Analytical chemistry

Lecture № 19

Complexation titration

Complexation titration - A titration in which the reaction between the analyte and titrant is a *complexation reaction.*

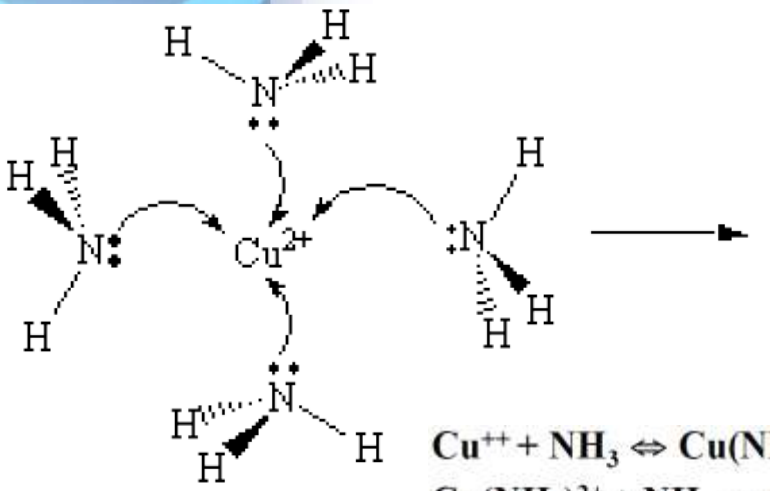
In this method, a simple ion is transformed into a complex ion and the equivalence point is determined by using metal indicators or electrometrically.

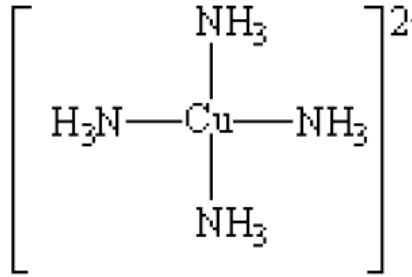
Definition of terms

Most metal ions can accept unshared pairs of electrons from an anion or molecule to form coordinate covalent bonds. Usually metals accept 2, 4 or 6 e- pairs (coordination number).

Molecule containing donor atom = ligand

Product resulting from reaction between metal ion and ligand = complex ion or (metal) complex





$Cu^{++} + NH_3 \Leftrightarrow Cu(NH_3)^{++}$ K_{f_1}

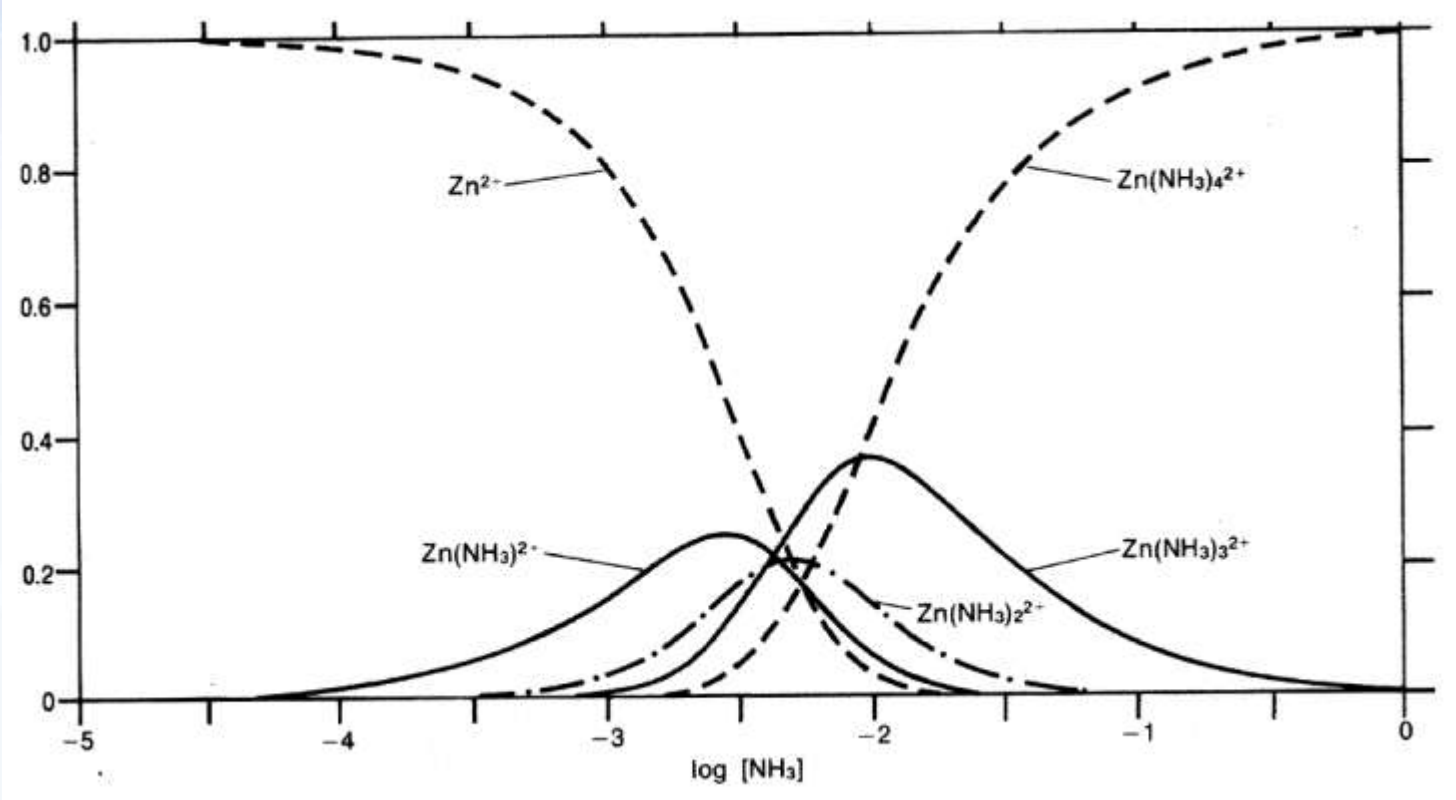
$Cu(NH_3)^{2+} + NH_3 \Leftrightarrow Cu(NH_3)_2^{2+}$ K_{f_2}

$Cu(NH_3)_2^{2+} + NH_3 \Leftrightarrow Cu(NH_3)_3^{2+}$ K_{f_3}

$Cu(NH_3)_3^{2+} + NH_3 \Leftrightarrow Cu(NH_3)_4^{2+}$ K_{f_4}

Ligands with a single donor atom - monodentate (CN^-, NH_3, F^-)

Multidentate ligands have multiple donor atoms and coordinate with a metal ion to form a ring structure - ***chelate*** ('claw')



- theoretically could titrate Zn with ammonia
- stepwise K very similar and small
- difficult to know stoichiometry
- to ensure all one form, need excess NH_3
- titration never gives good equivalence point
- can't use this monodentate ligand to titrate metals

Any complexation reaction can in theory be applied as a volumetric technique provided that:

- the reaction reaches equilibrium rapidly following each addition of titrant.
- interfering situations do not arise (such as stepwise formation of various complexes resulting in the presence of more than one complex in solution in significant concentration during the titration process).
- an complexometric indicator capable of locating equivalence point with fair accuracy is available

Complexation Titrations can be classified according to the type of ligands:

