
UNIT 13 GRAVIMETRIC ANALYSIS

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13.1 INTRODUCTION

In the last block you have studied about Redox titration and complexometric titration. This is the last block of this course which contains three units. Unit 12 deals with the precipitation titration in which you have studied about the precipitation titrations in detail. This unit deals with gravimetric analysis. There are two basic approaches for qualitative analysis one is by measurement of volume and other is based on measurement of mass, which is known as gravimetric analysis. First we will discuss about supersaturation then we will discuss precipitation and rate of precipitation. Coprecipitation is very important by product of precipitation which we will discuss later part of the unit. We will also discuss the method for minimizing the co-precipitation. After co-precipitation we will study about post-precipitation and precipitations from homogeneous solutions. Next we will discuss very important components of gravimetric analysis i.e., washing of precipitates. And in the last we will study about the classification.

Objectives

After studying this unit you should be able to:

- understand the mechanism of precipitate formation,

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- understand role of rate of precipitation and the purity of the precipitate,
- understand processes which make a precipitate impure,
- understand different approaches employed to control the rate of precipitation to improve the nature and purity of the precipitate,
- list of appropriate solutions to wash the precipitate from the adhering impurities and
- explain the role of organic precipitating agents in gravimetric analysis, their advantages and disadvantages.

13.2 GRAVIMETRIC ANALYSIS –A GENERAL INTRODUCTION

There are two basic approaches to quantitative analysis, one is by measurement of volume and the other is based on measurement of weight. In titrimetry the volume of a solution of accurately known concentration required to react quantitatively with the solution of the substance to be determined is measured. On the other hand the quantitative analysis by weight known as gravimetric analysis involves the process of isolating and weighing an element or a definite compound of the element in a pure form as possible. If we look at most of the gravimetric analyses the chemical species to be determined is transformed to a pure stable compound which can be converted to a form suitable for weighing. The separation of the elements or the compounds in a pure form from rest of the bulk is conventionally affected by precipitation. However, one should know that for carrying out separation of the element or compound of interest there are other known methods like volatilization and electroanalytical. As indicated above, normally the gravimetric analysis involves the separation of the desired constituent from the main bulk in the form of a pure precipitate. It should be remembered that in order to minimize the error in the analysis the precipitation of the analyte should be complete and the precipitate be very sparingly soluble. Gravimetric methods are widely applicable and employed for the quantification of both inorganic and organic entities.

In spite of wide applicability the gravimetric methods of analysis have certain limitations. Ideally a precipitating reagent should react specifically or if not that selectively with the analyte. One finds that the examples of specific reagent are very rare. The best known example of a specific reagent usually quoted is dimethylglyoxime which is used for precipitating Ni^{2+} . However, selective reagents which are more in number react with a limited number of species. The selectivity of certain group of reagents can be improved by controlling the conditions of precipitation. These may be the pH of the solution and the presence of masking agents. The arguments which are generally heard against gravimetric analysis are that it is very time-consuming and the sensitivity does not compete favourably with other analytical methods particularly instrumental. Gravimetric technique may be more accurate than an instrumental method which requires calibration or standardization. Instruments generally provide relative values and have to be calibrated on the basis of results of gravimetric or volumetric methods. Thus it becomes clear that gravimetric methods are imperative for standardization of standards or stock solutions which are used for calibration or checking the performance of instruments used for analysis. But you have to very clearly understand the different aspects of this technique to maintain the high level of accuracy inherent in these methods of analysis.

13.3 SUPERSATURATION AND NUCLEATION

13.3.1 Nucleation

Nucleation is a physical reaction which occurs when components in a solution start to

precipitated. In a simple example of nucleation, supersaturated sugar water is used to make rock candy, with the sugar crystals nucleating and growing into crystals.

Before discussing more about nucleation it may be important to know the dependence of solubility of particle size. The (solubility of a substance at a given temperature in a given solvent is the amount of substance dissolved by a known weight of the solvent when the substance is in equilibrium with the solvent.) The definition of solubility refers to particle size larger than 0.01 mm. For particle size smaller than 0.01 mm the solubility increases greatly with the decreasing particle size. In gravimetric analysis large particle size precipitates. They are less prone to surface adsorption, easy to filter and washed free from impurities.

The particle size of solids formed by precipitation varies largely. At one end there are colloidal suspensions whose tiny particles of the diameter $10^{-7} - 10^{-4}$ cm are invisible to the naked eye. These particles show no tendency to settle from solution and cannot be easily filtered. At the other end are the particles with the dimensions of the order of tenths of a millimeter or greater. The dispersion of such particles in the liquid phase is known as crystalline suspension. The particles of crystalline suspensions settle quickly and are readily filtered.

Such a condition is desired to be attained because it yields precipitate which can be easily filtered. Moreover, this precipitate is purer than a precipitate with relatively small size.

The mechanism of precipitate formation is much more complicated than you would comprehend. The discussion upto this stage clearly points out that for the purity of the precipitate the size of the particles is very critical. It is known that different experimental variables influence the particle size. Some of the important ones are:

- Precipitate solubility,
- Temperature,
- Reactant,
- Concentration and
- Rate at which they are mixed. The net effect of these variables can at least be qualitatively accounted for by a single property of the system known as relative supersturation.

13.3.2 Supersaturation

A supersaturated solution is one which contains greater concentration of the solute than permitted by the equilibrium solubility at the temperature under consideration. Essentially supersaturation is an unstable state just before the precipitation begins. This unstable state may be brought to a state of equilibrium by addition of a crystal of the solute or of some other substance or by mechanical means namely shaking or stirring.

SAQ 1

What are the two main reasons for not recommending precipitates with small particle size for gravimetric work?

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13.4 RATE OF PRECIPITATION

Von Weimarn was the first to make a systematic study of the relationship between the size of the particle of a precipitate and the rate of precipitation. It was proposed that the initial rate of precipitation is proportional to relative supersaturation.

Initial velocity of precipitation $\propto \frac{Q-S}{S}$, where Q is the concentration of a species at an instant and S is equilibrium solubility.

This Q-S represents the degree of supersaturation at the moment precipitation begins. The larger this term the greater is the number of nuclei and smaller the size of the particles of the precipitate. The term S represents the factor resisting precipitation. The greater the value of S the smaller the ratio and hence smaller the number of nuclei formed.

