GRAVIMETRIC ANALYSIS-By Dr.AdelSaeed

Preprint · January 2019

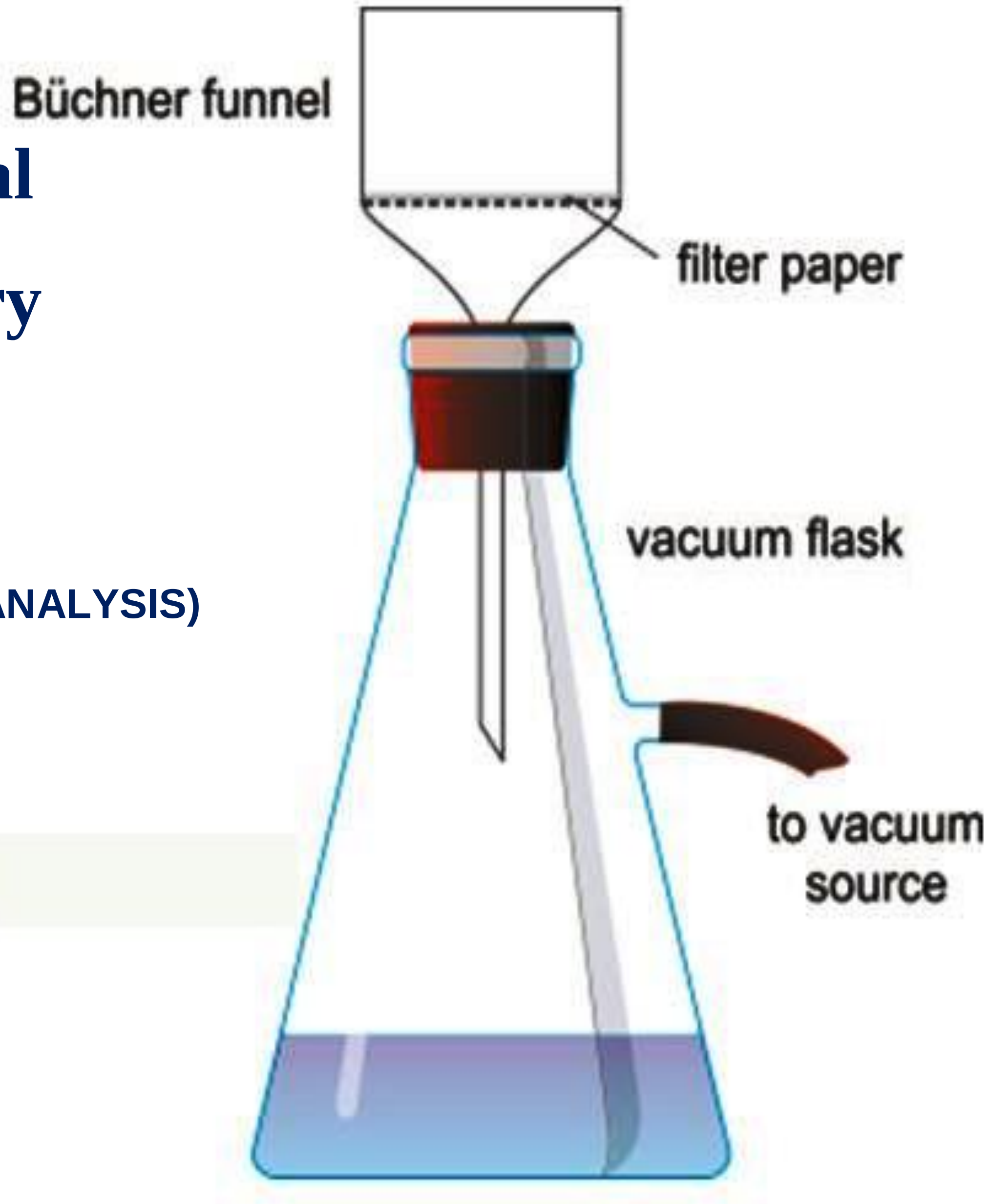
DOI: 10.13140/RG.2.2.36201.98403

Adel Saeed
Aden University

University of Aden

Faculty of Science

Analytical Chemistry (II)



(GRAVIMETRIC ANALYSIS)

By

Dr. Adel Ahmed Mohammed Saeed

2019-2020

BRIEF CONTENTS

BRIEF CONTENTS 1

LEARNING OUTCOMES (ILOs) 3

Introduction 4

Fig.1: Gravimetric analysis methods. 4

Steps in a Gravimetric Analysis: 6

Fig.2: Ostwald ripening improves the purity and crystallinity of the precipitate. 8

***Fig. 3:** Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.* 9

***Fig. 4:** Relastionship between solubility vs. concentration of the precipitates.* 10

***Fig. 5:** Preciptation steps.* 11

***Fig.6:** Precipitate formation stages.* 12

***Fig.7:** Successful precipitation factors.* 12

Nature of Precipitate 13

***Fig.8:** Detrmination of natrure of precipitates.* 13

***Fig.9:** Large molecules remain trapped inside a dialysis bag, whereas small molecules diffuse through the membrane in both directions.* 14

***Fig.10:** Charging colloidal particles.* 16

***Fig.11:** Scheme represents relationship between supersaturation & nucleation.* 17

Impurities in Precipitates 17

TABLE 1. Examples of GF. 19

Evaluation of Gravimetric Analysis 20

Advantages & Disadvantages of Gravimetric Analysis 20

TABLE 2. Representative gravimetric analyse. 21

Solubility and Solubility Product 23

TABLE 3. Solubility of aqueous solutions. 23

Gravimetric Factor (GF): 27

Some Concepts, Separating Mixtures Techniques & Processes Used in Gravimetric Analysis 28

TABLE 4. Mixtures types. 28

TABLE 5. Colloids main groups. 28

TABLE 6. Coagulation vs. flocculation. 30

TABLE 7. Coagulation vs. Peptization. 32

***Fig.14:** Filtration processes.* 33

***Fig. 15:** (1) Drying & ignition with filter paper, (2) Drying in a desiccator.* 33

***Fig.16:** Sublimation & deposition prosses to purify iodine.* 34

***Fig.17:** Extracting I_2 using separatory funnel.* 34

***Fig. 18:** Other speration methods from left to right (1) Centrifuging, (2) Using a magnet (3) Sieving.* 35

Types of Adsorption 35

TABLE 8. The differences between physical and chemical adsorption. 35

TABLE 9. Methods for homogeneous generation of precipitating agents. 36

TABLE 10. Some inorganic precipitating agents. 36

TABLE 11. Some reducing agents used in gravimetric methods. 37

TABLE 12 Some organic precipitating agents. 37

Gravimetric Analysis of Silver - Ag – 107.870 38

TABLE 13. Forms of determination of silver. 39

***Fig.19.**Thermo analytical curves of silver chloride precipitate heated in air.* 40

***Fig.20.**Thermo analytical curves of silver chloride precipitate heated in hydrogen gas atmosphere.* 41

TABLE .14. Silver determination in form of AgCl. 43

Fig.21.*Thermoanalytical curves of silver bromide precipitate.* *44*

Fig.22.*Thermoanalytical curves of metallic silver reduced by ascorbic acid.* *45*

TABLE .15. Silver determination with reduction by ascorbic acid. *46*

Gravimetric Analysis of Chlorine - Cl – 35.453; 46

Cl_2, HCI, HCIO, HCIOz, $HCIO_3$, $HClO_4$........ 46

TABLE .16. Forms of determination of chlorine. *47*

Biblography 49

Problems 50

LEARNING OUTCOMES (ILOs)

At the end of this book, the student is expected to be able to:

1- Understand the fundamentals of gravimetric analysis.

2- Follow the steps of the gravimetric analysis.

3- Choose the appropriate precipitating agent for a certain analyte.

4- Avoid or at least minimize the contamination of the precipitate.

5- Optimize the precipitation conditions in order to obtain a desirable precipitate.

6- Learn how to do accurate measurents.

7- Learn how to do calculations related to gravimetric analysis.

Students should know the following key words:

Gravimetric Analysis, Precipitation, Volatizaton, Digestion (or) Ostwald Ripening, Filtration, Washing, Drying, Igniting, Weighing.

Introduction

(Gravi + Metry) = Weigh +measure

Gravimetric methods (Fig.1) are quantitative methods (A **precipitation, volatilization, electrical, or particulate**) that are based on measuring the mass of a pure compound to which the **analyte** is chemically related. Since weight can be measured with greater accuracy than almost any other fundamental property, gravimetric analysis is potentially one of the most accurate classes of analytical methods . However, it is lengthy and tedious as a result, only a very few gravimetric methods are currently used. There are three fundamental types of gravimetric analysis.

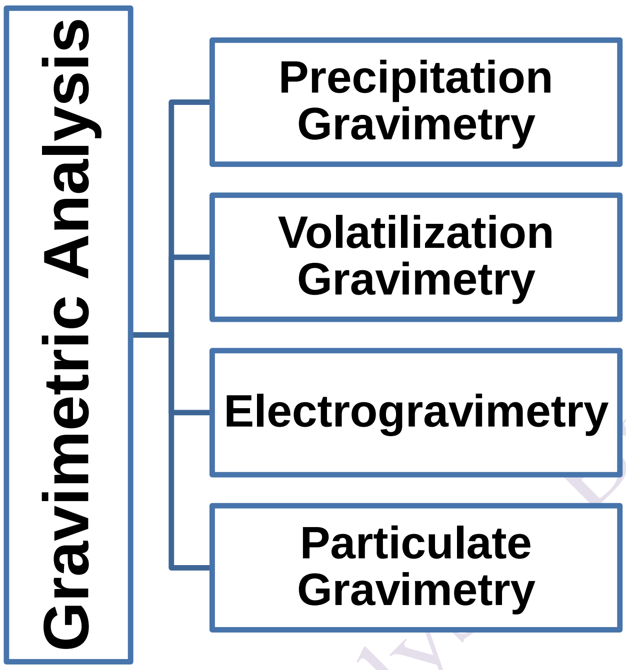


***Fig.1**: Gravimetric analysis methods.*

In **precipitation gravimetry**, which is our subject in this course, the analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.

In **volatilization gravimetry**, the analyte is separated from other constituents of a sample by conversion to a gas. The weight of this gas then serves as a measure of the analyte concentration. In **electrogravimetry**, the analyte is separated by deposition on an electrode by an electrical current. The mass of this product then provides a measure of the analyte concentration.

Finally, in **particulate gravimetry** we determine the analyte by separating it from the sample's matrix using a filtration or an extraction.

In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment, and weighed. For example, a precipitation method for determining calcium in natural waters involves the addition of $C_2O_4^{2-}$as a precipitating agent:

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s) \qquad \longrightarrow \qquad (1)$$

The precipitate CaC_2O_4 is filtered, then dried and ignited to convert it entirely to calcium oxide:

$$CaC_2O_4(s) \xrightarrow{\triangle} CaO\,(s) + CO\,(g) + CO_2(g) \qquad \longrightarrow \qquad (2)$$

After cooling, the precipitate is weighed, and the calcium content of the sample is then computed.

Why Gravimetry is Important:

The answer is that gravimetry is one of only a small number of **definitive techniques** whose measurements require only base SI units, such as mass or the mole, and defined constants. Although most analysts never use gravimetry to validate their results, they often verifying an analytical method by analyzing a standard reference material whose composition are traceable to a definitive technique. All precipitation gravimetric analysis is share two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to accurately reflect the analyte's mass. Second, the precipitate must be easy to separate from the reaction mixture.

Properties of Precipitates and Precipitating Reagents:

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.

Mechanism of Precipitate Formation:

The effect of relative supersaturation on particle size can be explained if we assume that precipitates form in two ways; by nucleation and by particle growth. The particle size of a freshly formed precipitate is determined by the mechanism that predominates.

In **nucleation**, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid (1 – 100 nm diameter). Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles. Further precipitation then involves a competition between additional nucleation and growth on existing nuclei (particle growth). If nucleation predominates, a precipitate containing a large number of small particles results; if growth predominates, a smaller number of larger particles are produced.

The rate of nucleation is believed to increase enormously with increasing relative supersaturation. In contrast, the rate of particle growth is only moderately enhanced by low relative supersaturations. Thus, when a precipitate is formed at high relative supersaturation, nucleation is the major precipitation mechanism, and a large number of small particles are formed. At low relative supersaturations, the rate of particle growth tends to predominate, and deposition of solid on existing particles occurs to the exclusion of further nucleation; a crystalline suspension results.

How to Perform a Successful Gravimetric Analysis?

The following factors determine a successful analysis by precipitation:

1. The precipitate must be so insoluble that no appreciable loss occurs when it is collected by filtration.

2. The physical nature of the precipitate must be much that it can be readily separated from the solution by filtration, and can be washed free soluble impurities.

3. The particles are of such size that they not pass through the filtering medium, and that the particles size is unaffected (or at least, not diminished) by the washing process.

4. The precipitate must be convertible into pure substance of definite chemical composition; this may be affected either by ignition or by a simple chemical operation, such as evaporation, with suitable liquid.

Steps in a Gravimetric Analysis:

The steps required in gravimetric analysis, after the sample has been dissolved, can be as follows:

1- Preparation of the Solution: The first step in performing gravimetric analysis is to prepare the solution. This may involve several processes. Some form of preliminary separation may be necessary to eliminate interfering materials. Also, we must adjust the **solution conditions** to maintain low solubility of the precipitate and to obtain it in a form suitable for filtration. Proper adjustment of the solution conditions prior to precipitation may also mask potential interferences. **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. The pH is important because it often influences both the solubility of the analytical precipitate and the possibility of interferences from other substances.

2- Precipitation: This requires addition of a precipitating agent solution to the sample solution. Upon addition of the first drops of the precipitating agent, supersaturation occurs, then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleus. At this point, addition of extra precipitating agent will either form new nuclei (precipitate with small particles) or will build up on existing nuclei to give a precipitate with large particles.

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.

Following nucleation, the initial nucleus will grow by depositing other precipitate particles to form a crystal's of a certain geometric shape. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.

This can be predicted by **Von Weimarn** ratio where, according to this relation the particle size is inversely proportional to a quantity called the relative supersaturation:

$$\text{Relative Supersaturation} = (Q - S) / S \quad \longrightarrow \quad (3)$$

The Q is the concentration of reactants before precipitation at any point, S is the solubility of precipitate in the medium from which it is being precipitated.

Therefore, in order to get particle growth instead of further:

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

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

Obviously, then, we want to keep Q low and S high during precipitation.

Several steps are commonly taken to maintain favorable conditions for precipitation.

The optimum conditions for precipitation to minimize supersaturation and obtain large crystals are:

a. Precipitation using dilute solutions to decrease Q.

b. Slow addition of precipitating agent to keep Q as low as possible.

c. Stirring the solution during addition of precipitating agent to avoid concentration sites and keep Q low.

d. Increase solubility S by precipitation from hot solution.

e. Adjust the pH in order to increase S but not too much increase as we do not want to loose precipitate by dissolution.

f. Precipitation from Homogeneous Solution: In order to make Q minimum we can, in some situations, generate the precipitating agent in the precipitation medium rather than adding it. For example, in order to precipitate iron as the hydroxide, we dissolve urea in the sample. Heating of the solution generates hydroxide ions from the hydrolysis of urea. Hydroxide ions are generated at all points in solution and thus there are no sites of concentration. We can also adjust the rate of urea hydrolysis and thus control the hydroxide generation rate. This type of procedure can be very advantageous in case of colloidal precipitates.

3- Digestion of the Precipitate: The precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested. Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics. This **digestion** process is also called **Ostwald ripening** (Fig.2) and is is illustrated in Figure below:

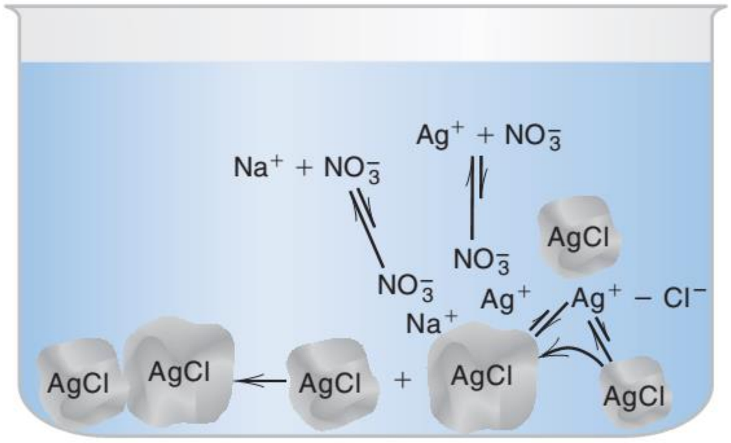


Fig.2*: Ostwald ripening improves the purity and crystallinity of the precipitate.*

An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate. Digestion forces the small colloidal particles to **agglomerate** (dissolve and reprecipitated on the surfaces of the larger crystals) which decreases their surface area and thus adsorption.

Digestion is usually done at elevated temperatures to speed the process, although in some cases it is done at room temperature. It improves both the filterability of the precipitate and its purity.

Many precipitates do not give a favorable Von Weimarn ratio, especially very insoluble ones. Hence, it is impossible to yield a crystalline precipitate (small number of large particles), and the precipitate is first colloidal (large number of small 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. As a precipitate forms, the ions are arranged in a fixed pattern. In AgCl, for example, there will be alternating Ag^+ and Cl^- ions on the surface (see Figure 3 next). While there are localized positive and negative charges on the surface, the net surface charge is zero. However, the surface does tend to adsorb the ion of the precipitate particle that is in excess in the solution, for example, Ag^+ if precipitating Cl^- with an excess of Ag^+; this imparts a charge. (With crystalline precipitates, the degree of such adsorption will generally be small in comparison with particles that tend to form colloids.) The adsorption creates a primary layer that is strongly adsorbed and is an integral part of the crystal. It will attract ions of the opposite charge in a counter layer or secondary layer so the particle will have an overall neutral charge. There will be solvent molecules interspersed between the layers. Normally, the **counter layer** completely neutralizes the **primary layer** and is close to it, so the particles will collect together to form larger particles; that is, they will **coagulate**. However, if the secondary layer is loosely bound, the primary surface charge will tend to repel like particles, maintaining a colloidal state.

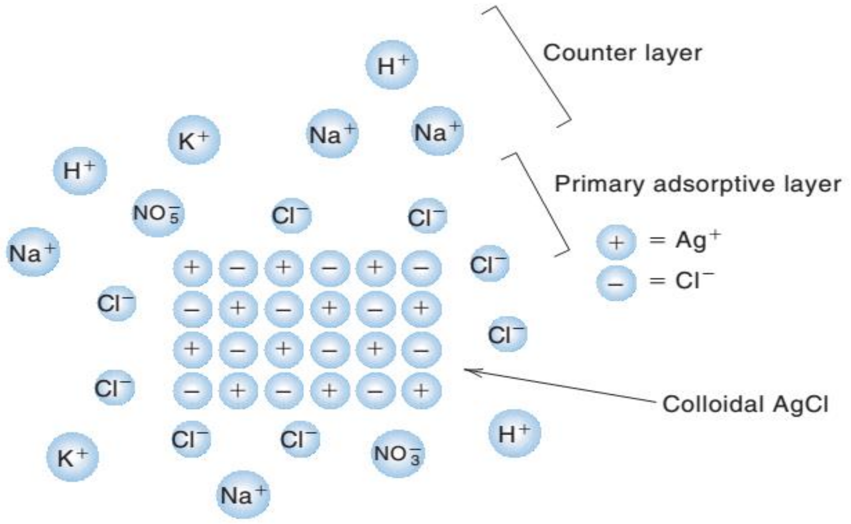


Fig. 3: *Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.*

The precipitate often contains ions that where trapped when the precipitate was formed. This is mostly a problem for crystalline precipitates. If the trapped ions are not volatile, then their presence will corrupt the weighing step. Concentration of interfering species may be reduced by digestion. Unfortunately, postprecipitation as we will see later will increase during digestion.

4-Washing and Filtering

When coagulated particles are filtered, they retain the adsorbed primary-and secondary ion layers along with solvent. Washing the particles with water increases the extent of solvent (water) molecules between the layers, causing the secondary layer to be loosely bound, and the particles revert to the colloidal state, this process is called **peptization**.

While all colloidal systems cause difficulties in analytical determinations, some are worse than others. Depending on the affinity of the dispsersed material for water, colloidal systems can be classified into **hydrophilic** (water loving) and **hydrophobic** (do not like water). While the former ones tend to produce stable dispersions in water, the latter ones tend to **aggregate**.

This results in the loss of part of the precipitate because the colloidal form may pass through on filtration, in case of colloidal precipitates we should not use water as a washing solution since peptization would occur. In such situations dilute volatile electrolyte such as nitric acid, ammonium nitrate, or dilute acetic acid may be used.

