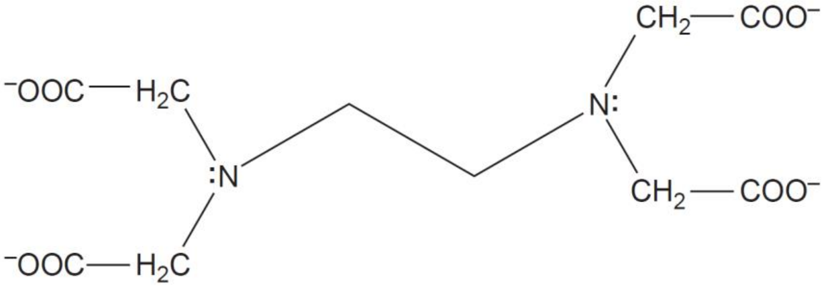
CHE-HC-4014: INORGANIC CHEMISTRY-III

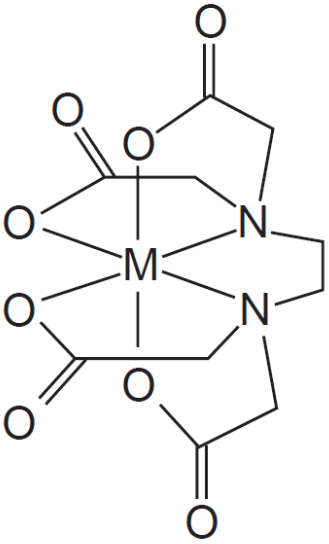
Topic: Theory of complexometric titrations

Semester IV

Chemistry and Properties of EDTA

- ☐ The most widely used complexing agent (complexone) is ethylenediaminetetraacetic acid, EDTA, which forms strong 1:1 complexes with many metal ions.
- ☐ It is an aminocarboxylic acid.
- ☐ It is a Lewis base, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons.
- ☐ Upon coordination to the metal center EDTA forms a cage-like structure around the metal ion.
- ☐ In practice, the disodium salt of EDTA ($Na_2H_2Y.2H_2O$) is used due to very low solubility of the acid in water.
- ☐ The formation constants of metal-EDTA complexes are quite large suggesting equilibrium position of the reaction towards the forward direction.





Advantages and Limitations of EDTA titrations

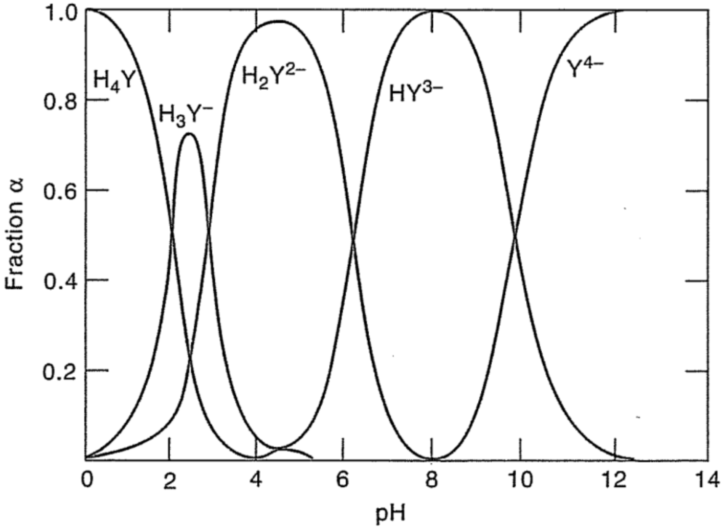
- EDTA forms stable complexes with various metal ions.
- Complexation occurs in a single step and hence titration of a metal produces sharp change in the metal ion concentration at the equivalence point.
- The metal-EDTA complexes are completely soluble in water so all the studies can be carried out in aqueous solution.
- EDTA forms strong 1:1 complexes with many metal ions irrespective of the charge of the metal ion.
- The stoichiometry for all metal ions is same.

Limitations

- Many Metal-EDTA titrations are carried out at relatively high pH, which may lead to leaching of certain metal ion from the complex.
- EDTA titrations are very unselective towards the metal ions.