$\frac{Q-S}{S}$ is low value, when Q is small or increasing S is large. A moderate decrease in

Q can be made by: i) Using reasonably dilute solutions and ii) Adding the precipitating reagent slowly.

S can be increased by making use of the factors namely temperature, pH, or the use of complexing agents which are known to generally affect the solubility. So we can say:

- i) Precipitation is usually carried out in hot solutions because the solubility generally increases with the rise in temperature.
- ii) It is generally recommended to carry the precipitation from dilute solutions and the reagent is added slowly with constant stirring. The slow addition of the reagent results in the formation of fewer numbers of primary particles which grow as more material precipitates. Constant stirring helps in coagulation of the colloidal particles and proper crystal growth of the precipitates. Stirring also helps in the distribution of the precipitant in the whole bulk of the solution thus avoiding the supersaturation to be attained rapidly in a particular zone of the solution.
- iii) In order to increase the solubility the addition of a suitable reagent is often recommended. This also leads to the formation of larger primary particles.

13.4.1 Digestion of the Precipitate with the Mother Liquor

In order to improve the nature of the precipitate the above approaches are adopted during the actual precipitation process. However, there is one other recourse available after the precipitation. This makes use of the fact mentioned in sub sec. 13.2.2 that smaller particles are more soluble than larger particles. The material of smaller particles that goes into solution reappears on larger particles making them even larger. This is achieved by digesting or aging the precipitate. It amounts to the fact that if the precipitate is allowed to stand in contact with the mother liquor frequently at elevated temperature for some time before filtration the smaller particles go into solution making it supersaturated with respect to larger particles. The equilibrium with respect to larger particles is achieved when the additional material leaves the solution and enters the solid phase. This additional material appears on larger particles making them to grow even larger. This process is often termed as Ostwald ripening. It has been observed that digestion does not significantly improve the nature of curdy precipitate like AgCl or gelatinous precipitate such as Fe(OH)₃. This happens when the compound is either very insoluble or the particles do not differ much in size. However, digestion at elevated temperatures before filtration is successful in increasing the particles size of crystalline precipitates like BaSO₄ and CaC₂O₄.

SAQ 2

Which one of the following precipitates is likely to improve significantly by digestion with the mother liquor.

- a) $Al(OH)_3$
- b) AgI
- c) ZnS
- d) $PbSO_4$

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13.5 COPRECIPITATION

Precipitates separating from a solution are not as a rule pure but contain larger amount of foreign substances including mother liquor. The precipitates may contain varying amounts of impurities depending upon the nature of the precipitate and the conditions of precipitation. The contamination of the precipitate by substances that are normally soluble under the conditions of precipitation is called coprecipitation. Contamination as a result of coprecipitation should be distinguished from contamination as a result of purely chemical precipitation. A typical example of coprecipitation is encountered when barium chloride is added to a solution of potassium sulphate the precipitated barium sulphate is found, after washing, to contain greater or lesser amounts of potassium sulphate inspite of the fact that this salt is freely soluble under the circumstances. Corecipitation prominently takes place by the two mechanism i.e.

- i) adsorption at the surface of the particles
- ii) occlusion by incorporation of foreign ions (and solvent)

13.5.1 Method of Minimizing Coprecipitation

In the foregoing discussion we have seen that precipitates predominantly become impure due to coprecipitation.

It may also be pointed out that there are no universal rules to reduce coprecipitation but in a fairly general way they can be enumerated as under.

- i) Precipitation should be carried out from dilute solutions keeping in mind the solubility, the time required for filtration and the subsequent operations to be carried out with the filtrate. If the precipitate is formed by mixing very concentrated solutions at room temperatures it separates out more or less as a flocculated colloid which is likely to be contaminated by surface absorption.
- ii) The reagents should be mixed slowly with constants stirring. This is how we can keep the degree of supersaturation low and will be able to get large crystals. Large crystals have lesser surface adsorption.
- iii) Precipitatuion should be carried out from hot solution provided the solubility and stability of the precipitates permit. Since:
 - the solubility increases the degree of supersaturation decreases.
 - coagulation of the precipitate is assisted thereby reducing the sol formation.

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- the velocity of crystallization is increased thus leading to better formed crystals.
- iv) Crystalline precipitates should be digested within the other liquor as long as practical except where postprecipitation may occur. Digestion of the precipitate may be done by leaving the precipitate in contact with the mother liquor either overnight or on a steam bath for some time. During digestion smaller crystals with larger surface area and more prone to adsorption go into the solution and the corresponding material reappears on larger crystals. It may be again emphasized here that digestion has little effect upon amorphous or gelatinous precipitates, the nature of the precipitates is hardly improved.
- v) By carrying out second precipitation less amount of foreign substances are involved and consequently the amount of impurities carried by the precipitate will be less.

13.5.2 Role of Coprecipitation for the Separation of Tracer Quantities

We have seen that coprecipitation is detrimental as far as the purity of precipitate is concerned, but it can be very useful for the separation of tracer quantities of radioisotopes. The radioisotopes produced by nuclear reaction are usually present in extremely small quantities and ordinary precipitation procedures generally fail at such a low concentration. The separation of unweighable amount of tracer material from macro quantities of target materials by coprecipitation usually involves two steps. First the tracer is separated and concentrated from the target material by coprecipitation. Thus the role of carrier is to carry the tracer amounts by surface adsorption. Second the tracer is separated and concentrated from the carrier. It is desired to use carrier substances that can be separated from the tracer easily in subsequent operations. Generally the tracers are coprecipitated by surface adsorption on unspecified carriers. The adsorption is due to large surfaces offered to tracer quantities by many scavenger type materials. Substances of high specific surface area are generally manganese dioxide, metal sulphides and hydrated oxides. Ferric hydroxide is a very useful scavenger and in the presence of excess of hydroxide ions it is negatively charged. The use of ferric hydroxide as a scavenger for the separation of barium radioisotope from cesium target used for the nuclear reaction illustrates the utility of coprecipitation. The separation of barium from cesium is made by coprecipitation barium on ferric hydroxide at pH10. The separation of barium from iron is made by dissolving the precipitate in acid and reprecipitation ferric hydroxide at pH 5.4. Barium remains in the supernatant liquid.