Usually, it is a good practice to check for the presence of precipitating agent in the filtrate of the final washing solution. The presence of precipitating agent means that extra washing is required. **Filtration** should be done in appropriate sized Goosh or ignition ashless filter paper. After the solution has been filtered, it should be tested to make sure that the analyte has been completely precipitated. This is easily done by adding a few drops of the precipitating reagent to the filtrate; if a precipitate is observed, the precipitation is incomplete.

The common ion effect can be used to reduce the solubility of the precipitate. When Ag^+ is precipitated out by addition of Cl^-

$$Ag^+ + Cl^- \rightarrow AgCl\ (s) \quad \longrightarrow \quad (4)$$

The (low) solubility of AgCl is reduced still further by the excess of Ag^+ which is added, pushing the equilibrium to the right. It is important to know that the excess of the precipitating agent should not exceed 50% of its equivalent amount , otherwise the precipitating agent may form a soluble complex with the precipitate:

$$AgCl + Cl^- \rightarrow AgCl_2^-\ (\text{ soluble complex }) \quad \longrightarrow \quad (5)$$

The following graph (Fig. 4) shows that most precipitates follow this pattern, but there are some anomalies such as Hg_2I and $BaSO_4$.

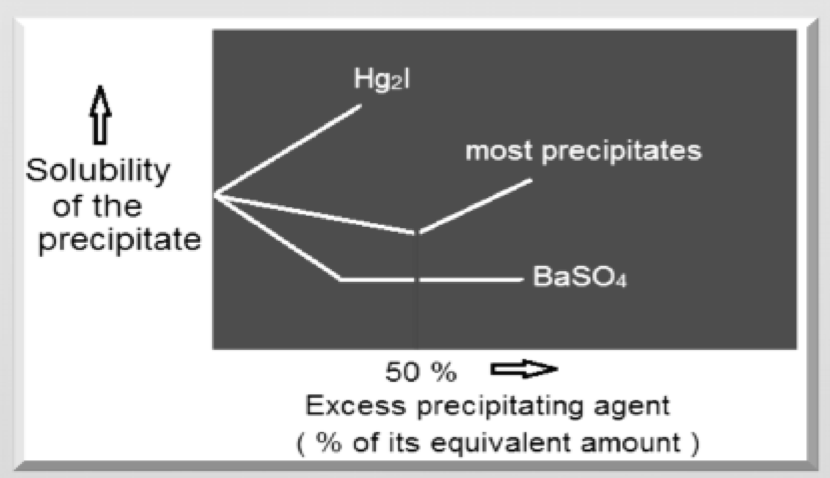


Fig. 4: *Relastionship between solubility vs. concentration of the precipitates.*

Example : To precipitate 10 moles of Ag^+ as Ag_2S, how many moles of the precipitating agent S^{2-} do you need to obtain complete precipitation ?

Solution : According to the following precipitation reaction:

$$2Ag^+ + S^{2-} \rightarrow Ag_2S \quad \longrightarrow \quad (6)$$

The equivalent amount of S^{2-}= 5 moles.

50% of the equivalent amount = 2.5 moles

So the total amount of S^{2-} needed for complete precipitation of Ag^+ = 5 +2.5 = 7.5 moles.

5- Drying and Ignition: The purpose of drying (heating at about 120-150 ^{o}C in an oven) is to remove the remaining moisture while the purpose of ignition in a muffle furnace at temperatures ranging from 600-1200 ^{o}C is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined . The precipitate is converted to a more chemically stable form. For instance, calcium ion might be precipitated using oxalate ion, to produce calcium oxalate (CaC_2O_4) which is hydrophil, therefore it is better to be heated to convert it into $CaCO_3$ or CaO . The $CaCO_3$ formula is preferred to reduce weighing errors.

It is vital that the empirical formula of the weighed precipitate be known, and that the precipitate be pure; if two forms are present, the results will be inaccurate.

6-Weighing the precipitate: The precipitate can not be weighed with the necessary accuracy in place on the filter paper; nor can the precipitate be completely removed from the filter paper in order to weigh it.

The precipitate can be carefully heated in a crucible until the filter paper has burned away; this leaves only the precipitate. (As the name suggests, "ashless" paper is used so that the precipitate is not contaminated with ash.) . If you use Goosh crucible then after the precipitate is allowed to cool (preferably in a desicator to keep it from absorbing moisture), it is weighed (in the crucible).

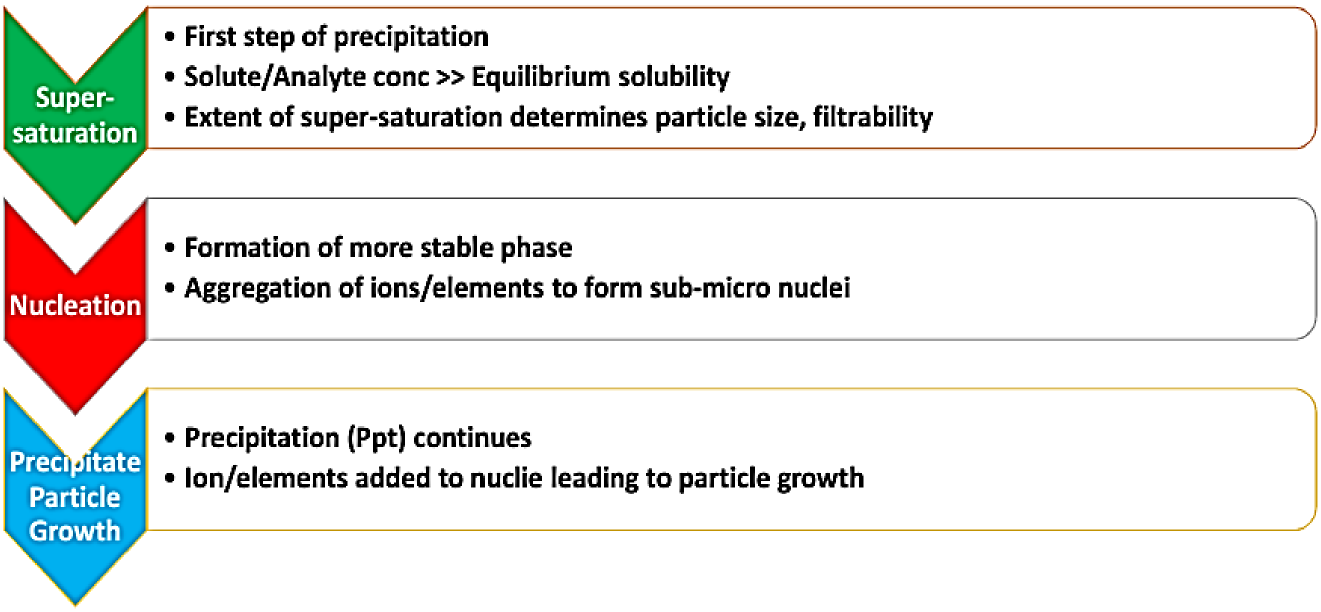
The mass of the crucible is subtracted from the combined mass, giving the mass of the precipitated analyte. Since the composition of the precipitate is known, it is simple to calculate the mass of analyte in the original sample.

To summery, gravimetric preciptation can followed the next routes.

1 • Preparation of the sample solution
2 • Precipitation process
3 • Digestion (or) Ostwald ripening
4 • Filtration
5 • Washing
6 • Drying
7 • Igniting
8 • Weighing
9 • Calculation

***Fig. 5:** Preciptation steps.*

Whereas, precipitate (ppt) formation follows several stages:



- First step of precipitation
- Solute/Analyte conc >> Equilibrium solubility
- Extent of super-saturation determines particle size, filtrability

- Formation of more stable phase
- Aggregation of ions/elements to form sub-micro nuclei

- Precipitation (Ppt) continues
- Ion/elements added to nuclie leading to particle growth

Fig.6: *Precipitate formation stages.*

Any successful precipitation depens on some factors such as insolubility, physical form and purity.

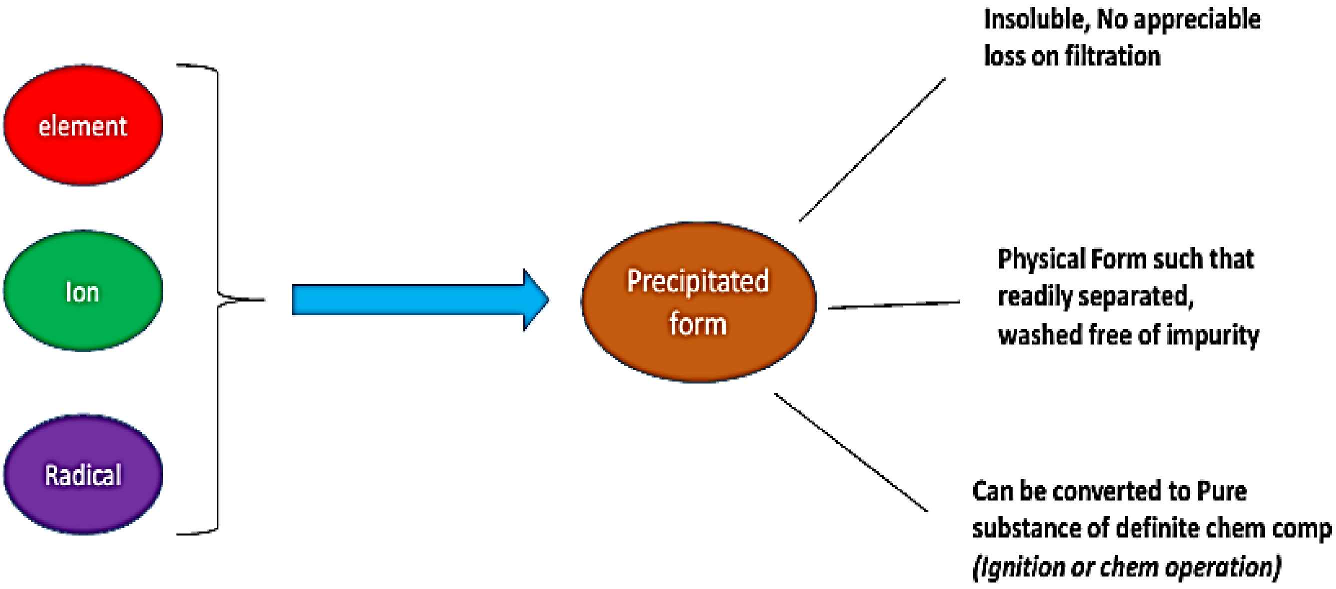


Fig.7: *Successful precipitation factors.*

Nature of Precipitate

Physical nature of precipitate will be determined by relative rates of nucleation and particle growth.

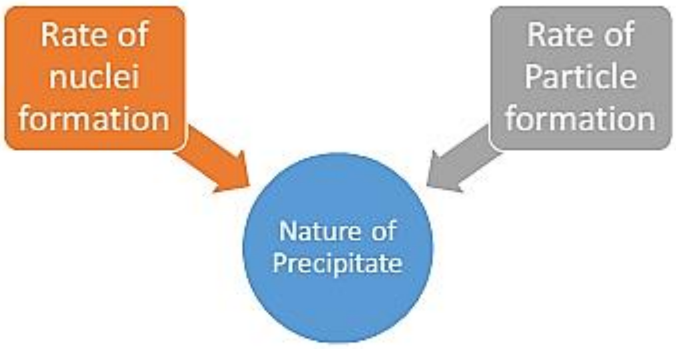


Fig.8: *Detrmination of natrure of precipitates.*

Colloids and Dialysis

Colloids are particles with diameters in the approximate range 1–100 nm. They are larger than molecules, but too small to precipitate. Colloids remain in solution indefinitely, suspended by the Brownian motion (random movement) of solvent molecules.

To make a colloid, heat a beaker containing 200 mL of distilled water to 70º–90ºC and leave an identical beaker of water at room temperature. Add 1 mL of 1 M $FeCl_3$ to each beaker and stir. The warm solution turns brown-red in a few seconds, whereas the cold solution remains yellow (Color Plate 2a). The yellow color is characteristic of low-molecular-mass Fe^{3+} compounds.

The red color results from colloidal aggregates of Fe^{3+} ions held together by hydroxide, oxide, and some chloride ions. These particles have a molecular mass of 10^5 and a diameter of ~10 nm, and contain ~10^3 atoms of Fe.

To demonstrate the size of colloidal particles, we perform a **dialysis** experiment (Fig. 9) in which two solutions are separated by a *semipermeable membrane* that has pores with diameters of 1–5 nm. The membrane has pores through which small molecules, but not large molecules (such as proteins) and colloids, can diffuse.

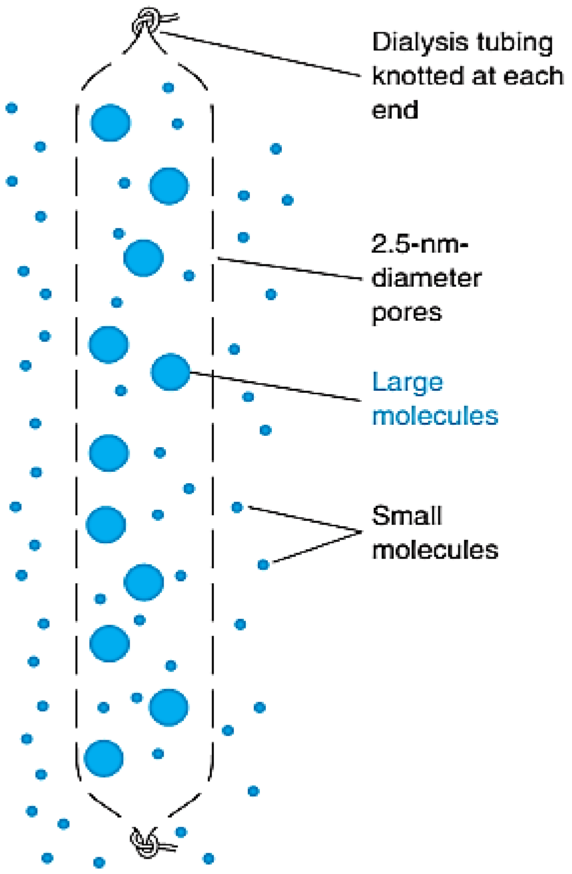


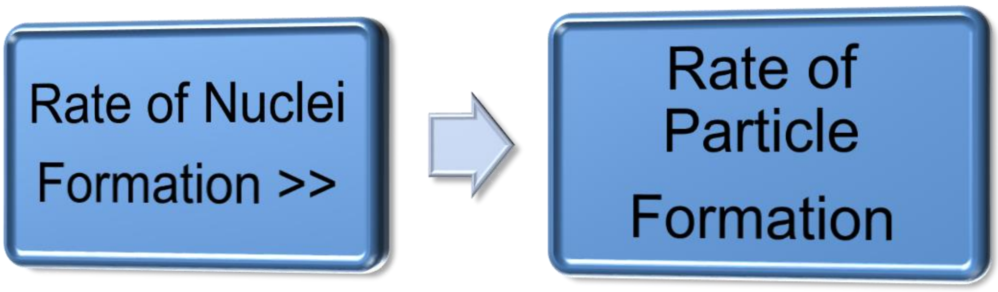
Fig.9: *Large molecules remain trapped inside a dialysis bag, whereas small molecules diffuse through the membrane in both directions.*

Cellulose dialysis tubing (such as catalog number 3787 from A. H. Thomas Co.) has 1–5 nm pores. Pour some of the brown-red colloidal Fe solution into a dialysis tube knotted at one end; then tie off the other end. Drop the tube into a flask of distilled water to show that the color remains entirely within the bag even after several days (Color Plates 2band 2c). For comparison, leave an identical bag containing a dark blue solution of 1M $CuSO_4.5H_2O$ in another flask. Cu^{2+} diffuses out of the bag, and the solution in the flask becomes light blue in 24 h. Alternatively, the yellow food coloring, tartrazine, can be used in place of Cu^{2+}. If dialysis is conducted in hot water, it is completed in one class period.

Dialysis is used to treat patients suffering from kidney failure. Blood is run over a dialysis membrane having a very large surface area. Small metabolic waste products in the blood diffuse across the membrane and are diluted into a large volume of liquid going out as waste. Large proteins, which are a necessary part of the blood plasma, cannot cross the membrane and are retained in the blood

To summary ,

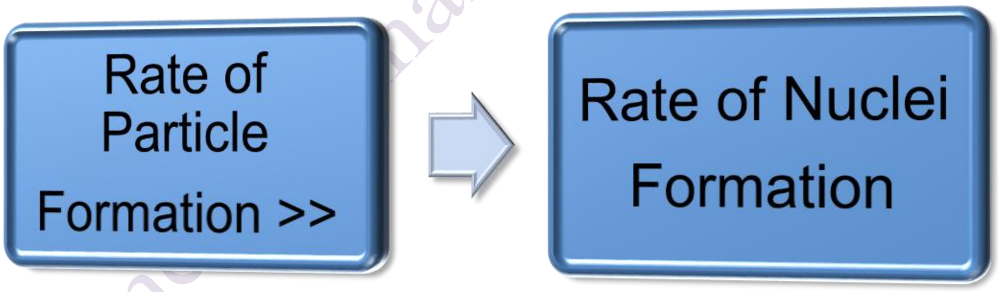
If



More number of nuclei formed.

- Smaller particle produced.
- Colloidal PPT formed (10^{-7}– 10^{-4} cm).
- Adsorbs impurity.
- Increased chance of imperfection in the crystal & surface area of precipitate increase this leads to easy trapping of impurities.
- Not easily filterable, do not settle.

If



- Coarse PPT formed.
- Particle diameter >10^{-3}cm).
- Easily filterable.

For a colloidal precipitate, where the rate of nuclei formation is bigger than the rate of particle formation, electrovalent particles can be attract common ions then surrounded by double layers as mention next:

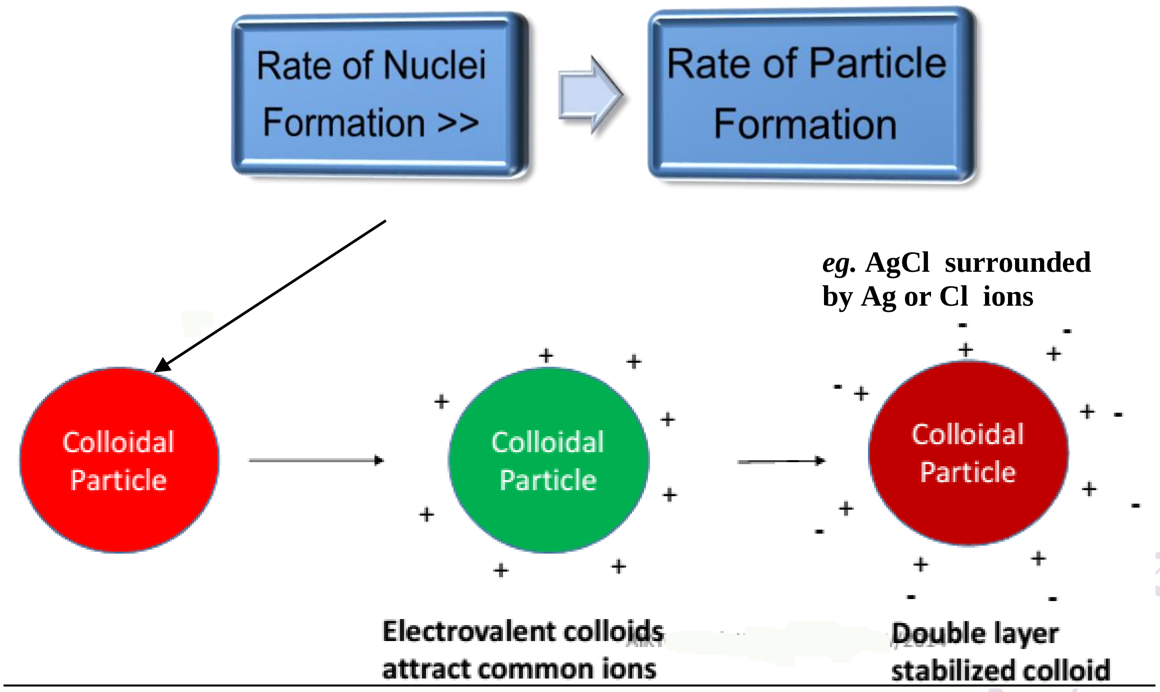


Fig.10: *Charging colloidal particles.*

- Solution to colloid formation:

1. Neutralize electrical double.
2. Remove adsorbed ions by heating/stirring.
3. Process called **<u>coagulation</u>** or **agglomeration.**

Relationship between particle sizes & supersaturation

Von weimarn – discovered that

Particle size of precipitate is <u>inversely proportional</u> to the relative super-saturation of the solution during the precipitation process

(Von weimarn ratio) Relative supersaturation = (Q-S) /S

☐ Q- concentration of mixed reagents before precipitation occurs(Degree of upersaturation)

☐ S- solubility of precipitate at equilibrium

☐ So in order to get particle growth instead of further nucleation we need to make the relative supersaturation ratio as small as possible

Relative supersaturation can affect nucleation size and number.