Effect of pH on EDTA equilibria

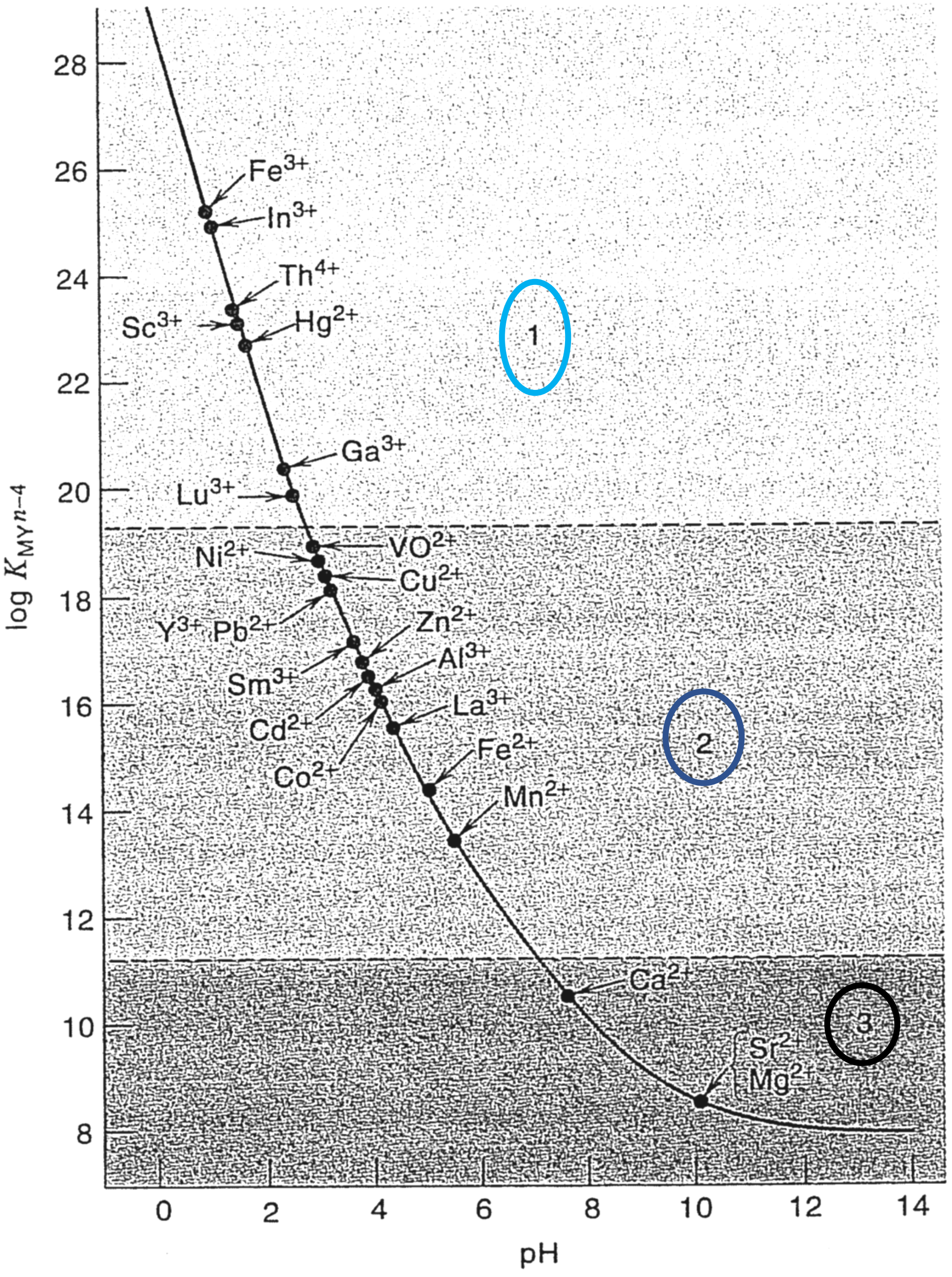
- ❑ A plot of fraction of EDTA species as a function of pH is shown below:



- ❑ Since Y^{4-} is the species involved in complex formation, the complexation equilibria is markedly affected by the pH.
- ❑ H_4Y has low solubility in water and therefore the disodium salt, Na_2H_2Y is generally used. It dissociates in solution to give predominantly H_2Y^{2-} and the pH of the solution is ca. 4 to 5.
- ❑ The disodium salt liberates of two equivalents of hydrogen ions when added to a metal ion solution $$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$
- ❑ According to Le Chatelier's principle, decreasing the acidity will favor formation of the chelate complex

Effect of pH on EDTA equilibria

- A plot of minimum pH for effective titration of various metal ions with EDTA.
- Only some metal chelates are stable enough to allow titration in acidic solution; others require basic condition.
- At the highest pH range, all the metals will react but not all can be titrated directly due to precipitation as hydroxides.
- At the lowest pH range, the first group can be titrated in the presence of all.



Metal EDTA Titration Curves

- ☐ The equivalence point of a complexometric titration refers to the stoichiometric equivalence of the analyte and the titrant that have reacted.
- ☐ In the EDTA titration, if pM (negative logarithm of the 'free' metal ion concentration: pM = -log[M^{n+}]) is plotted against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point.

