Paper: FS-201 (Forensic Chemistry)

Topic: Precipitations & Organic Precipitant

by

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Precipitations (Gravimetric Methods of Analysis):

1.One of the most accurate and precise methods of macro quantitative analysis. (II) Analyte selectively converted to an insoluble form (III) Measurment of mass of materials and correlate with chemical composition. Gravimetric analysis is one of the major divisions of analytical chemistry. The measurement step in a gravimetric method is a weighing. Ppt^n is a widely used technique for separating the analyte from the interference. Electro dialysis, solvent extraction and chromatography are other important methods are used for separation. Why (II) Simple (ii) Often required for high precision.

Principle: A gravimetric method of analysis is usually based on a chemical reaction such as

$$_aA + _rR \longrightarrow A_aR_r$$

where a molecule of the analyte, A react with r molecules of the reagent, R. The product AaRr, is usually a slightly soluble substance which can be weighed as such after drying or which can be ignited to another compound of known composition and then weighed. An excess of reagent R is normally added to repress the solubility of the precipitate.

Criteria for gravimetric method are successful:

1. The ppt should be slightly soluble, so it can be weighed as such.
2. The separation process should be sufficiently complete so that the quantity of analyte left unprecipitated is undetectable (usually 0.1mg or less should be detected by chemical balance).
3. The substance (ppt) should have definite composition (composition should not changed) and should be pure or very nearly so.
4. The pure form of the ppt is weighed and from this value the wt. of analyte in the sample is calculated.

In the usual gravimetric procedure a precipitate is weighed, and from this value the weight of analyte in the sample is calculated. The percentage of analyte A is then

$$\%\ A = \frac{\text{wt of A}}{\text{wt of sample}} \times 100$$

For Example: Calcium can be determined gravimetrically by precipitation of calcium oxalate and ignition of the oxalate to calcium oxide:

$$Ca^{2+} + C_2O_4^{2-} \longrightarrow CaC_2O_4(s)$$

$$CaC_2O_4(s) \longrightarrow CaO(s) + CO_2(g) + CO(g)$$

Desirable properties of Precipitate:

1. The ppt should be insoluble, so that no appreciable loss occurs, when it is collected by filtration. In practices this is usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary chemical balance.
2. The ppt must be easily separated from the solution by filtration and can be washed free of soluble impurities. The condition required that the particle are of such size that they do not pass through the filtering medium and that the particle size is unaffected (or at least not diminished) by the washing process.
3. The ppt must be convertible in to a pure substance of definite composition (this may be affected by ignition or by simple chemical operation such as evaporation with suitable liquids).

Theory/Ppt^n Process:

1. **Super saturation:** Super saturation is achieved by adding precipitant reagent to the solution. Supersaturation occurs when the solution phase contains more of dissolve precipitate that can be present at equilibrium. The greater the disparity the greater the relative super saturation.
2. **Nucleation:** When the some minimum number of ions or nuclei come together to form a stable second phase, this is the process of nucleation. The process of nucleation involves formation of the smallest particles of precipitate (the nuclei) that will grow spontaneously from the supersaturated solution.
3. **Crystal growth:** When the large number of nuclei is formed then these will close together to give a ppt which is curdy, eg. AgCl.

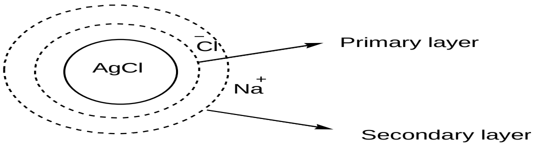
   When the less number of nuclei are formed, these nuclei act as a base for further growth of ppt deposited on the initially formed nuclei, so the crystal grown inside and we get the crystalline ppt. This is the best form of ppt.

Gelatinous ppt: Some colloids when coagulated carry down large quantity of water giving a gelly like ppt. "Those ppt which take along with them a large amount of water during ppt^n are gelatinous ppt. Ex. $Fe(OH)_3$, $Al(OH)_3$.