1. Titration methods based on the chemical reactions with monodentate ligands M – Lig

2. Titration methods based on the chemical reactions with multidentate ligands

Typical Inorganic Complex-Forming Titrations

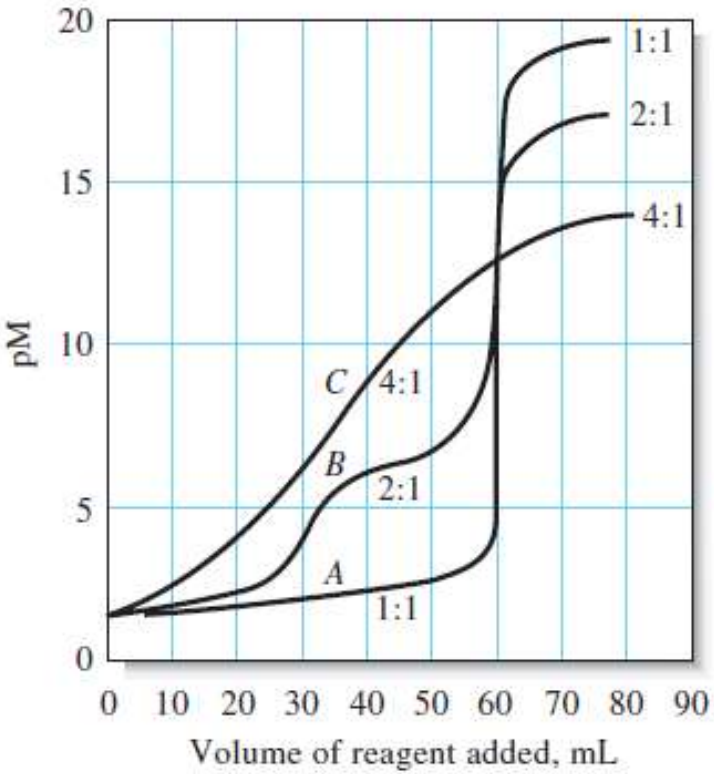
Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is AgI; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

The earliest titrimetric applications involving metal–ligand complexation were the determinations of cyanide and chloride using, respectively, Ag^+ and Hg^{2+} as titrants.
Both methods were developed by Justus Liebig (1803–1873) in the 1850s.

1. Argentometric titration - titrant $AgNO_3$

2. Mercurimetric titration - titrant $Hg(NO_3)_2$

Tetradentate or hexadentate ligands are more satisfactory as titrants than ligands with fewer donor groups because their reactions with cations are more complete and because they tend to form 1:1 complexes.



Titration curves for complexometric titrations. Titration of 60.0 mL of a solution that is 0.020 M in metal M with (A) a 0.020 M solution of the ***tetradentate ligand*** D to give MD as the product; (B) a 0.040 M solution of the ***bidentate ligand*** B to give MB_2; and (C) a 0.080 M solution of the ***unidentate ligand*** A to give MA_4. The overall formation constant for each product is 10^{20}.

Argentometric titration (titrant $AgNO_3$)

The earliest examples of metal–ligand complexation titrations are Liebig's determinations, in the 1850s, of cyanide and chloride using, respectively, Ag^+ and Hg^{2+} as the titrant. Liebig's titration of CN^- with Ag^+ was successful because they form a single, stable complex of $Ag(CN)_2^-$, giving a single, easily identified end point.

$$Ag^+ + 2CN^- \Leftrightarrow [Ag(CN)_2]^-$$

$$Ag^+ + [Ag(CN)_2]^- \Leftrightarrow \underset{white}{Ag[Ag(CN)_2]\downarrow}$$

$$n(AgNO_3) = n(2KCN)$$

Titrant: $AgNO_3$

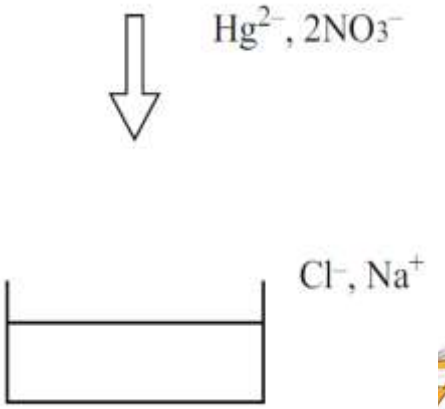
Indicator: no indicator (self indicator), a white precipitate appears at the end point

Conditions: Always to an analyzed solution (NaCN, KCN etc) titrant $AgNO_3$ should be added, and not vice versa.

Mercurimetry (Votocek–Dubsky's Method)

Mercurimetry groups all the titrimetric methods based on the use of titrant solutions consisting of ionized mercuric (II) salts. The most important one is that due to Votocek and Dubsky. This method is essentially a method of determining some halide ions by titration with a mercuric salt.

Votocek–Dubsky's method is based on the property exhibited by some mercuric "salts" to be very poorly ionized in solution because they actually are complexes. This property is shared by halide, cyanide, and thiocyanate ions. Oxygenated salts, however, are normally ionized (nitrate, sulfate). From another standpoint, ***sodium nitroprusside*** forms a white precipitate of mercuric nitroprusside with Hg^{2+} ions, that is, with oxygenated mercuric salts but not with halides or parent compounds because of their property of being complexes.



$$Hg^{2+} + 2X^{-} \rightarrow [HgX_2]$$

$$Hg^{2+} + 4X^{-} \rightarrow [HgX_4]^{2-}$$

When we progressively add a solution of a normally ionized mercuric salt (nitrate or sulfate) to a solution of sodium chloride, for example, the mercuric ions disappear with equivalent quantities of chloride ions as they give the complexes $[HgCl_4]^{2-}$, $[HgCl_3]^{-}$, $[HgCl_2]$, and $[HgCl]^{+}$. Close to the equivalence point, it is essentially $HgCl_2$ that is formed. After the equivalence point, free Hg^{2+} ions appear suddenly in the titrand solution. They are in sufficient quantity to be detected either

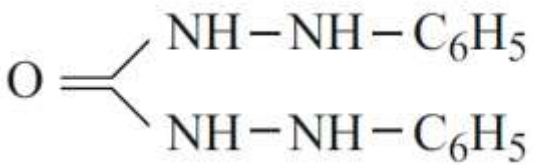
• by a turbidity indicator. They react with sodium ***nitroprusside*** according to the reaction

$$[Fe(CN)_5NO]^{2-} + Hg^{2+} \rightleftharpoons Hg[Fe(CN)_5NO]\downarrow$$

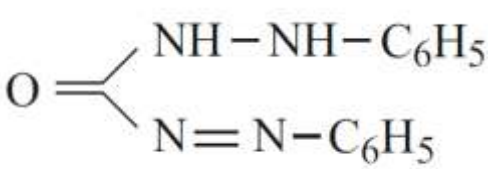
In this case excess of titrant leads to formation of *white precipitate*. This is ***Votocek's method***;

• with colored indicators:

