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عنوان المحاضرة باللغة العربية: التحليل الوزني

عنوان المحاضرة باللغة الإنكليزية : Gravimetric Analysis

3.1 Introduction

A gravimetric analysis is based upon the measurement of the weight of a substance of known composition that is chemically related to the analyte. Two types of gravimetric methods exist.

1- *Precipitation methods*: The species to be determined is caused to react chemically with a reagent to yield a product of limited solubility; after filtration and other suitable treatment, the solid residue of known chemical composition is weighed.

2-*Volatilization methods*: The substance to be determined is separated as a gas from the remainder of the sample; here the analysis is based upon the weight of the volatilized substance or upon the weight of the nonvolatile residue. Precipitation methods are more frequently encountered than methods involving volatilization, so we concentrate on the precipitation method.

3.2 Calculation of Results from Gravimetric Data

A gravimetric analysis requires two experimental measurements: specifically, the weight of sample taken and the weight of a product of known composition derived from the sample. Ordinarily these data are converted to a percentage of analyte by a simple mathematical manipulation.

If A is the analyte, we may write:

weight of A
% A =
$$----- \times 100$$
 (3-1)
weight of sample

Usually the weight of A is not measured directly. Instead, the species that is actually isolated and weight either contains A or can be chemically related to A. In either case, a *gravimetric factor* is needed to convert the weight of the precipitate to the corresponding weight of A.

Example 1

How many grams of Cl are contained in a precipitate of AgCl that weights 0.204 g? Atomic weights for Ag = 107.86, Cl = 35.45.

We write the equation:

AgNO₃ + NaCl

$$-AgC+\downarrow$$
 + NaNO₃
Cl⁻ $-AgC+$
 $35.45 \equiv 143.3$
x 0.204

$$x = 0.204 \times \frac{35.45}{143.3} = 0.0505 \text{ g}$$

The value $\frac{35.45}{143.3}$ is called the *gravimetric factor* (GF).

Example 2

To what weight of $AlCl_3$ would 0.204 g of AgCl correspond? Atomic weights for Ag = 107.86, Cl = 35.45, Al = 26.98.

We know that each AlCl₃ yield three AgCl. Therefore,

AlCl₃ = 3AgCl
133.3 = 3 × 143.3
x 0.204

$$x = 0.204 \times \frac{133.3}{3 \times 143.3} = 0.0633 \text{ g}$$

Example 3

What weight of Fe_2O_3 can be obtained from 1.63 g of Fe_3O_4 ? What is the gravimetric factor for this conversation? Atomic weights for Fe = 55.84, O = 16.

It is necessary to assume that all Fe in the Fe_3O_4 is transformed into Fe_2O_3 and ample oxygen is available to accomplish this change. That is:

 $2Fe_{3}O_{4} + [O] = 3Fe_{2}O_{3}$ $2Fe_{3}O_{4} \equiv 3Fe_{2}O_{3}$ $2 \times 231.5 \equiv 3 \times 159.7$ $1.63 \qquad x$

$$3 \times 159.7$$

x = 1.63 × _____ = 1.687 = 1.69 g
 2×231.5

gravimetric factor
$$\frac{3 \times 159.7}{2 \times 231.5} = 1.035$$

Example 4

A 0.703 g sample of a commercial detergent was ignited at a red heat to destroy the organic matter. The residue was then taken up in hot HCl which converted the P to H₃PO₄. The phosphate was precipitated as MgNH₄PO₄.6H₂O by addition of Mg²⁺ followed by aqueous NH₃. After being filtered and washed, the precipitate was converted to Mg₂P₂O₇ by ignition at 1000°C. This residue weighed 0.432 g. Calculate the percent P in the sample. Atomic weights for P = 30.97, Mg = 24.3, O = 16.

$$P \equiv Mg_2P_2O_7$$

$$30.97 \equiv 222.54$$

x 0.432

$$x = 0.432 \times \frac{2 \times 30.97}{= 0.120 \text{ g}}$$

$$222.54$$

$$0.120$$

% P = $----- \times 100 = 17.1\%$
 0.703

 $-Na_2 O_3 + CO$

Example 5

At elevated temperatures sodium oxalate is converted to sodium carbonate:

 $Na_2C_2O_4$

Ignition of a 1.3906 g sample of impure sodium oxalate yielded a residue weighing 1.1436 g. Calculate the percentage purity of the sample. Atomic weights for Na = 22.98, C = 12, O = 16.