Paneth- Fajans-Hahn's Rule: When the ionic product exceeds the solubility product, A^+ and B^- ions begin clinging together, forming a crystal lattice and growing sufficiently large to be pulled to the bottom of the content by the force of gravity.

$$\underset{10^{-8}\text{ cm}}{\text{Ions in sol}^n} \longrightarrow \underset{10^{-7}\text{-}10^{-4}\text{ cm}}{\text{Collidal sol}^n} \longrightarrow \underset{>10^{-4}\text{cm}}{\text{Precipitate}}$$

For Ex: Suppose that a drop of $AgNO_3$ is added to a solution of sodium chloride and the solubility product constant of AgCl is surpassed. When the first particle grows to colloidal size, there are a large number of Ag^+ and Cl^- ions on the surfaces. In the sol^n are Na^+, Cl^- and NO_3^- ions. As a general rule (Paneth- Fajans-Hahn's Rule**)** the ion in the solution which is more strongly adsorbed is the one in common to the lattice, in this case the Cl- ion (If no common ion present, this rule says that the ion in solution that forms the least soluble compound with one of the lattice ions is the most strongly adsorbed). Thus the surface of particle acquires a layer of chloride ion and the particle becomes negatively charged. The chloride ions are said to form the primary layer; they inturn attract sodium ions, forming a secondary layer. The secondary layer is held more loosely than the primary layer. The primary and secondary layers are considerable to constitute a electrical double layer which imparts a degree of stability to the colloidal dispersion. These layers cause colloidal particles to repel one another and the particles therefore resist combination to form larger particle which will settle from the solution.



Peptization: The phenomenon by which the ppt can revert back to colloidal state is known as peptization. This occurs due to the removal of charge, neutralization on the surface of ppt. This can be avoided by suitable electrolyte in the wash soln (electrolyte replace this ions).

Von Weimarn theory of relative super saturation:

Initial rate of ppt **α** Relative super saturation

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

Q= Total conc^n of substance (solute) which has been precipited

S= Equilibrium solubility

Q-S = represent degree of super saturation at the moment precipitation begins.

The term S in the denominator represents the force resisting precipitation or causing the precipitate to redissolve.

The larger the Q-S term, the greater is the number of nuclei and the smaller are the particles of ppts.

The greater the value of S, the smaller will be the ratio and smaller will be the number of nuclei formed

The value of S increases by heating the soln and saturation more. Value of S can be increased by increasing the temp, varying the pH or by the of complexing agent. (Analyst is interested in obtaining large particle; he should try to adjust conditions to make the ratio Q-S/S as small as possible.)

Chemical steps involved in gravimetry:

1. The sample being analysed is weighed first.
2. The wt sample is dissolve in to a suitable solvent
3. Species which interfere in actual measurement are often removed by suitable separation method.
4. Experimental environment is adjusted, this may include pH adjustment, concentrating or diluting the soln.'
5. A suitable inorganic precipitating reagent is added.
6. Ppt^n is carried out in hot soln (dil). The precipitating reagent being added very slowly with constant stirring, so that the initial form nuclei act as base for the further crystal growth.
7. Ppt is then separated from mother liquor by filtration.
8. Ppt is washed with suitable soln containing a suitable electrolyte.
9. The dried ppt/ ppt produced from the result of ignition are finally weight.

Types of Precipitation:

1. Coprecipitation: The process by which a normally soluble substance is carried down during the precipitation of the desired substance. **"**Contamination of the precipitate by other contaminants which are normally soluble in the mother liquor is called co-precipitations".

Coprecipitation may occur by the formation of mixed crystals or by the adsorptions of ion during the precipitation process. Coprecipitation is phenomenon by which impurities normally soluble in the solution are precipitated. This can occur by two ways:

3. **Adsorption:** this occurs when the impurities are present on the surface of the ppt. (the helding of one substance to the other substance).

3. **Occlusion:** The process by which an impurity is held within a crystal by growth of the crystals around it. Occlusion occurs during the process of crystal growth, solvent or some impurities present in the solution are incorporated or occluded in the crystal and further crystal growth occurs over these impurities. These impurities become in an internal part of the crystal structures. The occluded impurities can be removed by the process of digestion. Adsorption impurities can be removed by the washing.

