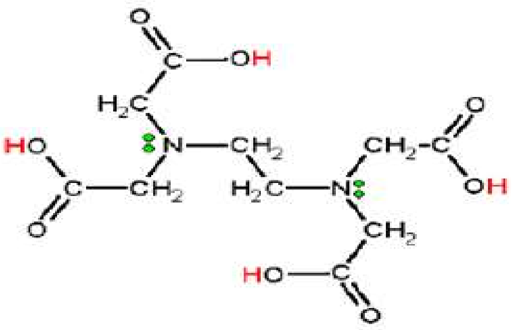
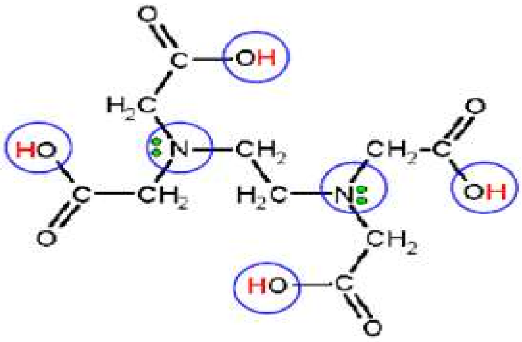
Structure of EDTA

EDTA structure (H_4A) – a ***hexadentate*** *(6 binding sites –* circled) ligand





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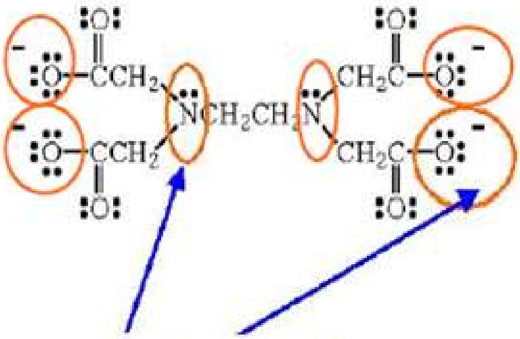
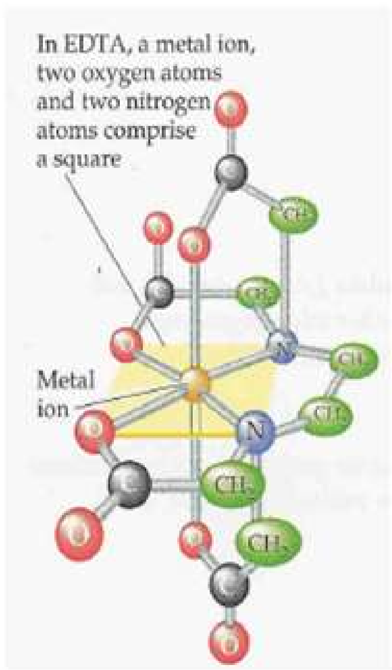
Fully deprotonated form, A^{4-}



Six metal binding sites: Amino-N (2) and carboxylate O (4)

Structure of metal ion-EDTA complex



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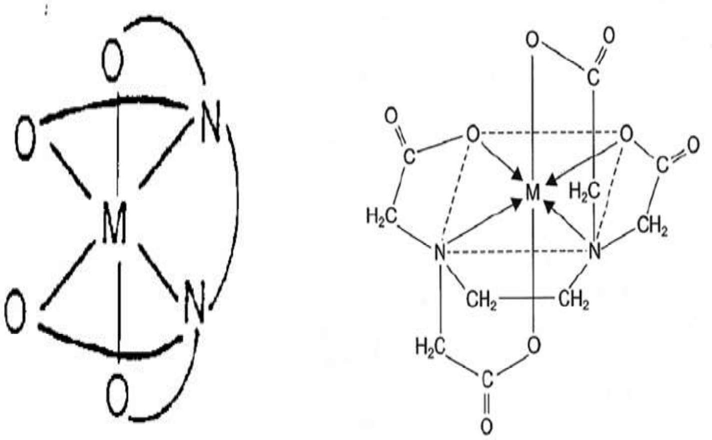
Structure of an EDTA chelate complex



H_6Y^{2+}

$$pK_1 = 0.0$$
$$pK_2 = 1.5$$
$$pK_3 = 2.0$$
$$pK_4 = 2.66$$
$$pK_5 = 6.16$$
$$pK_6 = 10.24$$

Structure of fully protonated EDTA

Complexometry

Complexometry is a titrimetric method that is primarily used for the determination of metal ions, with the aid of complex formation (mainly chelate) reactions.

The following conditions need to be met for the successful use of a complex reaction in titrimetry:

- the complex needs to be very stable, with a high formation constant so the reaction is stochiometric (chelates)

- the solution needs to be buffered

- the complex needs to be formed in 1:1 ratio (for a sharp end-point)

There are several useful complexons, but by far the most useful is ethylene-diammine tetraacetic acid or EDTA.