Here it must be assumed that the difference between the initial and final weights represents the carbon monoxide evolved during the ignition; it is this weight loss that forms the basis for the analysis. From the equation for the process, we see that:

1.3906 - 1.1436 = 0.247 weight of CO

$$Na_2C_2O_4 \equiv CO$$
$$133.96 \equiv 28$$
$$x \qquad 0.247$$

133.96

$$x = 0.247 \times \underline{\qquad} = 1.181 \text{ g}$$

$$28$$
% Na₂C₂O₄ = $\frac{1.181}{1.3906} \times 100 = 84.97\%$

Example 6

Calculate the percentage of SO₃ in a sample of gypsum of a 0.7560 g weight, produced 0.9875 g of BaSO₄ precipitate. Atomic weights for Ba = 137.34, O = 16, S = 32.

BaSO₄ = SO₃
233.34 = 80
0.9875 x

$$x = 0.9875 \times \frac{80}{233.34}$$

% SO₃ = $\frac{0.3385}{0.7560} \times 100 = 44.77\%$

3.3 Properties of Precipitates and Precipitating Reagents

The ideal precipitating reagent for a gravimetric analysis would react specifically with the analyte to produce a solid that would:

(1) have a sufficiently low solubility so that losses from that source would be negligible.

(2) be readily filtered and washed free of contaminants.

(3) be unreactive and of known composition after drying or, if necessary, ignition.

Few precipitates or reagents possess all these desirable properties; thus, the chemist frequently finds it necessary to perform analyses using a product or a reaction that is far from ideal.

3.4 Filterability and Purity of Precipitates

Both the ease of filtration and the ease of purification are influenced by the particle of the solid phase. The relationship between particle size and ease of filtration is straightforward, coarse precipitates being readily retained by porous media which permit rapid filtration. Finely divided precipitates require dense filters, low filtration rates result. The effect of particle size upon purity of a precipitate is more complex. A decrease in soluble contaminants is found to accompany an increase in particle size.

In considering the purity of precipitates we shall use the term coprecipitation, which describes those processes by which normally soluble components of a solution are carried down during the formation of a precipitate.

3.5 Factors That Determine the Particle Size of Precipitates

Enormous variation is observed in the particle size of precipitates, depending upon their chemical composition and the conditions leading to their formation.

* **Colloidal suspensions**, the individual particles of which are so small as to be invisible to the naked eye (10^{-6} to 10^{-4} mm in diameter). These particles show no tendency to settle out from solution, nor are they retained upon common filtering media.

* **Particles** with dimensions on the order of several tenths of a millimeter. The dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle out rapidly and are readily filtered.

No sharp discontinuities in physical properties occur as the dimensions of the particles containing the solid phase increase from colloidal to those typical of crystals. Indeed, some precipitates possess characteristics intermediate between these types.

The particle size of the solid that forms is influenced in part by experimental variables as the temperature, the solubility of the precipitate in the medium in which it is being formed, reactant concentrations, and the rate at which reagents are mixed. The particle size is related to a single property called relative supersaturation, where:

relative supersaturation =
$$\frac{Q - S}{S}$$
 (3-2)

Q is the concentration of the solute at any instant, and S is its equilibrium solubility.

During formation of sparingly soluble precipitate, each addition of precipitating reagent causes the solution to be momentarily supersaturated (that is Q > S). Under most circumstances, this unstable condition is relived, usually after a brief period, by precipitate formation. Experimental evidence suggests, however, that the particle size of the resulting precipitate varies inversely with the average of relative supersaturation that exists after each addition of reagent. Thus, when (Q - S) / S is large, the precipitate tends to be colloidal; when this parameter is low on the average, a crystalline solid results.

3.6 Mechanics of Precipitate Formation

The effect of relative supersaturation on particle size can be rationalized by postulating two precipitation processes, *nucleation* and *particle growth*. The particle size of a freshly formed precipitate is governed by the extent to which one of these steps predominates over the other.

Nucleation is a process whereby some minimum number of ions or molecules (perhaps as few as four or five) units to form a stable second phase. Further precipitation can occur either by formation of additional nuclei or by deposition of solid on the nuclei that are already present (particle growth). If the former predominates, a precipitate containing a large number of small particles results; if growth predominates, a smaller number of large particles will be produced.

