

# 8

## GRAVIMETRIC ANALYSIS

In gravimetric analysis, the weight of a product is measured and used to calculate the quantity of the original analyte. Despite its simplicity, it remains one of the most accurate methods in chemical analysis. A logical extension of the established gravimetric analysis is the combustion analysis. In combustion analysis, a sample is burned in excess oxygen and the products are analysed. This type of analysis is used in the 'CHNS analysis' of organic compounds.

Many gravimetric analyses involve precipitation reactions at controlled conditions to selectively precipitate a species. There is often the requirement to remove potentially interfering species prior to the measurement. This chapter describes the underlying principles of gravimetric analysis.

### 8.1 STEPS IN GRAVIMETRIC ANALYSIS

Typical gravimetric analysis consists of a number of steps (Figure 8.1). These include the dissolution of sample, precipitation, digestion, filtration and washing of precipitate, drying of precipitate, weighing and calculations.

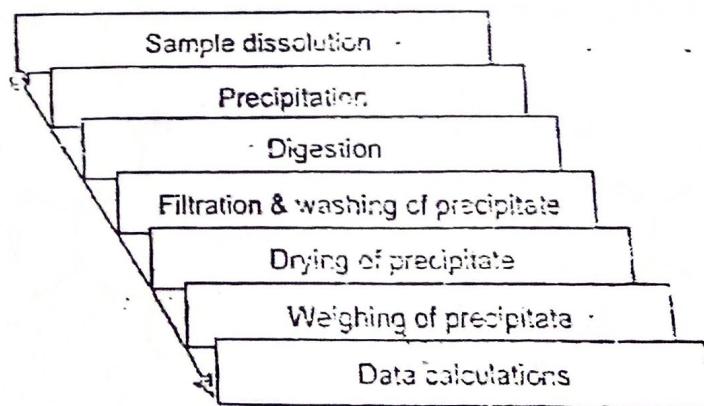


Figure 8.1 Steps in gravimetric analysis.

A sample for gravimetric analysis must be in solution form. For solid samples, suitable techniques should be used for dissolution of the sample. (See Chapter 4 and 5).

An ideal precipitate for gravimetric analysis should be:

- Insoluble
- Easily filterable
- Pure
- Known composition

For quantitative gravimetric analysis, the precipitate must have very low solubility and large particle size for easy filtration and washing. Large particle size also means smaller total surface area to minimize impurities caused by coprecipitation. Before we perform the gravimetric analysis, we have to know the solubility of the product; a soluble precipitate is not suitable for gravimetric analysis.

Few precipitates meet all the requirements. However, certain techniques can be used to optimize the properties of the measured substance. By considering the characteristics of an ideal precipitate, a number of factors must be controlled during preparation of solutions. These include the volume of the solution, the type of precipitating reagent and its concentration, the presence and the concentration of other species in solution that may affect the precipitation process, temperature and pH of the solution. These factors will be discussed in the following sections.

### Solubility

Different compounds can have different solubility. Table 8.1 gives the solubility of inorganic ions. The solubility of the low solubility salts can be determined from the solubility product ( $K_{sp}$ ) (Appendix 3). Inorganic salts of common metal cations can range from extremely soluble compounds such as  $\text{Pb}(\text{NO}_3)_2$  to slightly soluble salts and insoluble salts such as  $\text{PbCl}_2$  that have very low solubility in water ( $K_{sp} = 1.6 \times 10^{-5}$ ). It should be clear that the more soluble the precipitate the less suitable it is for gravimetric analysis.

### 8.2 PRECIPITATION AGENTS<sup>3</sup>

Gravimetric analyses of several species are listed in Table 8.2. The precipitating agents used in gravimetric analysis are inorganic and organic precipitants. Examples of inorganic precipitants are sulfate, sulfide, and chloride. Organic precipitants include 8-hydroxyquinoline, dimethylglyoxime, cupferron, and 1-nitroso-2-naphthol.

Some hydroxide precipitates are gelatinous and difficult to filter and weighed. Therefore, the precipitate is usually filtered, washed and ignited at high temperature. For example,

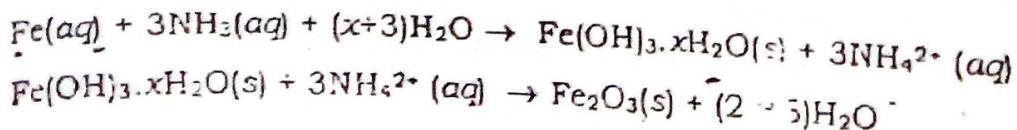


Table 8.1 Solubility of salts of common inorganic anions.

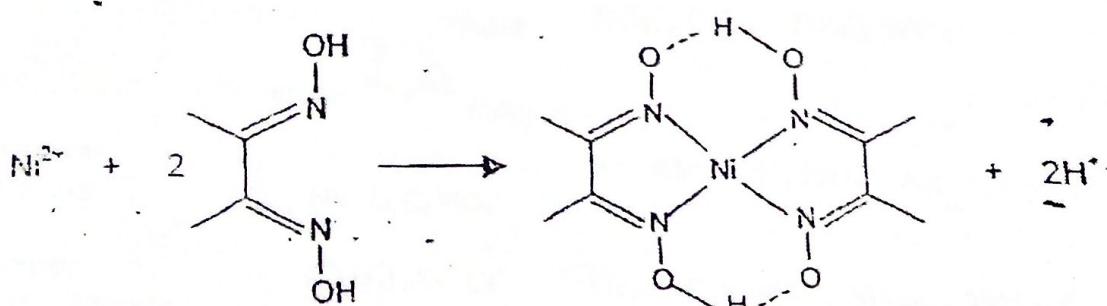
Anion	Soluble compounds	Insoluble compounds
$\text{OH}^-$	Hydroxide of Group IA elements, e.g. $(\text{NaOH})$ . For Group IIA elements, $\text{Sr}(\text{OH})_2$ , $\text{Ba}(\text{OH})_2$ , $\text{Ca}(\text{OH})_2$ are partially soluble.	All compounds except those stated on the left.
$\text{NO}_3^-$	All compounds.	Nil.
$\text{ClO}_4^-$	All compounds except $\text{KClO}_4$ .	$\text{KClO}_4$ is slightly soluble.
$\text{Cl}^-$	All except those stated on the left.	$\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ , $\text{PbCl}_2$ are slightly soluble
$\text{SO}_4^{2-}$	All except those stated on the right.	$\text{HgSO}_4$ , $\text{MgSO}_4$ , $\text{Ag}_2\text{SO}_4$ , $\text{PbSO}_4$ , $\text{CaSO}_4$ , $\text{SrSO}_4$ , $\text{BaSO}_4$
$\text{S}^{2-}$	Salts of Group IA elements, e.g. $(\text{Na}_2\text{S})$ . Salts of Group IIA ( $\text{CaS}$ ), $\text{NH}_4\text{HS}$ , and $(\text{NH}_4)_2\text{S}$ .	All except those stated on the left.
$\text{CO}_3^{2-}$	All salts of Group IA elements, except $\text{Li}_2\text{CO}_3$ , and salts of $\text{NH}_4^+$	All except those stated on the left.

### Organic precipitants

Precipitates with high molecular weight can be achieved using organic precipitant. Table 8.4 gives several organic precipitating agents. The use of organic precipitants is advantages for gravimetric analysis:

- The resulting precipitates are less soluble in water.
- Less impurity due to coprecipitation.
- High molecular weight – less error in weighing
- A few organic precipitant acts as a chelating agent to form colored complex for easy detection by colorimetry.

**Dimethylglyoxime (DMG).** It is a good example of a selective organic precipitant. It reacts with  $\text{Ni}^{2+}$  to form the red DMG-nickel complex in slightly alkaline solution.



$\text{Ni}$  (MW 58.60) DMG (FW 116.12) Bis(dimethylglyoximate)nickel(II)

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(FW 288.91)

Table 8.2 Examples of gravimetric analysis.

