ORGANIC REAGENTS USED IN INORGANIC ANALYSIS

Introduction

Reagent is a chemical compound, which used in the qualitative analysis for the detection and in quantitative analysis for the estimation of ions or molecules. The term organic reagents is used for such organic compounds which find extensive used in analytical chemistry for various purposes e.g. in gravimetric and colorimetric estimation.

For many years, organic reagents play an important role in the chemical and physicochemical methods of compounds (both organic and inorganic), as well as for separation, concentration, masking and other auxiliary operations that precede or accompany the analysis. The reagent for the determination of metals should, first of all contains a proper functional analytical group that enables its interaction with the determined element and subsequent observation of the respective analytical signal. Currently, several tons of such functional analytical groups are known and documented.

The determination of organic compounds requires that the reagent molecule contained specific groups able to react with functional groups of determined compounds (hydroxyl-carbonyl-, halogen-, and sulfur-, nitrogen containing) with the formation of intensely colored or luminescent products. Reagents used for the determination of functional groups differ considerably from those used for inorganic ions. In particular, the nature of the molecular core (aliphatic or aromatic) is important. Besides that, the course of many reactions depends substantially on the media and the reactions are not often sufficiently selective.

History

In the 17th century Boyle, who has been considered to the father of scientific method in analytical chemistry, used various organic reagents in inorganic analysis. They were mostly vegetable extracts; e.g. litmus was used as an acid-base indicator. He mentioned also the spot test for iron on papyrus soaked with oak-berry extract, as described by Pliny, in the first century A.D. In the 18th century, for example, the following applications of organic reagents were known: the detection of iron (III) with thiocynate or in the form of Prussian blue, the masking of the iron with the tartaric acid, oxalic acid or succinic acid, and the precipitation of calcium with oxalate.

The first ever reported organic reagent was α -nitroso- β -naphthol which was used as a reagent for the identification of cobalt. In the last century the colorimetric determination of the iron (III) with thiocynate was worked out and the titrimetric determination of silver using the same reagent was described. Glycerol was advocated for the titration of boric acid and the following organic reagents were employed: Morin in a fluorescence test for aluminium, flourescein as a fluorescent acid-base indicator, aniline for catalytic detection of vanadium, 1-nitroso-2-naphthol as precipitation reagent for cobalt,2,2'-bipyridyl and 1,10-phenanthroline as reagent for iron(II).

The systematic study of reactivity of organic reagents with inorganic ions was significantly stimulated by the development of the theory of complex compounds, the foundations for which had been laid by Werner in 1891, and by the discovery of the selective reaction of biacetyl dioxime with nickel (II) at the beginning of this century, which led to a successful gravimetric determination of the nickel.

Properties

Organic reagents are used in various ways in inorganic analysis. Some of common properties that are used in this way include the following:

Formation of a characteristic color of colored precipitates:

- Organic reagents form direct characteristic colored with the ions to be detected.
- For locating end point i.e. as indicators employed in volumetric titrations.
- Formation of precipitates due to difference in solubility: This may be made the basis of gravimetric method.
- > Extraction of organic solvent at controlled pH.

Masking Reagents:

This increases the selectivity of reagents.

- Difference in volatility.
- > Oxidation or reduction to other valence state.

- > Wash liquids.
- > Advantages of organic precipitating reagents

There are several ways in which organic reagents are better than inorganic reagents.

Advantages

There are some advantages to use organic reagents in inorganic analysis as following:

1. Selectivity

In many inorganic bases organic reagents are somewhat are specific. For example, cobalt from nickel u-nitroso-Rnaphthol or dimethylglyoxime (DMG), aluminium from iron using cupferron, cadmium from copper using quinaldinic acid and thiourea can be precipitated. In some cases adjustment of the pH will often cause precipitation of one constituent alone. By changing pH and solvent conditions, one constituent from after another can sometimes be quickly precipitated out.

2. Ease of Handling

Organic reagents produce compounds that have little infinity for water and are dried easily at temperature low enough to prevent decomposition.

3. **Co-precipitation**

Lack of ionic character of organic precipitation products greatly reduces co-precipitation, in most cases.