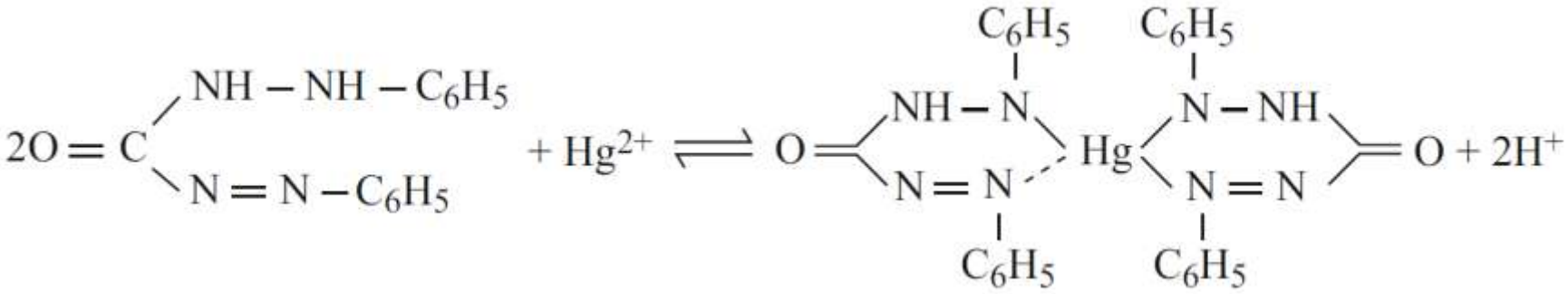
– diphenylcarbazid



- diphenylcarbazone

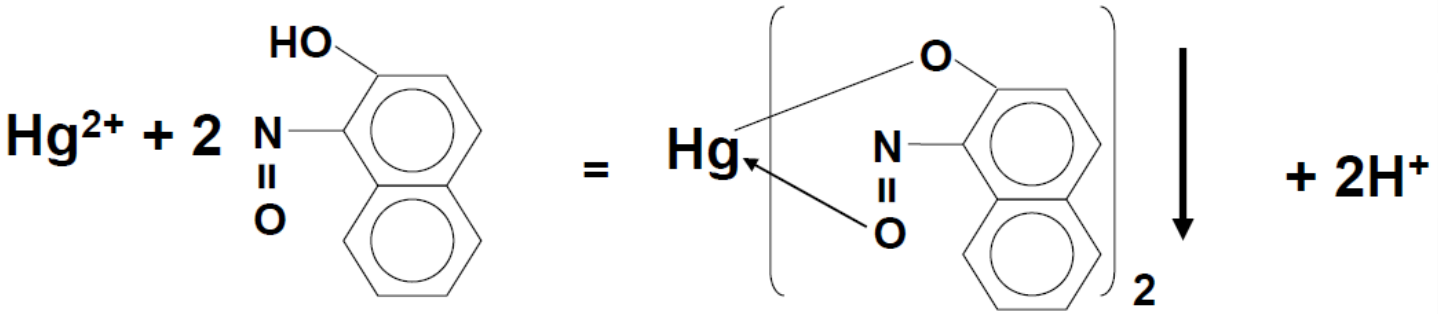


In this case excess of Hg^{2+} reacts with diphenylcarbazone giving complex compound of blue violet colour. This is ***Dubsky's method***



violet chelate

• Application of ***α-nitroso-β-naphthol*** as indicator. In this case excess of titrant leads to formation of red precipitate with indicator.



Red precipitate

Preparation of titrant $Hg(NO_3)_2$

Mercury (II) nitrate is not a primary standard. It should be standardized against dried sodium chloride.

$$Hg(NO_3)_2 + 2NaCl = HgCl_2 \downarrow + 2NaNO_3$$

$$n(\tfrac{1}{2} Hg(NO_3)_2) = n(NaCl)$$

Advantages of mercurimetric method:

- Determinations can be performed in acidic solution by direct technique
- Mercury salts are less expensive then silver compounds
- Less ions interference the determinations

Disadvantage– mercury compounds are toxic.

Applications

Votocek–Dubsky's method is useful when argentometry can no longer be used. It permits us to determinate 200 µg of chloride ions with a ±5% precision. This is a very sensitive method. It has been systematically used for penurious reasons of different origins, for example, that of silver. Furthermore, mercurimetry has been called the "argentometry of poor people." It permits the determination of Br^-, CN^-, and SCN^- ions. **F^-** ions cannot be determined in this way. It cannot be used to determine iodide ions because of the formation of the red precipitate of HgI_2 that begins too early. It gives good results in clinical chemistry for the determination of chloride ions in urine and in the cephalo-rachidian liquid, provided albumin and protides have been eliminated previously by defecation. Finally, let's recall that the titrant solution must be ***acidified*** to avoid the mercuric oxide precipitation after hydrolysis.

Applications

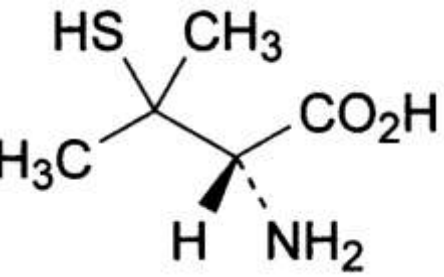
Mercurimetric titration of drugs.

Principle:

- Mercury (Hg) has the ability to complex two –SH group .
- All drugs which including Sulphadryl compounds react quantitative with Mercuric salts.
- Mercury II nitrate used in Pharmacopia as standard solution which reacted with the sulphadryl drugs according to the following reaction:

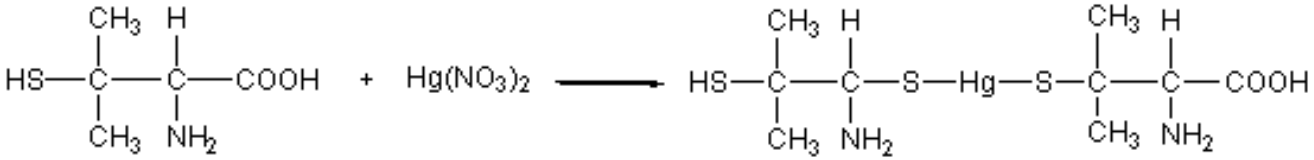
$$\mathbf{2\ R\text{-}SH + Hg(NO_3)_2 \rightleftarrows R\text{-}S\text{-}Hg\text{-}S\text{-}R + 2\ HNO_3}$$

- Diphenylthiocarbazone (dithizone) used as indicator



Penicillamine

Used in treatment of rheumatoid arthritis and in treatment of lead poisoning.



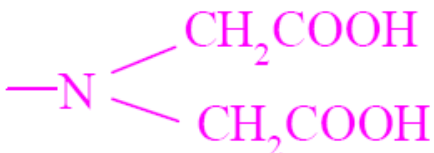
Complexometry II: Titrations with EDTA

In 1945, Schwarzenbach et al. initiated fundamental studies concerning the chelating properties of polyamino carboxylic acids in order to improve their interesting analytical properties. He named these new derivatives ***complexones***. *These studies* followed previous ones, begun in 1939, which had led to the discovery that these compounds did form stable and water-soluble complexes with plenty of metallic ions.

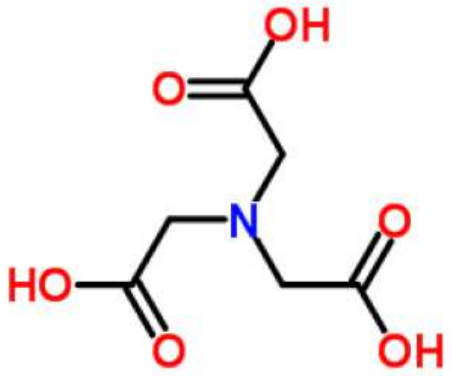
Among other complexones, ***ethylenediaminetetraacetic acid (H_4EDTA)*** and its derivatives are probably the most commonly used reagents in complexonometry. Their success originates from their chelating properties and also from the fact they give watersoluble complexes quasi-instantaneously. These attributes are required properties in titrimetry.