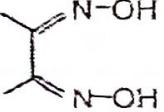
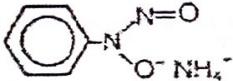
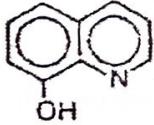
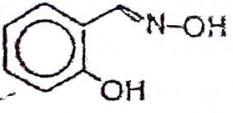
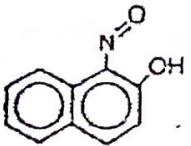
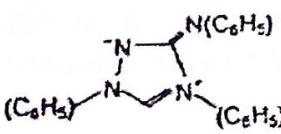
Species analyzed	Precipitated form*	Weighed form	Possible interfering species
$\text{Al}^{3+}$	$\text{Al}(\text{8-hydroxy-quinolate})_3$	$\text{Al}(\text{8-hydroxy-quinolate})_3$	Many metals
$\text{Ba}^{2+}$	$\text{BaSO}_4$	$\text{BaSO}_4$	$\text{Na}^+$ , $\text{K}^+$ , $\text{Li}^+$ , $\text{Ca}^{2+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Sr}^{2+}$ , $\text{Pb}^{2+}$ , $\text{NO}_3^-$
$\text{Ca}^{2+}$	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	$\text{CaCO}_3$ or $\text{CaO}$	Many metals except $\text{Mg}^{2+}$ , $\text{Na}^+$ and $\text{K}^+$
$\text{Ce}^{4+}$	$\text{Ce}(\text{IO}_3)_3$	$\text{CeO}_2$	$\text{Th}^{4+}$ , $\text{Ti}^{4+}$ , $\text{Zr}^{4+}$
$\text{Co}^{2+}$	$\text{Co}(\text{l-nitroso-2-naphtholate})_3$	$\text{CoSO}_4$ (by rxn. with $\text{H}_2\text{SO}_4$ )	$\text{Fe}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Zr}^{4+}$
$\text{Cr}^{3+}$	$\text{PbCrO}_4$	$\text{PbCrO}_4$	$\text{Ag}^+$ , $\text{NH}_4^+$
$\text{Cu}^{2+}$	$\text{CuSCN}$	$\text{CuSCN}$	$\text{NH}_4^+$ , $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Ag}^+$
$\text{Fe}^{3+}$	$\text{Fe}(\text{HCCO}_2)_3$	$\text{Fe}_2\text{O}_3$	Many metals
$\text{K}^+$	$\text{KB}(\text{C}_6\text{H}_5)_4$	$\text{KB}(\text{C}_6\text{H}_5)_4$	$\text{NH}_4^+$ , $\text{Ag}^+$ , $\text{Hg}^{2+}$ , $\text{Tl}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$
$\text{Mg}^{2+}$	$\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$	$\text{Mg}_2\text{P}_2\text{O}_7$	Many metals except $\text{Na}^+$ and $\text{K}^+$
$\text{Mn}^{2+}$	$\text{Mn}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$	$\text{Mn}_2\text{P}_2\text{O}_7$	Many metals
$\text{NH}_4^+$	$\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4$	$\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4$	$\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$
$\text{Ni}^{2+}$	Ni(dimethylglyoxime)	Same as ppt.	$\text{Pd}^{2+}$ , $\text{Pt}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Au}^{3+}$
$\text{Pb}^{2+}$	$\text{PbSO}_4$	$\text{PbSO}_4$	$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Ag}^+$ , $\text{HCl}$ , $\text{NH}_3$
$\text{Sn}^{4+}$	$\text{Sn}(\text{cupferron})_4$	$\text{SnO}_2$	$\text{Cu}^{2+}$ , $\text{Pb}^{2+}$ , $\text{As(III)}$
$\text{Ti}^{4+}$	$\text{Ti}(\text{5,7-dibromo-8-hydroxyquinoline})_2$	Same as ppt.	$\text{Fe}^{3+}$ , $\text{Zr}^{4+}$ , $\text{Cu}^{2+}$ , $\text{C}_2\text{O}_4^{2-}$ , citrate, HF
$\text{Zn}^{2+}$	$\text{Zn}(\text{NH}_4)\text{PO}_4 \cdot \text{H}_2\text{O}$	$\text{Zn}_2\text{P}_2\text{O}_7$	Many metals
$\text{Br}^-$	$\text{AgBr}$	$\text{AgBr}$	$\text{Cl}^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{S}^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{CN}^-$
$\text{Cl}^-$	$\text{AgCl}$	$\text{AgCl}$	$\text{Br}^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{S}^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{CN}^-$
$\text{ClO}_4^-$	$\text{KClO}_4$	$\text{KClO}_4$	$\text{KClO}_4$
$\text{CN}^-$	$\text{AgCN}$	$\text{AgCN}$	$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{S}^{2-}$ , $\text{S}_2\text{O}_3^{2-}$
$\text{CO}_3^{2-}$	$\text{CO}_2$ (by acidification)	$\text{CO}_2$	Note: the $\text{CO}_2$ is trapped with Ascarite and weighed
$\text{F}^-$	$(\text{C}_6\text{H}_5)_3\text{SnF}$	$(\text{C}_6\text{H}_5)_3\text{SnF}$	Many metals (except alkali metals); $\text{SiO}_4^{4-}$ , $\text{CO}_3^{2-}$
$\text{I}^-$	$\text{AgI}$	$\text{AgI}$	$\text{Cl}^-$ , $\text{Br}^-$ , $\text{SCN}^-$ , $\text{S}^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{CN}^-$
$\text{NO}_3^-$	Nitron nitrate	Nitron nitrate	$\text{ClO}_4^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{CrO}_4^{2-}$ , $\text{ClO}_3^-$ , $\text{NO}_2^-$ , $\text{Br}^-$ , $\text{C}_2\text{O}_4^{2-}$
$\text{PO}_4^{3-}$	$\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$	$\text{Mg}_2\text{P}_2\text{O}_7$	Many metals except $\text{Na}^+$ , $\text{K}^+$
$\text{SCN}^-$	$\text{CuSCN}$	$\text{CuSCN}$	$\text{NH}_4^+$ , $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Ag}^+$
$\text{SO}_4^{2-}$	$\text{BaSO}_4$	$\text{BaSO}_4$	$\text{Na}^+$ , $\text{K}^+$ , $\text{Li}^+$ , $\text{Ca}^{2+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Sr}^{2+}$ , $\text{Pb}^{2+}$ , $\text{NO}_3^-$

\* Refer to Table 8.4 for structures of precipitating agents. Key: rxn = reaction,  
ppt = precipitate.

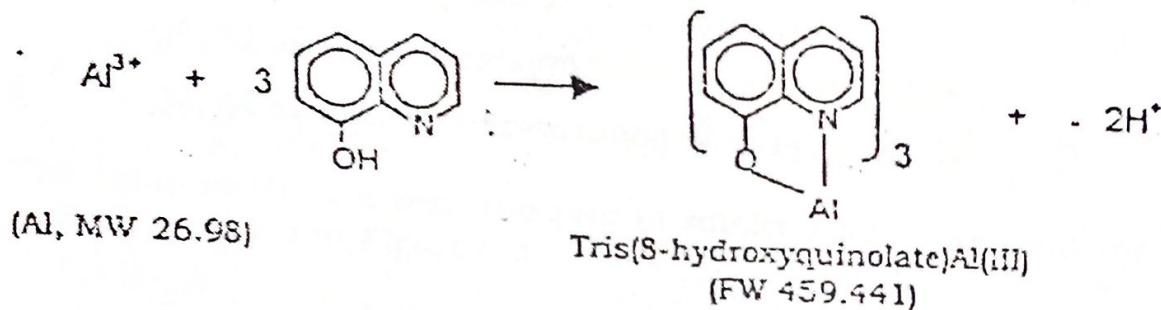
**Table 8.3** Several inorganic precipitation reagents, analytes, precipitate form and weighed form.

Reagent	Analyte	Precipitated form	Weighed form
HCl	Ag	AgCl	AgCl
NH <sub>4</sub> CH	Al	Al(OH) <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
AgNO <sub>3</sub>	Cl <sup>-</sup>	AgCl	AgCl
NaSO <sub>4</sub>	Ba	BaSO <sub>4</sub>	BaSO <sub>4</sub>

**Table 8.4** Several organic precipitating reagents.

Precipitating agent	Structure	Ions precipitated
Dimethylglyoxime		Ni <sup>2+</sup> , Pd <sup>2+</sup> , Pt <sup>2+</sup>
Cupferron		Fe, VO <sup>2+</sup> , Ti <sup>2+</sup> , Zr <sup>4+</sup> , Ce <sup>3+</sup> , Ga <sup>3+</sup> , Sn <sup>4+</sup>
8-hydroxyquinoline (oxine) (FM = C <sub>9</sub> H <sub>6</sub> NO)		Mg <sup>2+</sup> , Zn <sup>2+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup> , Al <sup>3+</sup> , Fe <sup>3+</sup> , Bi <sup>3+</sup> , Ga <sup>3+</sup> , Th <sup>4+</sup> , Zr <sup>4+</sup> , UO <sub>2</sub> <sup>2+</sup> , TiO <sup>2+</sup>
Salicyldaldoxime		Cu <sup>2+</sup> , Pb <sup>2+</sup> , Bi <sup>3+</sup> , Zn <sup>2+</sup> , Ni <sup>2+</sup> , Pd <sup>2+</sup>
1-Nitroso-2-naphthol		Co <sup>2+</sup> , Fe <sup>3+</sup> , Pd <sup>2+</sup> , Zr <sup>4+</sup>
Nitron		NO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , BF <sub>4</sub> <sup>-</sup> , WO <sub>4</sub> <sup>2-</sup>
Sodium tetraphenylborate	Na <sup>+</sup> B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	K <sup>+</sup> , Rb <sup>+</sup> , Cs <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Ag <sup>+</sup>
Tetraphenylarsonium chloride	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As <sup>+</sup> Cl <sup>-</sup>	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> , MnO <sub>4</sub> <sup>-</sup> , ReO <sub>4</sub> <sup>-</sup> , MoO <sub>4</sub> <sup>2-</sup> , WO <sub>4</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup> , I <sub>3</sub> <sup>-</sup>

**8-Hydroxyquinoline.** Sometimes called oxine, 8-hydroxyquinoline ( $C_9H_6NO$ ) is a common complexing reagent for more than 13 metal ions. It forms a 2:1 complex with a divalent metal ion such  $Mg^{2+}$  and a 3:1 complex with a divalent metal ion such as  $Al^{3+}$ .