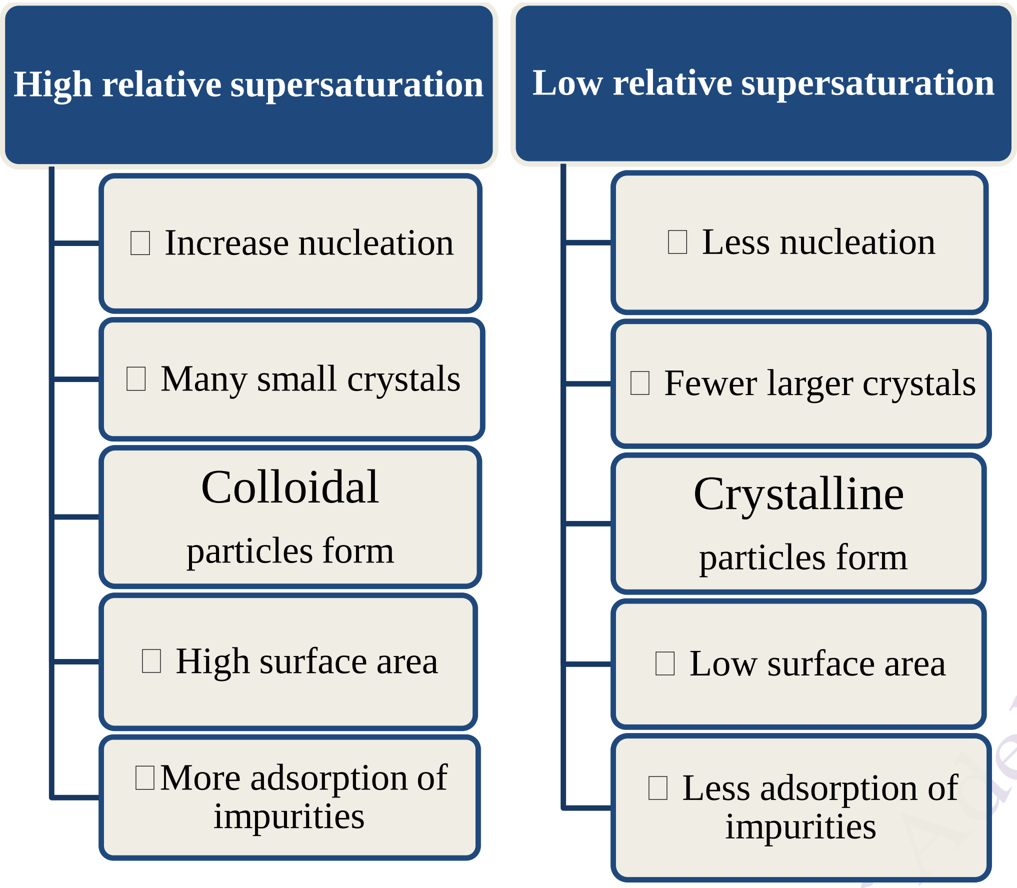


Fig.11: *Scheme represents relationship between supersaturation & nucleation.*

Impurities in Precipitates

No discussion of gravimetric analysis would be complete without some discussion of the impurities which may be present in the precipitates.

There are two typs of impurities:

a. Coprecipitation

This is anything unwanted which precipitates with the analyte during precipitation . Coprecipitation occurs to some degree in every gravimetric analysis (especially barium sulfate and those involving hydrous oxides). You cannot avoid it all what you can do is minimize it by careful precipitation and thorough washing:

1- Surface adsorption

Here unwanted material is adsorbed onto the surface of the precipitate. Digestion of a precipitate reduces the amount of surface area and hence the area available for surface adsorption. Washing can also remove surface material.

2- Occlusion

This is a type of coprecipitation in which impurities are trapped within the growing crystal.

And can be reduced by digestion and reprecipitation.

b. Postprecipitation

Sometimes a precipitate standing in contact with the mother liquor becomes contaminated by the precipitation of an impurity on top of the desired precipitate. To reduce postprecipitation filter as soon as the precipitation is complete and avoid digestion.

Precipitating Agents (Precipitation Reagents):

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 analyte to give a precipitate that has the preferred requirements which have been previously discussed.

Inorganic precipitating agents:

The inorganic precipitants e.g. S^{2-}, CO_3^{2-}, PO_4^{3-}…etc are usually not selective compared to the organic precipitants but it give precipitates with well known formula.

Organic precipitating agents:

Mostly precipitation reagents are organic. The organic precipitants such as dimethglyoxime and 8-hydroxyquinoline are more selective than inorganic precipitants. They produce with the analyte less soluble precipitate (small Ksp). They also have high molecular weight so that the weighing error is redued . The disadvantage of organic precipitants is that they usually form with the analyte a precipitate of unknown formula , therefore the precipitate is burned to the metal oxide.

Advantages of organic reagents

- PPT products sparingly soluble
- Colored
- High molecular masses, so more ppt

Solutions to problems in gravimetry

Process carried out in dilute solution

- Reagents mixed slowly with constant stirring
- PPT carried in hot solutions if stability permits

Advantages of heating:

- Solubility increased, reduction in degree of supersaturation
- Coagulation occurs
- Velocity of crystallization increased
- Crystalline ppt digested as long as possible
- Ppt should be washed with dilute solution of electrolyte

- If contamination high, re-dissolve in appropriate solvent & then rePPT for purity.

Digestion of precipitate

Digestion is a process keeping the precipitate within the mother liquor (or solution from which it precipitated) for a certain period of time to encourage densification of nuclei.

- During digestion, small particles dissolve and larger ones grow (Ostwald ripening).
- This process helps produce larger crystals that are more easily filtered from solution

Ostwald ripening improves the purity and crystallinity of the precipitate

7- Calculation of Results from Gravimetric Data:

The results of a gravimetric analysis are generally computed from two experimental measurements: the weight of sample and the weight of a known composition precipitate .The precipitate we weigh is usually in a different form than the analyte whose weight we wish to find . The principles of converting the weight of one substance to that of another depend on using the stoichiometric mole relationships. We introduced the **gravimetric factor (GF)**, which 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, that is,

$$GF = \frac{mw\ of\ analyte\ (g/mole)}{mw\ of\ precipitate\ (g/mole)}\ X\ R = \frac{g\ analyte}{g\ precipitate} \longrightarrow \quad (7)$$

Where R is the number of moles of analyte in one mole of precipitate.

TABLE 1. Examples of GF.

Analyte	ppt	GF
CaO	$CaCO_3$	$CaO/CaCO_3$
FeS	$BaSO_4$	$FeS/BaSO_4$
$UO_2(NO_3)_2$	U_3O_8	$3UO_2(NO_3)_2/U_3O_8$
Cr_2O_3	Ag_2CrO_4	$Cr_2O_3/2Ag_2CrO_4$

In gravimetric analysis, we are generally interested in the percent composition by weight of the analyte in the sample, that is,

$$\%\ analyte = \frac{weight\ of\ analyte\ (g)}{weight\ of\ sample\ (g)}\ X\ 100 \longrightarrow \quad (8)$$

We obtain the weight of analyte from the weight of the precipitate and the corresponding weight/mole relationship.

$$Weight\ of\ analyte\,(g) = weight\ of\ precipitate\ \ (g)\ X\ GF \longrightarrow \quad (9)$$

We can write a general formula for calculating the percentage composition of the analyte:

$$\%\ analyte = \frac{weight\ of\ precipitate\,(g)\ X\ GF\ (\ g\ analyte\,/\ g\ precipitate\,)}{weight\ of\ sample\,(g)}\ X\,100 \longrightarrow \quad (10)$$

Evaluation of Gravimetric Analysis

Gravimetric analysis, if methods are followed carefully, provides for exceedingly precise analysis. In fact, gravimetric analysis was used to determine the atomic masses of many elements to six figure accuracy. Gravimetry provides very little room for instrumental error and does not require a series of standards for calculation of an unknown. Also, methods often do not require expensive equipment. Gravimetric analysis, due to its high degree of accuracy, when performed correctly, can also be used to calibrate other instruments in place of reference standards . However , the long time needed for the analysis makes it tedious and time consuming for this reason, the volumetric analysis starts to overshadow gravimetry that is why we did not discuss gravimetry in more details. Gravimetric methods have been developed for most inorganic anions and cations, as well as for such neutral species as water, sulfurdioxide, carbon dioxide, and iodine. A variety of organic substances can also be easily determined gravimetrically.

Examples include lactose in milk products, salkylates in drug preparations, phenolphthalein in laxatives, nicotine in pesticides, cholesterol in cereals, and benzaldehyde in almond extracts.

Advantages & Disadvantages of Gravimetric Analysis

Advantages

- Extensive numbers of inorganic ions are determined with excellent precision and accuracy.
- Routine assays of metallurgical samples
- Relative precision 0.1 to 1%
- Good accuracy, relatively in-expensive

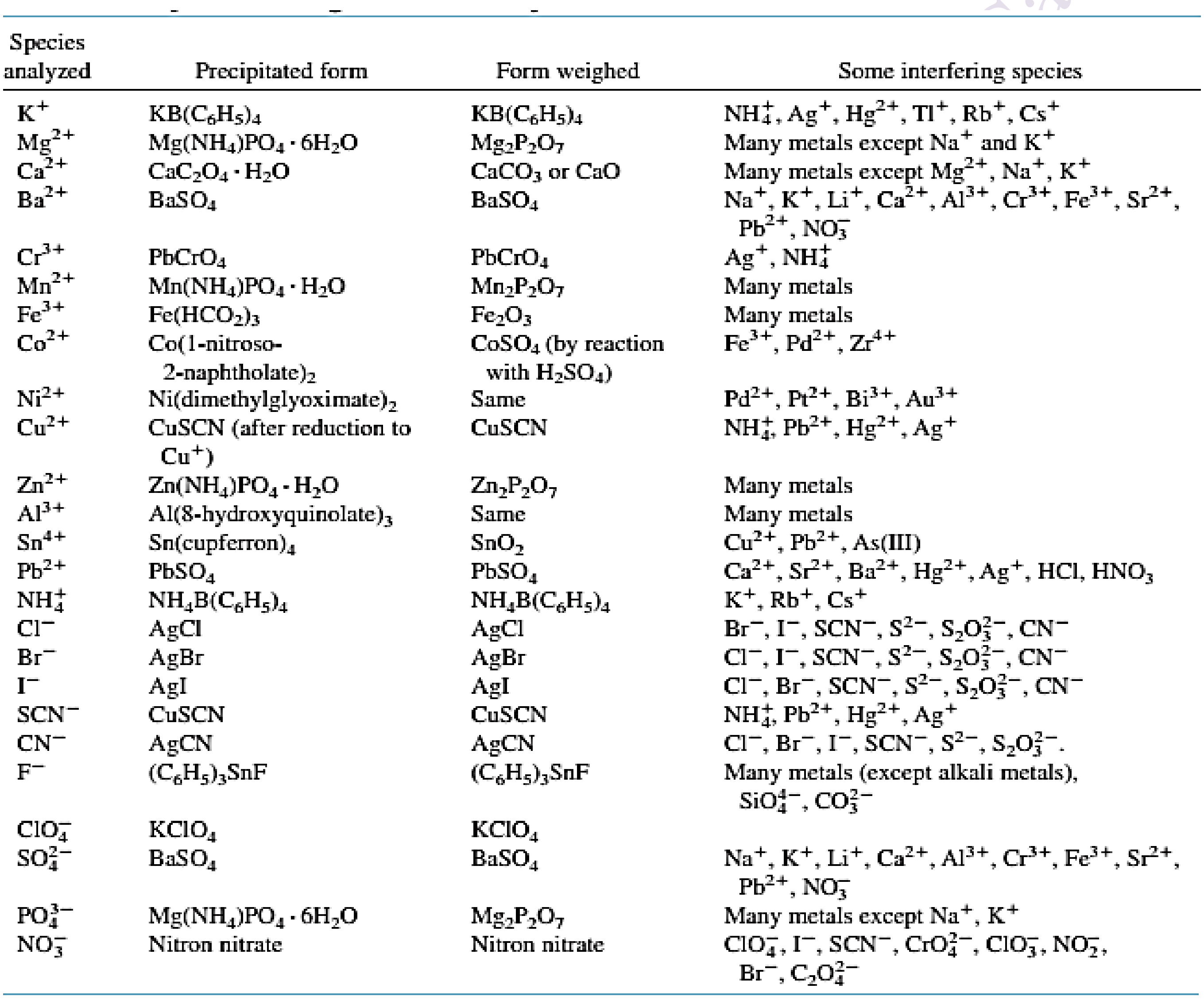
Disadvantages

- Careful and time consuming
- Scrupulously clean glassware
- Very accurate weighing
- Co-precipitation.

Applications

Representative analytical precipitations are listed in Table 2. Conditions must be controlled to selectively precipitate one species. Potentially interfering substances may need to be removed prior to analysis.

TABLE 2. Representative gravimetric analyse.



Species analyzed	Precipitated form	Form weighed	Some 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^-
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)$_2$	$CoSO_4$ (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 (after reduction to Cu^+)	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
Zn^{2+}	$Zn(NH_4)PO_4 \cdot H_2O$	$Zn_2P_2O_7$	Many metals
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^-, $C_2O_4^{2-}$

Assay of Nickel by Dimethylglyoximate (DMG):

Equation: $Ni^{2+} + 2H_2DMG \rightarrow Ni(HDMG)_{2\,(s)} + 2H^+$ ⟶ (11)

1. DMG insoluble in water, added as 1% solution in 90% ethanol.
2. 1 ml ppt 0.0025g of nickel.
3. Reagent added to hot acidic solution of nickel salt.
4. Only slight excess of reagent should be used.
5. PPT (Fig. 12) washed with cold water, dried at 110-120 ^{0}C.

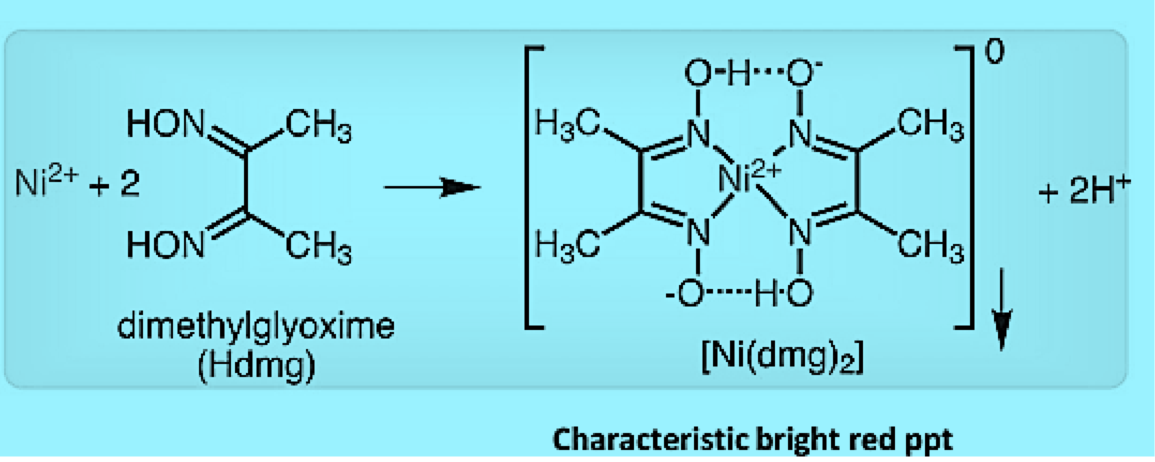


Fig. 12: The reaction between Ni ion and Hdmg.

Assay of Aluminium by Oxine (8-hydroxyquinoline):

Equation: 3 oxine + $Al^{+3} \rightarrow$ Al-oxinate $_{(s)}$ → (12)

- Separates Al from beryllium & other earth metals.
- 2 or 5 % solution of oxine in 2M ethanoic acid.
- 1 ml sol can ppt 3 mg of aluminium.

Procedure

1. Dissolve 0.4 g of Al ammonium sulphate in 100 ml of water.
2. Heat to 70 – 80 ^{0}C.
3. Add appropriate volume of oxime reagent.
4. Keep adding reagent to ensure complete ppt.
5. Allow to cool, collect Al-oxinate.
6. Wash with water, dry to constant weight at 110 ^{0}C

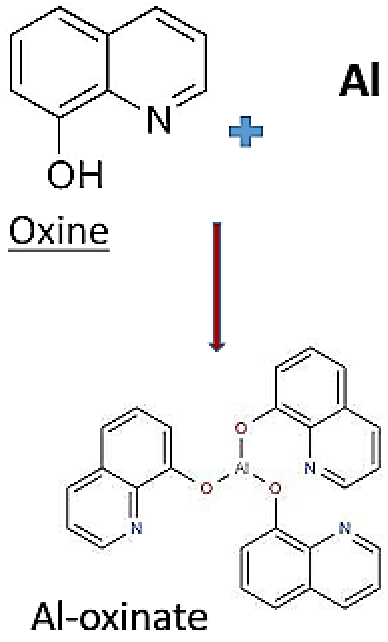


Fig. 13: Al/oxine reaction.

Assay of Barium as Barium sulphate:

Equation: $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_{4\,(s)}$ → (13)

- Slow addition of dilute solution of $BaCl_2$ to hot solution of sulphate.
- Acidic solution prevent other salts formation (Chromate, carbonate, phosphate)
- Process carried out at boiling temp for lower supersaturated.
- Ba has strong tendency to carry down other salts.
- Barium chloride, Barium nitrate are co-precipitated.
- Nitrate can be converted to oxide by ignition.
- Slow addition of Ba to SO_4 solution lowers formation of $BaCl_2$.

Solubility and Solubility Product

Solubility is the maximum amount of the substance, which will dissolve at a given temperature (at this point the solution is saturated).
A saturated solution is a solution in which dynamic equilibrium exists between undissolved and the dissolved solute.

- Unsaturated solution??
- Super saturated solution??

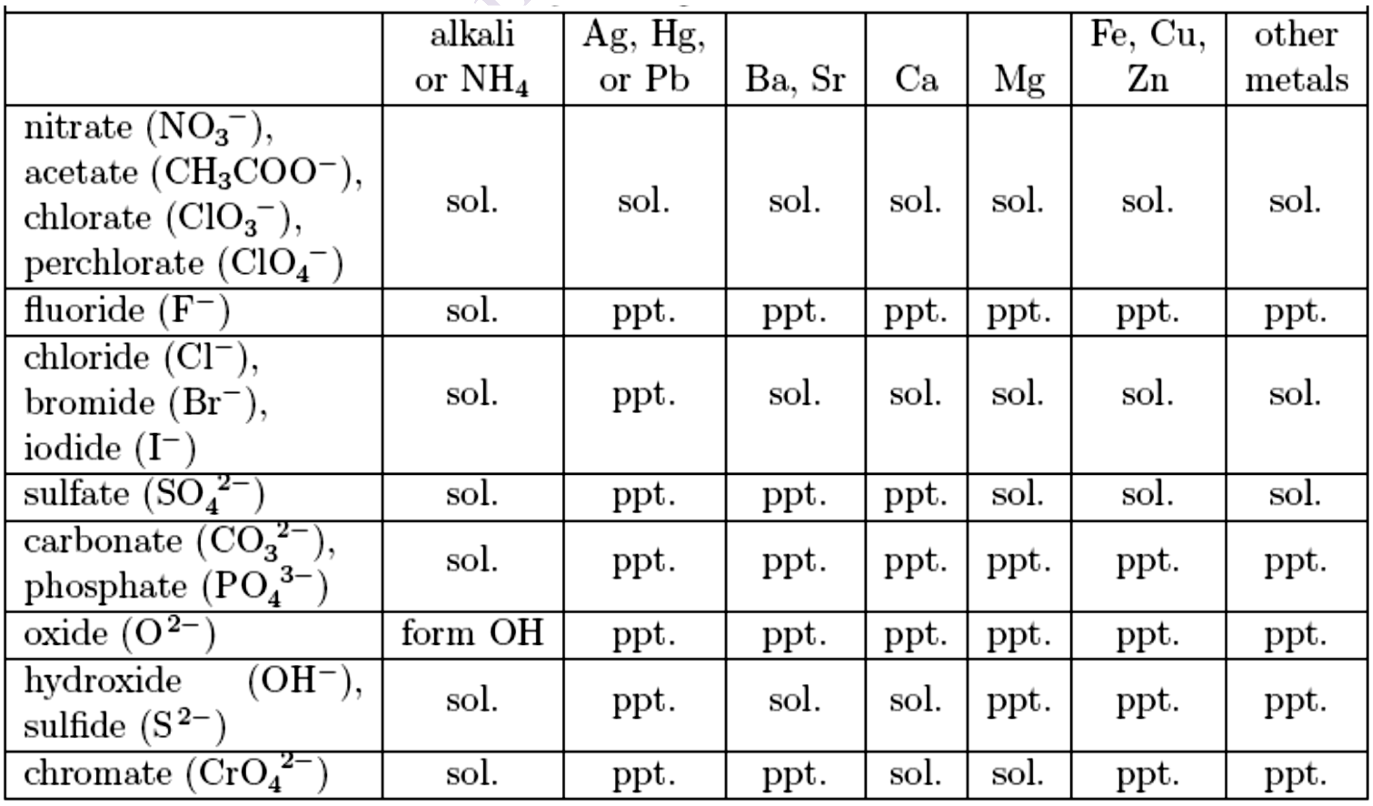
A substance is considered soluble if it will form a solution of concentration.at least 0.1 moles per litre at room temperature otherwise it is insoluble.