For example the co-precipitation of sodium and potassium with magnesium is much less when the later is precipitated by 6ydroxyquinoline than when it is precipitated by phosphate or oxalate. Reagents are usually insoluble in water, therefore, it is important not to add an excess of reagents. This is difficult because there is no way to tell when sufficient reagent, without excess, has been added. Any excess that is insoluble would add to the weight of precipitate.

Disadvantages

There are, unfortunately, some disadvantages to using organic reagents.

1. Volatility

This is the first practical disadvantage of organic reagents. Because chelated compound, are non-polar, the forces between individual molecules in the crystal are not very great. Thus, some of the metallic complexes which are precipitated and analytical chemistry are appreciably volatile above 130-150°C and most decompose above this temperature. Therefore, the drying of precipitate should be done below 130°C to avoid decomposition.

2. Impurities in Reagents

It is very difficult to prepare an organic reagent of the same degree of purity as say inorganic compounds. Impurities present in inorganic reagents may enter into the precipitate during the precipitation and cause undesirable reactions.

For example, Dimethylglyoxime (DMG) exist in three forms, i.e., α , β and r. Of these, only α form is specific for nickel while preparing dimethylglyoxime (DMG) y-form is also formed along α form. If the precipitation is carried out with this impure dimethylglyoxime (DMG), then nickel will be precipitated with some other metals because r-form is specific for nickel whereas r-form can precipitate other metals also.

3. Low Solubility of the Reagents in Water

This is the greatest disadvantage which organic precipitants have in comparison with inorganic precipitants.

4. High Molecular Weight

The very high molecular weights of chelate complexes formed with metal ions reduce, proportionately, small errors in precipitation and weighing.

5. Colored Compound

Chelate compounds are often highly colored and since they are usually soluble in organic solvents, they lend themselves to colorimetric or photometric methods of analysis.

6. Solubility in Organic Solvents

Because of their covalent nature, most metal complexes with organic reagents are soluble in non-polar solvents, chloroform being usually the best. Such solvents are used to extract the complexes for calorimetric determination, or they may be used for separating one element from another; thus the complex of cupferron with tripositive iron is very soluble in ether and chloroform, which allows one to remove large amounts of iron from solutions containing aluminium. In all these extractions, the pH must be carefully adjusted to give the desired separation.

Reactivity

The reactions of organic reagents with inorganic ions in solution can yields products of various properties; *for example,* they can exhibit a change in;

- color,
- luminescence,
- solubility &
- volatility

The reaction products may be complex compounds, or new organic substances (formed due to oxidation-reduction or catalytic action of inorganic ions), or the other forms of the reagent (acid-base indicator).

Besides these reaction types the organic reagents in solution can be adsorbed on a precipitate of an inorganic substances, the adsorption being accompanied by a color change of the reagent (adsorption indicators). Solid organic reagents which are insoluble in a given solvent constitute a special type (ion-exchange resins, chromatographic stationary phases, etc). The formation of a product which is insoluble in a given solvent (usually water) can be employed for the gravimetric determination, separation or precipitation titration of an ion.

If the reaction product is less soluble in water than in organic solvent immiscible with water, the reaction can be used for the solvent extraction of any of its parent constituents.

In many reactions of organic reagents a conspicuous color or fluorescence is developed, or conversely, a colored component in solution is decolorized during the reaction, or its fluorescence is quenched. Such reactions can be applied both for qualitative tests and for spectrophotometric (colorimetric) or fluorimetric determinations. Further, this type of reaction is also employed for end-point indication in the acid-base, oxidation-reduction, or complexometric titrations.

Masking is based on the formation of stable soluble complexes of interfering ions. Their concentrations is thus decreased to such a slow value that they no longer react with a given reagent – their interfering in a given reaction is eliminated. If the reaction product is volatile, the organic reagent can be used for an analytical separation based on distillation or sublimation.

Applications of Organic Reagents in Inorganic Analysis

The use of organic reagents in inorganic analysis is many-sidedthey can be applied in separations, qualitative tests, determinations, and for masking. The successful application of a given reagent requires the knowledge of background theory.