SAQ 3

Why does polymetallic manganese sea nodules found at ocean floor contain a very large number of metals at the trace level?

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13.6 POSTPRECIPITATION

Coprecipitation is important as far as the contamination of a precipitate with foreign materials is concerned. But there is another process called postprecipitation which makes a precipitate impure. In this case, as the name suggests the primary precipitate separates out in a pure form and the second phase of the foreign substance which is slightly soluble forms afterwards. The second phase is therefore, not coprecipitated but postprecipitated. Postprecipitation can occur only when the supernatant is supersaturated, with respect to some component which crystallizes fairly slowly. In other words it occurs with sparingly soluble substances which form supersaturated

solution and usually have an ion in common with the primary precipitate. In the precipitation of calcium as oxalate in the presence of magnesium a small amount of the latter is coprecipitated with the calcium oxalate. However, if the suspension is digested for a long time some magnesium oxalate appears on calcium oxalate. The longer the precipitate is allowed to stand in contact with the solution the greater is the postprecipitation of magnesium oxalate on calcium oxalate.

A typical example of postprecipitation is observed when H₂S is passed through a 0.2 N H₂SO₄ solution containing Cu²⁺ ions and a little amount of Zn²⁺ ions. Copper sulphide will precipitate first without carrying zinc. It means that there will not be any coprecipitation. However, if the precipitated copper sulphide is left with zinc ions in solution zinc sulphide is precipitated at the copper sulphide precipitate. The strong promoting effect of copper sulphide is due to the fact it has strong adsorptive properties towards hydrogen sulphide or other sulphides.

13.7 DIFFERENCES IN COPRECIPITATION AND POST PRECIPITATION

We have seen that both coprecipitation and postprecipitation make the precipitates impure and can cause serious problems but the two differ in several aspects.

- i) If the precipitate is left in connect with the mother liquor the contamination increases with time in postprecipitation the contamination increases the faster the solution is agitated by either the mechanical or thermal means. The reverse is generally the case with coprecipitation.
- ii) In the case of postprecipitation the contamination increases the faster the solution is agitated by either the mechanical or thermal means. The reverse is generally the case with coprecipitation.
- iii) The magnitude of contamination by postprecipitation may be much greater than by coprecipitation.

SAQ 4

Which one of the cations is likely to be coprecipitated most with BaSO₄ precipitate?

- a) Na⁺
- b) K⁺
- c) Ca⁺⁺
- d) Cu⁺⁺

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SAQ 5

PbSO₄ is soluble in ammonium acetate. PbSO₄ coprecipitated with BaSO₄ precipitte does not come out easily even after washing the host precipitates with ammonium acetate solution. Explain why.

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13.8 PRECIPITATION FROM HOMOGENEOUS SOLUTION

One of the major objectives of a precipitation reaction is the separation of a pure solid phase. In order to obtain a solid with a minimum contamination to is desirable to produce large well-defined crystals rather than microcrystals. In other words a compact and dense precipitate instead of a gelatinous precipitate is required. The guidelines to be used in the preparation fo precipitates with desired physical characteristics were offered by von Weimarn. The key lies in the fact that the degree of supersaturation should be dept minimum. This will bead to fewer nuclei and the material will grow on them. Ideally the precipitating reagent should be added in successive small increments until its concentration just reaches the threshold value to form the first stable solid particles. But the ideal rate is rarely attained in a direct precipitation process carried out in the usual manner. The problem has been sorted out by slowly generating the precipitant by a homogeneous chemical reaction within the solution instead of adding the precipitant externally. The technique is known as homogeneous precipitation. Different types of approaches have been adopted to carry out homogeneous precipitation. They can be broadly classified under four different categories.

- i) Generating the precipitating anions by slowly hydrolyzing the ester or some suitable compounds
- ii) Raising the pH of the solution by slowly boiling with area.
- iii) Synthesizing the reagents within the solution by reaction of the different components.
- iv) Releasing the cation slowly by changing its oxidation state or destroying its complex.

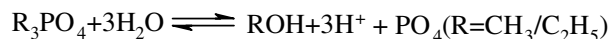
It should be noted that the above classification does not cover all the different examples available in the literature but provides a wide coverage.

13.8.1 Generating the Anions by Hydrolysis

Anions have been generated in solution to precipitate, insoluble salts, by controlled hydrolysis of corresponding esters or some suitable salts. In this class the esters have been mostly used. Let us discuss some important examples.

A. Precipitates of phosphates

Insoluble phosphates can be precipitated with phosphate generated from triethyl phosphate or metaphosphoric acid



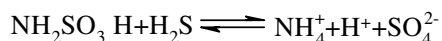
B. Precipitates of Oxalates

Esters of oxalic acid serve as a source of oxalate ions as per the equation below

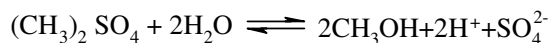


C. Precipitates of Sulphates

The hydrolysis of sulphamic acid serves as a convenient method for the generation of sulphate ion according to the reaction.

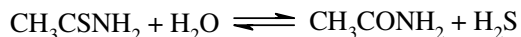


The reaction has been used for the separation and determination of barium ions. Hydrolysis of diethyl sulphate has been used to precipitate calcium, strontium, barium, and lead sulphate.



D. Precipitates of Sulphides

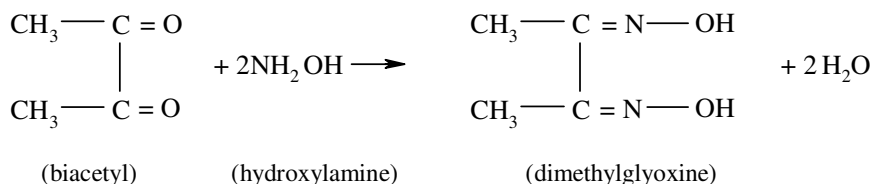
Many sulphur compounds have been suggested as the source of sulphide ions but thioacetamide is by far more popular and put to practical use. Thioacetamide hydrolyses to produce sulphide according to the reaction



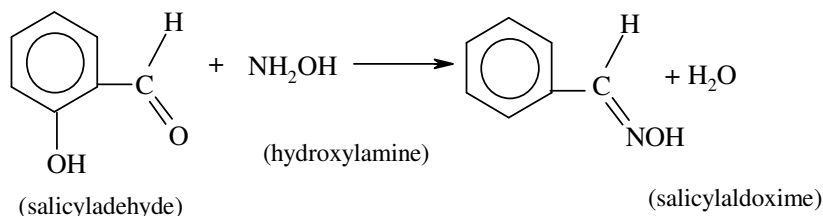
Determination of antimony, bismuth, molybdenum, copper, arsenic, lead, cadmium, tin and mercury using thioacetamide as a reagent has been reported.