Because 8-hydroxyquinoline is a weak acid, the stability of its complexes is different from one cation to another cation and it depends on the pH of the solution. For example,  $Al(C_9H_6NO)_3$  is stable at pH 4 while  $Mg Al(C_9H_6NO)_2$  is stable at higher pHs. By this virtue, a mixture of  $Al^{3+}$  and  $Mg^{2+}$  can therefore be separated by controlling the pH. The use of a high pH (-pH 9) however, will result in the coprecipitation of  $Mg(OH)_2$ .

### 8.3 PRECIPITATION

In gravimetric analysis, precipitates should have a large size for easy filtration. Very fine particles can pass through the filter or clog the filter that consequently can cause slower throughput. Generally, large crystals have less surface area per mass than small crystals. This means that when we have large size crystals, less foreign species may become attached to the particles. Extremely small particles (1-100 nm) can form a colloidal suspension that pass through most filters. Because of these factors, appropriate precipitation conditions must be used to obtain large particles sizes. These are discussed in the following sections.

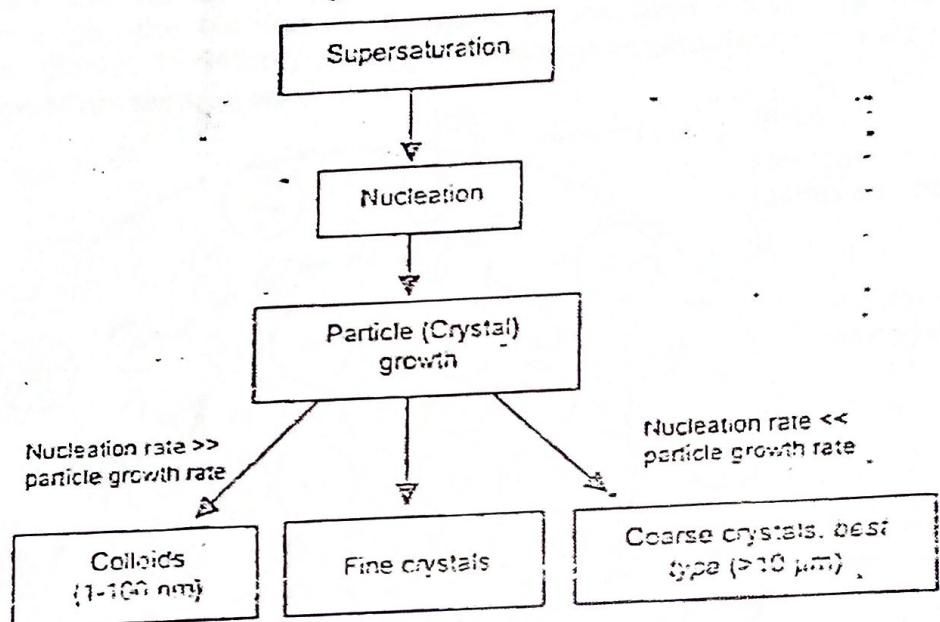
#### Crystal growth

Crystal growth occurs in a number of stages. It begins with the establishment of supersaturation, followed by nucleation, and particle growth (Figure 8.2).

- (a) There is a certain condition where a solution may contain more solute than should be present at equilibrium. The solution is said to be supersaturated. Supersaturation can be achieved by adding the precipitation reagent to the solution.
- (b) Nucleation is the process where molecules in solution combine randomly to form a small aggregate called nucleus. A nucleus is a very small particle which consists of a combination of perhaps a few ions.
- (c) Particle growth or Crystal growth is the process where more ions are added to the nucleus to form colloids or colloidal particles with sizes in the range of 1-100 nm in diameter.

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(d) Aggregation is the process of solid particle formation. The particles collide and stick together to form larger particles.



**Figure 8.2** Mechanisms of precipitation of ionic compounds from solution.

In a highly supersaturated solution, nucleation occurs faster than the particle growth. If the rate of nucleus formation is high compared to the particle growth rate, a colloid is formed in the solution. Colloid consists of a suspension of small-size particles in solution. In contrast, a less supersaturated solution allows slower nucleation and the nuclei have a chance to become larger, filterable particles. In general, a dilute solution with low supersaturation enhances particle growth that results in large particle size.

### Effect of Supersaturation

Precipitation occurs when there is a supersaturated solution. If  $Q$  denotes the solute concentration and  $S$  is the solubility of the solute, then the supersaturation conditions can be described by:

$$\text{Supersaturation} = Q - S$$

When the value of  $(Q - S)$  is high, it means that supersaturation is high and thus the formation of many nuclei having small particle size. The von Weimann principle states that the particle size of a crystal is inversely proportional to the relative supersaturation of the solution. The relative supersaturation is given by

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

Small-size precipitate or colloid is formed if the rate of nucleus formation is faster than the rate of particle growth.

$Q \uparrow, S \downarrow \Rightarrow$  High supersaturation  $\Rightarrow$  fine particles

$Q \downarrow, S \uparrow \Rightarrow$  Low supersaturation  $\Rightarrow$  large particles

The relationship between the rate of nucleus formation and the rate of particle growth is shown in Figure 8.3.

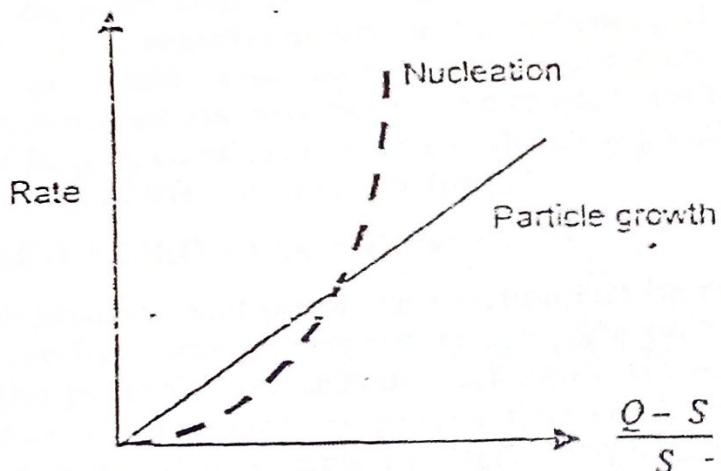
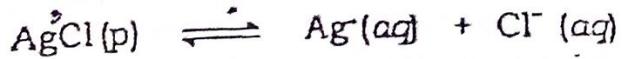


Figure 8.3 Effect of supersaturation on the rate of nucleus formation and particle growth.