For eg. When the sulphuric acid is added to a solution of barium chloride containing small amounts of nitrate ions, the ppt of barium sulphate is found to contain barium nitrate. It is said that the nitrate is co precipitated with sulphate**.** This type of contamination is called occlusion.

Digestion: The process in which a ppt stands in contact with the mother liquor to promote crystal growth.

Procedure That can be employed to minimize the co precipitation:

1. Methods of addition of two reagents. 2. Washing. 3. Digestion. 4. Reprecipitation. 5. Seperation. 6. Use of conditions that lead to larger particle size.

2. Post Precipitation: The process by which an impurity is deposited after the precipitation of the desired substance is termed post precipitation.

"The phenomenon by which a sparingly soluble substance presents in the solution in a supersaturated state which has an ion common with the initial ppt may be ppt over the ppt."

Post precipitation occurs when the solution is supersaturated with a foreign substance that precipitated very slowly. This can be prevented by filtering the ppt as soon as precipitation is complete. For eg.

1. Zinc sulfide does not readily precipitate from solution containing Zinc ion, hydrogen ion (0.1-0.2 M) and those that are saturated with hydrogen sulfide. However, if Hg(II) sulfide is precipitated under the same condition in the presence of Zinc, over 90 % of the Zinc comes down as the sulfide within 20 minutes. Apparently Zinc sulfide forms very stable supersaturated solution when Hg(II) sulfide is present. Sulfide ions are strongly adsorbed at the interface of the solid and solution.

2. When calcium oxalate is precipitated in the presence of Mg^{2+} ions, magnesium oxalate doesn't immediately ppt because it tends to form supersaturated solution. But it formed when the soln is allowed to stand for long time before filtration.

3. Copper sulfides will ppt in the presence of Zn^{2+} in acidic solution. Zn sulfide also precipitated if solution is allowed to stands for a long time.

Comparison of co precipitation and Post precipitation:

1.Co precipitation reduces with keeping the ppt in contact with mother liquor whereas post precipitation increases.

2.Co precipitation can be reduces by mechanical stirring or digesting the sol^n whereas post precipitation increases.

3.Concentrated amount of impurities can be introduced by the post ppt^n (increase the post ppt^n)

3. Isomorphous replacement: Isomorphous replacement occurs in crystalline ppt. Ion is replaced in lattice by another ion of same size and shape which is present in the sol^n.

Methods used for removal of impurities:

1.Methods of addition of two reagents: This method can be used to control the conc^n of impurities and the electric charge carried out by the primary particle of ppt. This method is using that cases in which the contaminants present. The soln containing contaminant is added to the another reagent, so in this case the primary form particle on nuclei, occluded less impurities during the process of growth . After this treatment we can minimize the impurities.

2.Washing: This is generally used for curdy and gelatinous ppt because the surface area is high exposed. Hence there is more probability of impurity to absorb. Washing is done to remove the absorb impurities but care has to be taken during washing that the filtrate do not revert back to the colloidal state.

3.Digestion: This process is used for the removal of impurities in crystalline ppt. In this case the ppt is kept in contact with mother liquor for few hrs at an elevated temp. The smaller particle which has larger solubility as compared to larger particle, they come back in to the soln, making the soln supersaturated with respect to the larger particles. Now to stabilize the equilibrium. Some of the smaller particles leave the soln and redeposited over the larger particles. This process of growth of larger particle at the expense of smaller particle is called as Ostwald ripening. The process of digestion having two advantages.

1.Crystal size increases.

2.Occluded impurities can be removed.

4. Reprecipitation: This method again washing and digestion is done.

5. Separation: The impurities may be separated or its chemical nature is changed by some reaction before the ppt is formed.

Precipitation from homogeneous soln: The best known example of this method is the use of the hydrolysis of urea to increase the pH and ppt hydrous oxide or salt of weak acid. Urea hydrolysed according the equ^n.