13.8.2 Synthesizing the Reagents by Reaction of the Different Components

Up to this point we have focused our attention mainly on the generation of inorganic anions to precipitate metal ions. But the fact remains that there is very huge list of organic reagents employed for the precipitation of cations. A detailed discussion on these reagents will be taken later in Section 13.8. It should be kept in mind that these organic reagents which mostly form insoluble metal chelates have overtaken inorganic anions as precipitants primarily because it is easier to attain selectivity in the former. One of the major drawbacks in the use of organic reagents is the nature of the precipitates. Most of these precipitates obtained by organic reagents are flocculent in nature. In view of certain inherent advantages of organic reagents serious efforts have been made to improve the nature of the precipitates substantially by synthesizing them in solution in the presence of metal ions. One the best example in this category is offered by the precipitation of Ni^{2+} by synthesizing dimethylglyoxime by the reaction between biacetyl and hydroxylamine.

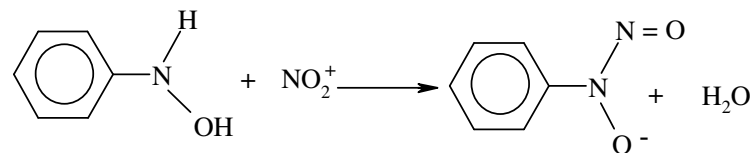


Another well-known reagent salicylaldoxime used for the precipitation of Cu^{2+} is generated by reaction between salicylaldehyde and hydroxylamine.



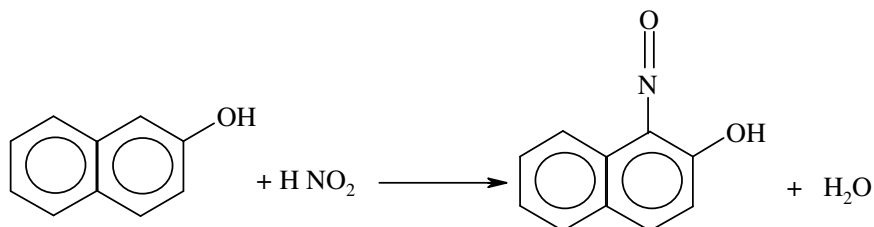
Cupferron has been synthesized in situ by the reaction between nitrate and phenylhydroxylamine to produce the insoluble precipitates of chelates of copper, iron and titanium from homogeneous solution.

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(phenylhydroxylamine)

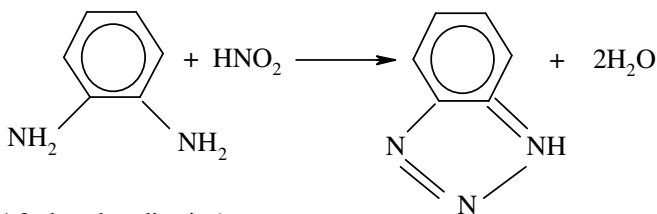
The action of nitrous acid with 2-naphthol led to a slow precipitation of cobalt 1-nitroso-2-naphtholate.



(2-naphthol)

(1-nitroso-2-naphthol)

This precipitate is stoichiometric and can be weighed directly while the conventional precipitate is contaminated and must be ignited to the oxide. When nitrous acid is reacted with 1, 2 phenylenediamine in aqueous solution in the presence of either copper or silver 1 H – benzotriazole slowly formed the precipitate of insoluble chelates of copper and silver from homogeneous solution.



(1,2 phenylenediamine)

(1 H-benzotriazole)

There are numerous such example where the reagent generated slowly in the solution precipitates the metal ion present there. The nature of the precipitate is markedly improved in terms of their easy filterability and purity.

SAQ 6

The hydrolysis of following reagents has been used for the homogenous precipitation of some cations.

- a) Trichloracetate
- b) 8-acetoxyquinoline
- c) Thioformamide

Citing the reaction, name the anion/ reagent which is generated. Also give the cation which can be precipitated.

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13.9 WASHING OF PRECIPITATE

When the precipitation is carried out from the solution invariably only one of the constituents is precipitated keeping many other in solution. The object of washing the precipitate is to remove the impurities contaminating the precipitate as completely as possible. In the process of washing only surface impurities will be removed. This means that under optimum condition the wash liquid will, in general, remove only the mechanically mixed and relatively loosely held impurities. Impurities which are strongly adsorbed by the precipitate may resist washing successfully and even some of the mechanically mixed supernatant liquid may remain protected by the capillary forces. The composition of the wash liquid, thus, becomes very critical. Moreover, in the light of some other constraints it should be carefully chosen. Water is used as a wash liquid but it should not be employed unless it is certain that it will not dissolve appreciable amount of precipitate or peptize it. Precipitates which have significant solubility in water may be washed with water containing an ion common to the precipitate. A typical example in this regard is that calcium oxalate is washed with an aqueous solution of ammonium oxalate. As in this particular case the dissolved constituent should be volatile. If the precipitate is somewhat soluble in water it may be washed with water-alcohol mixture. This treatment is suggested for some of the alkaline earth carbonates. It has been observed that sometimes a mixture of water and an organic solvent say ethanol or a dilute solution of an electrolyte is effective in reducing the solubility to negligible proportions. For washing PbSO_4 precipitate either dilute sulphuric acid or 50% aqueous ethanol is used.

Some of the precipitates have a tendency to become colloidal and passing through the filter paper. Such a tendency is frequently observed with gelatinous or flocculated precipitates. This process of peptization is rare with well-defined crystalline precipitates. For washing precipitates which peptize the wash solution should contain an electrolyte. The nature of the electrolyte should be such that it does not interfere during washing or ignition. Hydrated ferric oxide is washed with dilute ammonium nitrate solution and silver chloride precipitate with 1% HNO_3 .

