

5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

Mg_2Si

IV Filtration



(a)



(b)

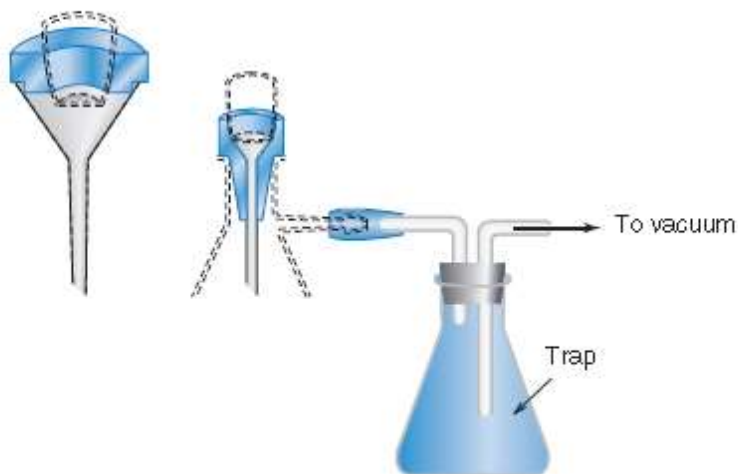
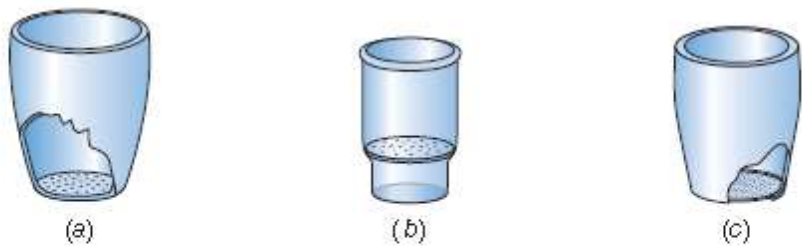


(c)