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3 \qquad \text{pH increases}$$

During mixture of Ca^{2+} and Mg^{2+}

$$Ca^{2+} + H_2C_2O_4 + H_2O \longrightarrow CaC_2O_4 + CO_2 + 2NH_3 \qquad \text{pH increases}$$

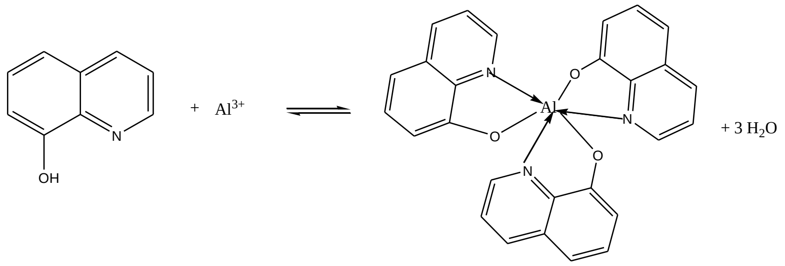
Ba^{2+} and Ca^{2+}: in this case pH decreases, Ba^{2+} will precipitated.

$$Ca^{2+} + H_2C_2O_4 + H_2O \longrightarrow CaC_2O_4 + CO_2 + 2NH_3 \qquad \text{pH increases}$$

$$(CH_3)_2SO_4 + 4\,H_2O \longrightarrow 2CH_3OH + SO_4{}^{2-} + 2H_3O^+ \qquad \text{pH decreases}$$

Organic Precipitant

Many inorganic anions can be precipitated with organic reagents called organic precipitant. A number of these reagents are useful not only for separation by precipitation but also by solvent extraction. Most of the organic precipitant combines with cations to form chelate rings. Neutral metal chelate compound insoluble in H_2O. 8-hydraxy quinoline (also called 8-quinolinol or oxine) form insoluble compounds with a number of metal ions (aluminium for one).



Mainly used for the group separation by controlling the pH. Aluminium replaces the acidic hydrogen of the hydroxyl group, at the same time the previously unshared pair of electron on the nitrogen is donated to the aluminium. Most of the better known organic precipitant which form chelate compounds with cations contains both an acidic and basic (electron donating) functional group. The metal interesting with both of these groups becomes itself one member of a heterorocyclic ring. Such types of chelate compounds are insoluble in water but soluble in less polar solvents such as $CHCl_3$ and CCl_4.

Separation of one or more inorganic ions from mixture may be made with the help of organic reagents with which they sparingly soluble and often colored compounds. These compounds usually have high m.w. so that small amounts of the ions will yield a large amount of the precipitats. It is difficult to give a rigid classification of the numerous organic reagents. The most important are those which form chelate complexes, which involve the formation of one or more (usually five or six membered) rings incorporating the metal ion, ring formation leads to a relatively great stability.

The ideal organic precipitant should be specific in character i.e. it should give a precipitate with only one particular ion.

Desirable property:

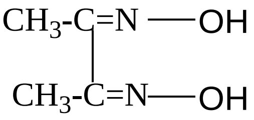
1. Many of the chelate compounds are very insoluble in ware so that the metal ions may be quantitatively precipitated.

2. The organic precipitant often has a larger m.w, thus a small amount of metal may yield a large weight of precipitate.
3. Some of the organic reagents are fairly selective, yielding precipitates with only a limited number of cations. Their selectivity can be easily enhanced by using controlling the pH and the conc^n of masking reagents.
4. Ppts obtained with organic reagents are often coarse and bulky and hence easily handled.
5. In some cases a metal can be precipitated with an organic reagent. The precipitate collected and dissolved and the organic molecule titrated, furnishing an indirect volumetric method for the metal.

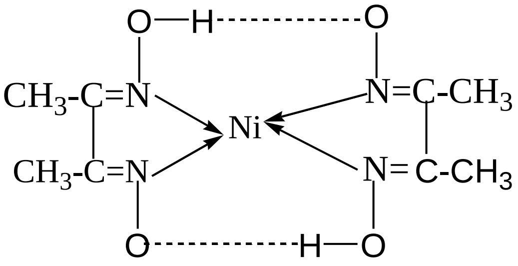
Disadvantage of organic precipitant:

1. The very limited aqueous solubility of most organic reagents themselves is often troublesome. It is generally necessary to add at least a slight excess of the precipitant, and the excess reagents contaminate the precipitate.
2. Many of the organic precipitants do not have good weighing form, largely because of uncertainty in the drying process. So weighing form can be changed.
3. A minor disadvantage is the fact that the precipitates are not easily wet by water and hence tend to float on the surface of the solution and to creep up the sides of glass vessel. The trouble can be alleviated by addition of a small amount of wetting agent to the solution before the filtration.