►Solubility Rules for Aqueous Solutions:

Compounds that are Soluble in Water
1. All common salts of the alkali metals (Group IA/1) or ammonium ($NH_4{}^+$) are soluble.
2. All common acetates (CH_3COO^-) and nitrates ($NO_3{}^-$) are soluble.
3. All binary compounds of a metal plus a halogen (Group VIIA/17) are soluble except for fluorides (F^-) and compounds containing silver (Ag), mercury (Hg), or lead (Pb).
4. All sulfates ($SO_4{}^{-2}$) are soluble except for those of barium (Ba), strontium (Sr), lead (Pb), calcium (Ca), silver (Ag), or mercury (Hg).

Compounds that are Insoluble in Water
1. All carbonates ($CO_3{}^{-2}$), phosphates ($PO_4{}^{-3}$), and oxides are insoluble except for alkalis (soluble compoounds rule #1).
2. All hydroxides (OH^-) and sulfides are insoluble except for alkalis (soluble compounds rule #1) and compounds containing calcium (Ca), strontium (Sr), or barium (Ba).
3. All chromates ($CrO_4{}^{-2}$) are insoluble except for alkalis (soluble compounds rule #1) and compounds containing calcium (Ca) or magnesium (Mg).

TABLE 3. Solubility of aqueous solutions.



	alkali or NH_4	Ag, Hg, or Pb	Ba, Sr	Ca	Mg	Fe, Cu, Zn	other metals
nitrate ($NO_3{}^-$), acetate (CH_3COO^-), chlorate ($ClO_3{}^-$), perchlorate ($ClO_4{}^-$)	sol.	sol.	sol.	sol.	sol.	sol.	sol.
fluoride (F^-)	sol.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
chloride (Cl^-), bromide (Br^-), iodide (I^-)	sol.	ppt.	sol.	sol.	sol.	sol.	sol.
sulfate ($SO_4{}^{2-}$)	sol.	ppt.	ppt.	ppt.	sol.	sol.	sol.
carbonate ($CO_3{}^{2-}$), phosphate ($PO_4{}^{3-}$)	sol.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
oxide (O^{2-})	form OH	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
hydroxide (OH^-), sulfide (S^{2-})	sol.	ppt.	sol.	sol.	ppt.	ppt.	ppt.
chromate ($CrO_4{}^{2-}$)	sol.	ppt.	ppt.	sol.	sol.	ppt.	ppt.

"Sol." means that more than 3 g of the substance dissolves in 100mL of water. "Ppt." indicates that the combination forms a precipitate.

General Solubility Rule

A low value of Ksp means the concentrations of ions are low at equilibrium. Hence the solubility must be low.

Solubility Product:

When a solid electrolyte is in a state of equilibrium with a saturated solution the concentration of a solid is a constant.

This new constant, equal to the products of the concentrations of all the ions present is called SOLUBILITY PRODUCT CONSTANT **(Ksp)**.

Calculating Ksp from Solubility:

Example1: Copper (I) Bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C. Calculate its Ksp value

Solution

$$CuBr\ (s) \leftrightarrow Cu^{+}_{(aq)} + Br^{-}_{(aq)}$$

$$Ksp = [Cu^{+}][Br^{-}]$$

$$[CuBr] = [Cu^{+}] = [Br^{-}]$$

$$[Cu+] = [Br-]$$

$$Ksp = (2.0 \times 10^{-4})(2.0 \times 10^{-4})$$

$= 4.0 \times 10^{-8}$ (There is no unit)

Or Set an ICE Table as Follows:

	$CuBr\ (s) \leftrightarrow$	$Cu^{+}_{(aq)}$	$+\ Br^{-}_{(aq)}$
Initial conc.	-	0	0
Change conc.	-	x	x
Equil Conc.	-	x	x

$x = 2.0 \times 10^{-4}$

$x = 2.0 \times 10^{-4}$

$$Ksp = [Cu^{+}_{(aq)}][Br^{-}_{(aq)}]$$

$$=(2.0 \times 10^{-4})(2.0 \times 10^{-4})$$

$$= 4.0 \times 10^{-8}$$

Example 2: Calculate the Ksp value for bismuth sulfide ($Bi_2S_{3(s)}$). Which has solubility of 1.0×10^{-15} mol/L at 25 °C.

Solution:

$$Bi_2S_{3(s)} \leftrightarrow [2Bi^{+3}\ (aq)][3S^{-2}\ _{(aq)}]$$

$$Ksp = [Bi^{3+}]^2[S^{-2}]^3.$$

Since no Bi^{3+} and S^{2-} ions were present in solution before the Bi_2S_3 dissolved,
$[Bi^{3+}]_0 = [S^{2-}]_0 = 0$
Thus the equilibrium concentration is determined by the amount of the salt that dissolved to reach equilibrium, which in this case is 1.0×10^{-15} mol/L

$Ksp = [Bi^{3+}]^2[S^{2-}]^3$
$= (2S)^2(3S)^3$

$=2(1.0 \times 10^{-15})^2 3(1.0 \times 10^{-15})^3$

$= (2.0 \times 10^{-15})^2(3.0 \times 1.0^{-15})^3$

$= 1.1 \times 10^{-73}$

OR Set an ICE table

	$Bi_2S_{3\,(s)} \leftrightarrow$	$2Bi^{3+}_{(aq)}$ +	$3S^{2-}_{(aq)}$
Initial conc.	-	0	0
Change conc.	-	2x	3 x
Equil Conc.	-	2x	3x

$x = 1.0 \times 10^{-15}$
$2x = 2(1.0 \times 10^{-15})$
$= 2.0 \times 10^{-15}$
$3x = 3(1.0 \times 10^{-15})$
3.0×1.0^{-15}
$Ksp = [Bi^{3+}{}_{(aq)}]^2[S^{2-}{}_{(aq)}]^3$

$=(2.0 \times 10^{-15})^2(3.0 \times 10^{-15})^3$

$= (4.0 \times 10^{-30})(2.7 \times 10^{-44})$

$= 1.1 \times 10^{-73}$

Calculating Solubility (s) from Ksp

When an ionic substance dissolves in water to form a saturated solution, equilibrium is created between the solid and its constituent ions.

- The concentration of the saturated solution is known as the SOLUBILITY OF THE SUBSTANCE

Example 3:
Calculate the solubility of zinc hydroxide at 25°C. The K_{sp} of zinc hydroxide(s) is 4.5×10^{-17} at 25°C

Solution:

$Zn(OH)_{2(s)} \leftrightarrow Zn^{2+}{}_{(aq)} + 2(OH)^-{}_{(aq)}$

$[Zn(OH)_{2(aq)}] = [Zn^{2+}{}_{(aq)}]$

The equilibrium expression is

$Ksp = [Zn^{2+}_{(aq)}][OH_{(aq)}]^2 = 4.5 \times 10^{-17}$

ICE Table

	$Zn(OH)_{2(s)} \leftrightarrow$	$Zn^{2+}_{(aq)}$ +	$2(OH)^-_{(aq)}$
Initial Conc	-	0	0
Change Conc	-	x	2x
Equili Conc.	-	x	2x

$Ksp = [Zn^{2+}_{(aq)}][OH_{(aq)}]^2 = 4.5 \times 10^{-17}$

$[(OH)^-_{(aq)}] = 2[Zn^{2+}_{(aq)}]$

$Ksp = [Zn^{2+}_{(aq)}]\,(2[Zn^{2+}_{(aq)}])^2$

$Ksp = (x)(4x^2)$

$4.5 \times 10^{-17} = (x)(4x^2)$

$4.5 \times 10^{-17} = (4x^3)$

$$x^3 = \frac{4.5 \times 10^{-17}}{4}$$

$$\mathbf{x} = \sqrt[3]{\frac{4.5 \times 10^{-17}}{4}}$$

$[Zn^{2+}_{(aq)}] = 2.24 \times 10^{-6}$

$[Zn(OH)_{2(aq)}] = [Zn^{2+}_{(aq)}] = 2.24 \times 10^{-6}$

Predicting Precipitation

Recall the use of the value of reaction quotient, Q, to determine the direction of equilibrium in a system.
It can also be used to predict whether a precipitate will form or not when we mix solutions. The reaction quotient is called a trial ion product in this case. We compare the Ksp of the salt of these ions to Q (trial ion product).
If Q is higher than Ksp, a precipitate will form, and if Q is smaller than Ksp, a precipitate will not form. Also, if Q is equal to Ksp, a precipitate will not form.

Example 4:
Predict whether a precipitate will form if 25.0 mL of 0.010 mol/L silver nitrate is mixed with 25.0 mL of 0.0050 mol/L potassium chloride
$AgNO_{3(aq)} + KCl_{(aq)} \rightarrow AgCl_{(s)} + KNO_{3(aq)}$

Solution:
This is a double displacement reaction. From above, AgCl(s) is relatively insoluble. But is the concentration of Ag^+ and Cl^- high enough to form a precipitate?
$AgNO_{3(aq)} \leftrightarrow Ag^+_{(aq)} + NO_3^-{}_{(aq)}$
$[Ag^+_{(aq)}] = [NO_3^-{}_{(aq)}] = 0.010$ mol/L (before mixing)

$KCl_{(aq)} \leftrightarrow K^+_{(aq)} + Cl^-_{(aq)}$

$[Cl^-_{(aq)}] = [KCl\ (aq)] = 0.0050\ mol/L$ (before mixing)

$[Ag^+_{\ (aq)}] = 0.010\ mol/L \times \frac{25\ mL}{50.0\ mL} = 5 \times 10^{-3}\ mol/L$ (after mixing-dillution rule)

$[Cl^-_{(aq)}] = 0.0050\ mol/L \times \frac{25\ mL}{50.0\ mL} = 2.5 \times 10^{-3}\ mol/L$ (after mixing)

Then Calculate Q for AgCl(s) Ksp = 1.8×10^{-10}

$AgCl(s) \leftrightarrow Ag+\ (aq) + Cl^-\ (aq)$

$Q = [Ag^+_{\ (aq)}][Cl^-_{\ (aq)}]$

$(5 \times 10^{-3})(2.5 \times 10^{-3}) = 1.25 \times 10^{-5}$

Since Q is higher Ksp, a precipitate will form.

Gravimetric Factor (GF):

The stoichiometric ratio between the analyte and the solid weighed in a gravimetric analysis.

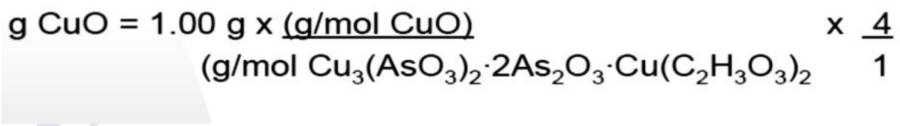
Gravimetric Factor Calculations

Example 5:

If you have a 1.00 g of $Cu_3(AsO_3)_2{\cdot}2As_2O_3{\cdot}Cu(C_2H_3O_3)_2$

☐How many grams of CuO produced from above sample?

A brief soultion:



$$g\ CuO = 1.00\ g \times \frac{(g/mol\ CuO)}{(g/mol\ Cu_3(AsO_3)_2{\cdot}2As_2O_3{\cdot}Cu(C_2H_3O_3)_2} \times \frac{4}{1}$$

Some Concepts, Separating Mixtures Techniques & Processes Used in Gravimetric Analysis

Mixtures (Table 4) can be true solution, colloidal solution or suspension.

TABLE 4. Mixtures types.

True Solution	Colloidal Solution	Suspension
(1) Particle size < 10 Â (<1 nm)	(1) Particle size 10 Â -1000 Â (1 nm-100nm)	(1) Particle size > 1000 Â (> 100 nm)
(2) Pass through filter paper as well as animal membrane.	(2) Pass through filter paper but not throught animal membrane.	(2) Pass throught nethier the two.
(3) Do not settle.	(3) Do not settle.	(3) Settle on standing.
(4) Particles are invisible.	(4) Particles scatter light.	(4) Particles are visible.
(5) Diffuse quickly.	(5) Diffuse slowly.	(5) Do not diffuse.
(6) Clear and transparent.	(6) Translucent.	(6) Opaque.

Colloids Types

Colloids are divided into two main groups, designated as lyophobic and lyophilic colloids. The chief properties of each class are summarized in Table 5, although it must be emphasized that the distinction is not an absolute one, since some gelatinous precipitates (e.g. aluminium hydroxide and other metallic hydroxides) have properties intermediate between those of lyophobic and lyophilic colloids.

TABLE 5. Colloids main groups.

Lyophobic Colloids	Lyophilic Colloids
(1) The dispersion (or sols) are only slightly viscous. Examples: sols of metals, silver halides, metallic sulphides, etc.	(1) The dispersions are very viscous; they set to jelly-like masses known as gels. Examples: sols of silicic acid, tin(IV) oxide. gelatin.
(2) A comparatively minute concentration of an electrolyte results in flocculation. The change is, in general, irreversible; water has no effect upon the flocculated solid.	(2) Comparatively large concentrations of electrolytes are required to cause precipitation ('salting out'). The change is, in general, reversible, and reversal is effected by the addition of a solvent (water).
(3) Lyophobic colloids, ordinarily, have an electric charge of definite sign, which can be changed only by special methods.	(3) Most lyophilic colloids change their charge readily, e.g. they are positively charged in an acid medium and negatively charged in an alkaline medium.
(4) The ultra-microscope reveals bright particles in vigorous motion (Brownian movement).	(4) Only a diffuse light cone is exhibited under the ultra-microscope.

The Purity of The Precipitate: Co-Preciptation

When a precipitate separates from a solution, it is not always perfectly **pure**: it may contain varying amounts of **impurities** dependent upon the nature of the precipitate and the conditions of precipitation. The **contamination** of the precipitate by substances which are normally soluble in the mother liquor is termed co-precipitation. We must distinguish between two important types of co-precipitation. The first is concerned with **adsorption** at the surface of the particles exposed to the solution, and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles.

With regard to surface **adsorption**, this will, in general, be greatest for gelatinous precipitates and least for those of pronounced macrocrystalline character. Precipitates with ionic lattices appear to conform to the Paneth- Fajans-Hahn adsorption rule, which states that the ion that is most strongly adsorbed by an ionic substance (crystal lattice) is that ion which forms the least soluble salt. Thus on sparingly soluble sulphates, it is found that calcium ions are adsorbed preferentially over magnesium ions because calcium sulphate is less soluble than magnesium sulphate. Also silver iodide adsorbs silver acetate much more strongly than it does silver nitrate under comparable conditions, since the former is the less soluble. The deformability of the adsorbed ions and the electrolytic dissociation of the adsorbed compound also have a considerable influence; the smaller the dissociation of the compound, the greater is the adsorption. Thus hydrogen sulphide, a weak electrolyte, is strongly adsorbed by metallic sulphides.

The second type of co-precipitation may be visualized as occurring during the building up of the precipitate from the primary particles. The latter will be subject to a certain amount of surface adsorption, and during their coalescence the impurities will either be partially eliminated if large single crystals are formed and the process takes place slowly, or, if coalescence is rapid, large crystals composed of loosely bound small crystals may be produced and some of the impurities may be entrained within the walls of the large crystals. If the impurity is isomorphous or forms a solid solution with the precipitate, the amount of co-precipitation may be very large, since there will be no tendency for elimination during the 'ageing' process. The latter actually occurs during the precipitation of barium sulphate in the presence of alkali nitrates; in this particular case X-ray studies have shown that the abnormally large co-precipitation (which may be as high as 3.5 per cent if precipitation occurs in the presence of high concentrations of nitrate) is due to the formation of solid solutions. Fortunately, however, such cases are comparatively rare in analysis.

Appreciable errors may also be introduced by post-precipitation. This is the precipitation which occurs on the surface of the first precipitate after its formation. It occurs with sparingly soluble substances which form supersaturated solutions; they usually have an ion in common with the primary precipitate. Thus in the precipitation of calcium as oxalate in the presence of magnesium, magnesium oxalate separates out gradually upon the calcium oxalate; the longer the precipitate is allowed to stand in contact with the solution, the greater is the error due to this cause. A similar effect is observed in the precipitation of copper or mercury(II) sulphide in 0.3M hydrochloric acid in the presence of zinc ions; zinc sulphide is slowly post-precipitated.

Post-precipitation differs from **co-precipitation** in several respects:

(a) The contamination increases with the time that the precipitate is left in contact with the mother liquor in post-precipitation, but usually decreases in co-precipitation.

(b) With post-precipitation, contamination increases the faster the solution is agitated by either mechanical or thermal means. The reverse is usually true with co-precipitation.

(c) The magnitude of contamination by post-precipitation may be much greater than in co-precipitation.

It is convenient to consider now the influence of digestion. This is usually carried out by allowing the precipitate to stand for 12-24 hours at room temperature, or sometimes by warming the precipitate for some time in contact with the liquid from which it was formed: the object is, of course, to obtain complete precipitation in a form which can be readily filtered. During the process of digestion or of the ageing of precipitates, at least two changes occur. The very small particles, which have a greater solubility than the larger ones, will, after precipitation has occurred, tend to pass into solution, and will ultimately re-deposit upon the larger particles; co-precipitation on the minute particles is thus eliminated and the total co-precipitation on the ultimate precipitate reduced. The rapidly formed crystals are probably of irregular shape and possess a comparatively large surface; upon digestion these tend to become more regular in character and also more dense, thus resulting in a decrease in the area of the surface and a consequent reduction of adsorption. The net result of digestion is usually to reduce the extent of co-precipitation and to increase the size of the particles, rendering filtration easier.

Conditions of Preciptation

No universal rules can be given which are applicable to all cases of precipitation, but, by the intelligent application of the principles enumerated in the foregoing paragraphs, a number of fairly general rules may be stated:

1. Precipitation should be carried out in **dilute solution**, due regard being paid to the solubility of the precipitate, the time required for filtration, and the subsequent operations to be carried out with the filtrate. This will minimize the errors due to **co-precipitation**.
2. The reagents should be mixed slowly and with constant stirring. This will keep the degree of **supersaturation** small and will assist the growth of large crystals. A slight excess of the reagent is all that is generally required; in exceptional cases a large excess may be necessary. In some instances the order of mixing the reagents may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of supersaturation .
3. Precipitation is effected in **hot solutions**, provided the solubility and the stability of the precipitate permit. Either one or both of the solutions should be heated to just below the boiling point or other more favourable temperature.

At the higher temperature:
(a) the solubility is increased with a consequent reduction in the degree of supersaturation,
(b) coagulation is assisted and sol formation decreased, and
(c) the velocity of crystallization is increased, thus leading to better-formed crystals.

4. Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of co-precipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.
5. The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water may tend to cause peptization.
6. If the precipitate is still appreciably contaminated as a result of co- precipitation or other causes, the error may often be reduced by dissolving it in a suitable solvent and then re-precipitating it. The amount of foreign substance present in the second precipitation will be small, and consequently the amount of the entrainment by the precipitate will also be small.

Numerous techniques have been developed to separate mixtures to study components.

Coagulation and **focculation** (Table 6) are two methods to separate out the **suspended particles** in a solution.

TABLE 6. Coagulation *vs.* flocculation.