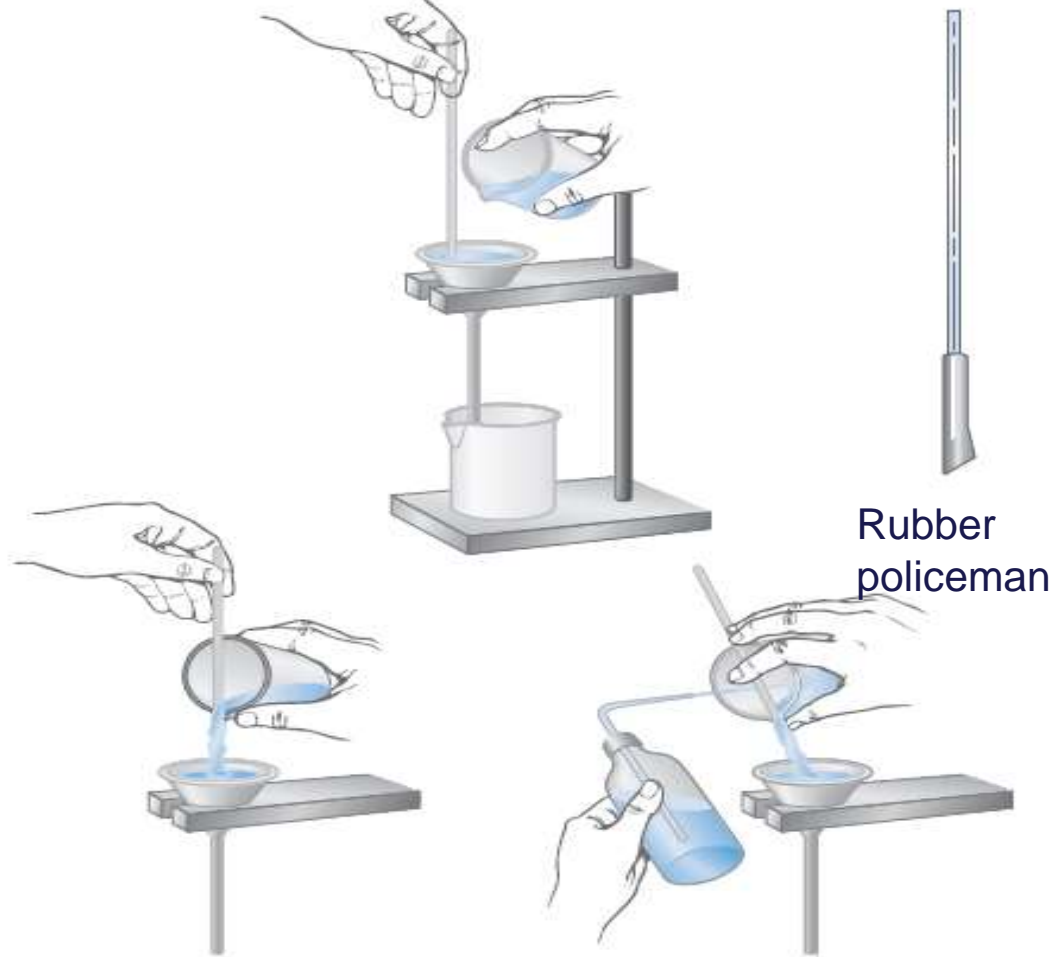


(d)



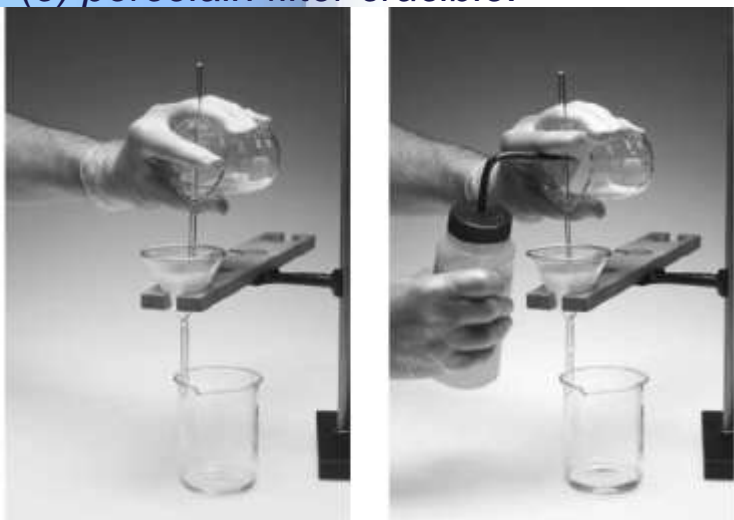


Filtering crucibles: (a) Gooch crucible; (b) *sintered-glass* crucible; (c) *porcelain filter crucible*.



Proper technique for transfer of a precipitate.

Decantation is the process of pouring a liquid gently so as to not disturb a solid in the bottom of the container.



V

Washing

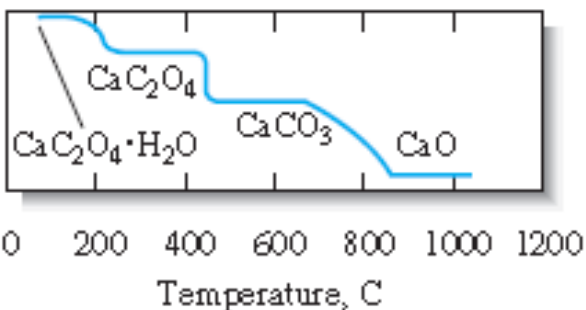
- Many precipitates cannot be washed with pure water, because **peptization occurs**.
- Add an strong electrolyte to the wash liquid, for example, HNO_3 or NH_4NO_3 for AgCl

The electrolyte must be one that is volatile at the temperature to be used for drying or ignition, and it must not dissolve the precipitate.

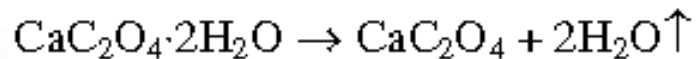


When you wash a precipitate, you should conduct a test to determine when the washing is complete. This is usually done by testing the filtrate for the presence of an ion of the precipitating reagent. After several washings with small volumes of the wash liquid, a few drops of the filtrate are collected in a test tube for the testing.