Complexes involving simple ligands, i.e., those forming only one bond are described as ***co-ordination compound***. A complex of a metal ion with 2 or more groups on a multidentate ligand is called a ***chelate or a chelate compound***. There is no fundamental difference between co-ordination compound and a chelate compound except that in a chelate compound, ring influence the stability of compound. Thus, a chelate can be described as a heterocyclic ring structure in which a metal atom is a member of ring. The stability of a chelate is usually much greater than that of corresponding unidentate metal complex.

Ligands having more than one electron donating groups are called ***chelating agents***. The most effective complexing agent in ligands are amino and carboxylate ions. All the multidentate ligands important in analytical chemistry contain the structure component as follows:

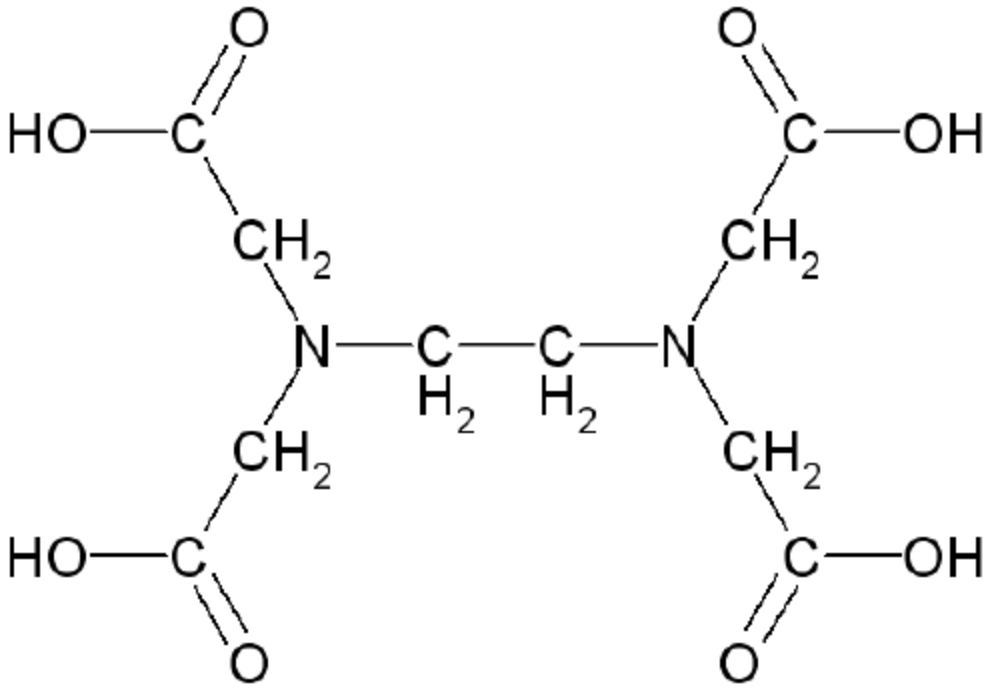


Other polydentate ligands:

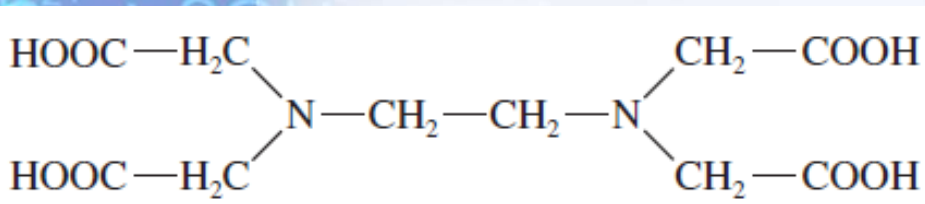


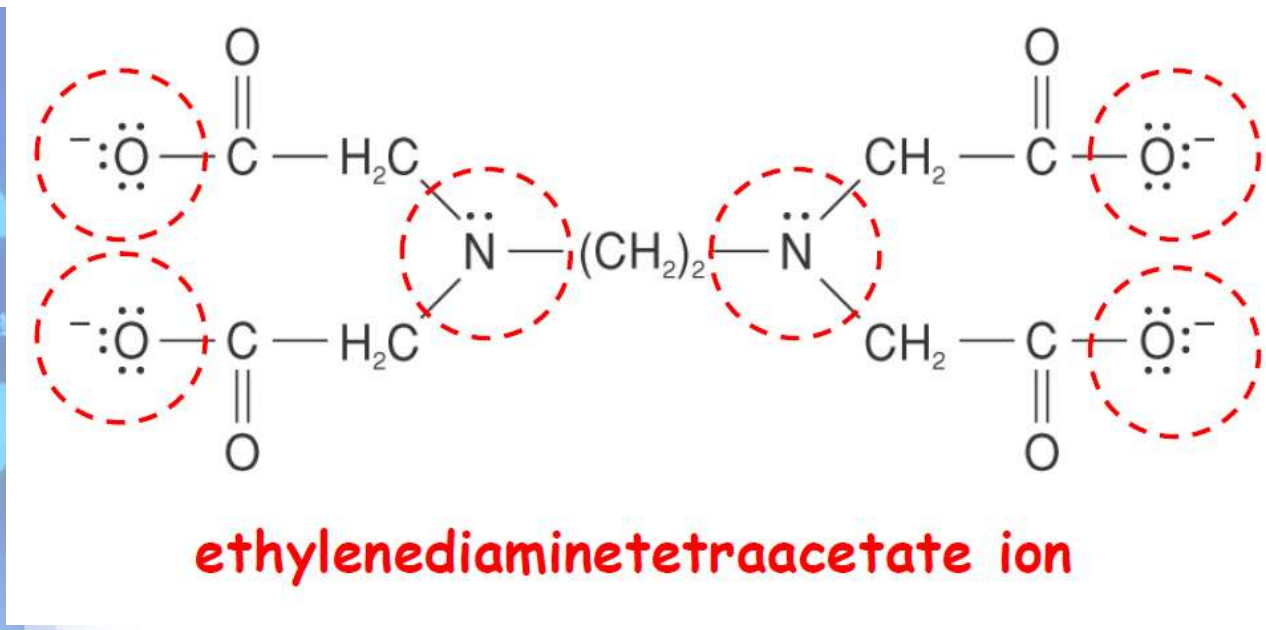
Nitrilotriacetic acid (NTA) is the aminopolycarboxylic acid with the formula $N(CH_2CO_2H)_3$. It is a colourless solid that is used as a chelating agent, which forms coordination compounds with metal ions (chelates) such as Ca^{2+}, Cu^{2+}, and Fe^{3+}.

EDTA



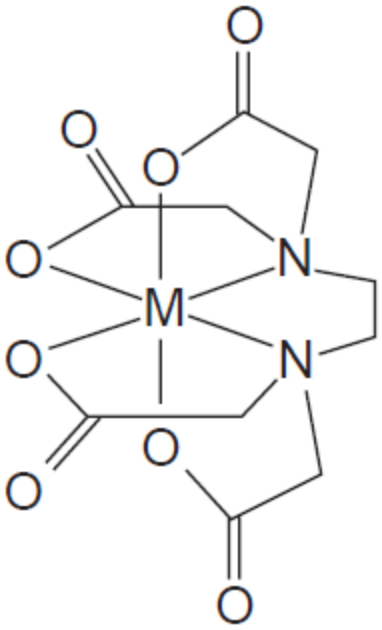
Chemistry and Properties of EDTA





ethylenediaminetetraacetate ion

Ethylenediaminetetraacetic acid, or EDTA, is an aminocarboxylic acid, which is a Lewis acid, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons. The resulting metal–ligand complex, in which EDTA forms a cage-like structure around the metal ion, is very stable. The actual number of coordination sites depends on the size of the metal ion; however, all metal–EDTA complexes have a **1:1** stoichiometry.