1. Separation by Precipitation

There are two modes of application of organic reagents as precipitants in separations.

Precipitates of Known Composition:

It is characterized by the formation of a stoicheiometrically defined compound (the weighing form), or the transformation of the isolated precipitate into such a form.

- *i.* **Co-precipitation:** In this type of separation the partitioning of a given component between the liquid phase (the solution) and the solid phase (the precipitate) is controlled by a particular partition (e.g. adsorption) isotherm.
- Distillation: It is of limited applicability in inorganic analysis. The volatility of some inorganic compounds (e.g. metal halides, RuO₄, OsO₄ and some non-metal compounds) can be used for separation procedures, but only seldom can the separations be based on volatile products from use of organic reagents.

Some metal chelates of β -diketones and of 8-hydroxyquinoline have been reported as volatile compounds; e.g. the oxinates of Cu (II), Pb (II), Ni (II), etc. can be sublimed within the temperature range 250-500°C in vacuo.

Extraction

Extraction is a versatile, useful, and popular separation technique because of its simplicity, speed, and applicability both to major and trace components. Organic reagents play an eminent role in extraction separations, because they can react with metal ions to give products having the basic prerequisite for extractability.

- Extraction systems are classified according to different criteria
- The type of extraction process or reaction in which the extractable species is formed (physical partition, salvation, formation of chelates of ionpairs, etc.).
- The kind of extractable species (simple covalent compounds, chelates, ion-association complexes etc.).
- > The type of extracting agent (neutral, acidic or basic).
- > The kinetics of the extraction.

Chromatography

A method of separation in which complexes formed with organic reagents are used, is chromatography. This is very wide field, so subdivided into particular techniques.

- 1. **Partition Chromatography:** Partition chromatography in which the formation of complexes and their properties are mainly applied includes liquid-liquid chromatography (LLC) and gas-liquid chromatography (GLC). The application of complexes is less frequent in adsorption chromatography which includes liquid-solid chromatography (LSC) and gas-solid chromatography (GSC).
- 2. Adsorption Chromatography: Despite the fact that adsorption chromatography is the oldest method known; it is often applied for separations of inorganic compounds in presence of organic reagents. In LSC a solution in an organic solvent of the substance to be separated, is applied to column or thin layer of the adsorbent. The choice of the solvent is an important factor in the efficiency of separation.
- 3. Ion-Exchangers

If organic reagents are defined as substances which take part in analytically useful reactions with the components being detected, determined or separated, then this definition also embraces organic ion-exchangers. This term is used to denote the solid organic polymers which are insoluble in water or common organic solvents, but are swollen, and which possess ionic groups able to bind ions of the opposite charge, exchanging them in solution for an equivalent amount of other counter-ions of the corresponding charge. Ion exchangers can be used as a stationary phase in an ion-exchange chromatography.

- a. The ion exchangers are classified by the type of the ions being exchanged, as cationic exchangers. Both types of ionexchanger may contain various functional groups.
- b. Thus cation-exchangers can be strongly acidic if they posses the group-SO₃H, or weakly acidic (usually possessing the groups –COOH or –OH).
- c. The anion-exchangers are similarly distinguished as strongly basic (e.g. containing the quaternary ammonium group NR³⁺ and weakly basic (e.g. containing the group –NH₂)*.

Following are the methods used in ion-exchangers technique.

- 1. Ion-exchange separations with the aid of complexing agents.
- 2. Separation on ion-exchangers saturated with complexforming lons.
- 3. Selective ion-exchangers

Qualitative Analysis

Organic reagents have found wide application in the qualitative analysis of inorganic substances because of the high degree of sensitivity and selectivity that can be achieved by proper choice of experimental conditions. Sometimes a test can be made specific.

Gravimetric Analysis

The use of organic reagents for gravimetric determination of inorganic substances offers a number of advantages, the outstanding feature being the high selectivity or even specificity.

The precipitates are easy to filter off and wash, and after drying can often be weighed directly, provided they have a defined stoichiometry.