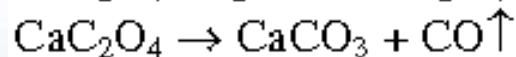
VI DRYING OR IGNITING



Gravimetric precipitate is heated until its mass becomes constant. Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also **ignited** to decompose the solid and form a compound of known composition. This new compound is often called the **weighing form**.



(200 °C)

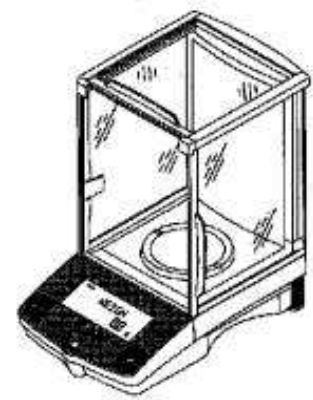


(475-525 °C)



(900-1000 °C)





Demands to weighed (gravimetric) form:

1. Composition stoichiometry corresponds to chemical formula.
2. Chemical stability. Not reacts with air components (CO_2 , O_2 , another gases) and not absorbs water steam.
3. Conclusion of analysed element must be the less. In this case measurement error not influence on calculation results.

VII

Weighing

VIII

Calculations

gravimetric factor (GF), represents the weight of analyte per unit weight of precipitate. It is obtained from the ratio of the formula weight of the analyte to that of the precipitate, multiplied by the moles of analyte per mole of precipitate obtained from each mole of analyte.

$$\text{GF} = \frac{\text{fw analyte (g/mol)}}{\text{fw precipitate (g/mol)}} \times \frac{a}{b} (\text{mol analyte/mol precipitate})$$
$$= \text{g analyte /g precipitate}$$

$$\% \text{ sought} = \frac{\text{weight of precipitate (g)} \times \text{GF (g sought/g precipitate)}}{\text{weight of sample (g)}} \times 100\%$$





The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4 . 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 (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

The mass of CaO is

$$26.7134\text{g} - 26.6002 = 0.1132\text{g}$$

The number of moles of Ca in the sample is equal to the number of moles of CaO , or

$$\begin{aligned}\text{amount of Ca} &= 0.1132\text{gCaO} \times \frac{1\text{molCaO}}{56.077\text{gCaO}} \times \frac{1\text{molCa}}{1\text{molCaO}} \\ &= 2.0186 \times 10^{-3}\text{molCa}\end{aligned}$$

$$\begin{aligned}\text{conc. Ca} &= \frac{2.0186 \times 10^{-3}\text{molCa} \times 40.078\text{gCa/molCa}}{200\text{mL sample}} \times \frac{100}{100} \\ &= 0.04045\text{g/100 mL sample}\end{aligned}$$





An ore containing magnetite, Fe_3O_4 , was analyzed by dissolving a 1.5419-g sample in concentrated HCl , giving a mixture of Fe^{2+} and Fe^{3+} . After adding HNO_3 to oxidize any Fe^{2+} to Fe^{3+} , the resulting solution was diluted with water and the Fe^{3+} precipitated as $\text{Fe}(\text{OH})_3$ by adding NH_3 . After filtering and rinsing, the residue was ignited, giving 0.8525 g of pure Fe_2O_3 . Calculate the %w/w Fe_3O_4 in the sample.

$$3 \times \text{moles Fe}_3\text{O}_4 = 2 \times \text{moles Fe}_2\text{O}_3$$

$$\frac{3 \times \text{g Fe}_3\text{O}_4}{\text{FW Fe}_3\text{O}_4} = \frac{2 \times \text{g Fe}_2\text{O}_3}{\text{FW Fe}_2\text{O}_3}$$

$$\frac{2 \times \text{g Fe}_2\text{O}_3 \times \text{FW Fe}_3\text{O}_4}{3 \times \text{FW Fe}_2\text{O}_3} = \frac{2 \times 0.8525 \text{ g} \times 231.54 \text{ g/mol}}{3 \times 159.69 \text{ g/mol}} = 0.82405 \text{ g Fe}_3\text{O}_4$$

$$\frac{\text{g Fe}_3\text{O}_4}{\text{g sample}} \times 100 = \frac{0.82405 \text{ g}}{1.5419 \text{ g}} \times 100 = 53.44\% \text{ w/w Fe}$$



Summary of Method

- A relative slow method of analysis – however, most time is spent waiting for 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.