Effect of pH: During a complexometric titration, the pH must be constant by use of a buffer solution. Control of pH is important since the H^+ ion plays an important role in chelation. Most ligands are basic and bind to H^+ ions throughout a wide range of pH. Some of these H^+ ions are frequently displaced from the ligands (chelating agents) by the metal during chelate formation.

Equation below shows complexation between metal ion and H^+ ion for ligand:

$$M^{2+} + H_2\text{-}EDTA^{2-} \rightleftharpoons M\text{-}EDTA^{2-} + 2H^+$$

EDTA is the most widely used complexing agent for routine analysis of water hardness and other applications. EDTA is a multidentate ligand that is represented by the formula H_4Y. Usually, EDTA titrations are conducted in alkaline conditions under which EDTA will be present in different forms including H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}. Therefore, controlling the pH is one major factor that affects complexation.

For EDTA to react with a metal ion, the hydrogens attached to the carboxylate groups must be removed. In strongly basic solution, these hydrogens are removed by reaction with hydroxide ion. In more acidic solutions, metal ions must be able to displace the hydrogens if a complex is to be formed. Since metal ions differ significantly in their ability to displace the hydrogens, the solution acidity can be used to "regulate" the reactivity of EDTA toward metal ions. For example, most metal ions react quantitatively with a stoichiometric amount of EDTA at pH 10, but only a few, such as Fe^{3+} and Hg^{2+}, also react quantitatively at pH 2.

Metal Ion Indicators

Metal ion indicators = compounds that change color when they bind to a metal ion (Table 3-3)

Desirable properties

- Must bind to the metal ion, but
- Must release the metal ion to EDTA at the equiv. point

  i.e. Metal-Indicator complex must be weaker (smaller K) than metal-EDTA complex

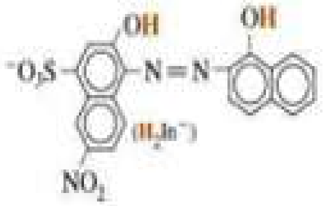
Equilibrium reaction: (Charges are omitted for simplicity)

$$\text{M-In} + \text{EDTA} \rightleftharpoons \text{M-EDTA} + \text{In}$$

M-In	EDTA	M-EDTA	In
Metal-indicator complex (Color 1)	(Colorless)		Free indicator (Color 2)

Indicators for EDTA Titration

Table 13-3 Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of meta ion complex
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}

Metal Ion Indicators – Cont.

M-In + **EDTA** ⇌ **M-EDTA** + **In**

Metal-indicator complex (Color 1) — EDTA (Colorless) — Free indicator (Color 2)

- **Beginning of titration:** Small amount of **In** added forms colored M-In complex
- **During titration:** EDTA (titrant) added ***binds first to M^{n+}*** that is not complexed with In
- **At the end point:** A small excess of EDTA ***displaces In*** from M-In complex; Color changes as In is released

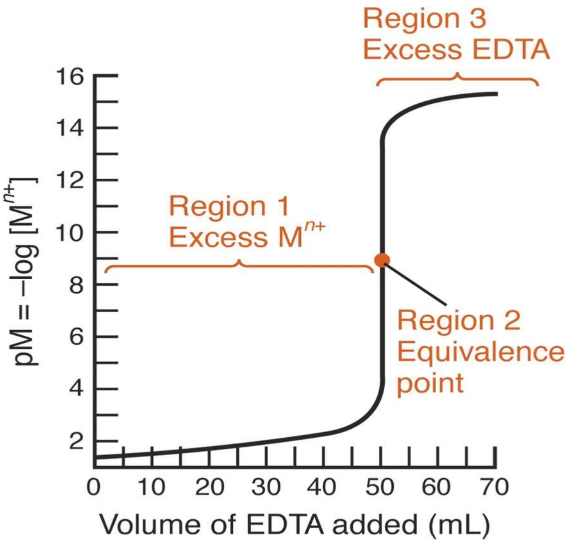
Three Regions of EDTA Titration

The curves are easily calculated by dividing the curve up into domains:

The pM before equivalence.

The pM at equivalence. •

The pM after equivalence. •



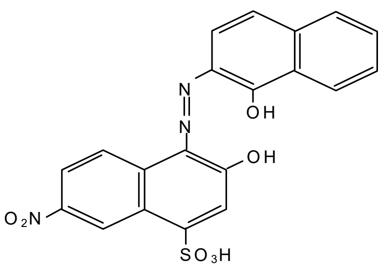
Examples:

Erichrome Black T

- **Eriochrome Black T is an azo dye, best used with Mg^{2+} and Zn^{2+} titrations.**
- **Excess EDTA causes a red to blue color change at near neutral pH.**
- **Eriochrome Black solutions decompose easily.**

MgIn + EDTA → MgEDTA + In

(red) (colorless) (blue)



Erichrome Black T (EBT)

- Useful in any titration were pH range is between 7 and 10, including calcium, magnesium and zinc
- EBT is triprotic and has a different structure at varying pH values
- Between pH 7 and 10 it exists as the dianion (Hin^{2-}) and is blue in colour
- It forms a red-purple complex with metals