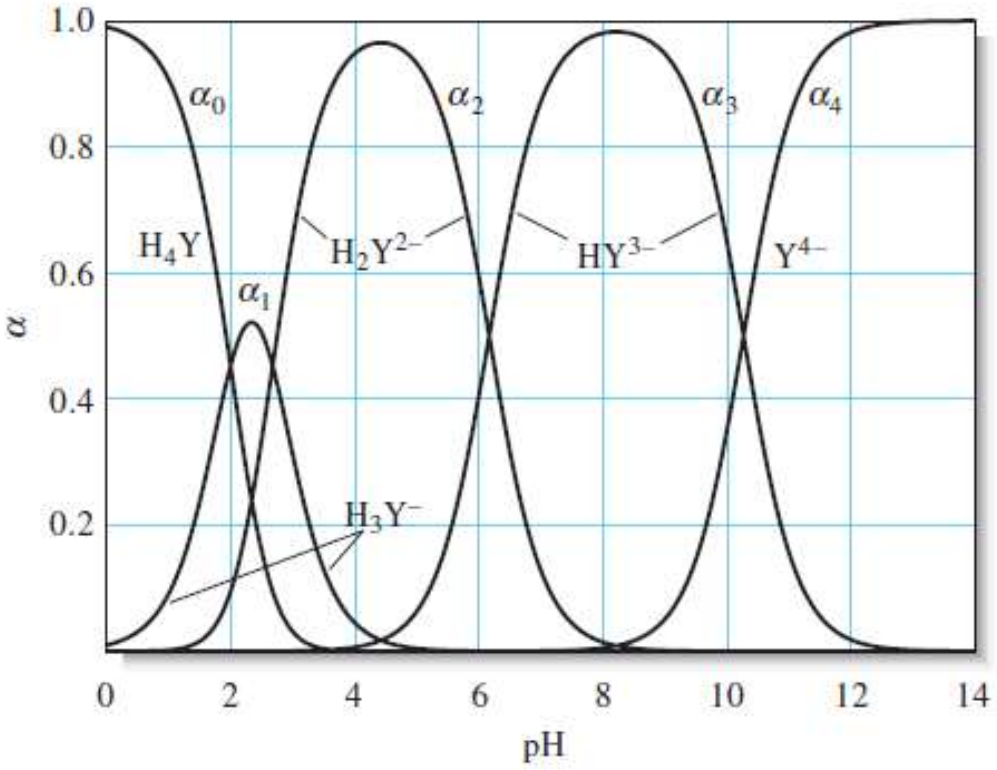
Thus, EDTA contains six complexing groups. We will represent EDTA by the symbol **H_4Y.** It is a tetraprotic acid, and the hydrogens in H_4Y refer to the four ionizable hydrogens belonging to the four carboxylic acid groups. At sufficiently low pH, the nitrogens can also be protonated and this diprotonated EDTA can be considered a hexaprotic acid. However, this occurs at a very low pH and EDTA is almost never used under such conditions. It is the unprotonated ligand Y^{4-} that forms complexes with metal ions, that is, the protons are displaced by the metal ion upon complexation.

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \quad K_{a1} = 1.0 \times 10^{-2} = \frac{[H^+][H_3Y^-]}{[H_4Y]}$$

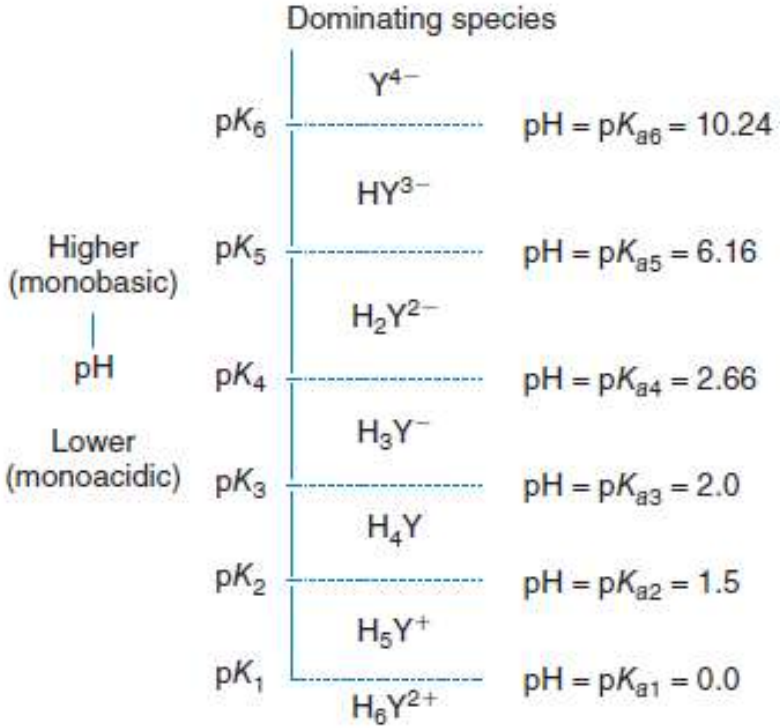
$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \quad K_{a2} = 2.2 \times 10^{-3} = \frac{[H^+][H_2Y^{2-}]}{[H_3Y^-]}$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{3-} \quad K_{a3} = 6.9 \times 10^{-7} = \frac{[H^+][HY^{3-}]}{[H_2Y^{2-}]}$$

$$HY^{3-} \rightleftharpoons H^+ + Y^{4-} \quad K_{a4} = 5.5 \times 10^{-11} = \frac{[H^+][Y^{4-}]}{[HY^{3-}]}$$



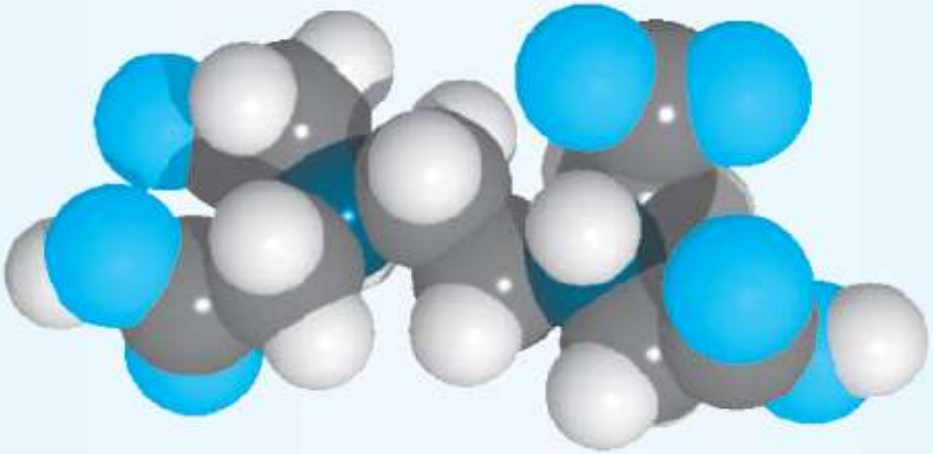
fraction of each form of EDTA as a function of pH



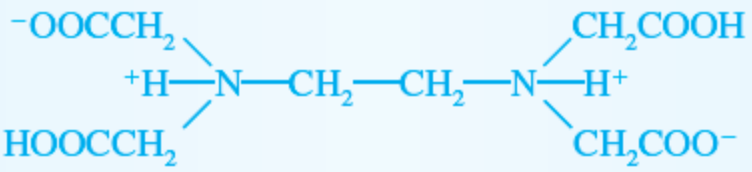
A ladder diagram for EDTA

The first four values are for the carboxyl protons, and the remaining two values are for the ammonium protons. The species Y^{4-} becomes the predominate form of EDTA at pH levels greater than 10.24. It is only for pH levels greater than 12 that Y^{4-} becomes the only significant form of EDTA.