The rate of nucleation is believed to increase enormously with increasing relativesupersaturation. In contrast, the rate of particle growth is only moderately enhanced by high relative supersaturations. At low relative supersaturations, growth predominates. When the supersaturation is great, the exponential nature of nucleation may cause this process to occur. These effects are illustrated in Figure 3-1.



Figure 3-1 Effect of Relative Supersaturation on Precipitation Processes

3.7 Experimental Control of Particle Size

Experimental variables that minimize supersaturation and thus lead to crystalline precipitate include:

Elevated temperature (to increase *S*).

Dilute solutions (to minimize *Q*).

Low addition of the precipitating agent and

Good stirring (also to lower the average value of *Q*).

The particle size of precipitates with solubilities that are pHdependent can often be enhanced by increasing *S* during precipitation.

3.8 Colloidal Precipitates

Individual colloidal particles are so small that they are not retained on ordinary filtering media; furthermore, Brownian motion prevents their settling out of solution under the influence of gravity. Fortunately, however, the individual particles of most colloids can be coagulate or agglomerate to give a filterable, noncrystalline mass that rapidly settles out from a solution.

* Coagulation of colloids

Three experimental measures induce the coagulation process are, **heating**, **stirring**, and **adding an electrolyte to the medium**.

The individual particles in a typical colloid bear either a positive or a negative charge as a consequence of *adsorption* of cations or anions on their surfaces. Adsorption of ions upon an ionic solid has the normal bonding forces that are responsible for crystal growth. When a silver ion adsorbed on the surface of a silver chloride particle, negative ions are attracted to this site by the same forces that hold chloride ions in the silver chloride lattice. Chloride ions on the surface exert an analogous attraction for cations in the solvent. Thus, a silver chloride particle will be positively charged in a solution containing an excess of silver ions, and it will have a negative charge in the presence of excess chloride ion for the same reason.

Figure 3-2 illustrates schematically a colloidal silver chloride particle in a solution containing an excess of silver ions. Attached directly to the solid surface are silver ions in the primary adsorption layer. Surrounding the charge particle is a region of solution called the counter-ion layer, within which there exists an excess of negative ions sufficient to balance the charge of the adsorbed positive ions on the particle surface. The counter-ion layer forms as the result of electrostatic forces.

The solution outside the secondary adsorption layer remains electrically neutral. **Coagulation** cannot occur if the secondary adsorption layer is too thick because the individual particles of AgCl are unable to approach one another closely enough. The primarily adsorbed silver ions and the negative counter-ion layer constitute an electric double layer that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.

Coagulation of a colloidal suspension can often be brought about by a short period of healing, particularly if accompanied by stirring. Heating deceases the number of adhered ions and thus the thickness of the double layer.

An even more effective way to coagulate a colloid is to increase the electrolyte concentration of the solution. If we add a suitable ionic compound to a colloidal suspension, the concentration of counter-ions increases in the vicinity of each particle. As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases.



Figure 3-2 Colloidal AgCl Particle Suspended in a Solution of AgNO₃

* Coprecipitation in coagulated colloids

Adsorption is the principal type of coprecipitation that affects coagulated colloids; other types are encountered with crystalline solids.

A coagulated colloid consists of irregularly arranged particles which form a loosely packed, porous mass. Within this mass, large internal surface areas remain in contact with the solvent phase. Adhering to these surfaces will be most of the primarily adsorbed ions which were on the uncoagulated particles.

* Peptization of colloids

Peptization is the process whereby a coagulated colloid reverts to its original dispersed state. Peptization occurs when pure water is used to wash such a precipitate. Washing is not particularly effective in dislodging adsorbed contaminants; it does tend to remove the electrolyte responsible for coagulation from the internal liquid in contact with the solid. As the electrolyte is removed, the counter-ion layers increase again in volume. The repulsive forces responsible for the colloidal state are thus reestablished, and particles detach themselves from the coagulated mass. The washing becomes cloudy as the freshly dispersed particles pass through the filter.

This problem is commonly resolved by washing the agglomerated colloid with a solution containing a volatile electrolyte which can subsequently be removed from the solid by heating. For example, silver chloride precipitates are ordinarily washed with dilute nitric acid. The washed precipitate is heavily contaminated by the acid, but no harm results since the nitric acid is removed when the precipitate is dried at $110 \,^{\circ}$ C.