Coagulation	Flocculation
(1) Coagulation means a process where the dispersed colloidal particles agglomerate	(1) Flocculants facilitate the agglomeration and, therefore, make larger floccules
(2) Coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on dispersed nonsettlable solids such as clay	(2) Flocculation, a gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. The microflocs are

and color-producing organic substances.	brought into contact with each other through the process of slow mixing. Collisions of the micro floe particles cause them to bond to produce larger, visible floes called pinflocs.
(3) Coagulation means a process where the colloidal particles agglomerate. The suspended particles are usually very small in size, and they may have electrical charges on them or between particles. Usually these are negative charges, which cause them to repel each other. Coagulants are used to neutralize these charges. They neutralize the repulsive electrical charges between the small particles by surrounding them. This allows the particles to come together and form larger clumps. Cationic coagulants are largely used for this. After coagulants are added, the mixture should be rapidly mixed in order to disperse the coagulants throughout the liquid. Coagulants can be metallic salts (e.g. alum) or polymers. Polymers can be cationic, anionic or nonionic.	(3) Flocculants are also added to facilitate the settling of very small in size, and they may have electrical charges on suspended particles in a solution. Flocculants facilitate the agglomeration and, therefore, make larger floccules. These tend to settle down due to gravitational force. Flocculants try to bridge the molecules forming clumps. For example, an anionic flocculent will react with a positively charge polymer and will adsorb those particles. This may cause destabilization due to charge neutralization or bridging. In flocculation, flocculants are added slowly and mixed gently. Therefore, small floes can agglomerate into larger particles.
(4) Coagulation refers to clotting of the blood and forming clots or large clumps.(also can refer to sour milk forming curds).	(4) Flocculation refers to the coming together of particles (floe means flake) Sometimes this needs to be observed under a microscope. Flocculation is also used in water purification by putting an alum in to help very tiny particles settle out.

Coagulating value is the minimum amount of electrolyte (in millimoles/litres) needed to coagulate the colloidal solution. Smaller the coagulating or flocculating value of an electrolyte, greater is its coagulating power.

$$\text{Coagulating power } \alpha \ 1 / \text{Flocculating value} \longrightarrow \quad (14)$$

Hardy-Schulz rule Greater the valency of the oppositely charged ions of the electrolyte, more will be its coagulating power, i.e. coagulating power α charge of ion, e.g., for As_2O_3 solution the order is

$$Sn^{4+} > Al^{3+} > Ca^{2+} > Na^{+}$$

Similarly, for TiO_2 sol, the order is $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

Colloidal suspensions can often be **coagulated** by heating, stirring, and adding an electrolyte.

Table 7 shows some differences between coagulation and peptization.

TABLE 7. Coagulation vs. Peptization.

Coagulation	Peptization
(1) Coagulation is a process of agitating together the colloidal particles so as to change them into large sized particles which ultimately settle as precipitate.	(1) Peptization is the process of converting a fresh precipitate into colloidal particles by shaking it wilh the dispersion medium in the presence of a small amount of suitable electrolyte.
(2) Coagulation is carried out by an electrolyte, whose one ion is oppositely charged to one ion of the sol.	(2) Generally electrolyte is added whose one ion is common with one ion of precipitate. The electrolyte used for this purpose is called peptizing agent.
(3) The particles of the sol take up the ions which are oppositely charged and thus get neutralized.	(3) The particles of the precipitate adsorb common ion of the electrolyte. Then they get dispersed due to electrostatic repulsion.
(4) Example: The negatively charged sol As_2S_3, can be coagulated with electrolyte $AlCl_3$.	(4) Example: A precipitate of silver iodide can be peptized by shaking with a dilute solution of silver nitrate or KI.

Sedimentation is a physical water treatment process using gravity to remove suspended solids from water.
Flotation is the separation of the components of crushed ore etc. by their different capacities to float.
Dialysis It is based upon the principle that impurities of **true solutions** can pass through the parchment paper or cellophane membrane while colloidal particles cannot.
In this process, dissolved substances are removed from the colloidal solution by means of **diffusion** through a suitable membrane.

Filtration (Fig. 14) can be used to separate an insoluble substance from a soluble substance.

Decantation is done to separate particulates from a liquid by allowing the solids to settle to the bottom of the mixture and pouring off the particle-free part of the liquid. Another method is to allow two immiscible liquids to separate and the lighter liquid is poured off.

Purification is "the process of making pure, free from anything that debases, pollutes, or contaminates".
Purification (Water) is "Steps taken to eliminate impurities and pollution from water".

Distillation is the process of evaporating a liquid and condensing its vapor usually using steam. The most common method used to obtain essential oils from plants".

- Separate a pure liquid from a solution.

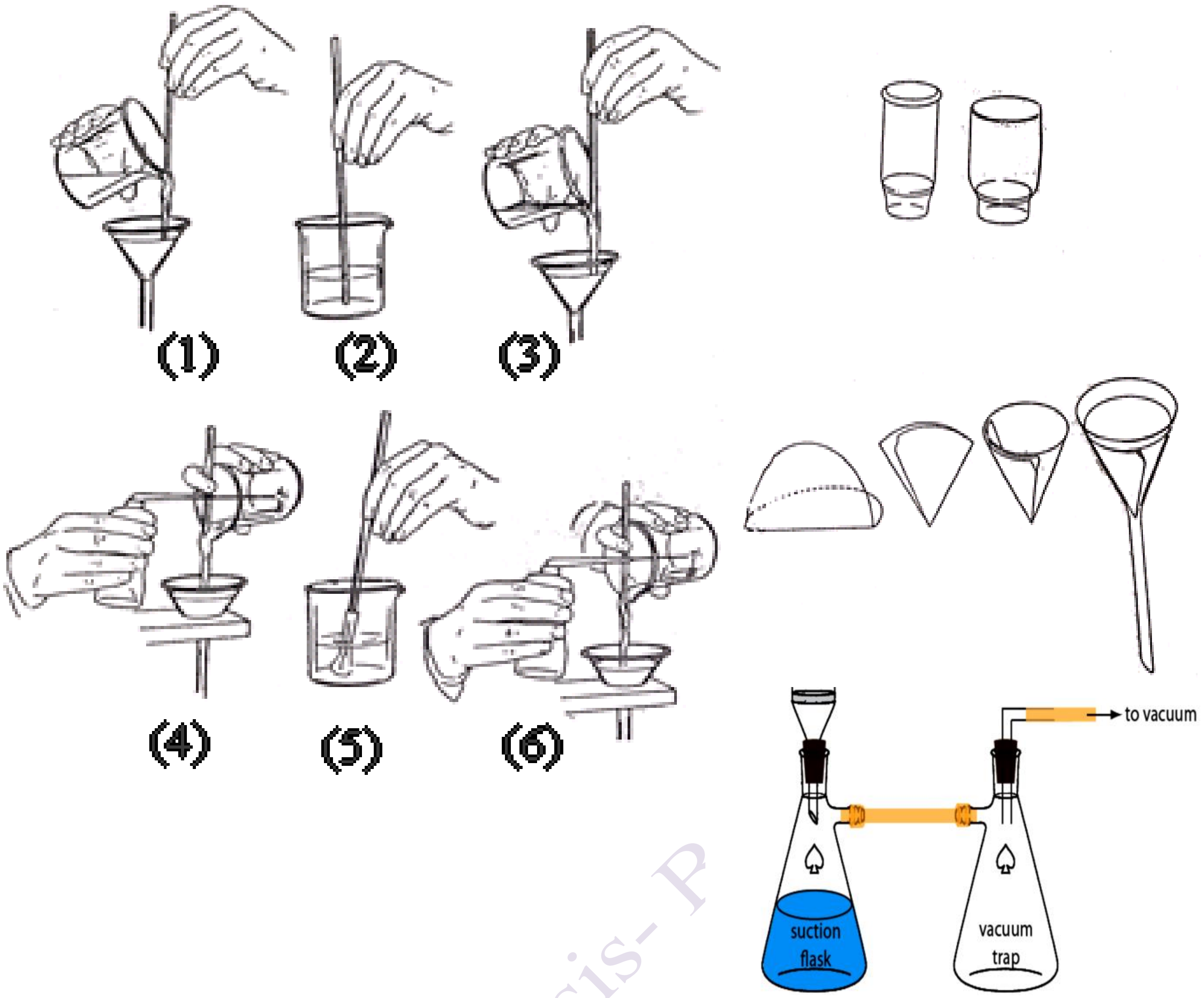


Fig.14: *Filtration processes.*

Chromatography is used to separate components of a mixture based on ability of each component to be drawn across the surface of another material.

Drying & Ignition (Fig. 15**)** is a separation technique that results in the evaporation/taking off water and ignition a filter paper to get **dryied solid.**

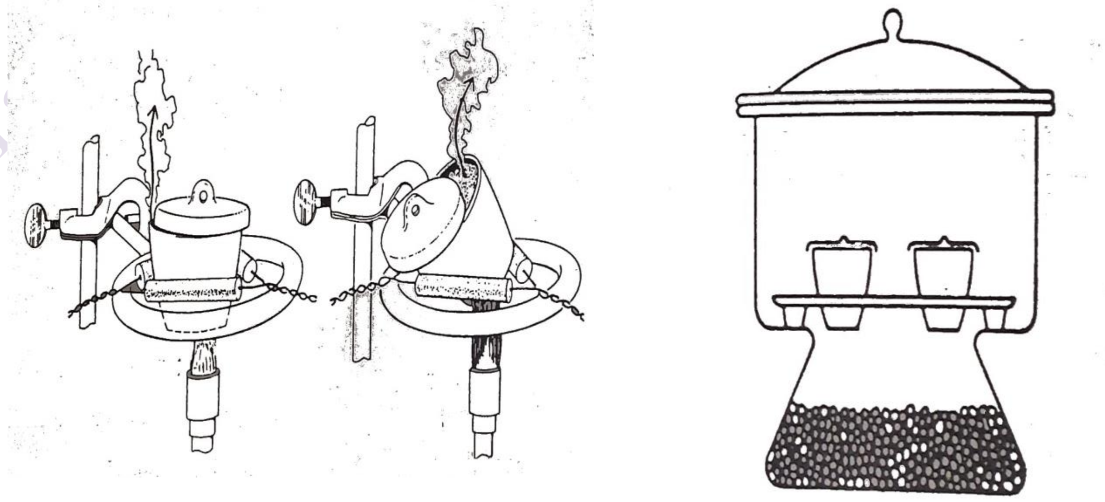


Fig. 15: *(1) Drying & ignition with filter paper, (2) Drying in a desiccator.*

Digestion is a process in which a precipitate is heated in the solution from which it was formed (the mother liquor) and allowed to stand in contact with the solution.
Mother liquor is the solution from which a precipitate was formed.

Crystallization is a separation technique that results in the formation of **high pure solid particles** from a solution containing the dissolved substance.
As one substance evaporates, the dissolved substance comes out of solution and collects as crystals.

Sublimation & Deposition
Figure 16, Sublimation can be used to purify volatile solids. The high vapor pressure of the solid substance causes it to sublime when heated. Crystals of purified substance are formed when the vapor is deposited to form solid on the cooler (upper) portion of the apparatus.

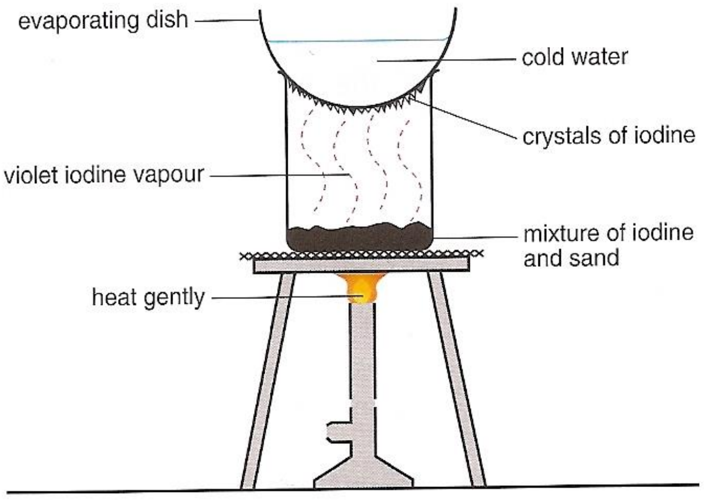


Fig.16: *Sublimation & deposition prosses to purify iodine.*

$$\text{solid} \xrightleftharpoons[\text{deposition}]{\text{sublimation}} \text{gas} \qquad \longrightarrow \tag{15}$$

Extraction (Fig. 17) is a separation method uses solvents called extraction or more specifically liquid-liquid extraction.

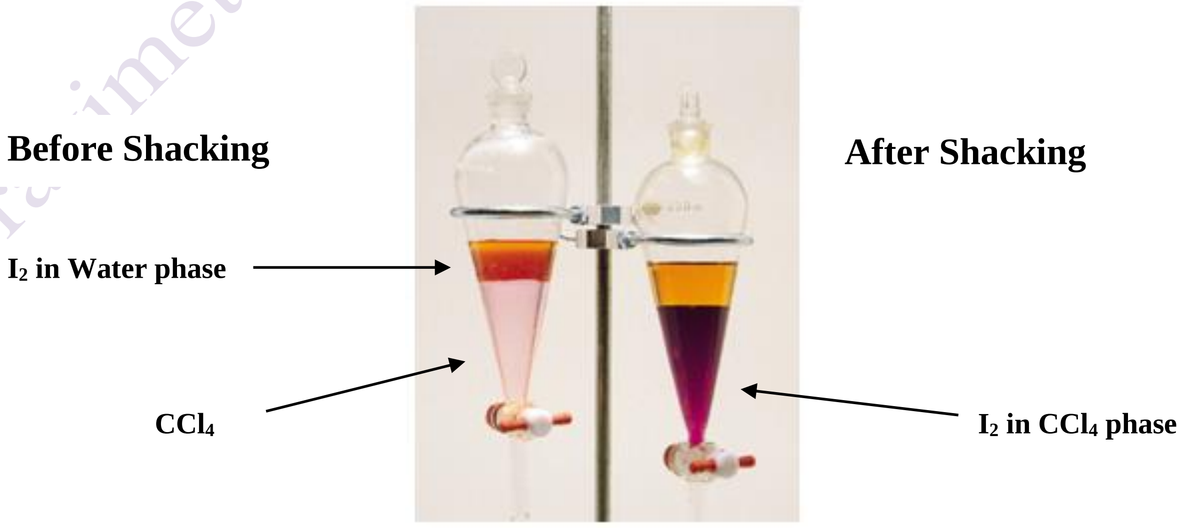


Fig.17: *Extracting I_2 using separatory funnel.*

Centrifuging is a separation technique uses centrifuges rotate containers of liquids to separate suspended materials with different densities.

Magnetization can be used to separate a magnetic substance from a non-magnetic substance by applying a magnetic field.

Sieving: A porous material is used to separate particles of different sizes.
This method is most commonly used to effect gross separations, as of liquids from suspended crystals or other solids.

- to accelerate filtration, pressure usually is applied.
- a series of sieves is stacked, with the screen of largest hole size at the top

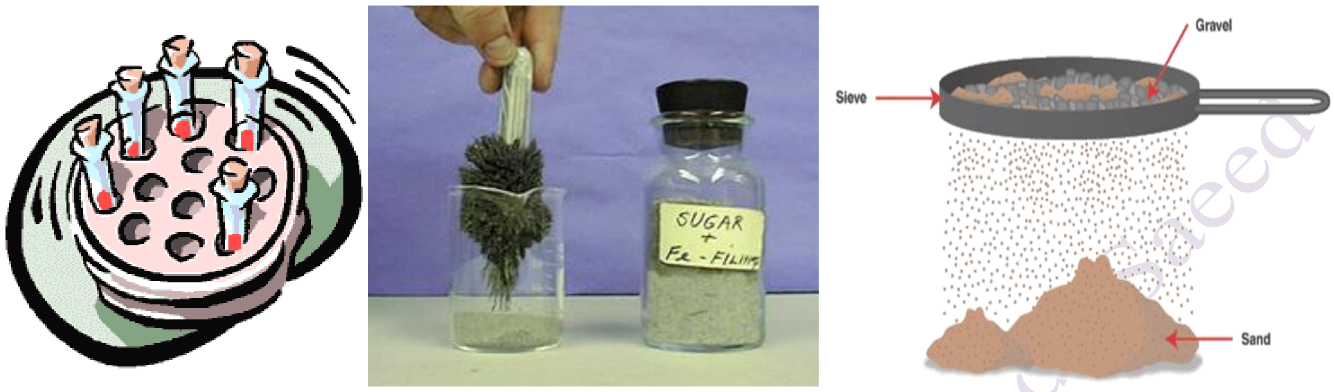


Fig. 18: *Other speration methods from left to right (1) Centrifuging, (2) Using a magnet (3) Sieving.*

Types of Adsorption
In physisorption, adsorbate is held to the adsorbent by weak van der Waals forces, and in chemisorption, adsorbate is held to the adsorbent by strong chemical bond. The chemical bonds may be covalent or ionic in nature and involves a high energy of activation. Almost all solids adsorb gases.

TABLE 8. The differences between physical and chemical adsorption.

Physical adsorption	Chemical adsorption
(1) The forces operating in this case are weak Vander wall's forces.	(1) The forces operating are chemical bonds (ionic or covalent bond).
(2) The heat of adsorption is low about 20- 40 Kj mol^{-1}.	(2) The heat of absorption are high about 40-400 Kj mol^{-1}.
(3) The process is reversible; desorption can be occurring by increasing tern. Or decreasing pressure.	(3) The process is irreversible. Efforts to free the adsorbed gas give different compounds.
(4) It does not require any activation energy.	(4) It requires activation chergy.
(5) It takes place at the low temperature and decreases with increase in the temperature.	(5) This type of adsorption first increases with increase in temperature.
(6) It is not specific in nature all gases adsorbes on all solids to same extent.	(6) It is highly specific in nature occurs only by the possibility of formation of chemical bond.
(7) It increases with the increase insurface area of the adsorbent.	(7) It also increases with the increases with the increase in surface area of adsorbent.
(8) It forms multimolecular layer.	(8) It forms unimolecular layer.

Precipitation from Homogeneous Solution

Precipitation from homogeneous solution is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative supersaturation is kept low during the entire precipitation.

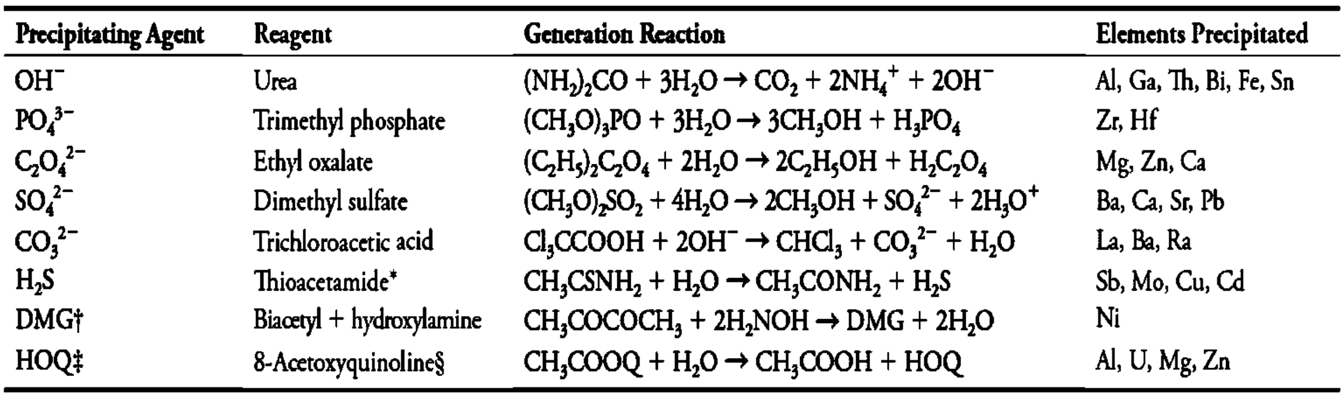
Urea is often used for the homogeneous generation of hydroxide ion. The reaction can be expressed by the equation

$$(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^- \qquad (16)$$

This hydrolysis proceeds slowly at temperatures just below 100°C, with 1 to 2 hours needed to complete a typical precipitation.

Representative methods based on precipitation by homogeneously generated reagents are given in Table 9.

TABLE 9. Methods for homogeneous generation of precipitating agents.