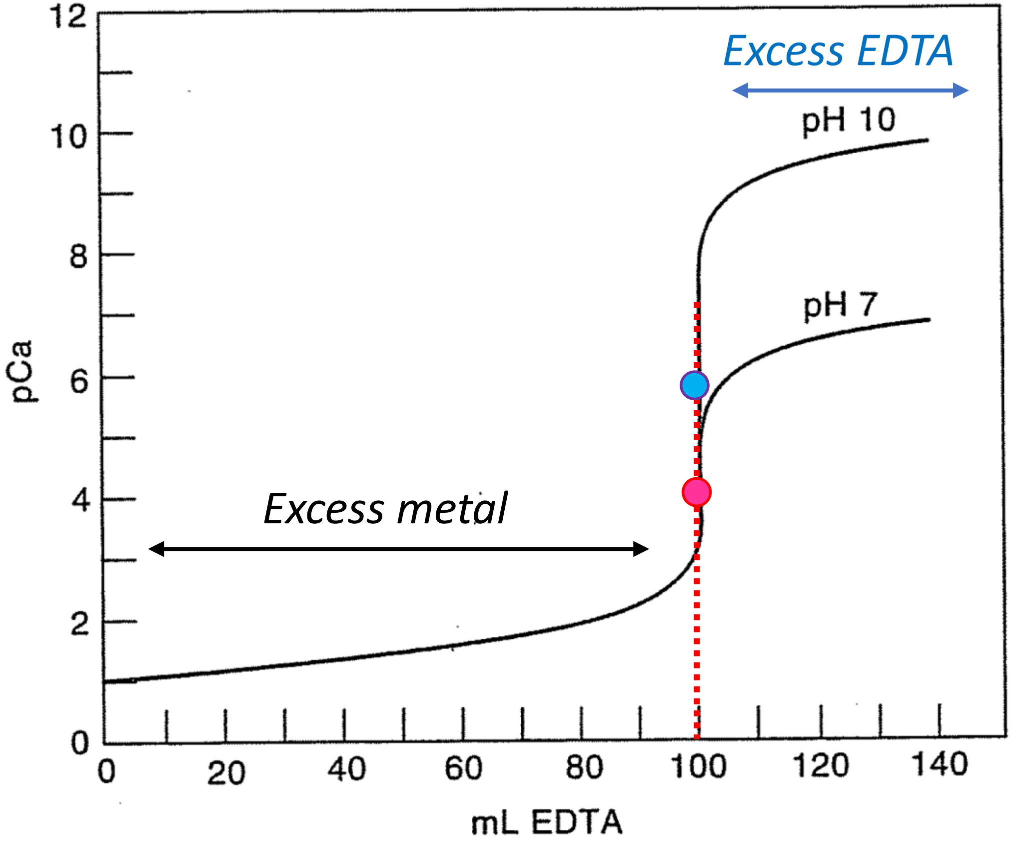
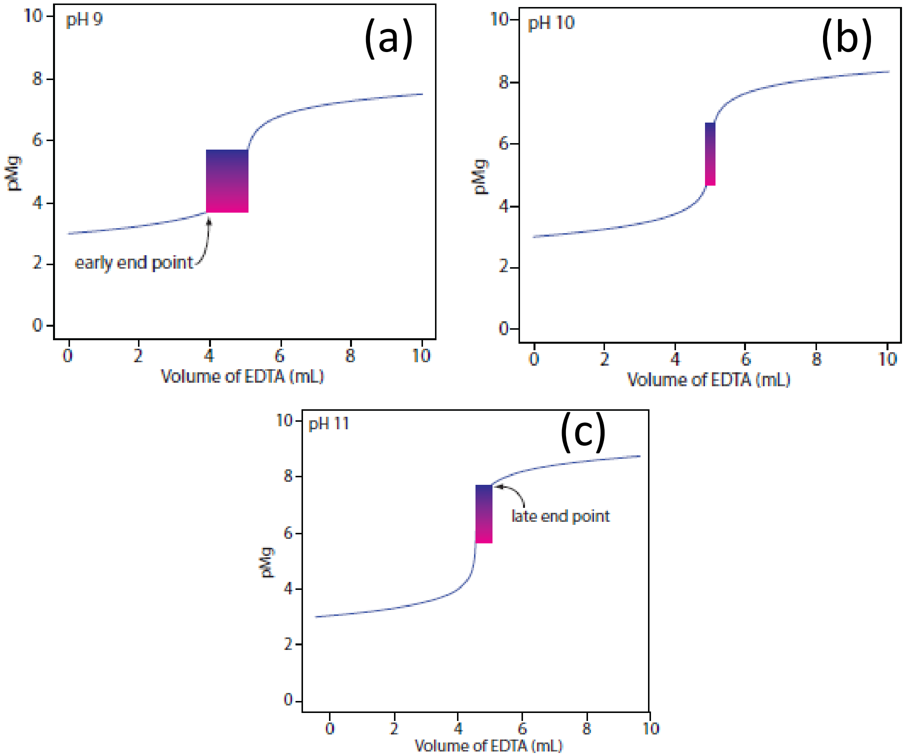


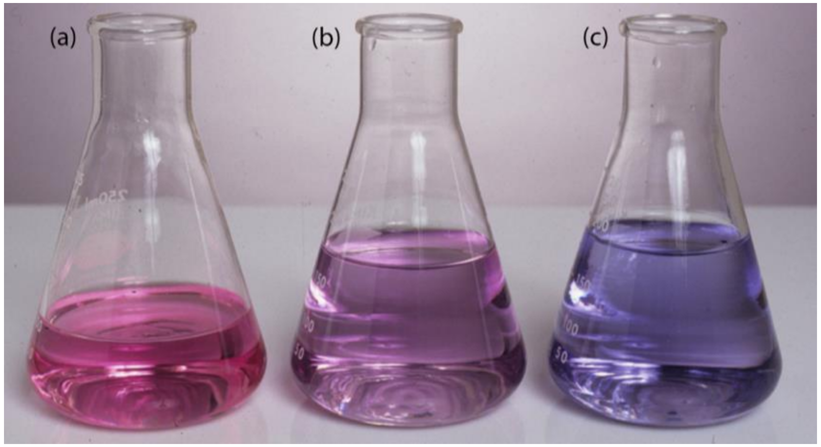
Fig: *Titration curve for 100 mL 0.1 M Ca^{2+} vs 0.1 M Na_2EDTA*