Example Applications

1. Inorganic precipitating agents.
2. Many cations and anions can be precipitated as groups.
3. With a proper design, you can use this to precipitate a single species.
4. Determination of humidity (moisture) of materials.
5. Determination of crystallisation water in hydrates.

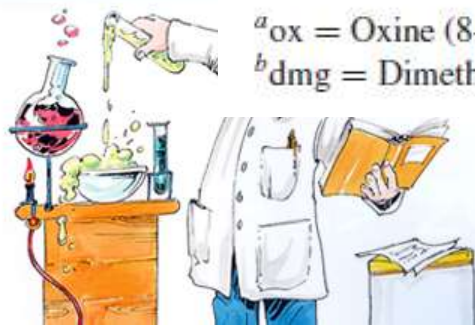


Some Commonly Employed Gravimetric Analyses

Substance Analyzed	Precipitate Formed	Precipitate Weighed	Interferences
Fe	Fe(OH) ₃ Fe cupferrate	Fe ₂ O ₃ Fe ₂ O ₃	Many. Al, Ti, Cr, etc. Tetravalent metals
Al	Al(OH) ₃ Al(ox) ₃ ^a	Al ₂ O ₃ Al(ox) ₃	Many. Fe, Ti, Cr, etc. Many. Mg does not interfere in acidic solution
Ca	CaC ₂ O ₄	CaCO ₃ or CaO	All metals except alkalis and Mg
Mg	MgNH ₄ PO ₄	Mg ₂ P ₂ O ₇	All metals except alkalis
Zn	ZnNH ₄ PO ₄	Zn ₂ P ₂ O ₇	All metals except Mg
Ba	BaCrO ₄	BaCrO ₄	Pb
SO ₄ ²⁻	BaSO ₄	BaSO ₄	NO ₃ ⁻ , PO ₄ ³⁻ , ClO ₃ ⁻
Cl ⁻	AgCl	AgCl	Br ⁻ , I ⁻ , SCN ⁻ , CN ⁻ , S ²⁻ , S ₂ O ₃ ²⁻
Ag	AgCl	AgCl	Hg(I)
PO ₄ ³⁻	MgNH ₄ PO ₄	Mg ₂ P ₂ O ₇	MoO ₄ ²⁻ , C ₂ O ₄ ²⁻ , K ⁺
Ni	Ni(dm _g) ₂ ^b	Ni(dm _g) ₂	Pd

^aox = Oxine (8-hydroxyquinoline) monoanion.

^bdm_g = Dimethylglyoxime monoanion.