Di -Methyl Glyoxime (DMG)



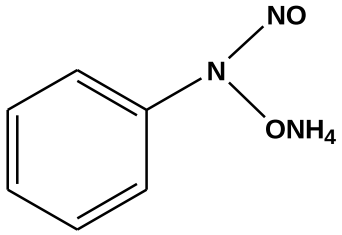
DMG

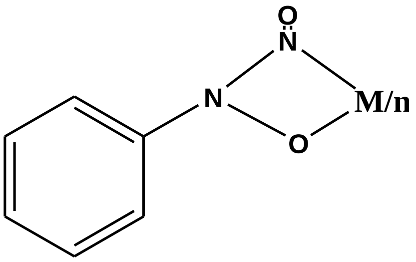


NiDMG

- Principally used for the determination of nickel in steel. It is colorless crystalline solid, which is sparingly soluble in water and highly soluble in alcohol and ether.
- At pH 12 and more than 12 i.e. alkali solution it behave as weak acid.
- Generally precipitation done in NH_3 sol^n or buffer sol^n containing CH_3COONH_4 and acetic acid and precipitate is dried at 110-120 °C.
- Generally large excess of reagent is avoided, as reagent it self precipitated (because insoluble in water). The interferences are Al, Fe, Bi, and they are masked by citrate and tartrate. For precipitation we can use 2-3 % of sodium salt of DMG in water (dark and red color).
- DMG is also used for the precipitation of Bi at pH 11-11.5 and gives a yellow ppt. exact composition is not known but assumes to be a polymer with a composition of $Bi_2 (C_4H_4N_2O_2)$. This precipitate is dried at 105-125 °C.
- In the presence of EDTA and of cyanide ion, metal ion Al, As, Bi, Ca, Cd, Cu, Pb, Mg, Hg, Ni, Pd, Pt, Ag, Sr, W and Zn do not interfere.
- Solution of palladium (II) salts gives a characteristic yellow ppt in dil. HCl or H_2SO_4 solution. The composition is similar to that of nickel *viz* $Pd(C_4H_7O_2N_2)_2$ and the ppt can be dried at 110-120 °C. The ppt is almost insoluble in hot water but dissolves readily in ammonia and cyanide ion.
- Gold is reduced to the metal by this reagent and platinum is partially precipitated either as a greenish complex compound or as the metal, upon the boiling the solution.
- The sodium salt of dimethylglyoxime $Na_2C_4H_6O_2N_2.8H_2O$ is available commercially. This is soluble in water and may be employed as 2-3 % aq. solution.

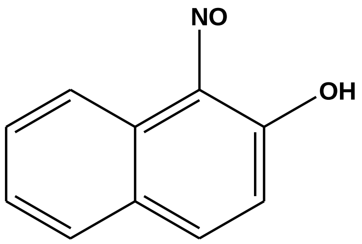
Cupferron (Ammonium salt of nitroso -N-phenyl hydraxylamine)