METAL ION INDICATORS

- In the EDTA titration a metal ion-sensitive indicator (abbreviated, to metal indicator or metal-ion indicator) is often employed to detect changes of pM.
- Such indicators (which contain types of chelate groupings and generally possess resonance systems typical of dyestuffs) form complexes with specific metal ions, which differ in colour from the free indicator and produce a sudden color change at the equivalence point.
- The end point of the titration can also be evaluated by other methods including potentiometric, amperometric, and spectrophotometric techniques.



End point for the titration of hardness (Mg^{2+}) with EDTA using calmagite as an indicator



METAL ION INDICATORS: General properties

- The colour reaction must be such that before the end point, when nearly all the metal ion is complexed with EDTA, the solution is strongly coloured.
- The colour reaction should be specific or at least selective.
- The metal-indicator complex must possess sufficient stability, however, be less stable than the metal-EDTA complex to ensure that, at the end point, EDTA removes metal ions from the metal indicator-complex.
- The colour contrast between the free indicator and the metal-indicator complex should be such as to be readily observed.
- The indicator must be very sensitive to metal ions (i.e., to pM) so that the colour change occurs as near to the equivalence point as possible.
- The above requirements must be fulfilled within the pH range at which the titration is performed.
- **Note:** *Indicators could equally take up protons, which also produces a colour change thus metal ion indicators are therefore not only pM but also pH indicators.*

METAL ION INDICATORS: Theory of Visual Use

- The use of a metal ion indicator in an EDTA titration (1:1 complex) may be written as:

$$\mathrm{M{-}In + EDTA \rightarrow M{-}EDTA + In}$$

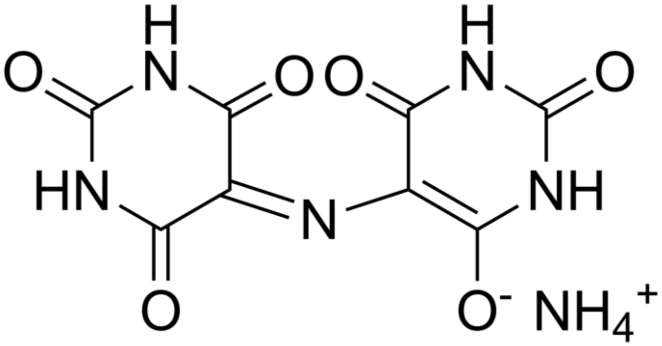
- This reaction will proceed if the metal-indicator complex M-In is less stable than the metal-EDTA complex M-EDTA.
- During the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M- In to leave the free indicator (In).
- The indicator colour change is affected by the hydrogen ion concentration of the solution.
- For example, solochrome black, which may be written as H_2In^-, exhibits the following acid-base behaviour:

$$H_2In^- \underset{5.3\text{-}7.3}{\overset{pH}{\rightleftharpoons}} HIn^{2-} \underset{10.5\text{-}12.5}{\overset{pH}{\rightleftharpoons}} In^{3-}$$

- In the pH range 7-11, in which the dye itself exhibits a blue colour, many metal ions form red complexes.
- The colours of metal indicators are extremely sensitive, for example, by the fact that 10^{-6}-10^{-7} molar solutions of magnesium ion give a distinct red colour with the indicator.

METAL ION INDICATORS: Some Examples

1. Murexide (ammonium salt of purpuric acid): 1st metal ion indicator



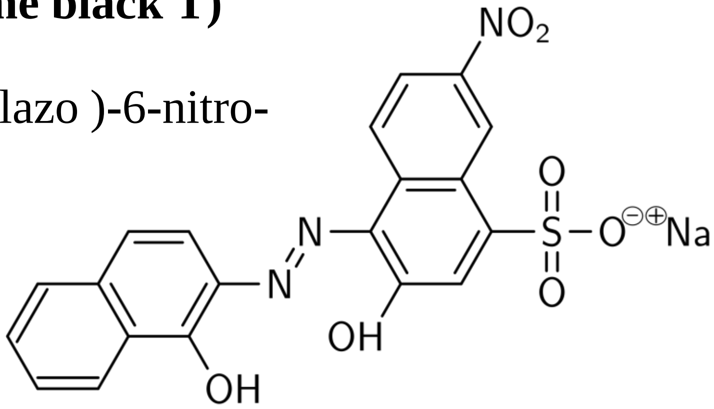
- ☐ Murexide forms complexes with many metal ions: only those with Cu, Ni, Co, Ca and the lanthanides are sufficiently stable to find application in analysis.
- ☐ Their colours in alkaline solution are orange (copper), yellow (nickel and cobalt), and red (calcium); the colours vary somewhat with the pH of the solution.
- ☐ The colour change in the direct titration of nickel at pH 10-11 is from yellow to blue-violet.