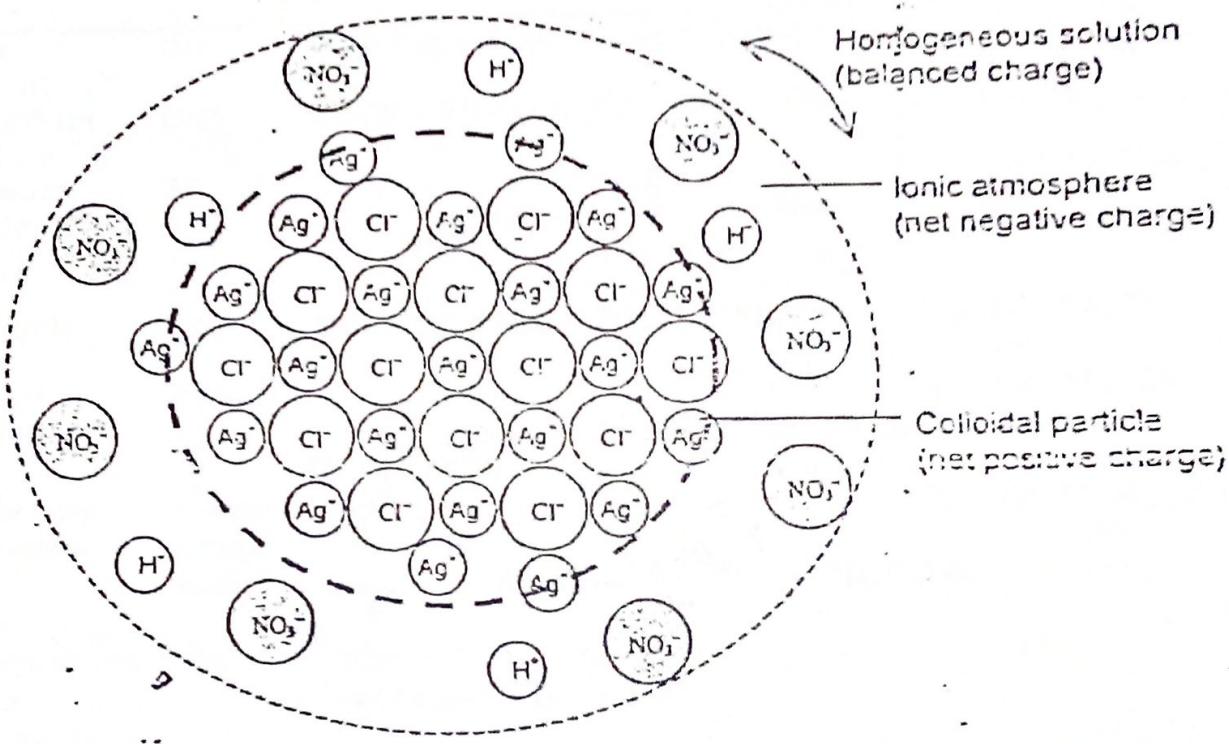
#### Illustration - precipitation of AgCl

As an illustration, let's now take a look at the analysis of chloride ion in a solution using  $\text{AgNO}_3$  as the precipitating agent.  $\text{AgCl}$  is usually precipitated in the presence of 0.1 M  $\text{HNO}_3$ .



During crystal formation, after the first stage of  $\text{AgCl}$  nucleus formation, the colloidal particle of  $\text{AgCl}$  is formed and the particles grow in solution containing excess  $\text{Ag}^+$ ,  $\text{NO}_3^-$  and  $\text{H}^+$ . The surface of the particle has an excess positive charge because of the adsorption of extra  $\text{Ag}^+$  on the exposed chloride ions (Figure 8.4). The positively charged surface attracts anions (such as  $\text{NO}_3^-$ ) and repels cations (such as  $\text{H}^+$ ) from the ionic atmosphere. The positively charged particle and the negatively charged ionic atmosphere together are called the electric double layer. The negatively charged ionic atmospheres of the particles repel each other. To coalesce, the colloidal particles must collide with each other with enough kinetic energy to overcome the repulsion.

One way of promoting coalescence is by heating the solution which increases the kinetic energy of the particles. By increasing the electrolyte concentration, the volume of the ionic atmosphere decreases that brings the particles closer. Therefore, most gravimetric precipitations are carried out in the presence of an electrolyte.



**Figure 8.4** Schematic diagram of a colloidal particle of  $\text{AgCl}$  growing in a solution containing excess  $\text{Ag}^+$ ,  $\text{H}^+$  and  $\text{NO}_3^-$ . The particles (white circles) have a net positive charge because of adsorbed  $\text{Ag}^+$  ions. The region surrounding the particle (ionic atmosphere) has a net negative charge because the particle attracts anions and repels cations.

#### Techniques to achieve low supersaturation

The experimental conditions should be controlled so as to minimize supersaturation (low  $Q$  and high  $S$ ). A few techniques can be used to promote particle growth. These include the following:

- Perform the crystallization at elevated temperature that to ensure low supersaturation.
- Add precipitant (precipitation agent) slowly with vigorous mixing to avoid local, highly supersaturated regions where the precipitant first enters the solution containing the analyte.
- Keep the volume of solution large to keep the analyte concentrations low.

The above measures must be controlled right from the solution preparation step to the precipitation process. In addition two other techniques can be used to obtain large-size particles:

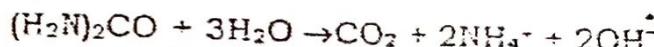
- Carry out homogeneous precipitation.
- After precipitation, subject the solution containing the precipitate to digestion.

These techniques are described below.

#### Homogeneous precipitation

The best method to ensure minimum supersaturation in precipitation is by generating the precipitation reagent slowly in the solution. In homogeneous precipitation, the precipitant is not added directly into the solution but generated slowly by a chemical reaction *in-situ*, in the solution. The chemical reaction takes place slowly enough thus avoiding high supersaturation.

Several compounds have been used to generate homogeneous precipitation reagent (Table 8.5). A classical example is the slow generation of OH<sup>-</sup> ions through the decomposition of urea in heated water.



The OH<sup>-</sup> concentration and pH of the solution can be raised gradually. It requires 1-2 hours to produce enough reagent for complete precipitation of the analyte. For example, in the precipitation of Fe(II) and Al(III), if the precipitant (OH<sup>-</sup>) is added directly, gelatinous precipitate is formed that contains considerable amounts of impurities and almost impossible to filter. With homogeneous precipitation with hydroxide ion, the precipitates formed have better filterability and purity.

Other examples of common homogeneous precipitation reagents include potassium cyanate, thioacetamide, sulfamic acid, dimethyl oxalate, and 8-acetoxyquinoline.

#### 8.4 IMPURITIES OF PARTICLES

Precipitates obtained in the gravimetric analysis are often impure. A precipitate is impure when a foreign substance is precipitated along with the analyte. Impurities can be in the form of adsorbed impurities or absorbed impurities.

Adsorbed and absorbed impurities are collectively known as coprecipitation. Coprecipitation is a process where the impurity is precipitated along with the desired precipitate, even though the solubility of the impurity has not been exceeded. Coprecipitation is important to be dealt with in gravimetric analysis because it is a major contributor to errors.

Coprecipitation is more serious in colloidal precipitates such as BaSO<sub>4</sub>, Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> which have large surface area. For example, if we add sulfuric acid into a solution containing BaCl<sub>2</sub> and FeCl<sub>3</sub>, we can expect only BaSO<sub>4</sub> is precipitated while Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> should remain in the solution. However, when the precipitate is filtered, washed and ignited, the residue is not white,

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characteristic of  $\text{BaSO}_4$  but contaminated with brown  $\text{Fe}_2\text{O}_3$  that resulted from the decomposition of coprecipitated  $\text{Fe}_2(\text{SO}_4)_3$  during heating.

Table 8.5 Common reagents employed in homogeneous precipitation.

Reagent	Precipitant	Reaction	Examples of elements precipitated
Urea	$\text{OH}^-$	$(\text{H}_2\text{N})_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$	Al, Ga, Th, Bi, Fe, Sn
Potassium cyanate	$\text{OH}^-$	$\text{HO}\text{CN} + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{CO}_2 + \text{OH}^-$	Cr, Fe
Thioacetamide	$\text{S}^{2-}$	$\begin{array}{c} \text{S} \\    \\ \text{CH}_3\text{C}\text{NH}_2 \end{array} + \text{H}_2\text{O} \rightarrow \begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{C}\text{NH}_2 \end{array} + \text{H}_2\text{S}$	Sb, Mo, Cu, Cd
Sulfamic acid	$\text{SO}_4^{2-}$	$\text{H}_3\text{N}^+\text{SO}_3^- + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{SO}_4^{2-} + \text{H}^+$	Ba, Ca, Sr, Pb
Dimethyl oxalate	$\text{C}_2\text{O}_4^{2-}$	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{CH}_3\text{OC}-\text{COCH}_3 \end{array} + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{H}^+ + \text{C}_2\text{O}_4^{2-}$	Ca, Mg, Zn
8-acetoxy-quinoline	8-hydroxyquinoline	$\begin{array}{c} \text{CH}_3\text{CO} \\   \\ \text{C}_6\text{H}_4-\text{N} \\    \\ \text{C}_6\text{H}_5 \end{array} + \text{H}_2\text{O} \rightarrow \begin{array}{c} \text{OH} \\   \\ \text{C}_6\text{H}_4-\text{N} \\    \\ \text{C}_6\text{H}_5 \end{array} + \text{CH}_3\text{CO}_2\text{H}$	Al, U, Mg, Zn
Chromic ion plus bromate	$\text{CrO}_4^{2-}$	$2\text{Cr}^{3+} + \text{BrO}_3^- + 5\text{H}_2\text{O} \rightarrow 2\text{CrO}_4^{2-} + \text{Br}^- + 10\text{H}^+$	Pb

Sometimes, a trace component is intentionally extracted by coprecipitation with a major component of the solution. The process is called gathering and the precipitate used to collect the trace component is called a gathering agent.