Another important advantage is that the precipitates are not hygroscopic. Also the high molecular weights of the complexes mean that the conversion factors are very favorable.

Titrimetric Analysis

Organic reagents find extensive applications in titrimetry. In acidbase titrations organic substances of the suitable properties are mainly applied as color or fluorescent pH change (sulphophthaleins, azocompounds, nitrophenols etc.), or as standards (oxalic acid, potassium hydrogen phthalate) or as titrants suited for non-aqueous media (tetraalkyl ammonium hydroxides).

Some are the examples of titrations mentioned below;

- Chelometric titrations
- Chelometric-back titrations
- Displacement titrations
- Potentiometric titrations
- Visual titrations
- Photometric titrations

Classification of organic reagents

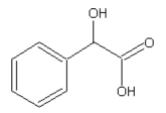
Organic reagents employed in Gravimetric analysis (Chelate forming Complexes)

i) Organic Reagents with the donor atoms O,O

1. Mandelic acid:

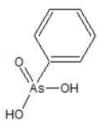
It is also known as alpha hydroxyphenyl acetic acid or phenylglycolic acid and has the formula $C_6H_5CHOH.COOH.It$ is white crystalline solid and has appreciable solubility in water.

Use: It is chiefly used to separate zirconium from Iron, aluminium, titanium and thorium but it is difficult to remove the excess of added acid from the precipitate of zirconium mandalate. This reagent is used in the form of 0.1% molar solution. *This compound is a buffering agent and a precursor to other organ arsenic compounds.*



2. Benzene arsonic acid:

This colourless solid is an organic derivative of arsenic acid, $AsO(OH)_3$, where one OH group has been replaced by a phenyl group.



Use: This compound is a buffering agent and a precursor to other organo arsenic compounds.

3. Oxalic acid:

Oxalic Acid (also called Ethanedioic Acid) is a colourless, crystalline, toxic organic compound belonging to the family of dicarboxylic acids; melting at 187 C; soluble in water, alcohol, and ether.

Use: oxalic acid (and formic acid) is readily oxidized and combine with calcium, iron, sodium, magnesium, or potassium to form less soluble salts called oxalates. As oxalic acid react with iron oxide to form water soluble iron oxalate complex ion.

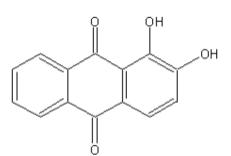
$$3H_2O(I)+Fe_2O_3(s)+6H_2C_2O_4(aq) \longrightarrow 2[Fe(C_2O_4)_3]^{-3}(aq)+6H_2O_3(s)+6H$$

$$\begin{array}{ccc}
O & O \\
\parallel & \parallel \\
H - O - C - C - O - H \\
Oxalic Acid, H_2C_2O_4
\end{array}$$

4. Alizarin:

The reagent contains phenolic OH and ketonic oxygen in appropriate position and hence forms colored lakes or solutions with those metal ions which either form amphoteric or weakly basic oxide.

Use: It gives purple coloured lakes with Al³, Sb², Bi, Co, Fe, Hg, Pt, orange lakes with Sn, Pd, yellow lakes with Cr, and blue lakes with Ti.

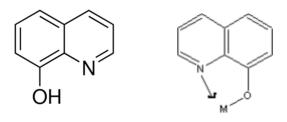


ii) Organic reagents with the donor atoms O,N

1. 8-Hydroxyquinoline(oxine):

It is popularly known as "oxine" and is sometimes also called 8quinolinol.It is a colourless crystalline solid with molecular formula $C_6H_7ON.It$ is almost insoluble in water and soluble in organic solvents.

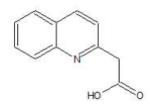
Use: The reagent is used to separate transition metals like Fe, Cu, Mo, Al, Ti, Zn etc in precipitation form by replacing acidic hydrogen of phenolic group with metal ion. It is used in the form of its 20% solution in 2N acetic acid. The precipitation is done by adding the reagent solution to a cold salt solution just in slight excess which is indicated by the yellow colour of the supernatant "liquid".