METAL ION INDICATORS: Some Examples

2. Solochrome black (eriochrome black T)

Sodium 1-(1hydroxy- 2-naphthylazo)-6-nitro-

2-naphthol-4-sulphonate



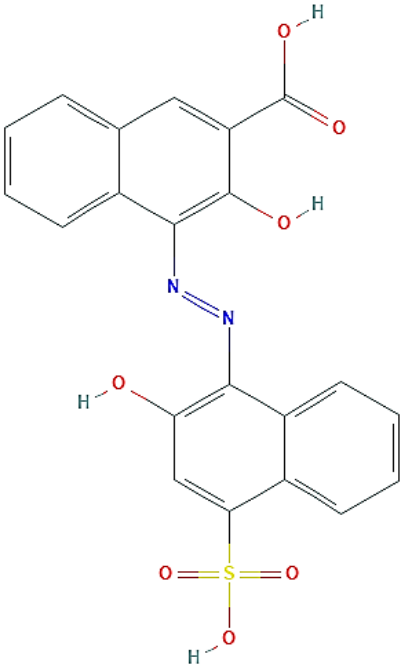
- The indicator is rarely applied in titrations of solutions more acidic than pH = 6.5.
- Below pH = 5.5, the solution of solochrome black is red (due to H_2D^-), between pH = 7 and 11 it is blue (due to HD^{2-}), and above pH = 11.5 it is yellowish-orange(due to D^{3-}).
- In the pH range 7-11 the addition of metallic salts produces a brilliant change in colour from blue to red:

$$M^{2+} + HD^{2-}\ \text{(blue)} \rightarrow MD^{-}\ \text{(red)} + H^{+}$$

- This colour change can be observed with the ions of Mg, Mn, Zn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and the Pt metals.
- To maintain the pH constant (ca 10) a buffer mixture is added, and most of the above metals must be kept in solution with the aid of a weak complexing reagent such as ammonia or tartrate.

METAL ION INDICATORS: Some Examples

3. Patton and Reeder's indicator



2-hydroxy-l-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid

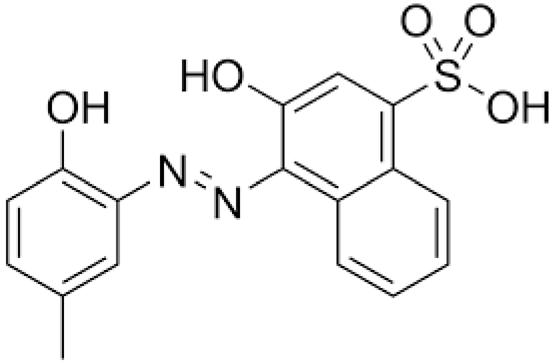
HHSNNA

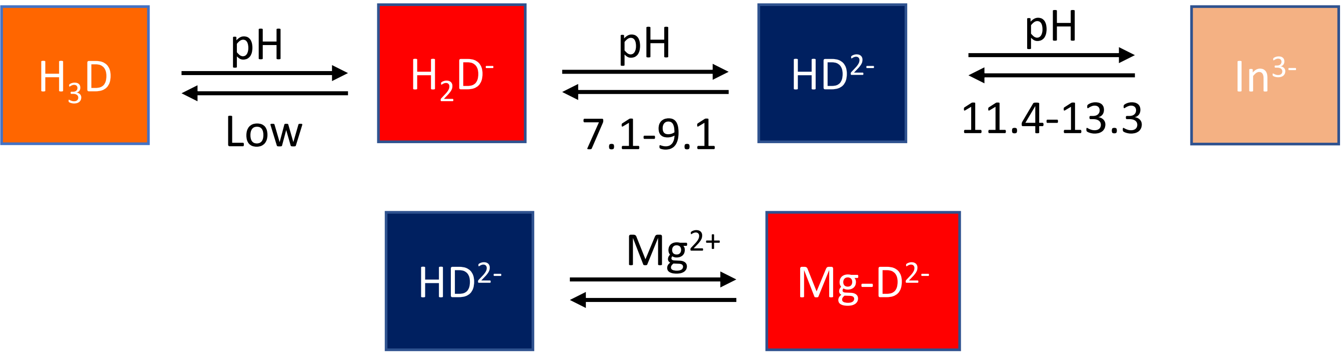
- ☐ Its main use is in the direct titration of calcium, particularly in the presence of magnesium.
- ☐ A sharp colour change from wine red to pure blue is obtained when calcium ions are titrated with EDTA at pH values between 12-14.
- ☐ This indicator may be used as an alternative to murexide for the determination of calcium.