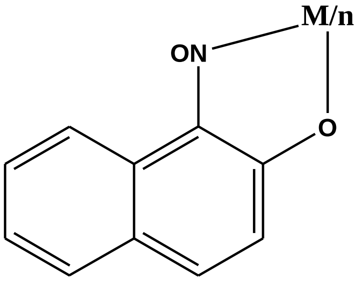




- Mainly used for separation of Iron and Titanium from Alluminium (The cupferron method is very satisfactory for the separation of iron, titanium, zirconium, vanadium, and in special cases tin, tantalum, uranium and gallium).
- It is most useful when employed in strongly acid solution (5-10 % by volume of HCl or H_2SO_4) and the precipitates iron(III), vanadium(V), titanium(IV), zirconium(IV), cerium(IV), niobium(V), tantalum(V), tungsten(VI), gallium(III) and tin(IV) separated these elements from aluminium, berilium, chromium, manganese, nickel, cobalt, zinc, uranium(VI) calcium, strontium and barium. The presence of tartrate and oxalate has no effect upon the precipitation of metals by cupferron (used as masking agent).
- Generally freshly prepared (6 % aqueous solution) sol^n of Cupferron is used because it dissociates keeping at long time.
- Cupferron form insoluble complexes with metals in both weakly and strongly acidic medium.
- Solid Cupferron should be stored in amber bottles containing a few lumps of ammonium carbonate to avoid decomposition (by photodecomposition).
- On heating Cupferron is decomposes to nitrobenzene, hence precipitation is done in cold soln.
- Filter precipitate as soon as possible because Cupferron is not stable in acidic soln.
- Nitric acid solution can not be used for the ppt^n, since oxidizing agent destroys the reagent.
- Macerated filter paper assists the filtration of ppt and also the subsequent gradual ignition.
- The precipitates can not be weighed after drying, but must be ignited to the corresponding oxide and weighed in this form. The ignition must be done cautiously in a large crucible with a gradual increase in temperature to avoid mechanical loss.

α- Nitroso-β-napthol



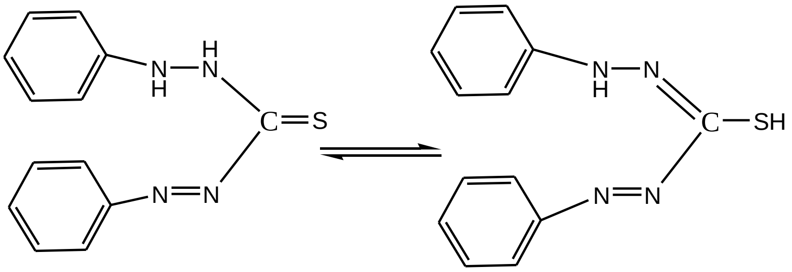


Principally used for the precipitation of cobalt in the presence of large amount of nickel after any iron(III) present has been removed. This reagent ppts quantitatively cobalt, Fe(III), Pd, Zr, from slightly acidic solutions. It ppts partially Tin, Silver, Bismuth, Chromium(III), Titanium, Tungusten(VI) Uranium(VI) and Vanadium(V).

- α- Nitroso-β-napthol is a brown powder, m.p. 109 °C. It is insoluble in water. The reagent is prepared by dissolving 4 g of α- Nitroso-β-napthol in 100 ml of glacial acetic acid and then adding 100 ml of hot distilled water. The cold filtered solution should be used immediately.
- Cobalt form a red-brown bulky ppt in dil. HCl. Composition of ppts is $Co(C_{10}H_6N)_3$ but doubtful whether the complex is pure.
- The ppt is carefully ignition in the presence of oxalic acid gives a cobalt oxide Co_3O_4. For larger amounts the cobalt oxide may be

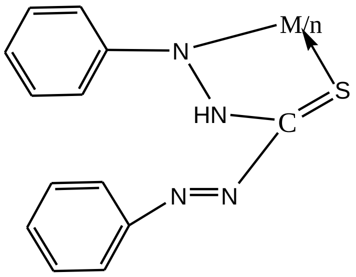
a. Reduced in hydrogen in a rose crucible and weighed as the metal. or
b. Treated with few drops of conc^n nitric acid to convert it in to nitrate, the excess of HNO_3 expelled by evaporating and then converted in to the sulphate by at least two evaporations with conc^n sulphuric acid followed by few drops of water and weighed as CoSO4 after heating for a short time at 450-500 °C. The cobalt solution may be also electrolyzed and the resulting metal weighed.