2. Quinoline-2-carboxylic (quinaldic) acid:

It is a yellow solid with MP 150°C which is insoluble in hot water and alkalies. The reagent is used as sodium salt and reagent solution is prepared by dissolving 5.63g of sodium salt in 150 ml of solution.

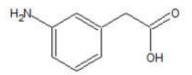
Use: The reagent gives insoluble precipitates with copper, cadmium, zinc, manganese, silver, cobalt nickel, platinium (II) and insoluble basic salts of Iron (III), Aluminium (III), Beryllium (II) and Titanium (IV).



3. 2-Aminobenzoic (anthranilic) acid:

It is a white pinkish colored solid with a melting point of 145°C which is insoluble in ether and ethanol.

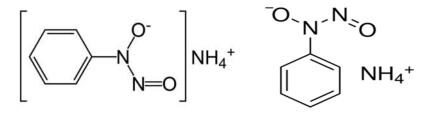
Use: It is used in the form of 3% aqueous solution of its sodium salt in weakly acidic or neutral solution the reagent precipitates Zn^2+,Pb^2+,Cu^2+ at pH 3.6-4.5.



4. N-nitroso-N-phenylhydroxylamine(cupferon):

In this reagent the nitrosyl and the ONH4 groups are both attached to the same aromatic amino nitrogen atom. It is a pale yellow solid of MP 163°C and is insoluble in water and ethanol.

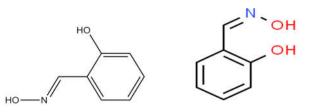
Use: This reagent forms insoluble compounds with a number of metals in both weakly and strongly acids solutions. Like in strongly acid solutions of tartarate and oxalate it can precipitate Iron (III), Vanadium (V), Titanium (IV), Cerium (IV) can be separated from metals like Alumminium, Beryllium, Chromium, Nickel.



5. Salicylaidoxime:

The reagent which is represented by formula $C_7H_7O_2H$, is a white crystalline of MP 57°C and is sparingly soluble in water.

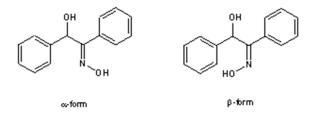
Use: The reagent is chiefly employed for the estimation of the bivalent copper. The solution of the reagent is prepared by dissolving 1.0g of the solid in 5ml of 90% ethanol, then adding 95ml water and keeping the temperature at 80°C, the reagent solution decomposes if kept and hence should be prepared a fresh before use.



6. Benzoin oxime (cupron):

The reagent is a white crystaline solid with MP 152°C and has the molecular formula C 14H13O2N. It is sparingly soluble in ethanol.

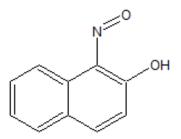
Use: It is specific reagent for copper which is detected as a green precipitate of composition Cu C14H11O2N from as ammonical solution containing some tartarate. It can also precipitate molydate and tungstate from acid solution quantitatively but precipitation of vandate and tantate is only partial.



7. 1-Nitroso-2-naphthol:

It is a brown powder with MP 109°C, and is insoluble in water, soluble in ethyl alcohol, ether, acetic acid and alkalies.

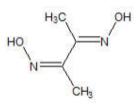
Use: This reagent precipitates quantitatively cobalt (below pH 8.74) palladium (below pH 11.82), thorium (pH 4.8-5.6), ferric ion (0.95-2) and ferrous ion from alkaline solution. The chief use of the reagent is in the separation of the cobalt from a nickel solution from which iron (III) has been removed.



iii) Organic reagents with the donor atoms N,N

1. Biacetyl dioxime:

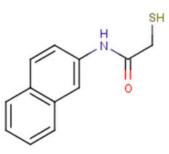
This reagent yields water insoluble chelates with nickel (II) and palladium (II). The palladium chelate is yellow and precipitated from dilute acid medium, whereas the red nickel (II) chelate can be brought down from a neutral medium.



2. Thionalide (2-marcapto-N-naphthylacetamide):

It is a white to ovy-colour needles like crystals. It is insoluble in water but soluble in many organic solvents.

Use: It is reagent use to precipitate copper, mercury, silver, thallium, and bismuth.