METAL ION INDICATORS: Some Examples

4. Calmagite:

1-(1-hydroxyl-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid



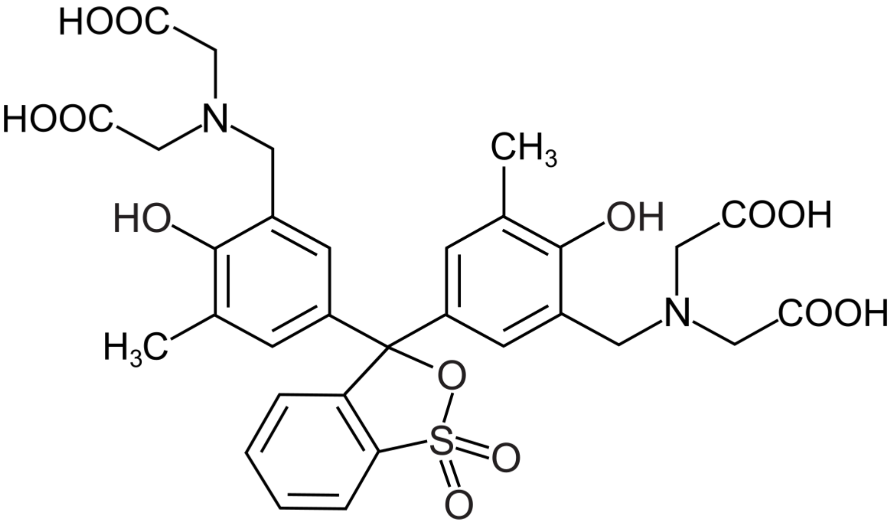


$$H_3D \underset{\text{Low}}{\overset{\text{pH}}{\rightleftharpoons}} H_2D^- \underset{7.1\text{-}9.1}{\overset{\text{pH}}{\rightleftharpoons}} HD^{2-} \underset{11.4\text{-}13.3}{\overset{\text{pH}}{\rightleftharpoons}} In^{3-}$$

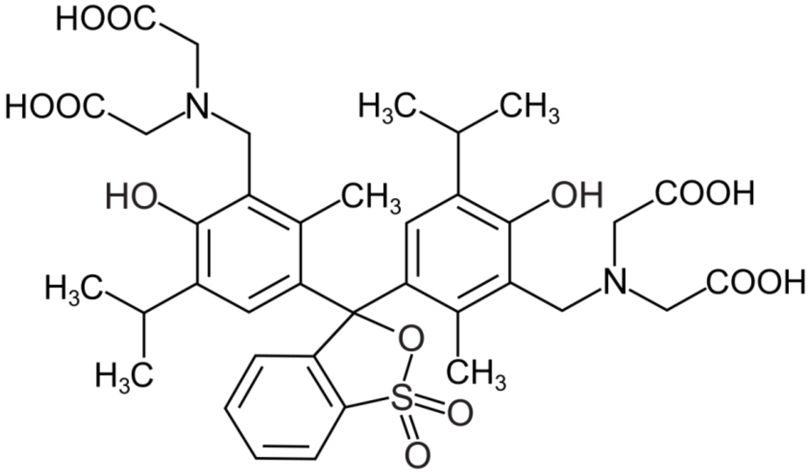
$$HD^{2-} \overset{Mg^{2+}}{\rightleftharpoons} Mg\text{-}D^{2-}$$

- It has the same colour change as solochrome black, but the colour change is somewhat clearer and sharper.
- It may be substituted for solochrome black without change in the experimental procedures for the titration of calcium plus magnesium.
- The pH of 10 is attained by the use of an aqueous ammonia-ammonium chloride buffer mixture.
- The combining ratio between calcium or magnesium and the indicator is 1:1; the magnesium compound is the more stable.

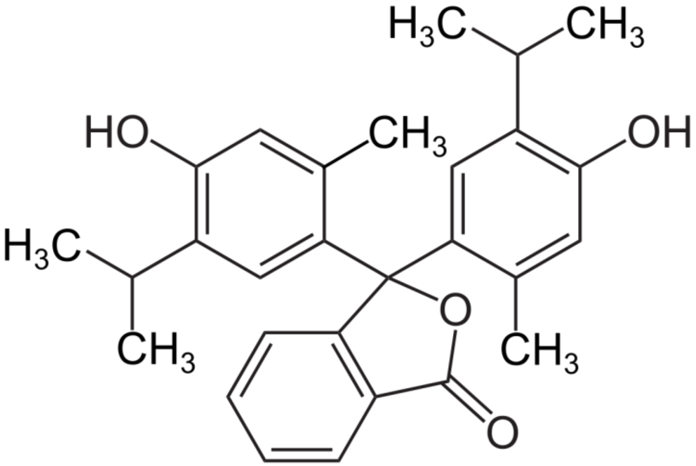
METAL ION INDICATORS: Some Examples



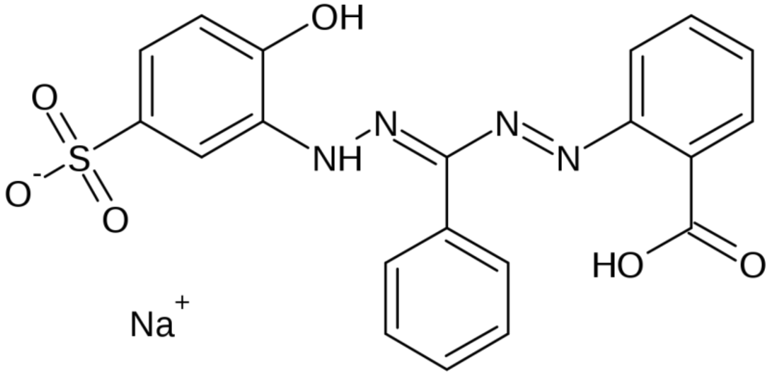
Xylenol orange



Thiomethyl blue



Thymolphthalein complexone



Zircon

Types of EDTA titrations

- **Direct Titrations:**

    i. The solution containing the metal ion to be determined is buffered to the desired pH (e.g., to pH = 10 with NH_4^+-aq. NH_3) and titrated directly with the standard EDTA solution.

    ii. It may be necessary to add auxiliary complexing agent, such as tartrate or citrate or triethanolamine to prevent precipitation of the hydroxide of the metal.

    iii. The equivalence point is generally determined by the change in color of a metal indicator or by amperornetric, spectrophotometric, or potentiometric methods.