Dithiazone (diphenyl thiocarbazone)



Thione

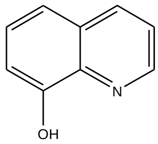
Thiol



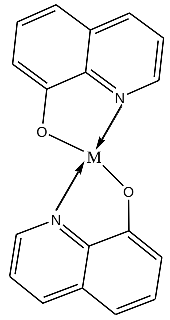
Metal Chelate

1. Dithiazone exists as a tautomer in solution. Dithiazone is a violet black solid which is insoluble in water. In solution the color of dithiazone is deep green.
2. Dithiazone and its metal chelates are highly insoluble in water but soluble in chloroform, CCl_4 and aq.ammonia.
3. Metal forming dithiazonates include, Mn, Fe, Co, Ni, Cu, Zn, Rd, Ag, Cd, Sn, and Pb. The chelate conc^n in extracts in normally determined spectrophotometrically.
4. Dithiazone can be used for separation of metal by controlling the pH and used as a masking reagent.
5. It behaves as monobasic acid up to pH 12. Acidic proton present in thiol form.
6. Ag, Hg, Pd, and Copper can be separated by controlling the pH.

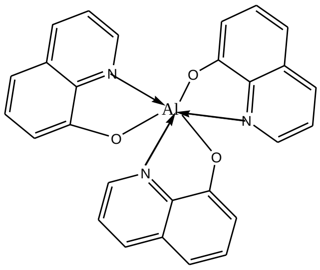
8-Hydroxy quinoline (Oxine)



Oxine



M = Mg , Cu, etc.



M= Al

1. Oxine forms sparingly soluble compounds with metallic ions which have the composition: $M(C_9H_6ON)_2$ If have coordination number 4(Mg, Zn, Cu, Cd, and Pb).
   $M(C_9H_6ON)_3$ If have coordination number 6 (Al, Fe, Bi, and Ga).
   $M(C_9H_6ON)_2$ If have coordination number 8 (Th and Zr).
   Exception: $TiO(C_9H_6ON)_2$, $MnO_2(C_9H_6ON)_2$, $Wo_2(C_9H_6ON)_2$ and $Uo_2(C_9H_6ON)_2$.
2. Oxine is colorless crystalline solid, M.P. 75-76 °C. It is insoluble in water.
3. Solution is prepared in alcohol (this reagents cannot be use for determination of alluminium) or acetic acid. Alcoholic solution may be use in cases where precipitation occurs at higher pH and acetic acid for precipitations at lower pH.
4. The ppt^n is done in cold sol^n or at temp 50-60 °C. The reagent is added in excess until the sol^n becomes yellow or orange which indicates the excess of reagents.
5. The precipitate is coagulated by a short period of heating at a temp not exceeding 70 ^{o}C.
6. The ppt may be filtered through filter paper or any variety of filtering crucible.
7. The filtrate should posses a yellow or orange color, indicating the presence of excess of precipitant. If a turbidity appears then the sol^n is heated. If on heating the turbidity disappears it may be assume to be due to excess of reagent crystallizing out and is harmless.
8. If turbidity remains as such, then it indicates incomplete precipitation and further addition of reagent is required. After complete ppt^n solution is heated up to 70 °C to coagulate the ppt. Precipitate is then washes with cold water and finally with alcohol until filtrate becomes colorless.
9. The washed ppt may be dried at 105-110 °C (usually hydrated oxinate) or at 130-140 °C (anhydrous oxinate). Frequently ignition to the oxide yields a more suitable form for weighing.

10. Since many oxinates are appreciably volatile, it is usually best to cover the complex with oxalic acid and heat gradually.
11. The determination may also be completed titrimetrically by dissolving the precipitate in dil.HCl and titrating with standard solution of potassium bromate.

Procedure to estimate aluminum:

1. Take 25 ml of solution which contain 0.2 g Al, then we adds 125 ml of water. Heat it to 50-60 °C then add excess of oxine until color becomes yellow or orange.
2. Cool and filtered through sintered crucible. Precipitate is dissolved in Conc^n HCl and few drops of methyl orange or methyl red.
3. Add excess (0.5-1.0 g) of KBr, Potassium bromate (0.1 N, $KBrO_3$). Then add KI (10 ml), the resulting I_2 is titrated with sodium thiosulphate solution (hypo) using starch as an indicator.