Some precipitates tend to oxidize during washing and such precipitates cannot be allowed to run dry. In order to circumvent the problem the precipitate should be washed with a special solution which reconverts the oxidized product into the original one. Cu^{2+} is not gravimetrically determined as sulphide but it is a known of separation of copper. The CuS precipitate which has a tendency to be oxidized to CuSO_4 should be washed with acidulated hydrogen sulphide water.

If the precipitate is a salt of a weak acid or a weak base it should be washed with a solution which prevents hydrolysis. For example if the precipitate is a salt of a weak acid and is lightly soluble it may show a tendency to hydrolyze and the soluble product of hydrolysis will be a base. In such a case the wash liquid should be a base. Take the case of $\text{Mg}(\text{NH}_4)\text{PO}_4$ it may hydrolyse to give phosphate, HPO_4^{2-} and hydroxide ion. It should be washed with dilute aqueous ammonia. On the other hand if the salts of a weak base such as hydrated ferric, chromic or aluminium ion are to be separated from a precipitate say silica by washing with water the salts may be hydrolyzed to their basic salts or hydroxide and acid.



The addition of an acid to the wash solution will prevent hydrolysis of ferric or similar salts.

In a nut-shell the wash solution should have the following characteristics.

- i) it should not have any dissolution action upon the precipitate but remove the foreign impurities easily,

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- ii) it should not peptize the precipitate,
- iii) it should not form any volatile or insoluble product with the precipitate,
- iv) it should be easily volatile at the temperature of drying of the precipitate, and
- v) it should not contain any substance which is likely to interfere with subsequent determinations in the filtrate.

During washing of the precipitate the following general protocol should be observed

- i) since no precipitate is absolutely insoluble minimum volume of the washing liquid required to remove the objectionable material should be used,
- ii) it is better to wash the precipitate with a number of small portions rather than one or two large portions, and
- iii) the wash liquid should be well drained between each washings rather than adding fresh portion of the washing whilst solution still remains on the filter.

SAQ 8

Suggest suitable wash liquids for the following precipitates giving explanation for the choice

- a) CaC_2O_4
- b) AgI
- c) SrSO_4

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**13.10 ORGANIC PRECIPITANTS, THEIR ADVANTAGES
AND DISADVANTAGES**

The organic reagents find a variety of applications in inorganic analysis. These applications encompass their utility as precipitant, titrant and indicator, colorimetric reagent, extractant and masking agent. Besides these there are some minor applications in various analytical methods. One of the major applications, in the real sense, is the use of the organic reagents as precipitating agents.

Separation of one or more ions from mixtures can be made with the aid of organic reagents with which they yield sparingly soluble and often coloured compounds. These organic compounds have high molecular weights and yield a relatively large amount of the precipitate with a small amount of the metal ion. This in turn will increase the sensitivity of the gravimetric procedure. Yield of a large amount of the precipitate minimizes weighing errors. Ideally the organic precipitant should be specific i.e. it should give a precipitate with one particular ion. But it is difficult to attain this ideal condition. However, it is usual that an organic reagent will react with a group of ions and frequently by rigorous control of experimental conditions it is possible to precipitate only one of the ions of the group.

The selectivity is often greatly enhanced by the control of pH and the concentration of the masking agents. The masking agent forms a more stable complex with the interfering cation than with the precipitating cation. The interfering cation thus remains in solution. Sometimes the precipitates obtained by organic reagents may be weighed after drying at a suitable temperature or in other cases where the precipitate

does not correspond to a definite composition it is converted either to the oxide of the metal or metal by ignition. In a few cases a titrimetric method is adopted after dissolving the quantitatively precipitated metal complex.

The earlier work on the search of the selective reagents for the metal ions was empirical in character but a more fundamental approach is now possible. Over the years a variety of reagents have been developed and it is difficult to give a rigid classification of these compounds.

13.10.1 Classification

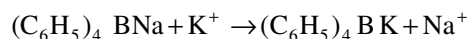
Five types of reactions have been identified with these organic reagents.

A. Formation of chelate compounds

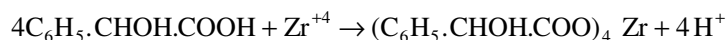
Probably the largest number of recorded cases of precipitation by organic compounds involves the formation of unionized chelate complexes. Most of the organic reagents which form chelates with the metal ions contain both an acidic and a basic functional group. The metal ion interacts with both of these groups and itself becomes a member of the heterocyclic ring. One of the best examples of this class of compounds is 8-hydroxyquinoline, also known as 8-quinolinol or oxine. It forms insoluble complexes with a number of metal ions.

B. Formation of salt-like compounds

Organic reagents also form salt-like compounds of low solubility with certain cations. Sodium salt of tetraphenyl boron precipitates K^+ ion.



Mandelic acid precipitates Zr^{+4}



C. Formation of adsorption complexes or lakes of indefinite composition

The lake appears to be formed between an organic reagent and the hydrated oxide of a metal. The nature of lake is not exactly known. Apparently the combination seems to take place on the surface of the colloidal particles of the oxide resulting in most of the cases in the production of a characteristic colour. There are many application of lake formation in colorimetric analysis with a few in gravimetric work. Tannin has been found useful in the precipitation of many metallic hydroxides. Cinchonine promotes complete precipitation of hydrated tungstic oxide.

D. Reduction to the metal

Some of the organic reagents have been used for the reduction of noble metals like platinum and gold etc. Hydroquinone and certain related compounds have been used for the reduction and determination of gold.

E. Use in homogeneous precipitation

The use of different organic reagents in homogeneous precipitation has been cited earlier in this chapter. Urea is a familiar example which raises the pH by slow hydrolysis to precipitate metal hydrous oxides and basic salts. Gradual hydrolysis of corresponding esters leads to the precipitation of phosphates, sulphates and oxalates. Thioacetamide is a convenient and inoffensive source of hydrogen sulphide to yield granular precipitates of metal sulphides.

