

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 it can be reduced by digestion and reprecipitation .

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 :

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 :

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

Organic precipitating agents :

The organic precipitants such as dimethylglyoxime and 8-hydroxyquinoline are more selective than inorganic precipitants . They produce with the analyte less soluble precipitate (small K_{sp}). They also have high molecular weight so that the weighing error is reduced . 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 .

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,

$$GF = \frac{mw \text{ of analyte (g / mole)}}{mw \text{ of precipitate (g / mole)}} \times R$$

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

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

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

ESTIMATION OF BARIUM SULPHATE

A certain barium halide exists as the hydrated salt $\text{BaX}_2 \cdot 2\text{H}_2\text{O}$. where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 mL) and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate , mw = 233.3) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.

The precipitate is barium sulfate . The first stage is to determine the number of moles of barium sulfate produced, this will, in turn give us the number of moles of barium in the original sample.

$$\text{Number of moles of Ba} = \text{Wt. of BaSO}_4 \text{ ppt.} / \text{mw of BaSO}_4 = 0.2533 / 233.3 = 1.09 \times 10^{-3}$$

This is the number of moles of barium present in the precipitate and, therefore, the number of moles of barium in the original sample. Given the formula of the halide, (i.e. it contains one barium per formula unit), this must also be the number of moles of the halide. From this information we can deduce the relative molecular mass of the original halide salt

$$\begin{aligned} \text{mw of BaCl}_2 \cdot 2\text{H}_2\text{O} &= \text{wt. of BaCl}_2 \cdot 2\text{H}_2\text{O} / \text{no. of moles of Ba in BaCl}_2 \cdot 2\text{H}_2\text{O} \\ &= 0.2650 / 1.09 \times 10^{-3} = 244.18 \end{aligned}$$

$$\begin{aligned} \text{Atomic wt. of Ba} + 2 \text{ X mw of H}_2\text{O} &= 137.327 + 2 \text{ X } 18 \\ &= 173.327 \end{aligned}$$

$$\text{aw of } 2\text{X} = 244.18 - 173.327 = 70.85$$

$$\text{aw of X} = 70.85 / 2 = 34.43$$

The atomic weight (am) of chlorine is 35.45 which is in good agreement with the result obtained and hence the halide salt is hydrated barium chloride and X = Chlorine