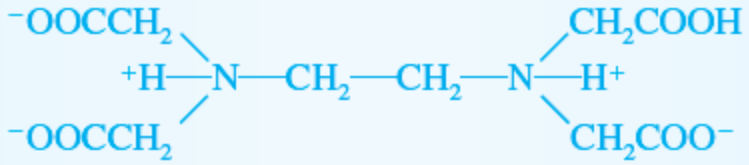
Since the anion Y^{4-} is the ligand species in complex formation, the complexation equilibria are affected markedly by the **pH.** H_4Y has a very low solubility in water, and so the disodium salt $\mathbf{Na_2H_2Y \cdot 2H_2O}$ is generally used, in which two of the acid groups are neutralized.



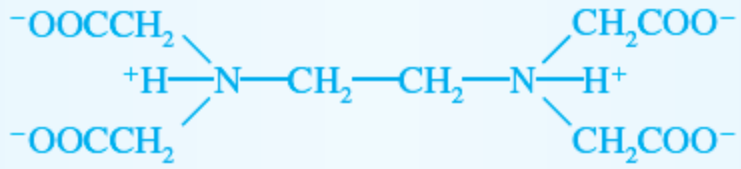
Molecular model of the H_4Y zwitterion.



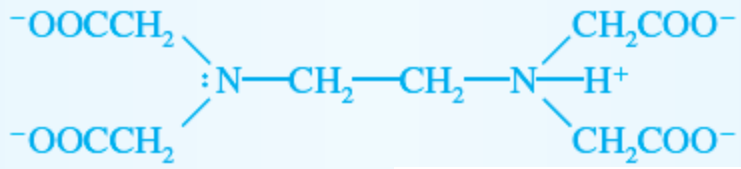
(a) H_4Y



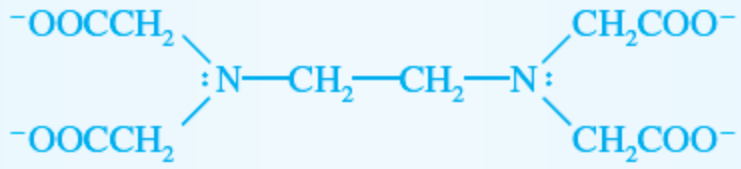
(b) H_3Y^-



(c) H_2Y^{2-}



(d) HY^{3-}



(e) Y^{4-}

Structure of H_4Y and its dissociation products. Note that the fully protonated species H_4Y exist as a double zwitterion with the amine nitrogens and two of the carboxylic acid groups protonated. The first two protons dissociate from the carboxyl groups, while the last two come from the amine groups.

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}}$$

Reagents for EDTA Titrations

The free acid H_4Y and the dihydrate of the sodium salt, $Na_2H_2Y \times 2H_2O$, are commercially available in reagent quality. The free acid can serve as a primary standard after it has been dried for several hours at 130°C to 145°C. However, the free acid is not very soluble in water and must be dissolved in a small amount of base for complete solution.

More commonly, the dihydrate, $Na_2H_2Y \times 2H_2O$, is used to prepare standard solutions. Standard EDTA solutions can be prepared by dissolving weighed quantities of $Na_2H_2Y \times 2H_2O$ and diluting to the mark in a volumetric flask.

- EDTA solutions should be standardized against $CaCO_3$, $ZnSO_4$ or $MgSO_4$ of very high purity. Water used in EDTA solution preparations should be distilled.
- The titration is conducted at a ***buffered solution*** at about pH 10.
- Another important note concerns storage of standardized EDTA solutions where these solutions should never be stored in soda based glass. Preferably, polyethlene bottles should always be used.
- A fresh solution should be prepared at least monthly, and the solution should be standardized fairly often (every one or two weeks) against a primary standard.

Complexes of EDTA and Metal Ions

The EDTA *combines with metal ions in a 1:1 ratio regardless of the charge on the cation.*

The great stability undoubtedly results from the several complexing sites within the molecule that give rise to a cagelike structure in which the cation is effectively surrounded and isolated from solvent molecules.

Formation Constants for EDTA Complexes

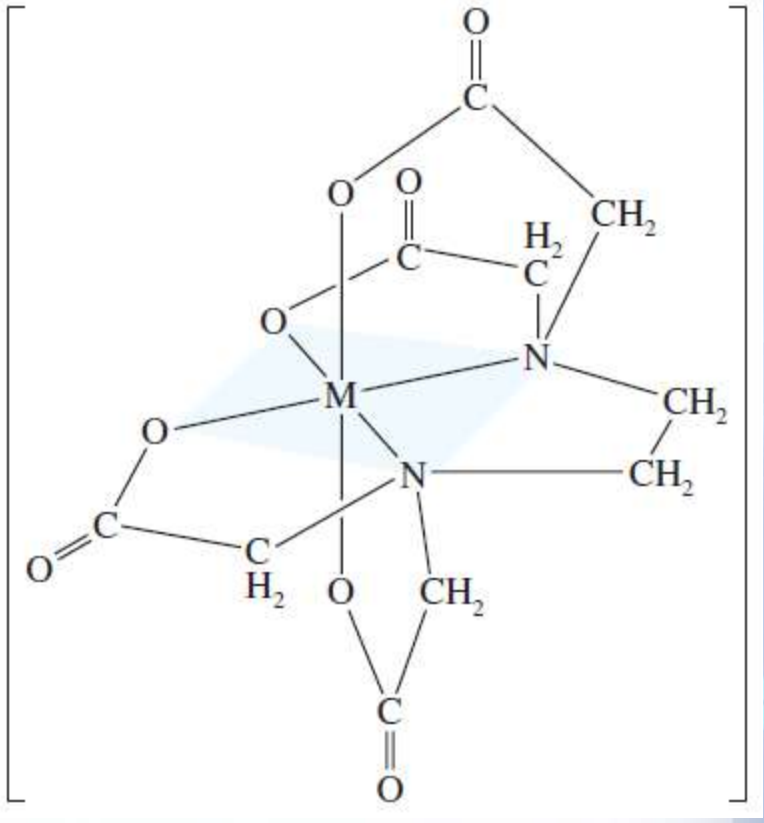
Cation	K_{MY}^*	log K_{MY}	Cation	K_{MY}
Ag^+	2.1×10^7	7.32	Cu^{2+}	6.3×10^{18}
Mg^{2+}	4.9×10^8	8.69	Zn^{2+}	3.2×10^{16}
Ca^{2+}	5.0×10^{10}	10.70	Cd^{2+}	2.9×10^{16}
Sr^{2+}	4.3×10^8	8.63	Hg^{2+}	6.3×10^{21}
Ba^{2+}	5.8×10^7	7.76	Pb^{2+}	1.1×10^{18}
Mn^{2+}	6.2×10^{13}	13.79	Al^{3+}	1.3×10^{16}
Fe^{2+}	2.1×10^{14}	14.33	Fe^{3+}	1.3×10^{25}
Co^{2+}	2.0×10^{16}	16.31	V^{3+}	7.9×10^{25}
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}

*Constants are valid at 20°C and ionic strength of 0.1.