Estimations Based On Precipitation and Gravimetry

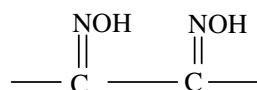
If one goes through the list of organic reagents employed for gravimetric work a majority of reagents belong to the first two of the above mentioned categories. It will be a improbable task to list the different organic reagents which have been used as metal ion precipitants. However, a majority of them are characterized by certain functional groups in molecules which are responsible for precipitation. Differences in parts of molecules may produce small changes in reactivity, solubility and colour. These changes can some time result in improvement in the utility of the reagent. Before taking a discussion on these functional groups it may be pertinent to point out that the discussion undertaken here is by means exhaustive but definitely gives an insight of the variations that have been introduced taking a few functional group as representative.

13.10.2 Reagents with Some Important Functional Groups

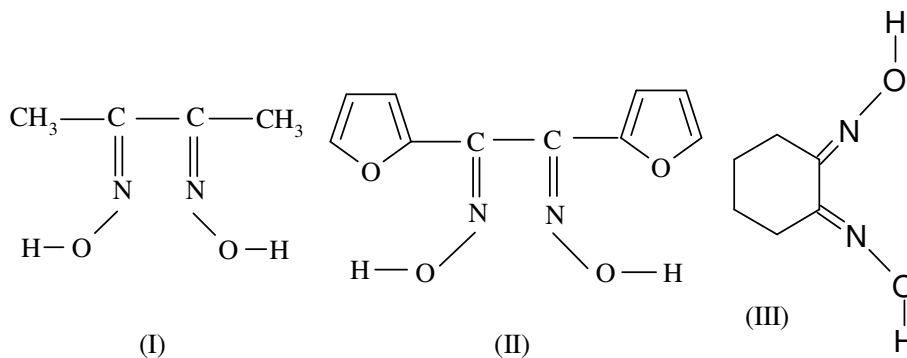
There are number of reagent but here we will discuss some important reagents

A. Dioximes

One of the most familiar examples of a metal chelate of this category is the red precipitate obtained in neutral or slightly alkaline medium by the addition of dimethylglyoxime (I) to nickel ion. This is probably the first chelate to be used for analytical purposes. It is strikingly selective for Ni (II) and Pd (II). The selectivity of the reaction is attributed to its configuration.



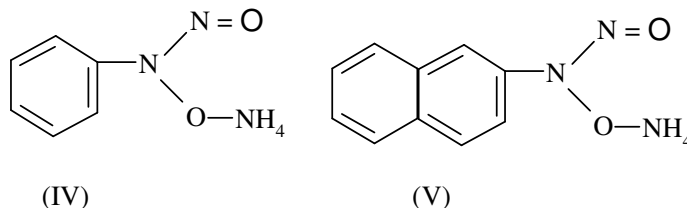
Many others α -dioximes such as furildioxime (II), bezildioxime (III), cyclohexane-1, 2-dionedioxime (III) and several others give similar reactions.



O-benzoquinonedioxime, however, does not precipitate nickel, so that the carbon atom in the dioxime configuration apparently cannot form part of an aromatic ring without the group losing its special reactivity. The reagent cyclohexane-1, 2-dionedioxime (nioxime) is a more sensitive reagent for the gravimetric determination of nickel than dimethylglyoxime. It is more soluble in water and possesses a more favourable gravimetric factor. It can be used as its aqueous solution and in a more acidic range than dimethylglyoxime. Its use is restricted because of its higher cost and the impurities accompanying the precipitate.

B. Nitroso compounds

The two well known derivatives of nitrosohydroxylamine are cupferron (ammonium salt of phenylnitrosohydroxylamine) (IV) and neocupferron (ammonium salt of naphthylanitrosohydroxylamine) (V).

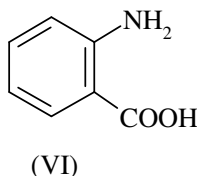


Both of these reagents react similarly but the second forms less soluble bulkier precipitates. They form precipitates with multivalent ions including Fe (III), Ga (III), Ti (IV), Zr (IV), Ce (IV), Nb (V), Ta (V), V (V) and W (VI) from moderately acidic solutions. From less acidic solutions some more metal ions may be precipitated. Both these reagents lack selectivity and therefore they are mainly used for separations. The precipitates formed with cupferron are of indefinite composition. If the metal ion is to be determined using this reagent the precipitate is to be ignited to an oxide.

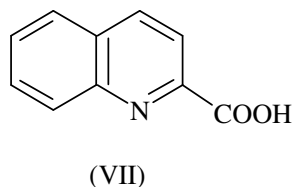
Two isomeric nitrosonaphthols, α – nitroso – β naphthol and β – nitroso – α – naphthol are particularly known as precipitating agents for Co(II). They have also been suggested for the determination of Cu (II), Pd (II), Fe (III), Zr (IV) from slightly acidic solutions. The composition of the precipitates seems to be doubtful therefore for quantitative work ignition to metal oxides is recommended. Similar nitrosonaphthylamines have also been suggested as precipitating reagents for Co (II), Ni (II) and Cu (II). The composition of CO (II) is closer to be theoretical and so the precipitate is recommended for direct weighing after drying.

C. Amino acids

Several aromatic amino acids have been employed as gravimetric reagents. Anthranilic acid (VI) precipitates a number of metal ions Cu (II), Zn (II), Cd (II), Co (II) and Ag (I).

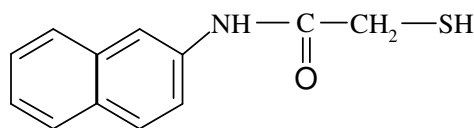


The reagent in the form of its water soluble sodium salt is to be used to precipitate metal ions. The precipitates are pure and easy to filter and wash. Because of lack of selectivity it is mostly used for the determination of metal ions in pure solutions. Quinaldic (VII) reacts quite similarly to anthranilic acid.

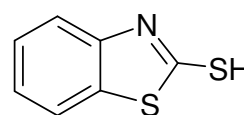


D. Sulphur compounds

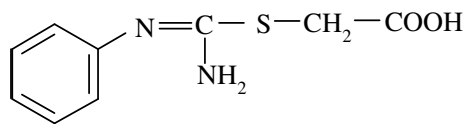
A number of sulphur compounds particularly those with sulphydryl group (-SH) have been recommended for gravimetric work. These may include thionalide (VIII), mercaptobenxthiozole (IX), phenylthiohydantonic acid (X), thiobarbituric acid (XI), thiophenol and several others. But none of the reagents of this group is popular.