### Adsorbed Impurities

Adsorbed impurities are attached to the surface of the crystal. Adsorption is a reversible process; a substance can be adsorbed and subsequently desorbed. The two opposing processes can reach an equilibrium. The equilibrium is governed by several factors:

- Surface area of adsorption
- Temperature
- Concentration of ions
- Characteristics of adsorbed ions

The amount of adsorbed substance on the surface is directly proportional to the surface area of the adsorbent. Therefore, adsorption is significant in colloidal or gelatinous precipitates. The adsorption increases with the concentration of the substance. Adsorption is an exothermic process. Therefore, increased temperature reduces the amount of adsorbed substance.

There are two types of adsorption. In primary adsorption, the precipitate adsorbs its own ions or isomorphous ions (ions having similar crystal structure and size). These ions form a monolayer on the surface of the particle to give a positive or negative net charge. The primary layer attracts counter ions that form a diffuse layer. This secondary adsorption increases with increasing charge on the adsorbed ions.

### Absorbed Impurities

These are impurities within the crystal and it can be classified as inclusion or occlusions.

#### Inclusions

Inclusions are impurity ions that occupy sites in the crystal lattice that are normally occupied by ions that belong to the crystal. The impurity is incorporated into the crystal by substituting the lattice site or located in between ions in the lattice. Inclusions are randomly distributed in the crystal lattice and are more likely to happen when the impurity ion has similar size and charge to those of the ions that belongs to the crystal. Such impurities are called **isomorphic impurities** (isomorphism refers to the similarity in crystal structure).

An example of isomorphic precipitate is  $\text{BaSO}_4$  in the presence of  $\text{Pb}^{2+}$  (Figure 8.5a). The lead ions are isomorphic and can be found substitute for barium ions in the lattice. Conversely, in the presence of  $\text{K}^+$  ions, a mixed crystal is not formed because of the differences in ionic charges. However, the potassium ions can be found distributed in between the  $\text{BaSO}_4$  crystal lattice (Figure 8.5b).

Inclusions are difficult to rectify. Digestion can help reduce inclusions in the precipitate but only to a small extent. Inclusions usually cannot be removed by washing but recrystallization of the precipitate may help reduce inclusions.

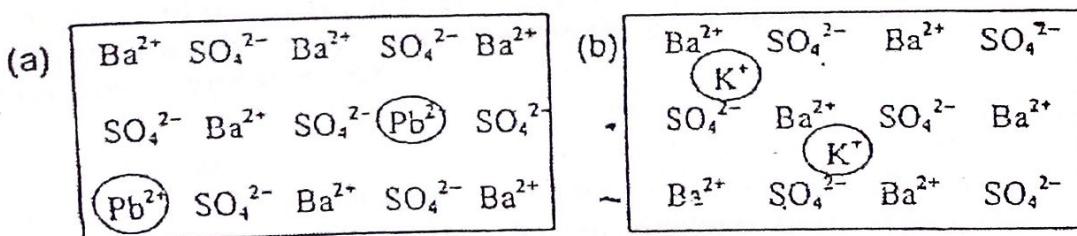


Figure 8.5 Schematic diagram showing inclusions of  $\text{BaSO}_4$  precipitate.  
 (a) Isomorphic impurities are distributed throughout the crystal lattice.  
 (b) Impurities distributed between the crystal lattice

### Occlusions

Occlusions are pockets of impurities that are trapped inside the rapidly growing crystal. It can occur in two forms.

(a) Crystalline occlusion. Impurities are trapped inside faults of a crystal. This is caused by *internal adsorption*. During the grow process, new layers can be precipitated onto the crystal surface. At the same time, impurities in the solution can also be adsorbed on the surface and precipitated. When the precipitate grows larger, the impurities are displaced by ions that form the crystal lattice but the displacement is not complete.

(b) Aggregate occlusion. Small-sized colloids or crystallites can aggregate by colliding with each other to form larger particles. The impurities from the solution can be trapped in voids between the crystallites as they aggregate (Figure 8.6).

The mixing sequence of two solutions can affect internal adsorption. For example, if  $\text{BaSO}_4$  is formed by slow addition of  $\text{H}_2\text{SO}_4$  to a solution of  $\text{BaCl}_2$ , the crystal will grow in a medium containing excess  $\text{Ba}^{2+}$  ions and the ion will be adsorbed on the precipitate with an overall positive charge and  $\text{Cl}^-$  as the counterions. Upon adding more  $\text{H}_2\text{SO}_4$ , the  $\text{Cl}^-$  ions are replaced by  $\text{SO}_4^{2-}$  ion. The displacement process is not complete and some adsorbed  $\text{Cl}^-$  ions remain trapped in the growing crystal. Thus, the precipitate is not pure  $\text{BaSO}_4$  but also contains some  $\text{BaCl}_2$  (see Figure 8.6). If the sequence is reversed, the crystal will grow in a medium of excess  $\text{SO}_4^{2-}$  ions. These ions are adsorbed on the surface of the growing crystal to give an overall negative charge. The negative charge in turn attracts positively charged counter ions i.e.  $\text{H}^+$ . Therefore, the precipitate also contains impurities  $\text{H}_2\text{SO}_4$ .

$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$
$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$
$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$
$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Cr Ba}^{2+} \cdot \text{H}_2\text{O}$		$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$
$\text{SO}_4^{2-}$	$\text{H}_2\text{O}$	$\text{H}_2\text{O}$	$\text{Ba}^{2+}$	$\text{Cl}^-$	$\text{Ba}^{2+}$
$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{Cl}^-$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$
$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$
	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$	
	$\text{SO}_4^{2-}$	$\text{Ba}^{2+}$			

Figure 8.6 Schematic diagram showing occlusion where a pocket of impurity (mixture of  $\text{H}_2\text{SO}_4$  and  $\text{BaCl}_2$ ) is trapped inside the growing crystal of  $\text{BaSO}_4$ .

### Postprecipitation

Another form of impurities is caused by postprecipitation. It usually involves a supersaturated impurity that does not ready to crystallize. Postprecipitation can occur even when the precipitate forms in a pure state. For example,  $MgC_2O_4$  crystals can be collected on  $CaC_2O_4$  particles.

### 8.5 WAYS TO MINIMIZE IMPURITIES

A number of techniques can be used to solve problems related to coprecipitation. Most impurities can be removed by washing or redissolving the precipitate followed by reprecipitation. Impurities can be minimized employing proper precipitation techniques and masking.

#### Digestion

Digestion is practiced in most gravimetric analysis. In the digestion process, the precipitate is allowed to keep in contact with the mother solution in which the precipitation takes place, usually with heating. Digestion promotes slow recrystallization of the precipitate and thus particle size increases and impurities tend to be excluded from the crystal.

#### Washing

Washing a precipitate on a filter tends to remove remaining liquid containing excess solute. Although some precipitates can be washed with water, most of them are washed with a solution containing a volatile or easily decomposed electrolyte to maintain coherence. The electrolytes replace the initial adsorbed electrolyte impurities. The surface charge of the particles is neutralized by the ionic solvent. If the electrolyte is washed by water, the counter-primary ion interaction is disturbed and the charged solid particles repel each other and the precipitate breaks up. The breaking up process is known as peptization and can end up in loss of product through the filter. For example,  $AgCl$  precipitate will peptize if washed with water. Thus it is usually washed with dilute nitric acid instead. The electrolyte used for washing of precipitate should be volatile so that it can be removed during the drying process. Commonly used electrolytes include  $HNO_3$ ,  $HCl$ ,  $NH_4NO_3$ ,  $NH_4Cl$  and  $(NH_4)_2CO_3$ .

#### Masking

Some impurities are prevented from reacting with the precipitant. This is carried out using a masking agent. Examples of gravimetric analysis that employ this technique are given in Table 8.6.

$Ca^{2+}$ Analyte	$+ 2RH$ Precipitant	$\rightarrow$	$CaR_2(s)$ + Precipitate	$2H^+$
$Mn^{2+}$ Impurity	$+ 6CN^-$ Masking agent	$\rightarrow$	$Mn(CN)_6^{4-}$ Stays in solution	

**Table 8.6** Several masking agents for gravimetric analysis.

Reagent	Analyte	Masking agent	Masked ion
<i>N</i> - <i>p</i> -chlorophenyl-cinnamohydroxamic acid (NCPCH acid)	Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup>	KCN	Ag <sup>+</sup> , Mn <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , Fe <sup>2+</sup> , and Ga <sup>3+</sup>
Same as above	Same as above	Mixture of citrate and oxalate	Pb <sup>2+</sup> , Pd <sup>2+</sup> , Sb <sup>3+</sup> , Sn <sup>2+</sup> , Bi <sup>3+</sup> , Zr <sup>4+</sup> , Ti <sup>4+</sup> , V <sup>5+</sup> , and Mo <sup>6+</sup>

## 8.6 DRYING

In gravimetric analysis, the final product must have a known, stable composition. After the filtration process, some precipitates are dried in an oven at 110–120°C for a period of about 1 hour to drive off excess solvent. Alternatively, the sample can be dried using a microwave oven for a relatively shorter period of time (in the order of a few minutes). A hygroscopic substance is difficult to weigh accurately as it adsorbs moisture from the surrounding air.