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]}$$

$$Cd^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons CdY^{2-}(aq)$$

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16}$$



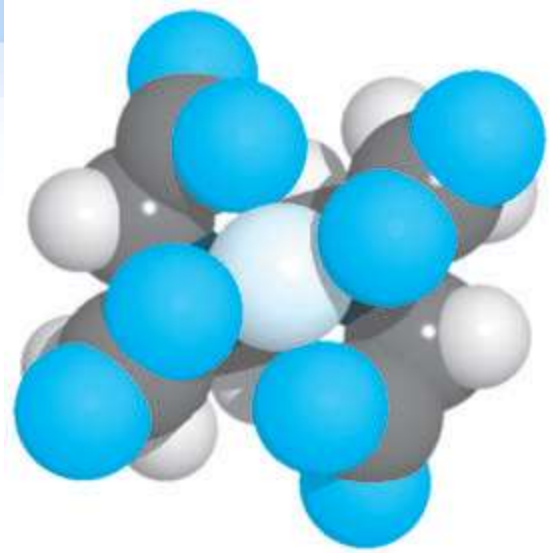
Structure of a metal/EDTA complex. Note that EDTA behaves here as a hexadentate ligand in that six donor atoms are involved in bonding the divalent metal cation.

$$M^{n+} + H_4Y \overset{K_1}{\rightleftharpoons} [MY]^{(n-4)+} + 4H^+,$$

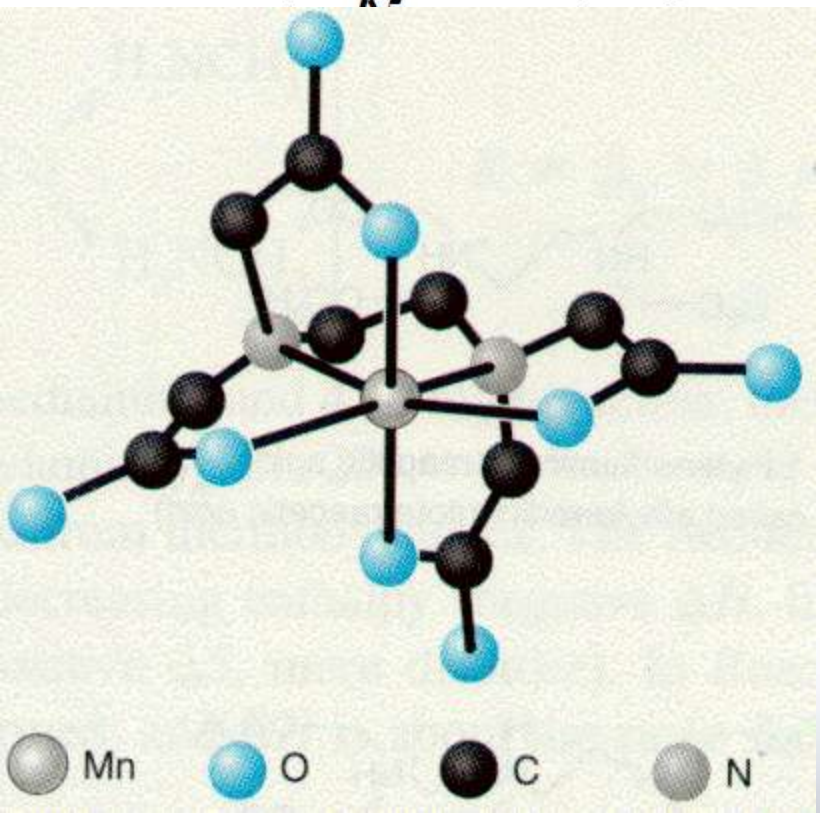
$$M^{n+} + H_3Y^- \overset{K_2}{\rightleftharpoons} [MY]^{(n-4)+} + 3H^+,$$

$$M^{n+} + H_2Y^{2-} \overset{K_3}{\rightleftharpoons} [MY]^{(n-4)+} + 2H^+,$$

$$M^{n+} + HY^{3-} \overset{K_4}{\rightleftharpoons} [MY]^{(n-4)+} + H^+,$$



Molecular model of NiY^{2-}



The more acidic the medium is, the less the complex with EDTA tends to form. Inversely, the more stable the chelate is, the more acidic the medium in which it will be formed may be. For example, according to the stability of the chelate, whether or not the titration of a metallic ion is possible depends on the solution's pH.

The conditional constant should be at least **10^6** to obtain a satisfactory end point with a 0.01 M solution of the metal ion.

Conditional Formation Constants

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$

$$c_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{3-}] + [H_4Y]$$

total molar concentration of *uncomplexed EDTA*

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T}$$

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

Conditional formation constants are pH dependent.

$$\alpha_4 = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

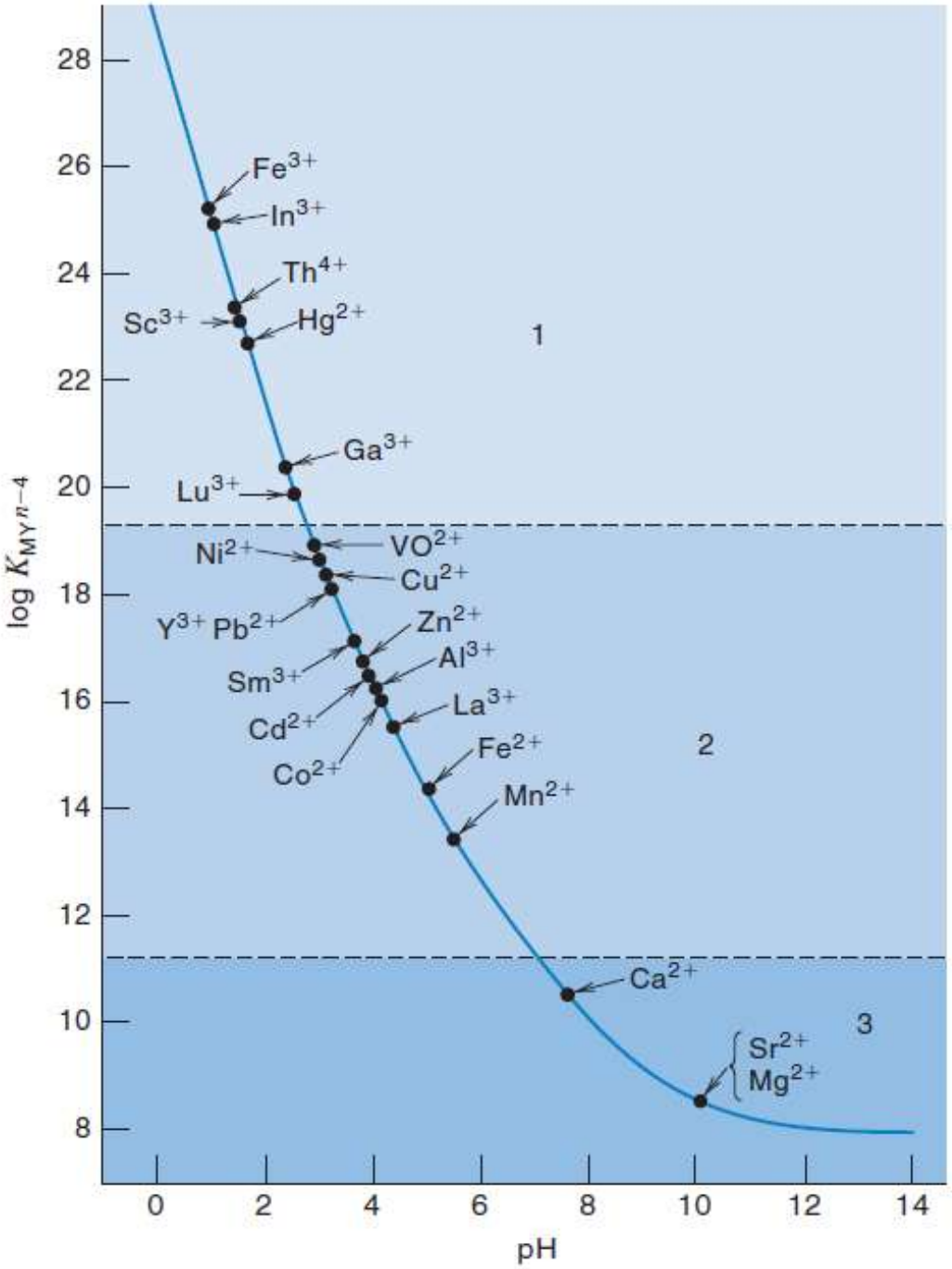
The term ***conditional formation constant*** *is used under specified conditions (e.g., at a* certain pH) and can be convenient for calculations. It takes into account that only a fraction of the total EDTA species are present as Y^{4-}.