- **Back Titrations:**

    i. Many metals cannot be titrated directly for various reasons such as *(a) formation of precipitates in the pH range; (b) formation of inert complexes or (c) unavailability of a suitable metal ion indicator.*

    ii. In such cases an excess of standard EDTA solution is added, the resulting solution is buffered to the desired pH, and the excess of the EDTA is back-titrated with a standard metal ion solution.

Types of EDTA titrations

❑ **Back Titrations:**

i. A solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose.

ii. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions.

❑ **Replacement or substitution titration:**

i. Substitution titrations may be used for metal ions that *(a) do not react with a metal indicator or (b) which forms EDTA complexes that are more stable than those of other metals such as magnesium and calcium.*

ii. The metal cation M^{n+} to be determined may be treated with the magnesium complex of EDTA, when the following reaction occurs:

$$M^{n+} + MgY^{2-} \rightleftharpoons (MY)^{(n-4)+} + Mg^{2+}$$

iii The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

Types of EDTA titrations

- **Replacement or substitution titration:**

  iv. An interesting application is the titration of calcium. In the direct titration of calcium ions, **solochrome black** gives a poor end point; if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point results.

- **Alkalimetric titration:**

  i. When a solution of disodium ethylenediaminetetraacetate, Na_2H_2Y, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion:

  $$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$

  ii. The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or a potentiometric end point.

  iii. Alternatively, an iodate-Iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution.

Titration of Mixtures: Masking and Demasking

- EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations.
- **Masking** may be defined as the process in which a substance, without physical separation of it or its reaction products, is so transformed that it does not enter into a particular reaction.
- **Demasking** is the process in which the masked substance regains its ability to enter into a particular reaction.
- By the use of masking agents, some of the cations in a mixture can often be 'masked' so that they can no longer react with EDTA or with the indicator.
- An effective masking agent is the cyanide ion; this forms stable cyanide complexes with the cations of Cd, Zn, Hg(II), Cu, Co, Ni, Ag, and the platinum metals, but not with the alkaline earths, manganese, and lead:

$$M^{2+} + 4CN^- \rightarrow [M(CN)_4]^{2-}$$

- It is therefore possible to determine cations such as Ca^{2+}, Mg^{2+}, Pb^{2+}, and Mn^{2+} in the presence of the above-mentioned metals by masking with an excess of potassium or sodium cyanide.

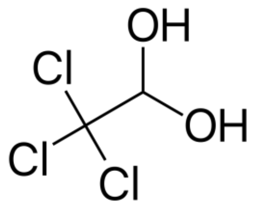
Titration of Mixtures: Masking and Demasking

- Titanium(IV), iron(III), and aluminium can be masked with triethanolamine
- Mercury with iodide ions
- Aluminium, iron(III), titanium(IV), and tin(II) with ammonium fluoride.
- Sometimes the metal may be transformed into a different oxidation state. For e.g., copper(II) may be reduced in acid solution by hydroxylamine or ascorbic acid which when titrated by EDTA with murexide as indicator without interference from the copper, which is now present as Cu(I).

Selective demasking

- The cyanide complexes of zinc and cadmium may be demasked with formaldehyde-acetic acid solution (3: 1) or, better, with chloral hydrate :