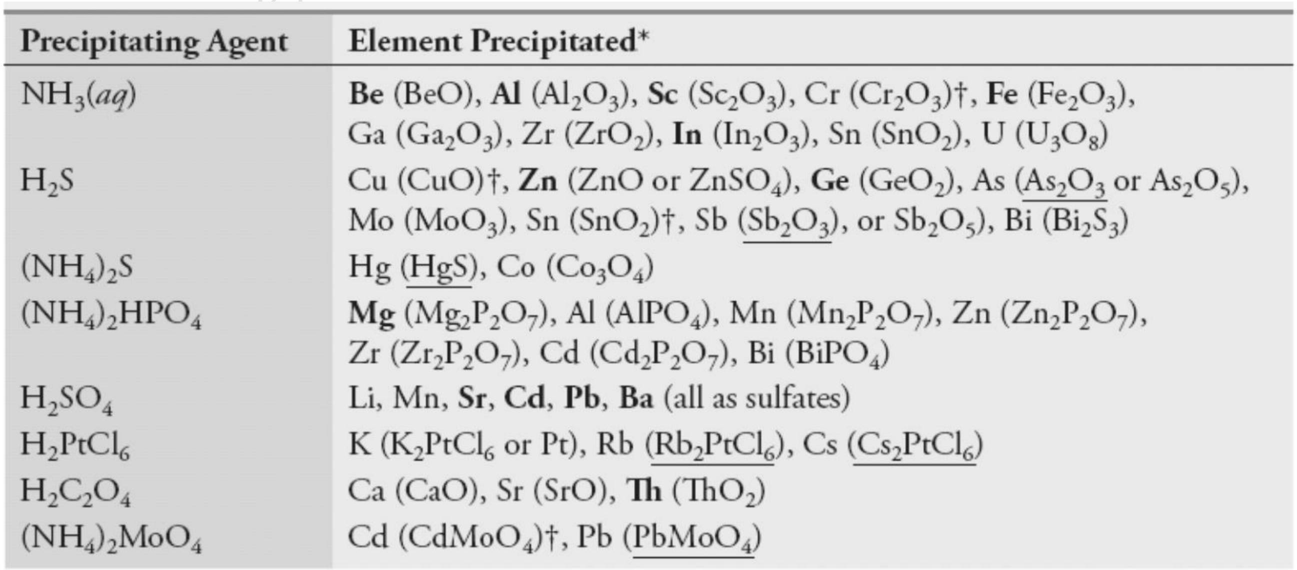
Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

Precipitating Agents:

(1) Inorganic Precipitating Agents

Table 10 lists common inorganic precipitating agents. These reagents typically form slightly soluble salts or hydrous oxides with the analyte. As you can see from the many entries for each reagent, few inorganic reagents are selective.

TABLE 10. Some inorganic precipitating agents.



Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), Cr (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO or $ZnSO_4$), **Ge** (GeO_2), As (As_2O_3 or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (Sb_2O_3), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg (HgS), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr**, **Cd**, **Pb**, **Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 or Pt), Rb (Rb_2PtCl_6), Cs (Cs_2PtCl_6)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($PbMoO_4$)

(2) Reducing Agents

Table 11 lists several reagents that convert an analyte to its elemental form for weighing.

TABLE 11. Some reducing agents used in gravimetric methods.

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

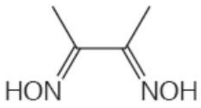
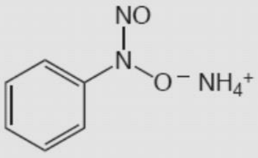
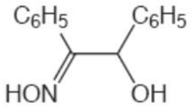
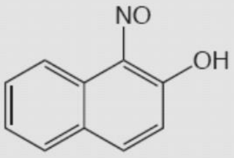
(3) Organic Precipitating Agents

Numerous organic reagents have been developed (Table 12) for the gravimetric determination of inorganic species. Some of these reagents are significantly more selective in their reactions than are most of the inorganic reagents listed in Table 8.

There are two types of organic reagents: one forms slightly soluble nonionic products called **coordination compounds**, and the other forms products in which the bonding between the inorganic species and the reagent is largely ionic.

In coordination compounds, reagents that form compounds of this type are called **chelating agents**, and their products are called **chelates.**

TABLE 12 Some organic precipitating agents.

Analyte	Precipitant	Structure	Precipitate Formed	Precipitate Weighed
Ni^{2+}	dimethylglyoxime		$Ni(C_4H_7O_2N_2)_2$	$Ni(C_4H_7O_2N_2)_2$
Fe^{3+}	cupferron		$Fe(C_6H_5N_2O_2)_3$	Fe_2O_3
Cu^{2+}	cupron		$CuC_{14}H_{11}O_2N$	$CuC_{14}H_{11}O_2N$
Co^{2+}	1-nitrso-2-napthol		$Co(C_{10}H_6O_2N)_3$	Co or $CoSO_4$
K^+	sodium tetraphenylborate	$Na[B(C_6H_5)_4]$	$K[B(C_6H_5)_4$	$K[B(C_6H_5)_4$

Gravimetric Analysis of Silver - Ag – 107.870

Silver is most frequently determined in alloys, and in its halides, the sulphide, telluride, arsenide, antimonide, cyanide or its sulpho salts. Frequently the silver content must be determined in mixtures or solutions of simple or complex salts, technical by-products (precious metal mud, anode mud), and silver-containing wastes (e.g. used fixing salt).

Dissolution of the sample. Metallic silver and its alloys containing less noble metals can be dissolved in moderately concentrated nitric acid (over 5%, best in **1 : 1).** Its alloys with gold or platinum can be dissolved in *aqua regia* (3 vol. of concentrated HCl and **1** vol. of concentrated HNO_3), but by this method most of the silver is precipitated as AgCl, and some remains dissolved in the form of $H[AgC1_2]$. Gold alloys containing more than 75% silver can be dissolved quantitatively with 1:1 HNO_3**.** For the dissolution of silver sulphides, and sulphidic ores, concentrated nitric acid is necessary, but in such a procedure precipitation of elementary sulphur often occurs. If the heating with concentrated nitric acid is continued, however, this sulphur can also be dissolved, or at least can be converted into a clear yellow form, and this ensures that it occludes no more undissolved silver. If the solution is diluted, after the evaporation of the excess nitric acid, silver sulphate precipitates, and this can only be dissolved in large volumes of water. If large amounts of sulphuric acid do not interfere in the subsequent determinations (titration according to Volhard, ascorbometric titration, electrogravimetry), the alloy or sulphidic ore can be dissolved in concentrated sulphuric acid, or in a mixture of concentrated sulphuric acid and nitric acid. Elementary sulphur which separates can be easily oxidized by adding concentrated nitric acid dropwise to the solution, which has previously been evaporated to sulphuric acid fumes.

Ores containing silver sulphide, silver thiocyanate, silver cyanide and silver halides (especially silver iodide) can be fused with a mixture of sulphur and anhydrous sodium carbonate. The sample must be fused with a 6- to 10- fold excess of this mixture in a porcelain crucible, and the silver is converted into silver sulphide which remains behind when the cold smelt is leached. The silver sulphide can then be dissolved by heating with 1:1 nitric acid. Silver halides can also be decomposed by fusion with sodium carbonate, and, after leaching, the residue can be dissolved in nitric acid. The fusion of ores, slags and precious metal residues containing selenide can be carried out with potassium cyanide and sodium carbonate, and the metal bead which remains behind can be dissolved easily in nitric acid. A similar result can be obtained with a mixture of borax and sodium carbonate.

Silver sulphide can be precipitated from solutions containing cyanide, and from used fixing solutions, by heating with sodium sulphide. After filtration the precipitate can be digested with the filter paper in a mixture of concentrated nitric and sulphuric acids. Natural sulphidic silver ores can be decomposed with bromine water or with a 1:1 mixture of bromine water and concentrated hydrochloric acid. Insoluble AgBr remains behind, while sulphur, antimony and arsenic are dissolved by the formation of their corresponding acids. The AgBr, (also AgCl and Ag_2S) can be reduced to metallic silver by heating in a hydrogen atmosphere in a Rose crucible. However, AgI cannot be reduced in this way. By this method silver can also be separated from insoluble material, if, after reduction, it is dissolved in nitric acid. Silver halide precipitates, or melted and cooled silver halides, can be reduced quantitatively to metallic silver with a piece of pure zinc or cadmium in the presence of dilute sulphuric acid.

For the determination of silver, the methods of determination shown in Table 13 can be used.

TABLE 13. Forms of determination of silver.

Ref. number	Form of precipitation	Precipitant	Reaction of the medium	Weighing form	Formula weight	Heat treatment °C
1.	AgCl	HCl (NaCl)	HNO_3	AgCl	143.337	70-455
2.	AgBr	(HBr) KBr NaBr	HNO_3	AgBr	187.796	70-422
3.	Ag	ascorbic acid	HNO_3	Ag	107.870	100-500
4.	Ag	electrolysis	HNO_3 H_2SO_4	Ag	107.870	room temperature

Determination in the form of Silver Chloride, AgCl

This is a very accurate method for the determination of silver, and can generally be used. From an acidic solution, containing nitric acid, silver chloride can be precipitated by the addition of a slight excess of hydrochloric acid:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \qquad \longrightarrow \quad (17)$$

The precipitate must be collected on a filter crucible, dried and weighed. From the *solubility product* of AgCl, ($K_{sp} = [Ag^+].[Cl^-] = 10^{-10}$), it can be calculated that, at 20°C, 1L of pure water dissolves 1.43 mg of silver chloride. At 100°C the solubility increases considerably (21.7 mg of AgCl per liter). The excess hydrochloric acid decreases the solubility by the commonion effect, but with a larger excess of HCl the solubility increases owing to the formation of the $H[AgC1_2]$ complex. At room temperature,

one liter of 1 % hydrochloric acid dissolves 0.2 mg of silver chloride
one liter of 5% hydrochloric acid dissolves 3.3 mg of silver chloride
one liter of 10% hydrochloric acid dissolves 55.5 mg of silver chloride

In order to decrease the solubility, hydrochloric acid must be added in excess, but a large excess of it must be avoided. A similar effect of increase in solubility can be experienced with alkali metal chlorides. Electrolytes, which do not react with silver chloride and do not contain ions common to the precipitate, (KNO_3), only effect a slight increase in solubility (foreign-ion effect), and cause no considerable error in ordinary analytical work.

The AgCl precipitate is a coagulated colloid having a microcrystalline structure. Coagulation usually takes place if an equivalent amount of hydrochloric acid is added, and can be helped by the addition of nitric acid, heating and stirring of the solution, or by allowing it to stand. Acidification with nitric acid also has the advantage that it prevents the precipitation of silver salts which are insoluble in a neutral medium (Ag_3PO_4, Ag_2CO_3), and partly represses the cation adsorption on the surface of AgCl colloid particles. If multivalent cations are present which have a strong tendency to adsorption [Al, Fe(III)], a higher concentration of nitric acid than usual must be employed. Under these conditions neither alkali metal nor alkaline earth ions are adsorbed to a measurable extent, even if they are present in excessive concentrations. If washed with water, AgCl is partly peptized and goes through the filter. Peptization can be easily avoided by using water which has been slightly acidified with nitric acid as a washing solution. The residue of nitric acid, which adheres to the surface of the silver chloride, can be easily removed by drying. It is advisable to test whether precipitation is complete by the addition of hydrochloric acid to the mother liquor above the precipitate and the completeness of the washing with silver nitrate in the small sample of the filtrate. Precipitation and washing must be carried out in an atmosphere which is free of hydrogen sulphide, otherwise the precipitate becomes contaminated with silver sulphide.

Because of the *light-sensitive* nature of silver chloride, working in direct sunlight or under strong light must be avoided. The wet precipitate is especially sensitive to light because chlorine is removed from the precipitate on irradiation, the weight of the strongly colored precipitate is less, and thus a negative error is incurred. The error is particularly high if the precipitate is stirred in strong daylight. This error reaches the value ~ 0.2% only when the precipitate is strongly colored. A slight photochemical decomposition, however, causes a relatively strong coloration because the decomposition occurs only in the surface layers. If the precipitate is violet or blue the error can be neglected. The error can be overcome, if, after weighing the precipitate, the bulk of it is placed in a porcelain crucible, re-weighed, and the metallic silver dissolved in nitric acid. The nitric acid is evaporated on an air-bath, 1-2 drops of concentrated hydrochloric acid are added, and it is then dried. The weight increase, calculated on the whole weight of the precipitate, yields a correction with which the error-free weight of the precipitate can be determined. The precipitate can be reduced to metallic silver by ignition in a hydrogen atmosphere, and the weight of the metal can be determined as a control.

The *thermal behavior* of the AgCl precipitate (see Figure 19, measurements of F. Paulik) shows that the precipitate, dried at 130- 150ºC, can be regarded as of constant weight. It contains, however, about 0·02% of water, and this can only be removed in the neighbourhood of its melting point (455 °C). According to Duval (1953) the weight of the precipitate when ignited at over 600°C is greater than

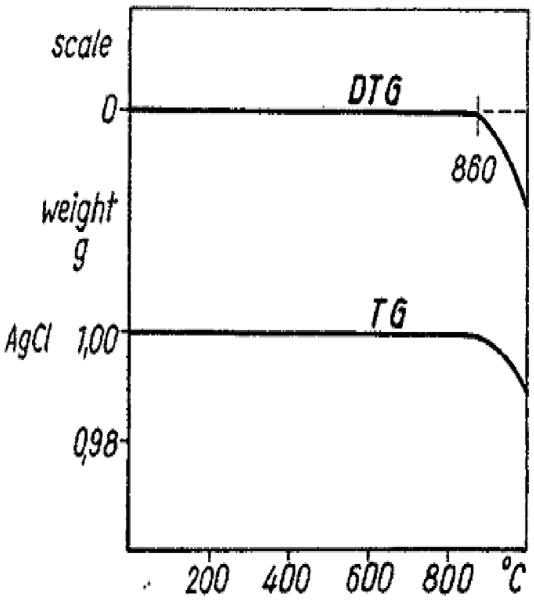


Fig.19.*Thermo analytical curves of silver chloride precipitate heated in air*.

calculated- (about 0.7%). The thermogravimetric TG curve obtained from our measurements does not reveal this weight increase, and therefore this does not always occur. At temperatures above 870°C the AgCl decomposes. The heating of the precipitate at above 150°C is usually inadvisable, because dust grains may reduce it to metallic silver. Ignition at higher temperatures, however, cannot be avoided, if filter crucibles are not used and the precipitate is collected on filter paper. When this method is used it is advisable to dissolve any reduced silver with nitric acid, and to convert it to silver chloride with hydrochloric acid. The silver chloride precipitate should not be washed with alcohol as reduction may occur.

Silver chloride decomposes slowly when heated at over 380°C in reducing gases, e.g. in a hydrogen atmosphere (see Figure 20, measurements of F. Paulik), and at over 880°C only metallic silver remains behind. The decomposition, according to the graph, proceeds in two stages, probably with the intermediate formation of silver subchloride, Ag_2Cl.

The determination of silver as silver chloride is *interfered* with by the following ions: Hg(I), Cu(I), Tl(I), Pb(II) and Pd(II) the chlorides of which are insoluble in dilute nitric acid. Salts of Bi(III), Sb and Sn hydrolyze in dilute acids and therefore may contaminate the precipitate. Cyanide and thiosulphate ions dissolve the silver chloride. These anions, as well as Hg(I) and Cu(I) ions, can be oxidized by evaporation with concentrated nitric acid before precipitation. Thallium(I) chloride is also insoluble in dilute nitric acid, but it can be oxidized to thallium(III) chloride by boiling with aqua reqia, and this is easily soluble in water or in nitric acid. Lead can be easily separated from silver in the form of lead sulphate, but the lead sulphate may be contaminated with considerable amounts of silver sulphate. A more accurate separation can be effected if silver chloride is precipi-tated from a solution containing small amounts of nitric acid and sodium acetate.

Lead chloride, which is also precipitated, can be washed out with hot water which has been acidified slightly with nitric acid until the filtrate no longer gives a positive lead reaction. If small amounts of lead are present, the AgCl precipitate, after washing with hot Ag water, must be dissolved in ammonia and re-precipitated by acidification with nitric acid. It is advisable in this instance, however, to reduce silver with ascorbic acid in the hot solution which contains nitric acid. In the presence of palladium the precipitate must be dissolved in ammonia, the solution filtered, and silver chloride must be re-precipitated from the filtrate with nitric acid. By a similar method silver can be separated from antimony and bismuth. Reduction with ascorbic acid can also be applied in these separations, but tartaric acid must be added to the solution to prevent the hydrolysis of antimony.

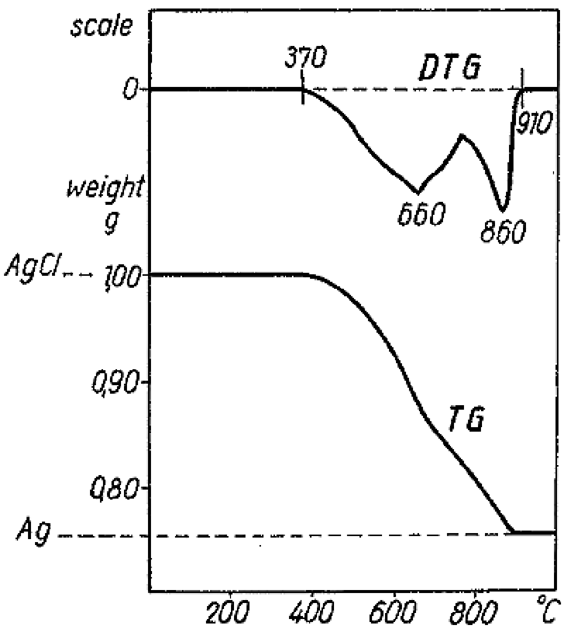


Fig.20.*Thermo analytical curves of silver chloride precipitate heated in hydrogen gas atmosphere.*

Among the anions, those which give insoluble precipitates with silver in an acidic solution will naturally interfere [Br^-,I^-, CNS^-, CN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, S^{2-}, $S_2O_3^-$]. Anions whose silver salts are soluble in slightly acidic media (CO_3^{2-}, PO_4^{3-}, CrO_4^{2-}, $C_2O_4^{2-}$) do not interfere. In the presence of these anions a higher acid-concentration must be used. Silicate ions must be separated previously as silicic acid by evaporation with nitric acid.

The *separation* of silver ions, if mercury(II) and lead ions are absent, can be achieved by the following procedure:

Silver ions must be precipitated as the sulphide, using hydrogen sulphide, from a solution acidified slightly with nitric acid. The filter paper which contains the precipitate must be stretched out on the bottom of a larger beaker, 0.2 g of powdered sulphur and 2-3 g of crystalline sodium sulphide placed on it, and the mixture heated cautiously with a small flame until it melts in the water of crystallization. The melt must then be leached out with water and filtered, the precipitate must be washed with water, and then dissolved in 2-5 ml of concentrated sulphuric and 2-10 ml of concentrated nitric acid. The mixture must then be boiled until sulphuric acid fumes appear, and then concentrated nitric acid added until precipitated sulphur dissolves and the filter paper is digested. After cooling and diluting, silver is then reduced to the metal with ascorbic acid, and can be weighed in this form, or it may be dissolved in nitric acid, converted into AgCI, and weighed in this form.

Procedure. Dilute a nearly neutral solution, containing 0.1-0.6 g of silver, to about 200 ml in a 400-ml beaker, add 5 ml [in the presence of excessive amounts of iron(III) or aluminium, 10-20 ml] of 2 N nitric acid and heat to approximately 70 °C. Remove the source of heat, and add a slight excess of 0•2 N hydrochloric acid dropwise from a pipette, with constant stirring. (For the precipitation of 100 mg of silver, 4.7 ml of 0.2 N hydrochloric acid is sufficient.) Heat and stir the mixture on a water bath away from strong light, until the initially turbid solution becomes clear and the precipitate separates. This occurs more easily when large amounts of precipitate are present, than with small quantities. Place the beaker, covered with a watch glass, in a dark place (e.g. laboratory desk), until the solution has cooled and the solubility equilibrium has been established.

After 4-5 hr the precipitate is usually filterable, but if the solution is turbid even after this time, it must be allowed to stand overnight. The presence of excess precipitant must be tested for once more by dropping 1-2 drops of 0.2 N hydrochloric acid along the wall of the beaker. Any turbidity which is formed can be seen easily in the clear part of the solution.

Filtration can be carried out with (a) G3 or G4 glass filter crucibles, No. 2 porcelain filter crucibles or with a Gooch filter by means of suction in each case; and (b) on filter paper.

(a) The filter crucible or filter funnel must be cleaned thoroughly before use. Approximately 20 ml of 0.2 N nitric acid and at least 50 ml of distilled water should be passed through it, after which it should be dried for 30-45 min at 130°C. Place the filter, in a covered beaker, near to the balance, and weigh after 30 min. Pour first the clear supernatant solution under slight suction.

Wash the precipitate by decantation with a total of 50 ml of cold 0.1 N nitric acid, using small portions, and transfer the precipitate on to the filter with the last portion. Continue the washing with 0.0l N nitric acid, until chloride ions cannot be detected in a small sample of the filtrate with silver nitrate.

Usually 50 ml of 0.01 N nitric acid is enough for the washing of the preci¬pitate. The washing of the precipitate should not be continued for long after the disappearence of the chloride reaction, because the removal of the common ion causes an increase in the solubility of the precipitate in the washing solu¬tion. Particles of precipitate which adhere to the wall of the beaker can be loosened by the use of a rubber-ended glass rod. When the solution is poured on to the filter the suction should be decreased. Finally, wash the internal wall of the filter crucible with 3-5 ml of distilled water added dropwise, and remove the remaining liquid as completely as possible by further suction for 2 min.