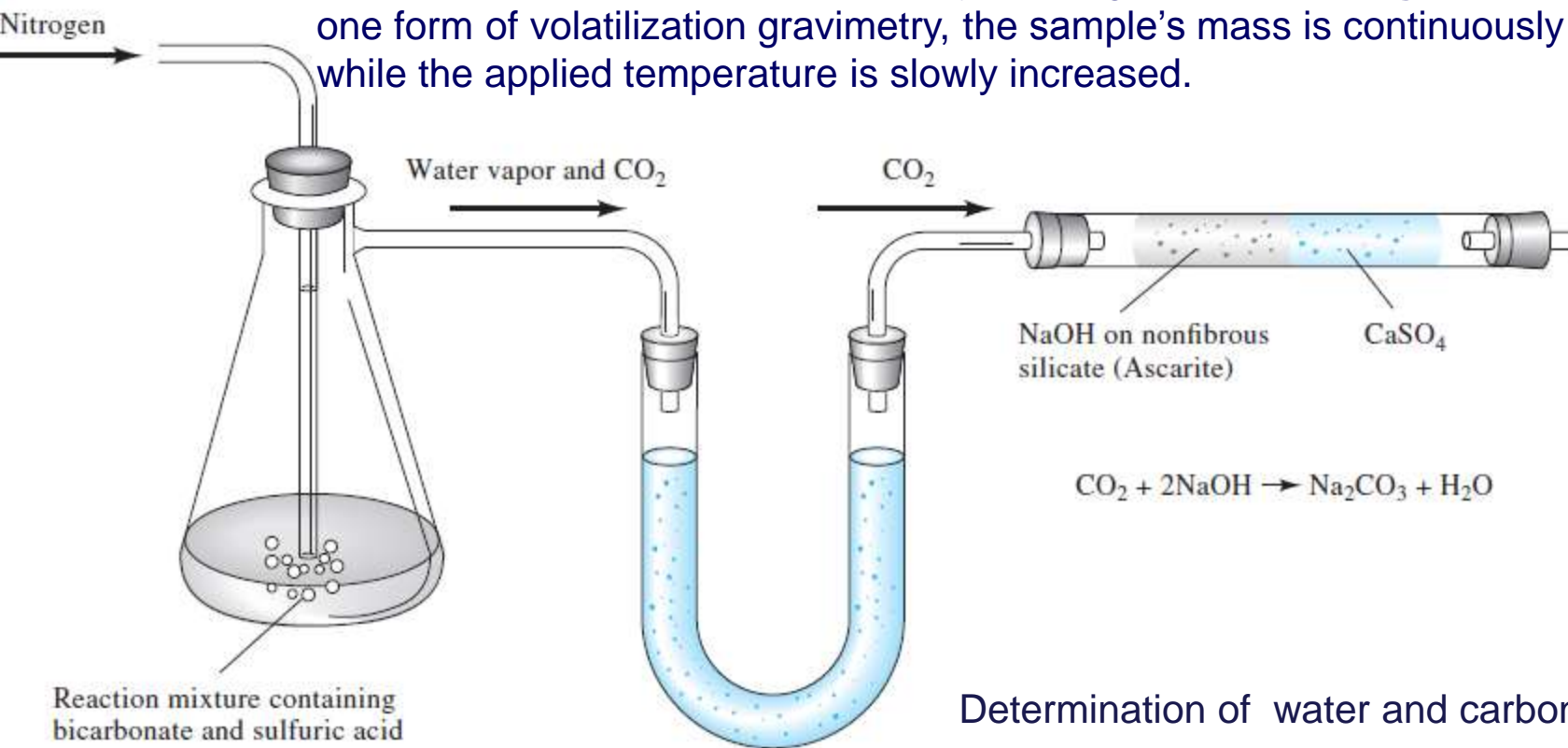
Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow R-CH=NNHC_6H_3(NO_2)_2(s) + H_2O$ (RCOR' reacts similarly)
Aromatic carbonyl	Mass of CO ₂ formed at 230°C in quinoline; CO ₂ distilled, absorbed, and weighed	$ArCHO \xrightarrow[CuCO_3]{230^\circ C} Ar + CO_2(g)$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH ₃ I or C ₂ H ₅ I	$\left. \begin{array}{l} ROCH_3 + HI \rightarrow ROH + CH_3I \\ RCOOH_3 + HI \rightarrow RCOOH + CH_3I \\ ROC_2H_5 + HI \rightarrow ROH + C_2H_5I \end{array} \right\} CH_3I + Ag^+ + H_2O \rightarrow AgI(s) + CH_3OH$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \frac{2}{3}Sn(s) + 6H^+ \rightarrow RNH_2 + \frac{2}{3}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN=NR' + 2Cu(s) + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$\begin{array}{c} O \\ \\ ROP(OH)_2 \end{array} + Ba^{2+} \rightarrow \begin{array}{c} O \\ \\ ROPO_2Ba(s) \end{array} + 2H^+$
Sulfamic acid	Mass of BaSO ₄ after oxidation with HNO ₂	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow ROH + BaSO_4(s) + N_2 + 2H^+$
Sulfinic acid	Mass of Fe ₂ O ₃ after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$ $(ROSO)_3Fe \xrightarrow{O_2} CO_2 + H_2O + SO_2 + Fe_2O_3(s)$



Volatilization Gravimetry

A second approach to gravimetry is to thermally or chemically decompose a solid sample. The volatile products of the decomposition reaction may be trapped and weighed to provide quantitative information. Alternatively, the residue remaining when decomposition is complete may be weighed. In **thermogravimetry**, which is one form of volatilization gravimetry, the sample's mass is continuously monitored while the applied temperature is slowly increased.



Determination of water and carbon dioxide



weighed absorbents

