Precipitant or precipitating agent

Precipitant or precipitating agent refers to the chemical that is used to cause precipitation. 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.

It is important to understand that the term specificity is used to tell something about the method's ability responding to one single analyte only, while selectivity is used when the method is able to respond to several different analytes in the sample.

Specifically react only with a single chemical species, i.e., Dimethylglyoxime – Ni^{+2}

Selectively react with a limited number of species, i.e., $AgNO^{3-}$ Cl^-, Br^-, I^- and SCN^-

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

Inorganic precipitating agents

Common inorganic precipitants can be used to determine several cations and anions. In some cases, the formation of the same precipitate can be used to determine the cation and the anion. For example, the reaction of barium and chromate ions to give barium chromate is used to determine both barium and chromate. However, precipitates such as hydroxides, oxalates, and metal ammonium phosphates are first converted to a weighable form. Precipitation methods can also be applied to determine organic functional groups such as organic halides, carbonyl, alkoxy groups, aromatic nitro, azo, and phosphate.

Organic precipitating agent

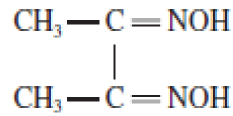
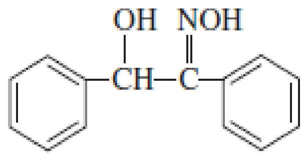
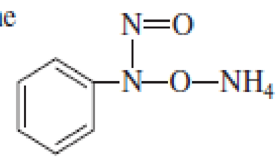
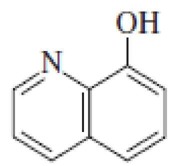
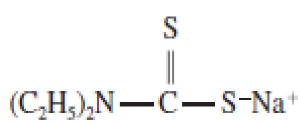
Organic precipitating agents have the advantages of giving precipitates with very low solubility in water and a favorable gravimetric factor. Most of them are **chelating agents** that form slightly soluble, uncharged chelates with the metal ions.

A chelating agent is a type of complexing agent that has two or more groups capable of complexing with a metal ion. The complex formed is called a chelate. Since chelating agents are weak acids, the number of elements precipitated, and thus the selectivity, can usually be regulated by adjustment of the pH. Some of these precipitates are not stoichiometric, and more accurate results are obtained by igniting them to form the metal oxides.

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 ($PbMoO_4$)
HCl	**Ag** ($AgCl$), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** ($AgCl$), Br ($AgBr$), I(AgI)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
$NaCl$, $Pb(NO_3)_2$	F ($PbClF$)
$BaCl_2$	**SO_4^{2-}** ($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-} ($Mg_2P_2O_7$)

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime		Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α -Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, $MoO_2{}^{+}$, $WO_2{}^{2+}$) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + nNH_4R \rightarrow \underline{MR_n} + nNH_4{}^+$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate		Many metals from acid solution ($M^{n+} + nNaR \rightarrow \underline{MRn} + nNa^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), $NH_4{}^+$, $RNH_3{}^+$, $R_2NH_2{}^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + NaR \rightarrow \underline{MR} + Na^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7{}^{2-}$, $MnO_4{}^-$, $ReO_4{}^-$, $MoO_4{}^{2-}$, $WO_4{}^{2-}$, $ClO_4{}^-$, $I_3{}^-$. Acidic solution ($A^{n-} + nRCl \rightarrow R_nA + nCl^-$)

Errors in Gravimetric analysis

There are different causes of errors in gravimetric analysis these are as follows:

- Inaccurate weighing.
- Incomplete and imperfect precipitation.
- Ignition of precipitate at either too low or too high temperature.
- Exposure of ignited precipitate to the atmosphere.
- Use of sub standard reagent and apparatus.
- Haste and impatience.

Precaution to avoid the errors in gravimetric analysis

Gravimetric analysis has several possible causes of error, however, a careful analyst with adequate technical skill would avoid frequent mistakes.

For a successful gravimetric analysis, the following precaution should be used.

- ✓ Since gravimetric analysis is a lengthy and tedious process, each step must be conducted with considerable patience.
- ✓ Dilute solutions should be used for the precipitation since they prevent co-precipitation.
- ✓ The precipitant should be slowly introduced with constant stirring. This helps in large crystal growth, and the level of super-saturation is also decreased.
- ✓ Precipitation should be performed under hot conditions since precipitation is most effective in hot solutions.
- ✓ A slight excess of the precipitant should be added throughout the precipitation process, but significant excess must be avoided since they will contaminate the precipitate.

Advantages of gravimetric analysis

1. Although there are numerous sources of inaccuracy in gravimetric analysis, when conducted correctly, this method remains the most accurate method for chemical analysis.
2. his procedure employs low-cost equipments.
3. It allows for very little instrumental error and does not necessitate a set of standards to calculate the constituent to be determined.
4. It is an analytical method that helps to determine the quantity of analyte based on the density of the solid.
5. This approach has been developed and standardized for practically all cations and anions.
6. This technique can also be used with neutral species like iodine, carbon dioxide, water, and sulfur dioxide.
7. This method has been successfully used to estimate a wider range of organic compounds, including lactose in milk products, salicylates in medications, nicotine in pesticides, and cholesterol in cereals, among others.
8. Possible sources of error i.e. presence of impurities can be checked easily.

Disadvantages of gravimetric analysis

1. It is a macroscopic approach since a large amount of sample is needed.
2. The study of a single element or small group of elements may generally only be done via gravimetric analysis at one time.
3. The steps in this method are frequently complex, and a single mistake in the process can frequently cause trouble for the study.
4. This method is time-consuming and difficult because it requires so many steps.

Requirements of gravimetric analysis

1. The component that needs to be estimated must be fully precipitated.
2. The precipitate should be pure before it weighs.
3. The precipitate must be suitable for handling, such as filtering, washing, weighing, etc.
4. The most fundamental requirement for the gravimetric analysis is the selection of an insoluble precipitate of the constituent to be determined which has sufficient stability and is suitable for manipulation.