Dry the filter crucible for 30 min at 100°C and then for 1 hr at 130-150°C. Place the crucible in a small, covered beaker near to the balance and weigh after 30 min. Test for constant weight after further drying for 30 min and then cooling for 30 min.

(b) The precipitate can also be collected on a filter paper. Filter the bulk of the solution on a medium-thick filter paper of 7 cm dia (Schleicher-Schull, white band), transferring the precipitate on to the filter while washing by decanta¬tion. Wash with 50 ml of 0.l N and afterwards with 0.01 N nitric acid, until the chloride test is negative. Place a wet filter paper over the mouth of the funnel and dry in an oven at 100°C for an hour. Remove the filter paper using forceps, pour the bulk of the precipitate on to a black glossy paper, and store it covered with a watch glass. Place the filter paper into a porcelain crucible which has been ignited, cooled and weighed, combust it on a small flame and then ignite the residue at under 445°C (the melting point of silver chloride) When cool, add 1 ml of l : 1 nitric acid to the crucible, and evaporate on an air bath. Repeat the evaporation with 1 ml of 2 N hydrochloric acid. Then, place the crucible on a second piece of black, glossy paper, transfer the bulk of the precipitate back into the crucible, without loss, with a small quill or fine brush and dry at 130-150°C for 1 hr. Place the crucible in a small beaker near to the balance, and weigh after cooling for 30 min.

Stoichiometric factors:

$$\frac{Ag}{AgCl} = 0.75263; \quad \frac{AgNO_3}{AgCl} = 1.1852. \quad \longrightarrow \quad (18)$$

Cleaning of filter crucibles. Most of the precipitate can be removed mechanically. Then pour on to the filter, which is placed in a small beaker, a hot mixture of 2 N sodium hydroxide and 2 N ammonia, add a few drops of formaldehyde solution and, placing the beaker on a water bath, allow the mixture to pass through the filter. Then pass distilled water through the filter, followed by hot, 1 : 1 nitric acid, which dissolves reduced silver from the pores. After a final washing with distilled water the filter can be dried in a drying oven.

TABLE .14. Silver determination in form of AgCl.

Number of measurements	Mean AgCl mg	True value AgCl mg	Deviation from true value Δ%	Standard deviation	
				mg	%
6	137•6	137.9	-0.20	±0·14	±0·10
6	275•4	275.8	-0.14	±0·22	±0-08
6	689·9	689.5	+0.06	±0·18	±0·025

Note. The method yields very accurate results. If the weight of the precipitate is greater than 0-5 g, the results are higher than the true value (for 1 g, 0.5 mg; and for 1.5 g, 0.8 mg). The results of our own measurements (E. Gegus and G. Beretka) are shown in Table 14.

Determination in the form of Silver Bromide, AgBr

The method is similar to the previous one:

$$Ag^+ + Br^- \rightarrow AgBr\downarrow \quad \longrightarrow \quad (19)$$

Because of the lower solubility of silver bromide (Ksp at 18° C = 4.1 x10^{-13}), the loss in weight due to washing is smaller. Sodium or potassium bromide solution can be used as precipitant. The light-sensitivity of the precipitate is greater than that of silver chloride, and therefore the determination must be carried out with even greater care.

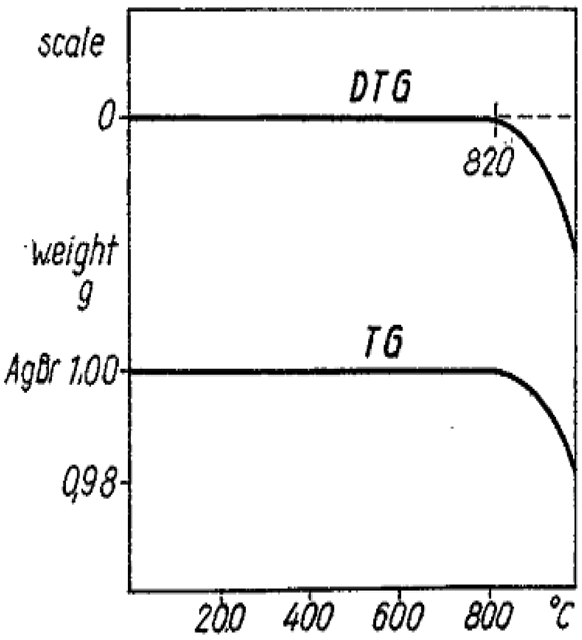


Fig.21.*Thermoanalytical curves of silver bromide precipitate.*

Thermoanalytical investigations of the precipitate (see Figure 21., measurements of F. Paulik) have proved that decomposition occurs only above 800°C. Metallic silver, formed on combustion of the filter paper, can be converted to silver bromide with a few drops of bromine water. Stoichiometric factor:

$$\frac{Ag}{AgBr} = 0.57445 \quad \longrightarrow \quad (20)$$

Note. Although the solubility of AgI is even less than that of silver bromide, it is not suitable for gravimetric determination because of its high light-sensitivity and tendency to peptization. Silver iodide is a suitable weighing form, however, when separation from lead ions is required.

Determination as Metallic Silver after Reduction with Ascorbic Acid

Ascorbic acid (Vitamin C) is a strong reducing agent, and will reduce silver to the metal even in the presence of excess nitric acid, with the formation of dehydroascorbic acid:

$$2AgNO_3 + C_6H_8O_6 = 2Ag\downarrow + C_6H_6O_6 + 2HNO_3 \quad \longrightarrow \quad (21)$$

The method has the great advantage, compared to other methods of silver determination, that it can be carried out rapidly, and, with the exception of gold, platinum metals and mercury, it effects a separation from other metals. Dehydroascorbic acid can easily be destroyed in the filtrate, and so does not interfere with the determination of other metals. It has the advantage, compared to other reduction methods for the determination of silver (NH_2OH, formaldehyde), that the medium need not be ammoniacal, and therefore the method is more specific. In contrast to the acidic reduction with hypophosphorous acid, no reagents which are difficult to remove are introduced into the mother liquor. The solubility of metallic silver is negligible in a mother liquor containing a slight excess of ascorbic acid, and when washing with water there is also no danger of even the slightest solubility. As Ag_2O decomposes at temperatures above 200°C, there is no danger of oxidation at temperatures higher than this. Thermogravimetric investigations on the finely distributed precipitate have proved, however, (see Figure 22, measurements of F. Paulik), that above 800°C a stepwise increase of weight occurs, and this may reach 3% dependent upon the state of distribution. Heat treatment should therefore be carried out between 200-500°C. Weight increase on heating can be explained by the fact that oxygen dissolves in silver as

Ag_2O, and this solubility increases with increase of temperature. If the determination is carried out with higher sample-weights (0.5 g of silver) the precision of the results is higher.

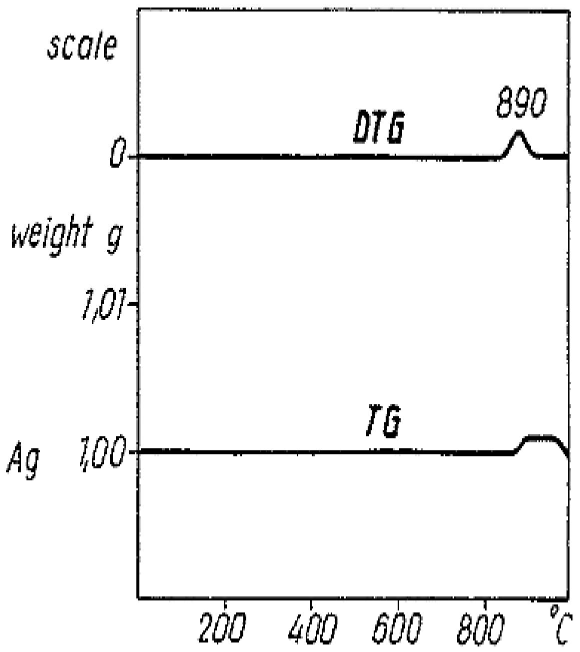


Fig.22.*Thermoanalytical curves of metallic silver reduced by ascorbic acid.*

Procedure. To a nearly neutral solution, containing 0.l-0.7 g of silver, add 5 ml of 1:1 nitric acid, and dilute to 50 ml in a 200-ml beaker. Heat the solution to 90-100° C, and dilute to 50 ml in a 200-ml beaker. Heat the solution to 90-100°0, and drop wise a freshly prepared, 5% solution of ascorbic acid in small excess. (For the precipitation of 100 mg of silver, 5 ml of 5% ascorbic acid is sufficient.) Allow the mixture to boil gently for 15 min, add a further 1 ml portion of 5% ascorbic acid, and filter the hot solution through a weighed porcelain filter crucible. Wash with 50 ml of hot water and then with 25 ml of cold water, used in small portions. Place the filter crucible into a larger porcelain crucible for protection, dry in a drying oven at 100°0, and finally ignite below 500° C for 1 hr.

It is advisable to carry out the ignition in a regulatable electric furnace. If this is not possible, the protecting crucible can be heated on a small flame so that its base glows just perceptibly (550° C). After cooling it must be placed near to the balance together with the protecting crucible for 30 min, and then weighed. The precipitate can also be collected on a filter paper. In this method the paper must be combusted separately from the precipitate, and, after replacing the bulk of the precipitate into the crucible, ignition can be carried out between 300 and 400°C.

Notes. (1) From the results of measurements carried out by E. Gegus and G. Beretka it can be seen (Table .15) that the results are higher than the theoretical values, which indicates that even 550°C is too high for the ignition of the precipitate. It is advisable therefore, when more accurate determinations are required, to carry out ignition on an aluminium block at 300-400° C. By this method the deviations can be corrected by -0-35%, if the weight of the sample is above 0.2 g. With this correction the method can be regarded as fairly precise. If this temperature-range is employed, the use of the streamline filter and the glass filter crucible can also be recommended. The lower precision with small sample sizes indicates that either the sample weight must be higher, or a semimiero-technique must be used, in which event the volume of precipitation and of washing solution would be reduced.

TABLE .15. Silver determination with reduction by ascorbic acid.

Number of measurements	Mean Ag mg	True value Ag mg	Deviation from true value Δ%	Standard deviation	
				mg	%
12	104·2	103·8	+0.4	±0-70	±0-67
6	209·3	208·4	+0.4	±0·19	±0-09
6	522,0	520·5	+0.3	±0·10	±0-02

(2) Some silver compounds, especially organic salts, can be decomposed by ignition, and the silver residue can be weighed. If silver chloride has been dissolved for some reason in ammonia, it is advisable to reduce it to the metal with hydroxylamine hydrochloride, rather than to re-precipitate it with nitric acid, because the ammonium salts present will dissolve the silver chloride to a slight extent. The metallic silver precipitate which is obtained can be heated by the method described above, for its weight also increases at temperatures over 600°C. The precipitate obtained using formaldehyde as reductant is not pure silver metal, and the compound formed only decomposes at temperatures above 600°C. At these temperatures the increase in weight mentioned above occurs, and therefore this method does not yield accurate results.

Gravimetric Analysis of Chlorine - Cl – 35.453; Cl_2, HCI, HCIO, HCIOz, $HCIO_3$, $HClO_4$

Gaseous chlorine can be obtained from the liquid form which is available commercially in steel containers. Chlorine is used in the textile industry for decolorization and whitening. The insecticide industry (DDT), and also the plastic industry (polyvinyl chloride, chlorinated rubber) use large amounts of chlorine. Chlorine is also used to disinfect water, and can be absorbed in calcium hydroxide or other alkalies and used as hypochlorite in decolorization and the production of chloroform. It occurs naturally most often as chloride, together with sodium, potassium and magnesium. These salts are found in sea water and in salt mines. Soil water, streams and rivers also contain small amounts of dissolved chlorides. Chloride ions are also found in plants and animal tissues. The following minerals contain chloride: rock salt (halite, NaCl); sylvine (KCI); ammonium chloride (NH_4CI); chlorocalcite ($CaCl_2$); chloromagnesite ($MgCl_2$); lawrencite [$(FeNi)Cl_2$]; scacchite ($MnCl_2$); molizite ($FeCl_3$); carnallite ($KCI\text{-}MgCl_2.6\ H_2O$); taohidrite ($CaCl_2.2MgCl_2.l2H_2O$); matlochite (PbCIF); cotumnite ($PbCl_2$); chlorargyrite (AgCl); atacamite [$CuCl_2.3Cu(OH)_2$].

Chlorine may be present in analytical samples as elementary chlorine (Cl_2); hydrochloric acid (HCl); hypochlorous acid (HCIO); chlorous acid ($HCIO_2$); chloric acid ($HClO_3$); and perchloric acid ($HCIO_4$); or as the salts of these acids or organic substances containing chlorine. Of the methods shown in Table. 16, only some are suitable for the gravimetric determination of chlorine, and of these the silver chloride method is usually preferred. A number of fairly accurate volumetric methods (argentimetric), however, are available for the determination of chloride ions. Redox titrations are usually used for the determination of hypochlorite, chlorite and chlorate ions. Perchlorate ions can also be determined by direct gra vi¬metric methods ($KCIO_4$, nitron perchlorate).

The preparation of samples containing chlorine thus consists of the following perations: (a) dissolution of the sample, and (b) transformation to chloride.

Dissolution of the sample. Most inorganic chlorine compounds, particularly chlorides, are easily soluble in water. The chlorides of the following ions are insoluble, or lightly soluble: Ag, Hg(I), Cu(I), Pb, Tl(I), Au(I), Pt(Il), and also the following basic chlorides: BiOCl, SbOCl and Hg_2Cl_2O. Hygroscopic chlorides ($CaCl_2$, LiCl), and mercury(Il) chloride are soluble in absolute ethanol, and even in higher alcohols (amyl alcohol). KCI, NaCl and $BaCl_2$ are only slightly soluble in concentrated hydrochloric acid, and thus can be separated from other chlorides if their aqueous solution is saturated with gaseous hydrogen chloride and the solution is filtered. Most metal chlorides are insoluble in ether; the chlorides of Fe(Ill), Hg(Il), Sn(Il, IV) and Au(III), however, are soluble. All chlorides, with the exception of silver chloride, can be dissolved in *aqua regia*.

TABLE .16. Forms of determination of chlorine.

No.	Ions	Forms of precipitation	Precipitant	Reaction of the of the medium	Weighing form	Formula weight	Heat treatment ºC
I.	Cl^-	AgCl	$AgNO_3$	nitric acid	AgCl	143.337	70-600
2.	Cl^-	Hg_2Cl_2	$Hg_2(NO_3)_2$	nitric acid	Hg_2Cl_2	472.13	< 130
3.	ClO_2^-	$Pb(ClO_2)_2$	$Pb(NO_3)_2$	weak nitric acid	$Pb(ClO_2)_2$	342.124	< 77
4.	ClO_3^-	$C_{20}H_{16}N_4.HClO_3$	nitron(1-4-diphenyl endanilo triazole)	weak sulphuric acid	$C_{20}H_{16}N_4.HC1O_3$	396.845	105
5.	ClO_4^-	$KClO_4$	KCl	hydrochloric acid	$KClO_4$	138.557	110
6.	ClO_4^-	$C_{20}H_{16}N_4.HClO_4$	nitron (1-4-diphenyl endanilo triazole)	weak sulphuric acid	$C_{20}H_{16}N_4.HClO_4$	412.845	105 (40-232)

Most minerals containing chloride are insoluble in water, but can be fused with a five-fold excess of chloride-free sodium carbonate. The cold melt must be leached in water, filtered, and the filtrate made just acid to methyl orange with nitric acid. If the solution also contains silicate it must be made alkaline with ammonia, and a small amount of zinc nitrate added. The solution must then be boiled and filtered. The precipitate is washed with hot water and the filtrate is acidified with nitric acid.

Lead chloride can be decomposed by boiling with sodium carbonate or sodium bicarbonate solution.

Silver chloride can be decomposed by igniting the material with a three-fold excess of chloride-free sodium carbonate until sintering occurs.

When the cold melt is leached with water, sodium chloride dissolves; the residue consists of silver carbonate and silver metal. The filtrate can then be acidified with nitric acid and the chloride can be determined by one of the recommended methods.

Mercury(I) chloride can be decomposed by boiling with sodium hydroxide, and after the mercury(I) oxide has been filtered off, the solution may be acidified with nitric acid, and the chloride determined.

Gaseous chlorine (Cl_2), is quite soluble in water; at 10°C, 1 volume of water dissolves 3 volumes of chlorine at I atmosphere pressure. The vapour pressure of the chlorine above the chlorine water, however, is considerable. Chlorine can be removed completely from the solution by boiling. Chlorine is absorbed in alkalis with the formation of chloride and hypochlorite. In the cold, hypochlorite is slowly converted to chlorate; the reaction is rapid in hot solution. Hypochlorites, chlorites, chlorates and perchlorates can be dissolved in water. When silver nitrate is added to the solution of chlorine, only part of the chlorine is precipitated:

$$3Cl_{2(g)} + 6AgNO_3 + 3H_2O \rightarrow 5AgCl(s) + AgClO_3 + 6HNO_3 \longrightarrow \quad (22)$$

Thus, when chlorine is to be determined gravimetrically, the solution must be made alkaline with ammonia and boiled. Chlorine reacts with ammonia with the formation of chloride and hypochlorite:

$$Cl_2 + 2NH_4OH \rightarrow NH_4Cl + NH_4OCl + H_2O \qquad \longrightarrow \quad (23)$$

Ammonium hypochlorite decomposes on boiling:

$$3NH_4OCl + 2NH_3 \rightarrow 3NH_4Cl + N_2 + 3H_2O \qquad \longrightarrow \quad (24)$$

After acidification with nitric acid the chlorine can be precipitated quantitatively as silver chloride.

Chlorine cannot be precipitated quantitatively from a solution containing *hypoclorite* (CIO^-) and *chlorite* (ClO_2^-) with silver nitrate, because partly soluble silver chlorate is formed. If hydrogen peroxide is added to the alkaline solution, however, and the mixture is boiled until the liberation of gas ceases, the hypochlorite and chlorate are reduced to chloride. Aged hypochlorite and chlorite solutions, however, always contain chlorate also, and it is advisable first to add sulphurous acid or sodium hydrogen sulphite to the solution.

Chlorates (ClO_3^-) do not form precipitates with silver nitrate in dilute aqueous solutions, because silver chlorate is partly soluble in water. Chlorates can be reduced by iron(Il) sulphate, sulphurous acid or metallic zinc. Dry alkali chlorates, when evaporated several times with ammonium chloride, form chlorate-free alkali chlorides.

(a) *Reduction with iron(II) sulphate*. To 100 ml of the solution, containing about 0.2 g of chlorate, add 50 ml of 10% iron(Il) sulphate solution, and boil for 15 min with constant stirring. Cool the solution, dissolve the precipitate of basic iron(III) sulphate in nitric acid, and precipitate chloride. with silver nitrate. If the solution contains sufficient excess of nitric acid there is no danger of the reduction of silver ions by iron(II) sulphate.

(b) *Reduction with sulphurous acid*. Add excess sulphurous acid to the slightly acidic or neutral solution of the chlorates, and boil the solution until the smell of sulphur dioxide disappears. Acidify the solution with nitric acid and precipitate the chloride with silver nitrate.

(c) *Reduction with metallic zinc*. Make the solution of the chlorates strongly acid with acetic acid, add excess of cut or granulated zinc to the solution, and boil for 1hr. Dissolve the excess zinc in nitric acid and precipitate the chloride in the filtrate with silver nitrate.

Perchlorate, (ClO_4^-) cannot be reduced using the above reducing agents, but reduction can be effected with titanium(III) sulphate. A much easier method, however, is to ignite the solid alkali perchlorates with ammonium chloride in a platinum crucible:

$$3KCIO_4 + 8\,NH_4Cl \rightarrow 3KCl + 8HCl\,(g) + 4N_2\,(g) + 12H_2O\,(g) \longrightarrow \quad (25)$$

Platinum also acts *as* a catalyst in the reaction.

Procedure. Take about 0.40 g of the solid alkali perchlorate, or evaporate to dryness a solution containing the same amount, add 1.5 g of analytically pure ammonium chloride, mix well, cover the crucible with a watch-glass, and heat on an air-bath for about l hr. Repeat the evaporation with l.5 g of ammonium chloride. When the ammonium salts have been completely removed dissolve the residue in a small volume of water, remove any traces of platinum by filtration on a small filter paper, acidify the filtrate with a small volume of nitric acid, and precipitate the chloride with silver nitrate.

Biblography

- A.I. Vogel, *A Textbook of Macro & Semimicro Qualitative Inorganic Analysis*, 5th ed. 1979.

- A.I. Vogel, *Vogel's Textbook of Quantitative Chemical Analysis*, 1994.

- D. Harvey, *Modern Analytical Chemistry*, The McGraw-Hill Companies 1st ed., 2000.