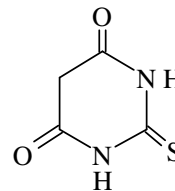
(VIII)



(IX)



(X)



(XI)

E. Salt like compounds

There is a wide variety of reagents which form salt-like compounds to be used for gravimetric work. It is not possible to categorize them as has been the case for reagents forming chelates. The important ones in this list are phenylarsonic acids and derivatives for Ti^{4+} , Sn^{4+} , Th^{4+} , mandelic acid and derivatives for Zr^{4+} , Hf^{4+} , tetraphenylboron sodium for K^+ , Rb^+ , Cs^+ and benzidine and similar compounds for SO_4^{2-} , WO_4^{2-} . Like many organic acids phenylarsonic acid and mandelic acid and their derivatives form insoluble salts. These salts are extremely insoluble salts. These salts are extremely insoluble and that explains as to why multivalent metal ions can be precipitated by these reagent from fairly acidic solutions. Under these conditions the concentration of free phenylarsonate or mandelate will be too low to allow the attainment of solubility product constant of the salts of many other metallic ions. This results in attaining partial selectivity.

13.10.3 Advantages and Disadvantages

The entire discussion in this section is able to project an overview on the use of organic precipitants in inorganic gravimetric analysis. With the available information it may be easy for you to enumerate the advantages and disadvantages associated with the use of these reagents. The disadvantages are primarily due to some problems which cannot be easily overcome.

A. Advantages

1. The organic precipitants for the metal ions offer a wide variety and the list is very large to supposedly meet different eventualities particularly with reference to interferences.
2. Many of the complexes are very insoluble and the metal ions can be quantitatively precipitated.
3. A good number of reagents are fairly selective yielding precipitates with only a limited number of cations. The selectivity of organic reagents can often be enhanced by controlling the pH or using appropriate masking agents.
4. The organic precipitants have often a high molecular weight and yield large amount of precipitate with a small amount of metal ion. This minimizes the weighing error.

5. A number of organic reagents yield precipitates with metal ions which are coarse and bulky and therefore easy to handle for gravimetric work.
6. An organic reagent with a metal ion may yield a precipitate which may not be suitable for weighing after drying. This precipitate without much problem can be ignited to yield the oxide or metal. In some cases the collected precipitate can be dissolved and the liberated organic molecule is titrated providing a tribimetric method for the indirect determination of the metal ion.

B. Disadvantages

1. With all the advantages cited above the fact remains that the use of organic reagent is not free of problems and there are some which need serious consideration.
2. As pointed out earlier one of important problems with these reagent their purity. It has to be ascertained before the use. The solutions of a number of organic reagent degenerates with time. In such cases a fresh solution is to be prepared each time before use.
3. Several of the organic reagents have a limited aqueous solubility and therefore, there is a danger of these reagents contaminating the metal complex precipitates used for metal ion separations.
4. Many of the metal complexes do not offer a suitable weighing form of definite composition and therefore can only be used for the separation of metal ions.

SAQ 8

What are the two ways to attain selectivity in the use of organic precipitants? Which one is better and why?

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SAQ 9

Which in your opinion are the two main drawbacks of organic reagents for inorganic gravimetric analysis?

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13.11 SUMMARY

In this unit you have learnt that gravimetric analysis is a technique of quantification of a variety of inorganic and organic at the macro levels. Its prime importance lies in its

Estimations Based On Precipitation and Gravimetry

utility for the standardization of stock solutions used for the calibration or checking the performance of instruments employed for analysis. In gravimetric analysis the sparingly soluble precipitate of the desired constituent should separate out from the bulk in a pure form and it should be possible to weigh it in a form corresponding to a definite composition. A major portion of discussion in this unit is devoted toward achieving these goals. The purity of the precipitate, to a large extent, is controlled by the rate of precipitation or the rate at which supersaturation is attained. The slower the rate of precipitation smaller is the number of the primary nuclei of precipitates. The material remaining in the solution appears on these particles making them bigger. The large well defined crystalline precipitates thus formed are easy to filter and less prone to contamination. If you look at the recommended procedures for most of the routine gravimetric analyses it is apparent that conditions are created to keep the degree of supersaturation low. In order to improve the nature of the precipitates it is a sometimes recommended to digest it with the mother liquor. Two main processes, namely coprecipitation and postprecipitation can significantly affect the purity of the precipitates. Coprecipitation is precipitation of impurities which normally would have been soluble along with the main precipitate while in postprecipitation impurities are precipitated after the main precipitate is formed. After having known the mechanism of these two processes conditions are identified to keep their contribution low. One significant point that emerges out of the discussion is that in order to obtain pure crystalline precipitates the rate of precipitation is to be controlled. A significant advancement in this direction is the introduction of technique of homogeneous precipitation. In homogeneous precipitation, within the solution, either the precipitant is slowly generated or the cation is slowly released. It has been impressed within the text of the unit that the selection of the liquid to be used for washing the precipitate and the temperature for its drying or ignition is very important. Water is a common wash liquid but it should not be used unless it is certain that it will not dissolve an appreciable amount of the precipitate or peptize it. A vast amount of information on drying or ignition temperatures for precipitates is available from TGA data. But, data it has to be used with caution as the shape of a thermogram depends upon several variables. The list of organic reagents used as precipitating agents for inorganic analysis is very large and offers a wide choice under different experimental conditions. It may be easier to attain selectivity with these reagents. A discussion on some of the important categories of these reagents is presented. Some theoretical and practical aspects associated with the utility of these precipitants are highlighted.

13.12 TERMINAL QUESTIONS

1. Give suitable explanations for the following:
 - a) Thermogravimetric analysis data should be used a little caution to assign drying or ignition temperature range for precipitates.
 - b) Dimethylglyoxime forms a more stable complex with copper than with nickel but it is a well-known selective reagent for nickel.
 - c) 8-hydroxyquinoline forms precipitates with a large number of metal ions but 7-trifluoromethyl-8-hydroxyquinoline fails to form precipitates with many of the metal ions with which the parent compound forms.
2. What are the different methods to reduce the extent of coprecipitation?
3. Give two examples of homogeneous precipitation for each of the following cations:
 - a) Ni^{2+}
 - b) Ba^{2+}
 - c) Cu^{2+}

- What should be the characteristics of a wash liquid to be used for washing a precipitate for gravimetric analysis?
- What are the different ways by which the metal contents of a precipitated metal oxinate can be determined?
- Mention the important advantages of organic precipitating agents over inorganic ones.