3.9 Crystalline Precipitates

In general, crystalline precipitates are more easily handled than coagulated colloids. The particle size of crystalline solids can be improved by keeping the relative supersaturation low during the period in which the precipitate is formed. From Equation 3-2, it is apparent that minimizing Q or maximizing S, or both, will accomplish this purpose.

The use of dilute solutions and the slow addition of precipitating agent with good mixing tend to reduce the supersaturation in the solution. Ordinarily, *S* can be increased by precipitating from hot solution.

* Types of impurities in crystalline precipitate

The specific area of crystalline precipitates is relatively small; consequently, coprecipitation by direct adsorption is negligible. However, other forms of coprecipitation, which involve incorporation of contamination within the interior of crystals, may cause serious errors. There are two types of coprecipitation:

1- *Inclusion:* Interfering ions whose size and charge are similar to a lattice ion may substitute into the lattice by chemical adsorption. The impurities are randomly distributed, in the form of individual ions or molecules, throughout the crystal. Inclusions are difficult to remove since the included material is chemically part of the crystal lattice. The only way to remove included material is through reprecipitation.

2- Occlusion: It involves a nonhomogeneous distribution of impurities, consisting of numerous ions or molecules of the contaminant, within imperfections in the crystal lattice. Occlusion occurs when whole droplets of solution containing impurities are trapped and surrounded by a rapidly growing crystal. Because the contaminants are located within the crystal, washing does little to decrease their amount. A lower precipitation rate may significantly lessen the extent of occlusion by providing time for the impurities to escape before they become entrapped. Digestion of the precipitate for several hours is even more effective in eliminating contamination by occlusion.

* Digestion of crystalline precipitates

The heating of crystalline precipitates (without stirring) for some time after formation frequently yields a product with improved purity and filterability. The improvement in purity results from the solution and recrystallization that occur continuously and at an enhanced rate at elevated temperatures. During these processes, many pockets of imperfection become exposed to the solution; the contaminant is thus able to escape from the solid and more perfect crystals result.

Solution and recrystallization during digestion are probably responsible for the improvement in filterability as well. Bridging between adjacent particles occur to yield larger crystalline aggregates which are more easily filtered.

3.10 Direction of Coprecipitation Errors

Coprecipitated impurities may cause the results of an analysis to be either too high or too low. If the contaminant is not a compound of the ion being determined, positive errors will always result. Thus, a positive error will be observed when colloidal silver chloride adsorbs silver nitrate during a chloride analysis. On the other hand, where the contaminant contains the ion being determined, either positive or negative errors may be observed. In the determination of barium ions by precipitation as barium sulfate, for example, occlusion of barium salts occurs. If the occluded contaminant is barium nitrate, a positive error will be observed, since this compound has a greater formula weigh than the barium sulfate. If barium chloride were the contaminant, a negative error would arise because its formula weight is less than that of the sulfate salt.

3.11 Drying and Ignition of Precipitates

After separating the precipitate from its supernatant solution the precipitate is dried to remove any residual traces of rinse solution and any volatile impurities. The temperature and method of drying depend on the method of filtration, and the precipitate's desired chemical form. A temperature of 110 °C is usually sufficient when removing water and other easily volatilized impurities. A conventional laboratory oven is sufficient for this purpose. The temperature required to produce a suitable product varies from precipitate to precipitate.

3.12 Applications of Gravimetric Method * Inorganic precipitating agents

Table 3-1 lists some of the common inorganic precipitating agents. These reagents typically cause formation of a slightly soluble salt or a hydrous oxide. The weighing form is either the salts itself or else an oxide. The lack of specificity of most inorganic reagent is clear from the many entries in the table.

| Precipitating Agent | E lement Precipitated |
|-----------------------------------|--|
| NH3(aq) | Be (BeO), Al (Al ₂ O ₃), Fe (Fe ₂ O ₃), Sn (SnO ₂) |
| H ₂ S | Cu (CuO), Zn (ZnO), Ge (GeO ₂), Sn (SnO ₂) |
| (NH ₄) ₂ S | Hg (HgS), Co (Co ₃ O ₄) |
| H ₂ SO ₄ | Li, Mn, Sr, Cd, Pb, Ba (all as sulfates) |
| HC1 | Ag (AgCl), Hg (Hg ₂ Cl ₂), Na (NaCl), Si (SiO ₂) |
| AgNO ₃ | Cl (AgCl), Br (AgBr), I (AgI) |
| NH ₄ SCN | Cu (Cu ₂ (SCN) ₂) |
| HNO3 | Sn (SnO ₂) |
| | |

Table 3-1 Some Inorganic Precipitating Agents

* Reducing reagents

Table 3-2 lists several reagents that convert the analyte to its elemental form for weighing.