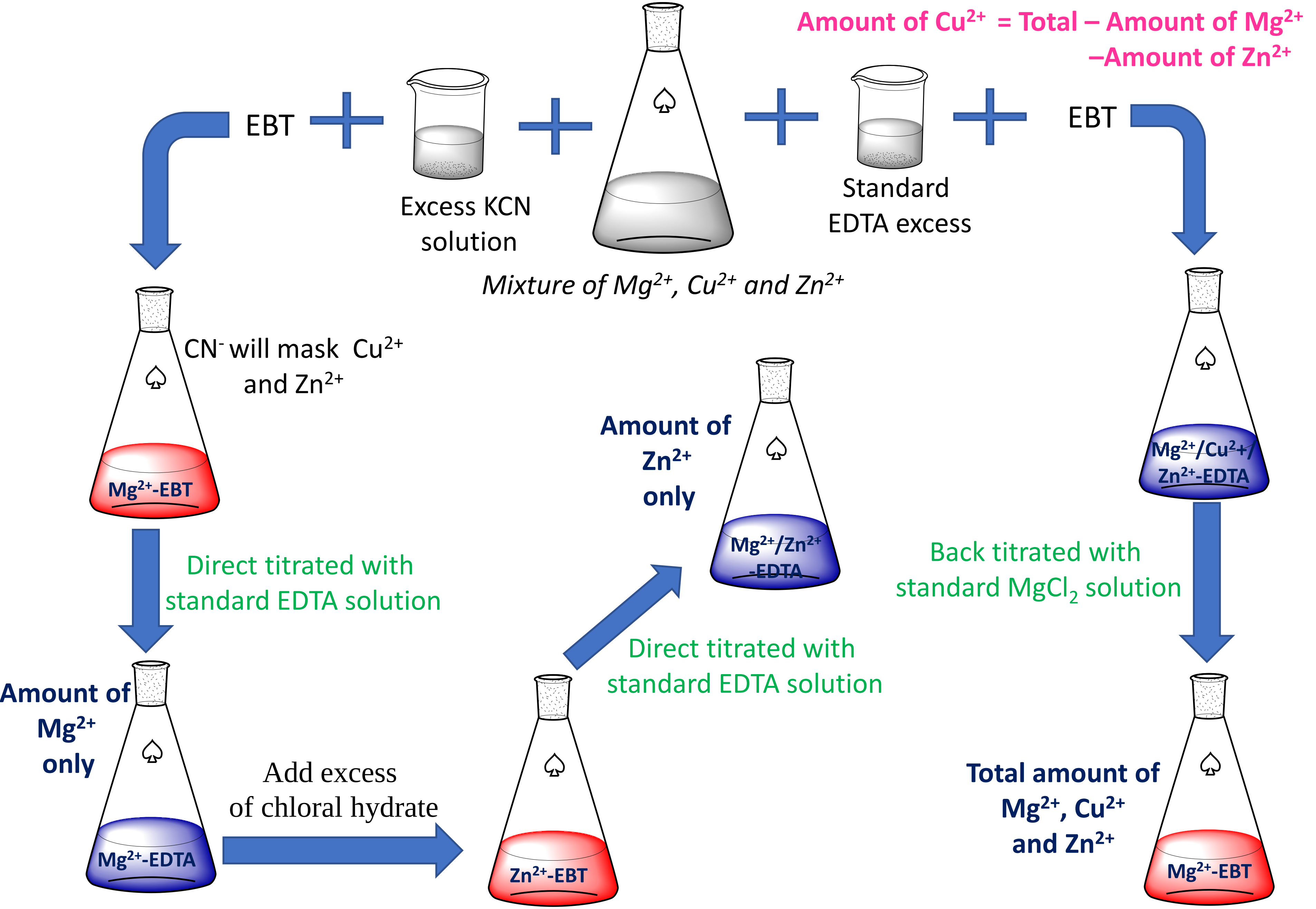
$$[\mathrm{Zn(CN)_4}]^{2-} + 4\mathrm{H}^+ + 4\mathrm{HCHO} \rightarrow \mathrm{Zn}^{2+} + 4\mathrm{HO \cdot CH_2 \cdot CN}$$



chloral hydrate

- The use of masking and selective demasking agents permits the successive titration of many metals

A practical use of Masking and Demasking Agents



Amount of Cu^{2+} = Total – Amount of Mg^{2+} –Amount of Zn^{2+}

EBT + Excess KCN solution + *Mixture of Mg^{2+}, Cu^{2+} and Zn^{2+}* + Standard EDTA excess + EBT

CN^- will mask Cu^{2+} and Zn^{2+}

Direct titrated with standard EDTA solution

Amount of Mg^{2+} only

Add excess of chloral hydrate

Direct titrated with standard EDTA solution

Amount of Zn^{2+} only

Back titrated with standard $MgCl_2$ solution

Total amount of Mg^{2+}, Cu^{2+} and Zn^{2+}

QUESTION: ***Why small amount of Mg salt added to the EDTA solution in the titration of calcium with solochrome black indicator?***

- When calcium ions are titrated with EDTA a relatively stable calcium complex is formed:

$$Ca^{2+} + H_2Y^{2-} \rightleftharpoons CaY^{2-} + 2H^+$$

- With calcium ions alone, no sharp end point can be obtained with solochrome black indicator and the transition from red to pure blue is not observed.
- With magnesium ions, a somewhat less stable complex is formed:

$$Mg^{2+} + H_2Y^{2-} \rightleftharpoons MgY^{2-} + 2H^+$$

- The magnesium indicator complex is more stable than the calcium-indicator complex 'but less stable than the magnesium-EDTA complex.
- Consequently, during. the titration of a solution containing magnesium and calcium ions with EDTA in the presence of solochrome black the EDTA reacts first with the free calcium ions, then with the free magnesium ions, and finally with the magnesium indicator complex.

$$MgD^- \text{ (red)} + H_2Y^{2-} = MgY^{2-} + HD^{2-} \text{ (blue)} + H^+$$

- If magnesium ions are not present in the solution containing calcium ions they must be added, since they are required for the colour change of the indicator.

Determination of hardness of water

http://vlabs.iitb.ac.in/vlabs-dev/labs/nitk_labs/Environmental_Engineering_1/experiments/determination-of-hardness-nitk/theory.html