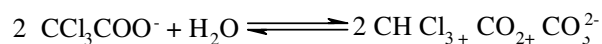
13.13 ANSWERS

Self Assessment Questions

- Precipitates with smaller particle size are not recommended for gravimetric work because:
 - they are not easy to filter
 - they are more prone to surface adsorption.
- d) precipitation from high pH rather than low pH
- d) PbSO_4
- c) Ca^{2+}
- PbSO_4 is occluded within BaSO_4 and forms a solid solution (mixed crystal), hence difficult to remove.

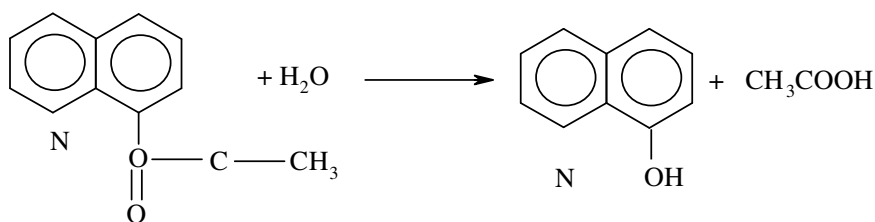
Hydrous manganese oxide is the main constituent of the polymetallic manganese sea nodules. It is a very good scavenger and during its precipitation in the water it carries with it different metal ions present in sea water by coprecipitation. As a matter of fact it is suggested to be a potential source for extracting some metal ions.

- Source of CO_3^{2-} ions according to the reaction.



Used for the precipitation of rare earth carbonates.

- Source of 8-hydroxyquinoline according to the reaction.



Used for the precipitation of magnesium, aluminium and zinc.

- Source of S^{2-} ions according the reaction
Used for the precipitation of sulphide forming elements like cadmium, tin, lead, mercury, arsenic etc.
- 0.1-0.2% aqueous ammonium oxalate solution to minimize solubility losses
 - 1% aqueous nitric acid to avoid peptization of the precipitate.

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- c) First with 75% ethanol with a few drops of H_2SO_4 and then pure ethanol to make it free from
3. The selecting can be achieved by
- Adjustment of pH for precipitation
 - Use of masking agents is better.
- Use of masking agent is better than pH adjustment because well defined pH to achieve selectivity (i) in precipitation reactions is difficult to ascertain. Moreover, by following (i) coprecipitation may take place.
4. The two main drawbacks of organic reagents are
- Many of them have poor aqueous solubility and therefore likely to contaminate the metal complex precipitates
 - Many of the metal complexes do not offer a suitable drying or ignition temperature range. Such precipitates can only find application for separations of metal ions.

Terminal Questions

1. a) One has to be cautious in using the information provided by TGA curves for assigning drying or ignition temperature range for the following reasons.
- Thermograms are recorded by continuous heating. These conditions are not necessarily valid for the laboratory procedures of gravimetric analysis where the precipitate is heated at a fixed temperature for some time.
 - Several factors like the rate of heating, furnace atmosphere, geometry of the sample holder and weight and particle size of the sample may affect the shape of the thermograms.
 - The pyrolysis curves are for precipitates obtained under specified conditions of precipitation and the conditions of precipitation have a significant effect on thermograms.
- b) The stability of copper – dimethylglyoxime complex is more than that of nickel complex but the latter possesses high lattice energy due to special arrangement of the molecules in the crystal. Accordingly Ni (II) – DMG complex possesses a low solubility and dimethylglyoxime becomes a selective precipitating reagent for Ni (II).
- c) 8-hydroxyquinoline is very liberal in its reactivity towards different metal ions but 7-trifluoromethyl-8-hydroxyquinoline is not. The lack of reactivity in case of trifluoromethyl derivative is attributed to steric problem faced in the formation of chelates due to bulk of $-\text{CF}_3$ group adjacent to hydroxy group.
2. See sub Sec. 13.5.3.
3. a) Ni^{2+}
- By synthesizing dimethylglyoxime by the reaction between biacetyl and hydroxylamine. For chemical reaction see sub sec. 13.8.3
 - By raising the pH of an acidic solution containing Ni(II) and dimethylglyoxime by boiling with urea.

- b) Ba^{2+}
- By generating SO_4^{2-} ions by controlled hydrolysis of sulphamic acid or dimethyl/diethyl sulphate. For chemical reaction see sub sec. 13.8.1(c).
 - By raising the pH of an acidic solution containing Ba^{2+} and CrO_4^{2-} ions by boiling with urea.
- c) Cu^{2+}
- By synthesizing salicylaldehyde by the reaction between salicylaldehyde and hydroxylamine. For chemical reaction see sub Sec. 13.8.3.
 - By synthesizing cupferron by the reaction between nitrate and phenylhydroxylamine. For chemical reaction see sub Sec. 13.8.3.
4. See sub sec. 13.9
5. There are three ways of determining the metal content of a precipitated metal oxinate.
- By weighing the oven-dried metal oxinate corresponding to a definite composition.
 - By igniting the metal oxinate at higher temperatures to weigh it as a metal oxide.
 - By dissolving the metal oxinate in hot concn. HCl and titrating the liberated oxine against potassium bromate – bromide solution which furnishes bromine for oxidation of oxine.
- $$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$$
- $$2\text{Br}_2 + \text{C}_9\text{H}_7\text{ON} \rightarrow \text{C}_9\text{H}_5\text{ON} + \text{Br}_2 + 2\text{H}^+ + 2\text{Br}^-$$
- (5,7-dibromo-8-hydroxyquinoline)
- The end point is detected by adding KI and starch and titrating against sodium thiosulphate Oxine reacts with 4 equivalents of bromine to give the dibromo product. Hence 1 mole of oxinate of a divalent metal will require 8-equivalents of bromine and that of a trivalent metal will need 12 equivalents.
6. See Sub sec. 13.11.3 (A)