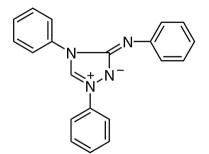


iv) Organic cations or organic anions giving insoluble salts with inorganic ions

1. Nitron:

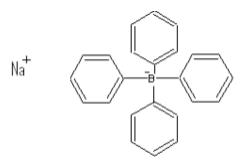
It is a crystalline yellow solid which is insoluble in water but soluble in acetic acid. It is very strong base and is specific gravimetric reagent for NO-³ with which it yields a sparingly soluble crystalline precipitate.

Use: It forms precipitate with large number of other ions such as oxalate, chromate, tangstate, chlorate and iodate.



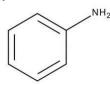
2. Sodium tetraphenylborate:

It is the organic compound with the formula $NaB(C_6H_5)_4$. It is a salt, wherein the anion consists of four phenyl rings bonded to boron. This colourless crystalline solid is used to prepare other tetraphenylborate salts, which are often highly soluble in organic solvents. The compound is used in inorganic and organometallic chemistry as a precipitating. agent.



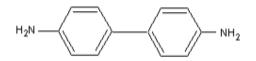
3. Aniline:

It is an organic base which has been used for estimation of iodide ions which is precipitated in the presence of Sulphuric acid.



4. Benzidine:

This base used in the form of its dihydrochloride to precipitate SO₄²-, WO4²-, MoO4²-, PO4³- but is most sensitive for SO4²-. The sulphate ion are precipitated from highly acidic solution and composition of precipitate is $[C_{12}H_{12}N_2H_2]^2$ + SO₄²- while that of free compound is $C_{12}H_{12}N_2H_4$.

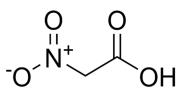


v) Organic reagents used for Masking or Sequestration

1. Nitroacetic acid:

It is a yellow crystalline solid. It is insoluble in water but soluble in organic solvents.

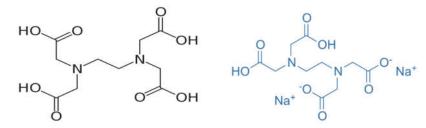
Use: It is a polydentae ligand and form complexes with metals like Ca, Sr, Ba and Mg. These complexes are stable hence precipitated out.



2. EDTA (Ethylene diaminetetracetic acid):

It is a polyaminocarboxylic acid and is a colorless compound. It is a water soluble acid.

Use: It is used in colorimetric analysis and for the titration of metallic ions. It is also used as masking agent as it is a polydentate ligand and form complexes with metals like calcium, barium, and magnesium. It also used for the determination of ions.



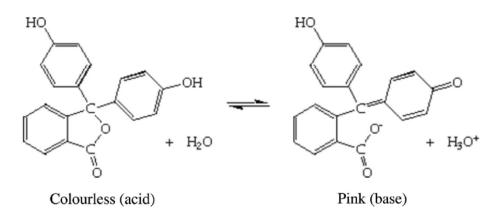
vi) Organic reagents used as Indicators

Acid-base Indicators

1. Phenolphthalein:

It is a white crystalline solid which melts at 254°C.It is insoluble in water but soluble in alcohol. Its unionized form is colourless in acidic medium and it ionizes to form pink ions in alkaline medium.

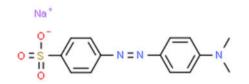
Use: It is weak organic acid used in titration of acids with strong alkalies and it is most commonly added to the solution of alkali taken in conical flask.



2. Methyl orange:

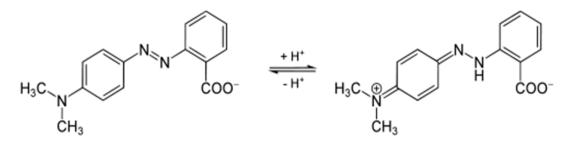
It is an orange colour solid which is soluble in water and ethanol.

Use: It is a weak base and used in the form of aqueous alcohlic solution in the titration of acids with weak bases. e.g. Titration of Sulphuric acid against sodium carbonate or bicarbonate.