Some other precipitates contain a variable quantity of water and must be dried under conditions that give a known stoichiometry of water. Drying is often carried out to a constant weight. Strong heating also known as ignition is used to change the chemical form of certain precipitates. For example,  $\text{Fe}(\text{HCO}_3)_3 \cdot n\text{H}_2\text{O}$  is ignited to 850°C for 1 hour to give  $\text{Fe}_2\text{O}_3$  and  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$  is ignited to give  $\text{Mg}_2\text{P}_2\text{O}_7$ .

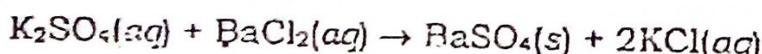
In thermogravimetric analysis (TGA), a sample is heated and its mass is measured as a function of temperature. The composition of the product depends on the temperature and duration of heating.

## 8.7 GRAVIMETRIC CALCULATIONS

In gravimetric analysis, the weighed substance is often different from that of the analyte. Some relationship must exist between them. In this section, we discuss how to relate the mass of a gravimetric precipitate to the quantity of the original analyte.

### Mass of product – mass of reactant relationship

The gravimetric factor relates mass of product to mass of analyte. Suppose we would like to determine the sulfate content of an impure  $\text{K}_2\text{SO}_4$  sample by precipitating the sulfate ion as  $\text{BaSO}_4$ .



The weight of the sample containing  $K_2SO_4$  and the weight of the  $BaSO_4$  precipitate are recorded. From these data, the percent of  $K_2SO_4$  in the sample is calculated.

$$\frac{wt\ K_2SO_4\ (g)}{FW\ K_2SO_4\ (g/mol)} = \frac{wt\ BaSO_4\ (g)}{FW\ BaSO_4\ (g/mol)}$$

$$wt\ K_2SO_4\ (g) = wt\ BaSO_4\ (g) \times \left( \frac{FW\ K_2SO_4\ (g/mol)}{FW\ BaSO_4\ (g/mol)} \right)$$

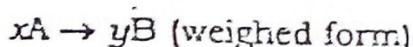
The term in brackets, which is the ratio of the molecular weights, is called the gravimetric factor. It is used to convert the weight of one chemical formula to another based on the stoichiometric relationship between the two. Thus,

$$\%K_2SO_4 = \frac{wt\ BaSO_4 \left( \frac{FW\ K_2SO_4\ (g/mol)}{FW\ BaSO_4\ (g/mol)} \right) \times 100}{wt\ of\ sample}$$

If the percent sulfur in the sample is desired, then,

$$\%S = \frac{wt\ BaSO_4 \left( \frac{FW\ S\ (g/mol)}{FW\ BaSO_4\ (g/mol)} \right) \times 100}{wt\ of\ sample}$$

For a general chemical equation



$$\%A = \frac{wt\ B \left( \frac{x \times FW\ A\ (g/mol)}{y \times FW\ B\ (g/mol)} \right) \times 100}{wt\ of\ sample}$$

where  $x$  and  $y$  are the coefficients of A and B, respectively, in the chemical equation showing the stoichiometric conversion. The values of  $x$  and  $y$  are chosen so that the numerator and denominator contain the same number of atoms common to A and B. When there is no atom common to substance A and B, it is important that all the chemical reactions for the transformation of A and B are known.

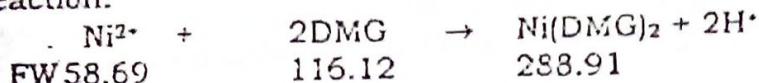
#### EXAMPLE 8.1 – Nickel in Steel

In the analysis of nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion which maintains iron in solution. The solution is heated to about 70-80°C and dimethylglyoxime (DMG) is added to precipitate the red DMG-nickel complex quantitatively. The product is filtered, washed with cold water and dried at 110°C for one hr.

**Q1.** If the nickel content is known to be approximately 3.2% w/w and you would like to analyze 1.2 g of the alloy, what volume of 1.0% w/w alcoholic DMG should be used to give a 50% excess of DMG for the analysis? Assume that the density of the alcohol is 0.79 g/mL.

**Solution**

Reaction:



1 g of alloy contains  $(3.2\% / 100\%) \times 1 \text{ g} = 0.032 \text{ g}$  of nickel  
 $0.032 \text{ g nickel} \equiv (0.032 \text{ g} / 58.69 \text{ g mol}^{-1}) = 5.45 \times 10^{-4} \text{ mol nickel}$

1 mol Ni requires 2 mol DMG.

$$\therefore \text{Amount of metal required} = 2(5.45 \times 10^{-4}) (116.12 \text{ g DMG} / 1 \text{ mol Ni}) \\ = 0.127 \text{ g DMG}$$

To give a 50% excess, amount of DMG required =  $(0.127 \text{ g} \times 1.5) = 0.190 \text{ g}$ 

This amount is DMG present in the alcoholic solution of 1.0%

Wt of solution =  $0.190 \text{ g DMG} / (0.010 \text{ g DMG/g solution}) = 19.0 \text{ g solution}$ Volume of solution =  $17.8 \text{ g solution} / (0.79 \text{ g/mL solution}) = 21 \text{ mL}$ 

**Q2.** If 1.3484 g of steel gave 0.2375 g of precipitate, what is the percentage of Ni in the steel?

**Solution**

1 mol Ni ≡ 1 mol ppt

58.69 g Ni ≡ 288.91 g ppt

$$\text{Wt of nickel in ppt} = 0.2375 \times \frac{58.69 \text{ g Ni}}{288.91 \text{ g ppt}} = 0.04825 \text{ g Ni}$$

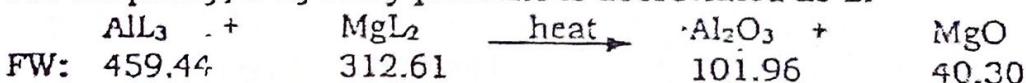
$$\begin{aligned} \text{Percent of Ni in sample} &= (0.04825 \text{ g Ni} / 1.3484 \text{ g alloy}) \times 100 \\ &= 3.116\% \end{aligned}$$

**EXAMPLE 8.2 - A mixture of two components**

A mixture of  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  ions is precipitated as 8-hydroxyquinoline complex weighing 0.9893 g. The complex mixture was ignited in the presence of air to give a residue of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  weighing 0.1084 g. What is the weight percent of  $\text{Al}(\text{C}_9\text{H}_5\text{NO})_3$  in the complex mixture?

**Solution**

For simplicity, 8-hydroxyquinoline is abbreviated as L.

Let  $x$  be the mass of  $\text{AlL}_3$  and  $y$  be the mass of  $\text{MgL}_2$ . Thus,

$$\text{Mol of Al} = x/459.44$$

$$\text{Mol of Mg} = y/312.61$$

$$\text{Mol of Al}_2\text{O}_3 = \frac{1}{2} (x/459.44)$$

$$\text{Mol of MgO} = y/312.61$$

$$\begin{aligned} \text{Mass of AlL}_3 + \text{mass of MgL}_2 &= 0.9893 \text{ g} \\ x + y &= 0.9893 \text{ g} \end{aligned}$$

$$\text{mass of Al}_2\text{O}_3 + \text{mass of MgO} = 0.1084$$

$$\frac{1}{2} (x/459.44)(101.96) + (y/312.61)(40.30) = 0.1084 \text{ g}$$

## Principles of Chemical Analysis

$$\frac{1}{2} \frac{x}{459.44} (101.96) + \frac{y}{321.61} (40.30) = 0.2084 \text{ g}$$

Substituting  $y = 0.9893 - x$  into the equation above gives

$$\frac{1}{2} \frac{x}{459.44} (101.96) + \frac{0.9893 - x}{321.61} (40.30) = 0.1084 \text{ g}$$

$$0.11096x + 0.12397 - 0.12531x = 0.1184 \text{ g}$$

$$-0.01435x = -0.00557 \Rightarrow x = 0.3882 \text{ g}$$

$$0.3882/0.9893 \times 100 = 39.24 \% \text{ of the total complex mixture}$$

**EXAMPLE 8.3** A limestone ( $\text{CaCO}_3$ ) sample (1,0000 g) was dissolved and the calcium was precipitated as the oxalate. The precipitate was ignited and weighed as  $\text{CaO}$ . If the  $\text{CaO}$  weighed 0.5110 g, determine the percent of  $\text{CaCO}_3$  in the sample.