- D. A. Skoog, *Fundamentals of Analytical Chemistry*, Brooks, Cole; 9th ed., 2014.

- D. C. Harris, *Exploring Chemical Analysis*, W. H. Freeman and Company, 4th ed., 2009.

- L. Erdey, *Gravimetric Analysis Parts I-III*, in Analytical Chemistry Series, Vol 7, Pergamon Press, Oxford,1965.

Problems

Part I. Multiple choice:

Q1.

During a gravimetric analysis experiment to determine the salt content of a chicken soup sample, a precipitate of silver chloride was produced, dried and weighed. The sources of error in the analysis include:
I. The precipitate was not washed before it was dried.
II. The precipitate was not dried and reweighed until a constant mass was obtained.
III. Some precipitate remained in the reaction flask after the filtration process.
Which of these errors could account for a greater than expected mass of silver chloride precipitate?
a I only
b I and II only
c I, II and III
d III only

Q2.

Analysis of a 3.817 g sample of nitroglycerine yielded 0.605 g of carbon, 0.0841 g of hydrogen, 0.706g of nitrogen and 2.421g of oxygen. The empirical formula of nitroglycerine is:
a $CH_2N_1O_3$
b $C_3H_6NO_8$
c $C_3H_5NO_9$
d $C_6H_1N_7O_{24}$

Q3.

Which of the following represent example(s) of quantitative analysis?
i A sample of ‘fries seasoning’ contains salt, chicken extract, rice flour, paprika and chilli.
ii Dry air contains 78% nitrogen vol/vol.
iii A sample of iron ore weighs 23.5 kg.
iv A chocolate biscuit contains 2.3 g protein, 6.6 g fat and 24.4 g carbohydrate per 100 g serve.
a IV only
b I and IV
c II and IV
d II, III and IV

Part II. Analysis by mass:

Q1.

a Why we heat the soup sample to 110°C?
b Why was it necessary to weigh the sample four times?

Q2.

Some laboratories use microwave ovens in place of conventional ovens to dry samples. What advantage could this have?

Q3.

Soy sauce weighing 74.6 g was heated in an oven to constant mass. The final mass was 14.2 g. What percentage of water did the sauce contain?

Q4.

Three brands of dog food were heated and dried to constant mass. The data recorded are shown in Table 3.1.

Table 3.1 Determination of water content of dog food.

Dog food tested	**Mass of dog food sample (g)**	**Final mass (g)**
Phydeaux Deluxe	19.8	3.9
K9 Budget	7.4	1.9
Fresh meat – buffalo mince	15.0	3.8

a Which brand contained the highest percentage of water?

b Do you consider that water content is a good guide to the relative value of different dog foods? What other factors might be important?

Q5.

A student determined the water content of a sample of jam. The following measurements were obtained:

Mass of evaporating dish:20.22 g
Mass of jam and evaporating dish
before heating: 30.95 g
after heating: 27.22 g
after more heating: 26.50 g
after more heating: 26.49 g
What was the percentage, by mass, of water in the jam?

Q6.

Calculate the amount (in mole) of:

a NaCl in 5.85 g of salt
b Fe atoms in 112 g of iron
c CO_2 molecules in 2.2 g of carbon dioxide
d Cl^- ions in 13.4 g of nickel chloride ($NiCl_2$)
e O^{2-} ions in 159.7 g of iron(III) oxide (Fe_2O_3)

Q7.

Calculate the mass of:

a 3.0 mol of oxygen molecules (O_2)
b 1.2 mol of aluminium chloride ($AlCl_3$)
c 2.0 mol of nitrogen atoms

Q8.

A small oxygen cylinder carried by an ambulance has an internal volume of 1.42 L. What mass of oxygen is present at a pressure of 15 000 kPa and temperature of 15.0°C?

Q9.

Calculate the mass of the following gases:
a 3.5 L of argon at SLC
b 250 mL of ammonia (NH_3) at STP

Q10.

Determine the percentage composition of the following compounds:
a lead(IV) oxide (PbO_2)
b sodium carbonate (Na_2CO_3)

Q11.

A gaseous hydrocarbon that is used as a fuel for high-temperature cutting and welding of metals contains 92.3% carbon.
a Determine its empirical formula.
b If the molar mass of the hydrocarbon is 26 g mol^{-1}, find its molecular formula.

Q12.

When 1.66 g of tungsten (W) is heated in excess chlorine gas, 3.58 g of tungsten chloride is produced. Find the empirical formula of tungsten chloride.

Q13.

A sample of blue copper(II) sulfate crystals weighing 2.55 g is heated and decomposes to produce 1.63 g of anhydrous copper(II) sulfate. Show that the formula of the blue crystals is $CuSO_4 \bullet 5H_2O$.

Q14.

Magnesium reacts with hydrochloric acid according to the equation:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

If 10.0 g of magnesium reacts completely, calculate:
a the mass of magnesium chloride that forms
b the mass of hydrogen that forms

Q15.

Iron metal is extracted in a blast furnace by a reaction between iron(III) oxide and carbon monoxide:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

To produce 1000 kg of iron, calculate:
a the mass of iron(III) oxide required
b the volume of carbon dioxide produced at SLC (25°C and 101.3 kPa)

Q16.

A solution containing 10.0 g of silver nitrate is mixed with a solution containing 10.0 g of barium chloride. What mass of silver chloride precipitate is likely to be produced?

$$2AgNO_3(aq) + BaCl_2(aq) \rightarrow 2AgCl(s) + Ba(NO_3)_2(aq)$$

Q17.

A chemist determined the salt content of a sausage roll by precipitating chloride ions as silver chloride. If an 8.45 g sample of sausage roll yielded 0.636 g of precipitate, calculate the percentage of salt in the food. Assume that all the chloride is present as sodium chloride.

Q18.

An impure sample of iron(II) sulfate, weighing 1.545 g, was treated to produce a precipitate of Fe_2O_3. If the mass of the dried precipitate was 0.315 g, calculate the percentage of iron in the sample.

Q19.

Find the number of mol of:

a Ca atoms in 60.0 g of calcium
b NH_3 molecules in 22 g of ammonia
c H_2O molecules in 20.0 g of $CuSO_4{\bullet}5H_2O$
d Cl^- ions in 34 g of $FeCl_3$

Q20.

Find the mass of:

a 0.30 mol of zinc atoms
b 0.16 mol of iron(III) oxide (Fe_2O_3)
c 1.5 mol of ammonium phosphate ($(NH_4)_3PO_4$)

Q21.

A brand of toothpaste contains 0.22% by mass sodium fluoride (NaF). Calculate the mass of fluoride ions in a tube containing 120 g of the paste.

Q22.

6.00 g of helium gas was blown into a fairground balloon. On the day, the temperature was 28.0°C and the pressure inside the balloon was 103.4 kPa. Assuming it is infinitely elastic, to what volume did the balloon inflate?

Q23.

Calculate the volume of the following gases:

a 1.50 mol of oxygen at STP
b 28.0 g of nitrogen at STP
c 17 g of sulfur dioxide at SLC
d 1.2×10^{22} atoms of helium at SLC

Q24.

A 1.22 g sample of pure gas extracted from the gases from a car exhaust occupied 991 mL at 24.0°C and 1.00 atmosphere pressure.

a Calculate the amount of gas, in mol, present in the sample.
b What is the molar mass of the gas?
c Suggest the identity of the gas.

Q25.

Solutions of silver nitrate and potassium chromate react to produce a red precipitate of silver chromate:

$$2AgNO_3(aq) + K_2CrO_4(aq) \rightarrow Ag_2CrO_4(s) + 2KNO_3(aq)$$

If 0.778 g of precipitate is formed in a reaction, find:

a the mass of potassium chromate that reacted
b the mass of silver nitrate that reacted.

Q26.

Magnesium in distress flares burns in air according to the equation:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

If 10.0 g of magnesium burns in air, calculate:

a the mass of magnesium oxide produced
b the mass of oxygen that reacts.

Q27.

Lithium peroxide may be used as a portable oxygen source for astronauts. Calculate the volume of oxygen gas, measured at 25°C and pressure of 101.3 kPa, that is available from the reaction of 0.500 kg of lithium peroxide with carbon dioxide according to the equation:

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$

Q28.

A power station burns coal at 45.5 tonnes per hour (1 tonne = 10^6 g). Assuming the coal is pure carbon and that all the coal is oxidised completely to carbon dioxide gas on combustion, what volume of carbon dioxide is released to the atmosphere per hour when the atmospheric pressure is 758 mmHg and the temperature is 19.0°C?

Q29.

Silicon steel is an alloy of the elements iron, carbon and silicon. An alloy sample was reacted with excess hydrochloric acid and the following reaction occurred:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

The carbon and silicon in the alloy did not react with the acid. If an alloy sample with a mass of 0.160 g produced 62.0 mL of hydrogen gas, measured at SLC, calculate:

a the amount of hydrogen evolved in the reaction
b the mass of iron that reacted to produce this amount of hydrogen
c the percentage of iron in the alloy.

Q30.

Explain the meaning of the following terms:

a relative atomic mass
b relative molecular mass
c mole
d Avogadro’s number
e molar mass
f precipitate
g gravimetric analysis
h ionic equation

Q31.

If 16.0 g of hydrogen sulfide is mixed with 20.0 g of sulfur dioxide and they react according to the equation:

$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$

a What mass of sulfur is produced?
b What mass of reactant is left after the reaction?

Q32.

Calculate the volume of carbon dioxide gas produced, at SLC, when 5.00 g of calcium carbonate is added to a solution containing 5.00 g of nitric acid.

Q33.

The following compounds are used in fertilisers as a source of nitrogen. Calculate the percentage of nitrogen, by mass, in:

a ammonia (NH_3)
b ammonium nitrate (NH_4NO_3)
c urea ($CO(NH_2)_2$).

Q34.

Find the empirical formula of:

a a compound that contains 65.2% scandium and 34.8% oxygen by mass
b an oxide of copper that contains 89% copper by mass
c a polymer used to make plastic drain pipes, which contains 38.4% carbon, 4.84% hydrogen and 56.7% chlorine by mass.

Q35.

Gypsum is hydrated calcium sulfate ($CaSO_4{\bullet}xH_2O$). A residue of 5.65 g of anhydrous calcium sulfate is obtained by heating 7.15 g of gypsum. Determine the empirical formula of gypsum.

Q36.

A 2.203 g sample of an organic compound was extracted from a plant. When it was burned in oxygen, the hydrogen in the compound was converted to 1.32 g of water and the carbon was oxidised to 3.23 g of carbon dioxide.

a Find the empirical formula of the compound.
b Another sample was analysed in a mass spectrometer. The mass spectrum produced showed that the molar mass of the compound was 60.0 g mol^{-1}. What is its molecular formula?

Q37.

What mass of barium chloride ($BaCl_2$) will remain after a 15.0 g sample of the hydrated salt $BaCl_2{\bullet}2H_2O$ is heated to drive off all of the water?

Q38.

A student is given solutions of lead(II) nitrate, copper(II) chloride and barium hydroxide.

a Name the precipitates that could be made by mixing together pairs of solutions.
b Write full and ionic equations for each of the reactions.

Q39.

Design a flowchart to show how the salt content of a savoury spread could be determined by gravimetric analysis.

Q40.

The iodide ions in a solution containing 0.300 g of sodium iodide were precipitated as silver iodide. What mass of silver iodide was formed?

Q41.

A precipitate of Fe_2O_3, of mass 1.43 g, was obtained by treating a 1.5 L sample of bore water. What was the concentration of iron, in mol L^{-1}, in the water?

Q42.

The chlorine in a 0.63 g sample of a chlorinated pesticide, DDT ($C_{14}H_9Cl_5$), is precipitated as silver chloride. What mass of silver chloride is formed?

Q43.

A 0.693 g sample of a silver alloy used to make cutlery is dissolved completely in nitric acid. Excess sodium chloride solution is added to produce a precipitate of silver chloride. The precipitate is filtered, dried and found to weigh 0.169 g.

a Find the percentage of silver in the alloy.

b If the precipitate was not completely dry when weighed, what effect would this have on the answer for part **a**?

Q44.

A 0.500 g sample of sodium sulfate (Na_2SO_4) and a 0.500 g sample of aluminium sulfate ($Al_2(SO_4)_3$) were dissolved in a volume of water, and excess barium chloride was added to precipitate barium sulfate.
What was the total mass of barium sulfate produced?

Q45.

Water pollution can result from the phosphates added to washing powders to improve the stability of their suds. The phosphorus in a 2.0 g sample of washing powder is precipitated as $Mg_2P_2O_7$. The precipitate weighs 0.085 g.

a What is the percentage, by mass, of phosphorus in the washing powder?

b Suppose you were in charge of an advertising campaign to promote the washing powder. Would you advertise the percentage of phosphorus or phosphate in the product? Explain.

Q46.

A 2.10 g sample of a commercial antacid powder is treated with excess hydrochloric acid. The volume of carbon dioxide evolved is 430 mL, measured at 21.0°C and 109.6 kPa pressure. If magnesium carbonate is the active ingredient in the antacid, calculate the percentage of magnesium carbonate in the sample.

Q47.

When 0.100 g of white phosphorus is burned in oxygen, 0.228 g of an oxide of phosphorus is produced. The molar mass of the oxide is 284 g mol^{-1}.

a Determine the empirical formula of the phosphorus oxide.
b Determine the molecular formula of the phosphorus oxide.

Q48.

Excessive salt intake in the diet can cause high blood pressure and heart disease. The salt content of a 14.96 g sample of powdered chicken soup was determined by dissolving it in water to make a volume of 250.0 mL. A 20.00 mL volume of this stock solution was pipetted into a conical flask and excess silver nitrate was added. The silver chloride precipitate that formed was then filtered, washed and dried. Its mass was 0.246 g.

a Write an ionic equation for the formation of the silver chloride precipitate.
b Calculate the amount, in mol, of silver chloride that was produced.
Assume all the chloride in the powdered soup came from sodium chloride (common salt).
c Determine the amount of sodium chloride in the 20.00 mL volume of stock solution in the conical flask.
d Calculate the amount of sodium chloride in 250.0 mL of the stock solution.
e What mass of sodium chloride was in the sample?

Q49.

A 523.1-mg sample of impure KBr is treated with excess $AgNO_3$ and 814.5 mg AgBr is obtained. What is the purity of the KBr?

Q50.

What weight of Fe_2O_3 precipitate would be obtained from a 0.4823-g sample of iron wire that is 99.89% pure?

Q51.

The aluminum content of an alloy is determined gravimetrically by precipitating it with 8-hydroxyquinoline (oxine) to give $Al(C_9H_6ON)_3$. If a 1.021-g sample yielded 0.1862 g of precipitate. what is the percent aluminum in the alloy?

Q52.

Iron in an ore is to be analyzed gravimetrically by weighing as Fe_2O_3. It is desired that the results be obtained to four significant figures. If the iron content ranges between 11 and 15%, what is the minimum size sample that must be taken to obtain 100.0 mg of precipitate?

Q53.

The chloride in a 0.12-g sample of 95% pure $MgCl_2$ is to be precipitated as AgCl. Calculate the volume of 0.100 M $AgNO_3$ solution required to precipitate the chloride and give a 10% excess.

Q54.

Ammonium ions can be analyzed by precipitating with H_2PtCl_6 as $(NH_4)_2PtCl_6$ and then igniting the precipitate to platinum metal, which is weighed [$(NH_4)_2PtCl_6 \xrightarrow{heat} Pt + 2NH_4Cl(g) + 2Cl_2(g)$]. Calculate the percent ammonia in a 1.00-g sample that yields 0.100 g Pt by this method.

Q55.

A sample is to be analyzed for its chloride content by precipitating and weighing silver chloride. What weight of sample would have to be taken so that the weight of precipitate is equal to the percent chloride in the sample?

Q56.

Pyrite ore (impure FeS_2) is analyzed by converting the sulfur to sulfate and precipitating $BaSO_4$. What weight of ore should be taken for analysis so that the grams of precipitate will be equal to 0.1000 times the percent of FeS_2?

Q57.

A mixture containing only BaO and CaO weighs 2.00 g. The oxides are converted to the corresponding mixed sulfates, which weigh 4.00 g. Calculate the percent Ba and Ca in the original mixture.

Q58.

A mixture containing only $BaSO_4$ and $CaSO_4$ contains one-half as much Ba^{2+} as Ca^{2+} by weight. What is the percentage of $CaSO_4$ in the mixture?

Q59.

A mixture containing only AgCl and AgBr weighs 2.000 g. It is quantitatively reduced to silver metal, which weighs 1.300 g. Calculate the weight of AgCl and AgBr in the original mixture.

Q60.

The ratio of the weight of silicon tetrachloride to the weight of an equivalent amount of silver has been found to be 0.393802 Assuming Cl = 35.457 and Ag = 107.880, calculate the atomic weight of silicon.

Q61.

How many milliliters of silver nitrate solution containing 20.00 grams of $AgNO_3$ per 100 ml. are required to precipitate all the chloride as AgCl from a solution containing 2.012 grams of dissolved $BaCl_2.2H_2O$?

Q62.

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 $Fe_2O_3 . xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

Q63.

(a) Theoretical Percentage: Calculate the theoretical percentage of water in barium chloride dihydrate.
(A.wt.: Ba= 137.3, Cl=35.5, O=16.0, H=1.00).

(b) Experimental percentage: A 1.250 g sample of barium chloride dihydrate has a mass of 1.060 g after heating. Calculate the experimental percentage of water.

(c) Water of crystallization: Calculate the water of crystallization for an unknown hydrate that is found to contain 30.6 % water. The formula mass of the anhydrous salt (AS) is 245 amu.

Q64.

Suppose 6.25g of blue hydrated copper(II) sulphate, $CuSO_4.xH_2O$, (x unknown) was gently heated in a crucible until the mass remaining was a constant 4.00g. Find the % water of crystallisation, the formula and formula mass of the salt.

Q.65.

If 1.51 g of hydrated sodium carbonate was used. If the average titre (0.1M HCl) reading was 10.6 cm^3, calculate the value of x in $Na_2CO_3.xH_2O$.

Q.66.

A 0.6113-g sample of Dow metal, containing aluminum, magnesium, and other metals, was dissolved and treated to prevent interferences by the other metals. The aluminum and magnesium were precipitated with 8-hydroxyquinoline. After filtering and drying, the mixture of $Al(C_9H_6NO)_3$ and $Mg(C_9H_6NO)_2$ was found to weigh 7.8154 g. The mixture of dried precipitates was then ignited, converting the precipitate to a mixture of Al_2O_3 and MgO. The weight of this mixed solid was found to be 1.0022 g. Calculate the %w/w Al and %w/w Mg in the alloy.

Q.67.

An impure sample of Na_3PO_3 weighing 0.1392 g was dissolved in 25 mL of water. A solution containing 50 mL of 3% w/v mercury(II) chloride, 20 mL of 10% w/v sodium acetate and 5 mL of glacial acetic acid was then prepared. The solution containing the phosphite was added dropwise to the second solution, oxidizing PO_3^{3-} to PO_4^{3-} and precipitating Hg_2Cl_2. After digesting, filtering, and rinsing, the precipitated Hg_2Cl_2 was found to weigh 0.4320 g. Report the purity of the original sample as %w/w Na_3PO_3.

Q.68.

A lawn fertilizer contains mainly ammonium sulfate ($(NH_4)_2SO_4$) and potassium sulfate (K_2SO_4). A 1.87 g sample of the fertiliser was dissolved in water and the sulfate precipitated as barium sulfate ($BaSO_4$). The dried $BaSO_4$ had a mass of 2.41 g.

a Write a balanced ionic equation for the precipitation reaction.

b Draw a flowchart to show the steps involved in this gravimetric analysis.

c State two reasons why $BaSO_4$ is a suitable precipitate to use in this analysis.

d Calculate the percentage by mass of sulfur in the fertilizer.

e The labelling on the fertilizer stated that the sulfur content was 16% rn/m. Suggest two possible reasons why the value obtained in **d** is greater than 16% m/m.

Q.69.

In order to determine the molecular formula of a compound known to contain only carbon, hydrogen and oxygen, two experiments were carried out. In the first experiment, a 0.80 g sample of the compound was burnt in excess oxygen. When the gases evolved were passed through anhydrous $CaCl_2$ its mass increased by 0.48 g. The remaining gases, when bubbled through a NaOH solution increased its mass by 1.2 g. In the second experiment, a 1.32 g sample of the compound was vaporized. The vapour occupied 0.574 L at 130°C and 1.28 x 10^5 Pa.

a. Determine the mass of carbon in 0.80 g of the compound.

b. Determine the mass of hydrogen in 0.80 g of the compound.

c. Determine the mass of oxygen in 0.80 g of the compound.

d. Determine the empirical formula of the compound.

e. Determine the molar mass of the compound.

f. Determine the molecular formula of the compound.