Table 3-2 Some Reducing Reagents Employed in Gravimetric Methods

| Reducing Agent | Analyte |
|-------------------------------------|--|
| SO ₂ | Se, Au |
| SO ₂ +H ₂ NOH | Те |
| H ₂ NOH | Se |
| $H_2C_2O_4$ | Au |
| H ₂ | Re, Ir |
| HCOOH | Pt |
| NaNO ₂ | Au |
| TiCl ₂ | Rh |
| SnCl ₂ | Hg |
| Electrolytic reduction | Co, Ni, Cu, Zn, Ag, In, Sn, Sb, Cd, Re, Bi |
| | |

* Organic precipitating agents

In general, these reagents tend to be more selective in their reactions than many of the inorganic reagents listed in Table 3.1.

Two types of organic reagents are encountered. One forms slightly soluble nonionic complexes called coordination compounds. The other forms products in which the bonding between the inorganic species and the reagent is largely ionic.

Organic reagents which yield sparingly soluble coordination compounds typically contain at least two functional groups, each of which is capable of bonding with the cation by donation of a pair of electrons. The functional groups are located in the molecule in such a way that a five- or six-membered ring results from reaction. Coordination compounds which form complexes of this type are called chelating agents; their products with a cation are termed chelates.

Neutral coordination compounds are relatively nonpolar; as a consequence, their solubilities are low in water but high in organic liquids. Chelates usually possess low densities and are often intensely colored. Three examples of coordination reagents are considered here.

8-Hydroxyquinoline. Approximately two dozen cations form sparingly soluble coordination compounds with 8-hydroxyquinoline, which is also known as oxine.



Typical of these is the product with magnesium:



The solubilities of metal oxinates vary widely from cation to cation and, moreover, are pH dependent because proton formation always accompanies the chelation reaction. Therefore, by control of pH, a considerable degree of selectivity can be imparted to 8hydroxyquinoline.

α-Nitroso-β-naphthol. This was one of the first selective organic reagents; its structure is:



The reagent reacts with cobalt(II) to give a neutral cobalt(III) chelate having the structure CoA₃. The most important application of α -nitroso- β -naphthol has been for the determination of cobalt in the presence of nickel. Other ions that precipitate with the reagent include bismuth(III), chromium(III), mercury(II), tin(IV), titanium(III), tungsten(VI), uranium(VI), and vanadium(V).

Dimethylglyoxime. An organic precipitating agent of unparalleled specificity is dimethylglyoxime.



Its coordination compound with palladium is the only one that is sparingly soluble in acid solution. Similarly, only the nickel compound precipitates from a weakly alkaline environment. Nickel dimethylglyoxime is bright red and has the structure:



Sodium Tetraphenylboron. Sodium tetraphenylboron, $(C_6H_5)_4B^-Na^+$, is an important example of organic precipitating reagent that form saltlike precipitates. In cold mineral acid solutions, it is a near-specific precipitating agent for potassium ion and for ammonium ion. The precipitates can be brought to constant weight at 105 to 120°C. Only mercury(II), rubidium, and cesium interfere and must be removed by prior treatment.

Benzidine. Another salt-forming reagent is benzidine.

Benzidine precipitates sulfate from a slightly acidic medium as $C_{12}H_{12}N_2.H_2SO_4$. The solubility of this precipitate increases rapidly with temperature and also with the acidity of the environment; both variable must be carefully controlled. Instead of being weighed as a gravimetric precipitate, benzidine sulfate may be titrated with a standard solution of sodium hydroxide. Yet another method for completion of the analysis calls for titration of the benzidine with a standard solution of permanganate. The methods succeed in the presence of copper, cobalt, nickel, zinc, manganese(II), iron(II), chromium(III), and aluminum ions. Benzidine is well suited to the rapid, routine analysis of sulfate.