**Solution**

$$\begin{aligned} \text{Wt. CaCO}_3 &= \text{wt. CaO} \times \frac{\text{MW CaCO}_3}{\text{MW CaO}} \\ &= 0.5110 \times \frac{100.09}{56.08} = 0.9120 \text{ g} \end{aligned}$$

$$\% \text{ Wt. CaCO}_3 = \frac{0.9120}{1.0000} \times 100 = 91.20\%$$

### 8.8 GRAVIMETRIC COMBUSTION ANALYSIS

The combustion analysis is a form of gravimetric analysis for the determination of carbon and hydrogen in organic compounds. In this technique, the organic compound is burned in excess oxygen and the volatilized products are weighed to determine the C and H compositions. The microdetermination is based on the Pregl combustion system (Figure 8.7).

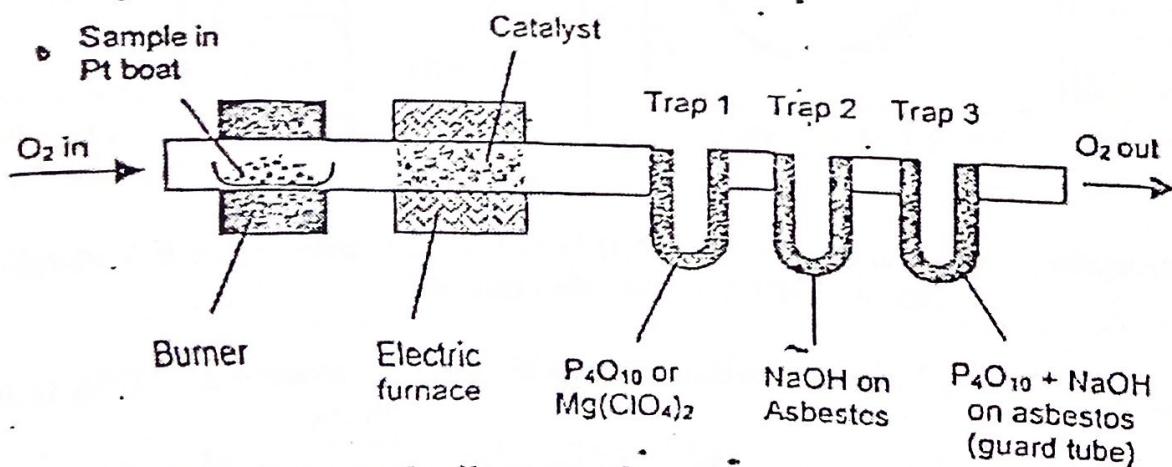
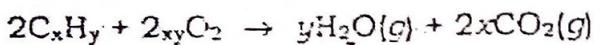


Figure 8.7 Schematic diagram of gravimetric combustion analysis for carbon, hydrogen, and nitrogen.

### Principles of Combustion Analysis

In gravimetric analysis, the sample placed in a platinum boat is first partially combusted in the burner in a stream of oxygen. The products are passed through a catalyst such as heated Pt gauze,  $\text{PbO}_2$  or  $\text{MnO}_2$  to complete the oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



The combustion products are flushed through a series of traps. Trap 1 contains phosphorous pentoxide ( $\text{P}_4\text{O}_{10}$ ) which absorbs water. Trap 2 contains  $\text{NaOH}$  on asbestos which absorbs  $\text{CO}_2$ . Trap 3 is the guard tube which prevents water and carbon dioxide from entering the chambers. To determine the amount of water and carbon dioxide from the sample, the tubes are weighed before and after adsorption. The mass increase of Trap 1 and Trap 2 can be related to the quantity of hydrogen and carbon, respectively. If the sample contains only elements C, H and N, the difference between the sample mass and the sum of the mass of H and C gives the mass of nitrogen.

### EXAMPLE 8.4 Combustion analysis

In a gravimetric combustion analysis, a compound (6.783 mg) produced 16.884 mg of  $\text{CO}_2$  and 2.962 mg of  $\text{H}_2\text{O}$  upon complete combustion. Calculate the weight percent of C and H in the sample.

#### Solution

$$\% \text{C} = \frac{\text{wt CO}_2 \left( \frac{\text{FW C (g/mol)}}{\text{FW CO}_2 (\text{g/mol})} \right)}{\text{wt of sample}} \times 100$$

$$= \frac{16.884 \text{ mg} \left( \frac{12.011}{44.010} \right)}{6.783 \text{ mg}} \times 100$$

$$= 67.93\%$$

$$\% \text{H} = \frac{\text{wt H}_2\text{O} \left( \frac{2 \times \text{FW H (g/mol)}}{\text{FW H}_2\text{O (g/mol)}} \right)}{\text{wt of sample}} \times 100$$

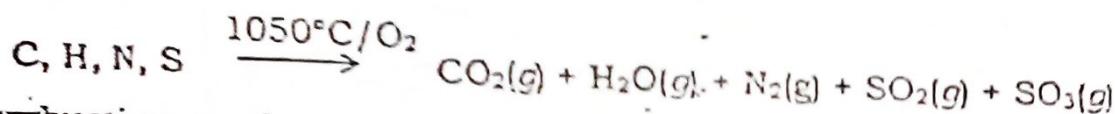
$$= \frac{1.962 \text{ mg} \left( \frac{2 \times 1.008}{18.015} \right)}{6.783 \text{ mg}} \times 100$$

$$= 4.89\%$$

### Modern combustion analysis

In the modern gravimetric combustion analysis, gas chromatographic separation thermal conductivity detection is used for the determination of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This method allows much faster analysis than the gravimetric combustion technique.

Figure 8.8 shows an instrument that measures C, H, N, and S in a single operation. An accurately weighed sample (~2 mg) is sealed in a tin capsule. Initially, a measured excess of oxygen is added to the helium stream. The sample capsule is placed into a preheated ceramic crucible, where the capsule melts and the sample is rapidly oxidized.



The combustion products pass through a series of zones: Zone 1 contains hot  $\text{WO}_3$  catalyst to complete the combustion of carbon to  $\text{CO}_2$ . Zone contains metallic

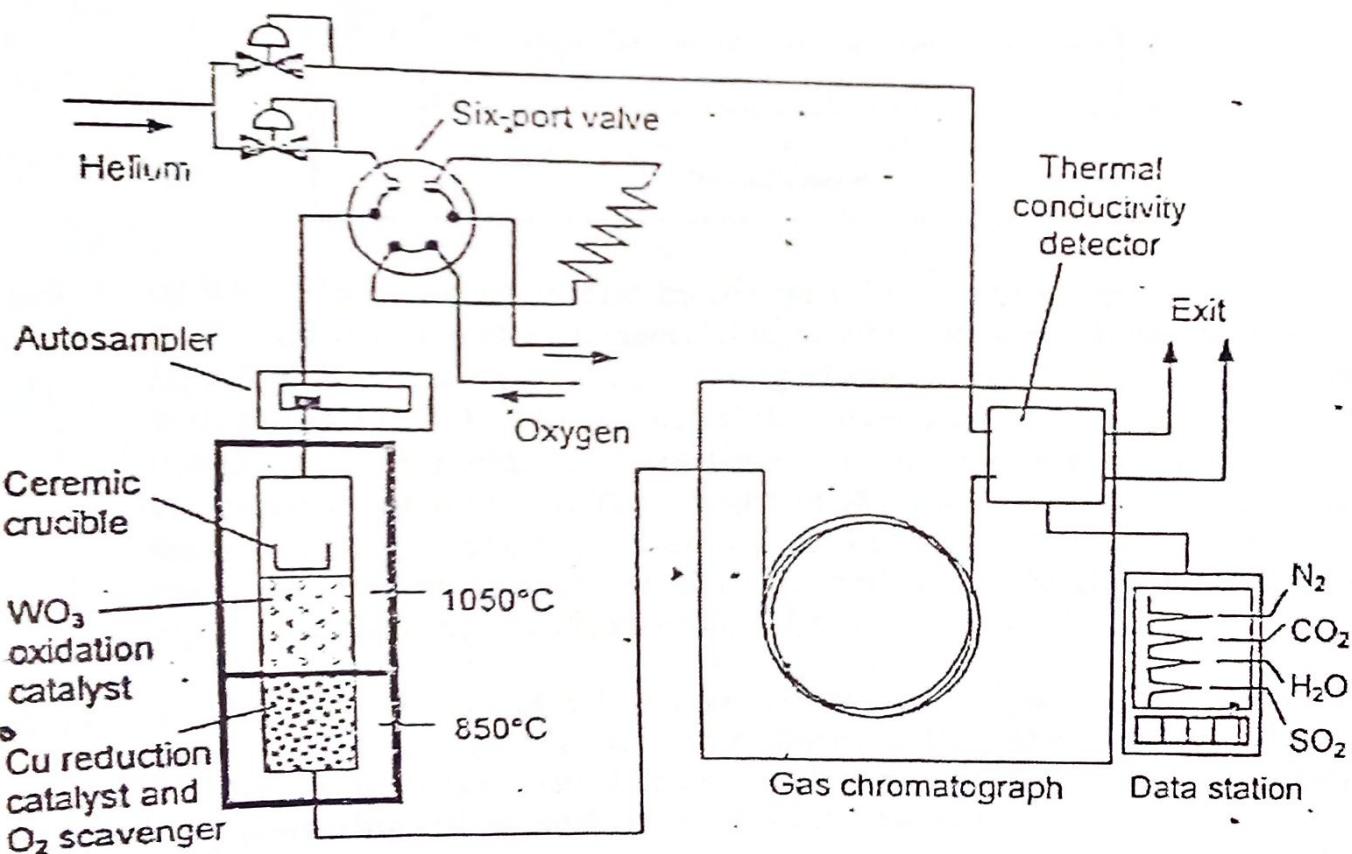
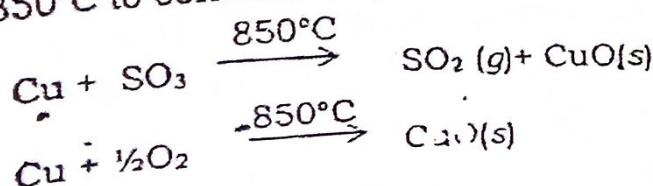