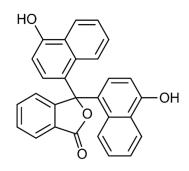
3. Methyl red:

This act in pH range 4.2-6.3 and is red in acidic and yellow in alkaline medium. The solution may be made by dissolving 1g of indicator in 1000ml of 80% ethanol.



4. α-naphtholphthalein:

The indicator acts in the pH range 7.3-8.7 and is pink in acidic and blue in alkaline solution. Its solution is prepared by dissolving 1g of indicator in 500 ml of ethanol and diluting with 500ml of water.

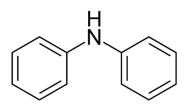


Redox Indicators

1. Diphenylamine:

It is redox indicator. It is used in the estimation of Fe²⁺ by titration against potassium dichromate. It is coloured crystalline solid which melts at 54°C and is insoluble in water but soluble in ethanol and ether.

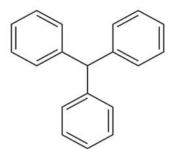
Use: When ferrous iron solution containing diphenylamine is titrated with potassium dichromate ferrous ions are first oxidized due to difference between redox potential of two system.



2. Triphenylmethane:

It is the hydrocarbon with the formula $(C_6H_5)_3$ CH. This colorless solid is soluble in nonpolar organic solvents but not in water.

Use: This dye form coloured complexes with transition metals.

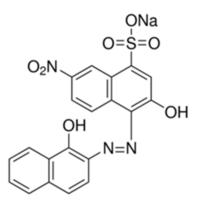


Metal-ion Indicators.

1. Eriochrome black-T:

It is an azodye or sodium 1-(I-hydroxy-2-naphylazo)-6-nitro-2-napthol-4 sulphonate also known as solochrome black.

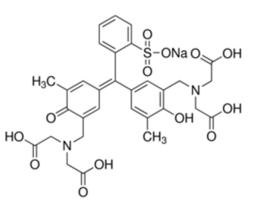
Use: It is used in the titration of magnesium with which it forms complex of wine red colour.



2. Xylenol Orange:

The indicator has lemon yellow colour in acid solution and that of its metal complex is red.

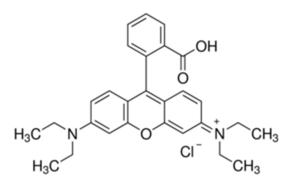
Use: It can be used in the titration of Bi, Cd, Pb with EDTA but is most specific for Co.



3. Rhodamine-B:

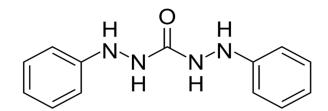
The compound in composition is tetraethyl rodhamine used as its hypochlorite. It is orange colour in solid and gives red solution.

Use: It is used in qualitative analysis for identifying antimony in pentavalent state in presence of tin.



4. Diphenyl Carbazide: This compound is insoluble in water but soluble in ethanol. In neutral or acetic acid medium gives red colour products with number of metals.

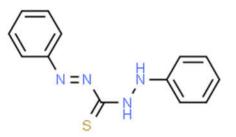
Use: It is used to detect chromium and mercury as chromate ion. If reagent is added in mercuric salt solution blue colour is observed which confirms mercury. Chromate ions produces a violet colour and chromium is thus identified as chromate by oxidation of chromium.



5. Dithizone:

This is diphenyl thiocarbazone which forms coloured precipitates with metal like lead, silver, copper, mercury, cadmium.

Use: It is commonly used to confirm lead with which it forms a red colour complex in neutral medium. The most important use of reagent is colorimetric determination of lead which forms a red colour complex. Zinc also form a complex of same colour and if present must be separated by back extraction with aqueous potassium thiocyanate.



6. Pyridine:

It is a simple 6-membered heterocyclic compound which is colorless liquid boiling at 115°C.It is miscible with water in all proportion.

Use: It is used in precipitate from as ferric hydroxide. It may also be used for gravimetric estimation of copper as it forms an insoluble complex. While for the estimation of germanium and silicon these are first to be converted into germano and silicomolybdates which are then precipitated with pyridine.