Figure 8.8 Schematic diagram of C,H,N,S elemental analyzer. [Adapted from E. Pella, Am Lab., August 1990, p. 28]

Cu at  $850^\circ\text{C}$  converts  $\text{SO}_3$  to  $\text{SO}_2$  and removes excess  $\text{O}_2$ .



## Chapter 8. Gravimetric Analysis

The mixture of the gas products are separated by gas chromatography and each component is measured with a thermal conductivity detector. Another type of CHNS analyzer uses infrared absorbance to measure  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$  and thermal conductivity for  $\text{N}_2$ .

In combustion analysis must incorporate dynamic flash combustion that create burst of gaseous products instead of slow release of gaseous products. This feature is essential because gas chromatography requires rapid injection of the mixture at once to minimize the injection zone. Otherwise, if the injection zone is too broad the products cannot be separated.

### QUESTIONS AND PROBLEMS

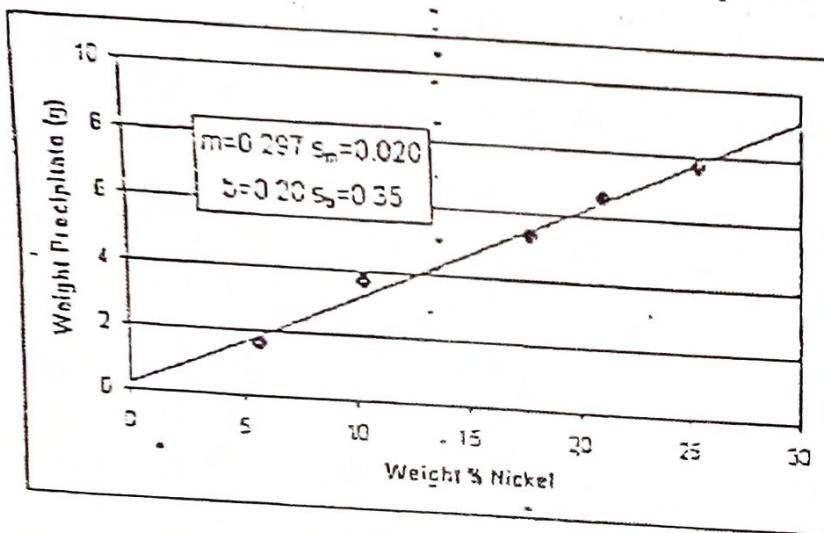
- 8.1 What do the following terms mean when applied to a gravimetric procedure: (a) digestion, (b) homogeneous precipitation, (c) ignition?
- 8.2 Write the balanced equation for the following:  
 a) The precipitation of chloride in sample by adding silver nitrate.  
 b) The precipitation of sulfate in a sample by adding barium chloride.  
 c) The gelatinous precipitate of ferric hydroxide is ignited to ferric oxide.
- 8.3 Why should  $\text{AgCl}$  be washed with dilute  $\text{HNO}_3$  in a gravimetric analysis?
- 8.4 A 50 ml solution of  $\text{NaBr}$  was treated with excess  $\text{AgNO}_3$ . The weight of the  $\text{AgBr}$  (M. W. 187.772) precipitate obtained was 0.2146 g. Calculate the molarity of the  $\text{NaBr}$  solution.
- 8.5 (a) Precipitation from homogeneous solutions is the most commonly used gravimetric method of analysis? Briefly discuss the requirements for a successful analysis.  
 (b) Discuss the advantages and disadvantages of using gravimetry in analysis?
- 8.6 Calculate to four significant figures the gravimetric factors for the following analyses:  
 (a) Mn precipitated with KOH and weighed as  $\text{Mn}_3\text{O}_4$   
 (b) Lu precipitated with  $\text{C}_2\text{O}_4^{2-}$  and weighed as  $\text{Lu}_2\text{O}_3$   
 (c) Ca precipitated with  $\text{C}_2\text{O}_4^{2-}$  and weighed as  $\text{CaCO}_3$   
 (d) Sr precipitated with  $\text{SO}_4^{2-}$  and weighed as  $\text{SrSO}_4$   
 (e)  $\text{Cr}_2\text{O}_3$  precipitated as  $\text{BaCrO}_4$  and weighed as  $\text{BaCrO}_4$   
 (f)  $\text{Bi}_2\text{S}_3$  precipitated as  $\text{BaSO}_4$  and weighed as  $\text{BaSO}_4$
- 8.7 A 0.5962 g iron ore sample was dissolved in hot perchloric acid and then filtered. The iron was oxidized to the ferric state,  $\text{Fe}^{3+}$  (AW 55.85). The solution was made basic with ammonium hydroxide,  $\text{NH}_4\text{OH}$ , and the iron subsequently precipitated as ferric hydroxide. This gel was filtered in a cistern-glass crucible, rinsed with dilute ammonium hydroxide, ignited, cooled in a desiccator, and weighed. The resulting ferric oxide,  $\text{Fe}_2\text{O}_3$  (FW 159.69) weighed 0.3210 g.

## Principles of Chemical Analysis

- (a) Why is the solution filtered after perchloric acid dissolution?  
 (b) Why rinse with ammonium hydroxide solution?  
 (c) Why use a dessicator during cooling?  
 (d) What is the wt. % of iron in the sample if the analysis produced 0.3210 g  $\text{Fe}_2\text{O}_3$ ?

8.8

Gravimetric analysis of nickel by precipitation with dimethylglyoxime gave the linear ( $y = mx + b$ ) calibration shown below. Regression values for the slope and intercept, and their standard deviations, are given in the inset box. Calculate the weight % nickel, and estimate the error using propagation formulas, for a sample with precipitate weight  $5.120 \pm 0.001\text{g}$ .



8.9

- (a) What do you understand by the term "co-precipitation"?  
 (b) Briefly discuss the process through which co-precipitation occurs.  
 (c) 0.6407 g of a sample containing chloride and iodide ions were treated with excess  $\text{AgNO}_3$ . The weight of the silver halide precipitate obtained was 0.4430 g. This precipitate was then strongly heated in a stream of  $\text{Cl}_2$  gas to convert  $\text{AgI}$  to  $\text{AgCl}$ . The weight of the precipitate after this treatment was 0.3181 g. Assuming that the conversion of  $\text{AgI}$  to  $\text{AgCl}$  is complete calculate the percentage of chloride and iodide in the sample. (Relative atomic masses Ag = 108, Cl = 35.5, I = 127)

8.10

- A 3.6670 g sample of a foot powder was wet-ashed and the zinc in it was precipitated as  $\text{ZnNH}_4\text{PO}_4$ . After filtration the precipitate was ignited to  $\text{Zn}_2\text{P}_2\text{O}_7$ , which weighed 0.2824 g. What gravimetric factor would you use in calculating the %  $\text{Zn}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$  in the sample.

8.11

- The phosphate in a 1.1020 g sample of fertilizer was precipitated as  $\text{MgNH}_4\text{PO}_4$ . Ignition at  $900^\circ\text{C}$  converted the precipitate to  $\text{Mg}_2\text{P}_2\text{O}_7$ , which weighed 0.2416 g. What is the % P in the fertilizer. Show your work.

8.12

- Calculate the gravimetric factor you would use for calculating the %  $\text{Fe}_3\text{O}_4$  from the gravimetric analysis in which  $\text{Fe}_2\text{O}_3$  results from igniting the  $\text{Fe}(\text{OH})_3$  precipitate.