Table 1 Values of $\alpha_{Y^{4-}}$ for Selected pHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
2	3.7×10^{-14}	8	5.4×10^{-3}
3	2.5×10^{-11}	9	5.2×10^{-2}
4	3.6×10^{-9}	10	0.35
5	3.5×10^{-7}	11	0.85
6	2.2×10^{-5}	12	0.98
7	4.8×10^{-4}	13	1.00

Table 2 Conditional Formation Constants for CdY^{2-}

pH	K'_f	pH	K'_f
2	1.1×10^{3}	8	1.6×10^{14}
3	7.3×10^{5}	9	1.5×10^{15}
4	1.0×10^{8}	10	1.0×10^{16}
5	1.0×10^{10}	11	2.5×10^{16}
6	6.4×10^{11}	12	2.8×10^{16}
7	1.4×10^{13}	13	2.9×10^{16}



Minimum pH for effective titration of various metal ions with EDTA.

The points on the curve represent the pH at which the *conditional formation constant K_f for each metal is 10^6 (log K_f= 6)*, which was arbitrarily chosen as the minimum needed for a sharp end point. Note that the smaller the K_f, *the more alkaline* the solution must be to obtain a K_f *of 10^6 (i.e., the larger α4 must be). Thus, Ca^{2+}* with K_f *only about 10^{10} requires a pH of ~≥ 8. The dashed lines in the figure divide* the metals into separate groups according to their formation constants. One group is titrated in a highly acidic *(pH < ~3) solution, a second group at pH ~3 to 7, and a* third group at pH > *7. At the highest pH range, all the metals will react, but not all* can be titrated directly due to precipitation of hydroxides.

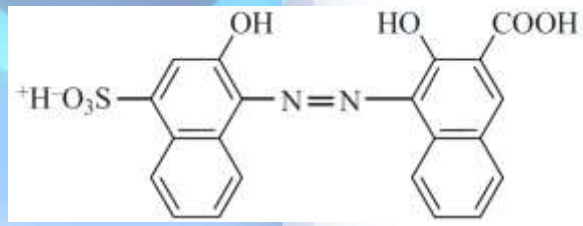
Selecting and Evaluating the End Point

I. Finding the End Point with a Visual Indicator.

Most indicators for complexation titrations are organic dyes that form stable complexes with metal ions. These dyes are known as ***metallochromic indicators*.** To function as an indicator for an EDTA titration, the metal–indicator complex must possess a color different from that of the uncomplexed indicator. Furthermore, the formation constant for the metal–indicator complex must be less favorable than that for the metal–EDTA complex.

1. Azo Derivatives Possessing a Phenol Function

- ***Eriochrome black T*** (solochrome black). It is used in the pH range 7–11.



- Patton and Reeder's indicator

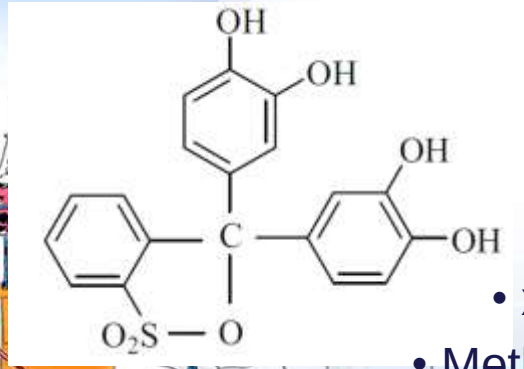
  It permits the titration of Ca^{2+} in the presence of Mg^{2+} in the pH range 12–14. In a direct titration, it turns pure blue at the endpoint. Before, the solution is wine red.

- eriochrome blue black or calcon (solochrome dark blue);
- calmagite;

2. Triphenylmethane Derivatives

- Catechol violet or pyrocatechol violet

  As a result, there is a sharp color change from blue-green to yellow at the endpoint of a direct titration with EDTA. It is used for titrations of bismuth and thorium.



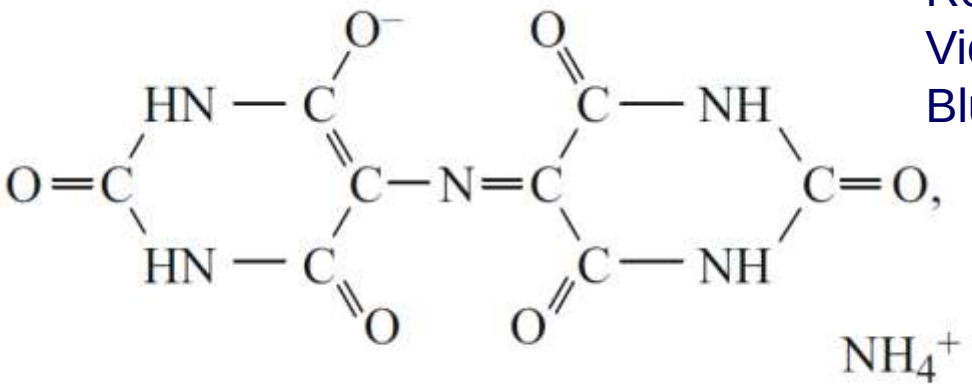
- xylenol orange;
- Methylthymol blue;

It can form complexes with metal cations even in acidic solution 3<*pH*<5.

Derivatives of Miscellaneous Structures

- ***Zincon*** A specific indicator of Zn^{2+}. At pH = 9−10, it gives a blue color.
- ***Murexide***, which is an indicator of a particular structure. It is the ammonium salt of purpuric acid:

Murexide forms complexes with numerous metal cations such as Cu^{2+}, Ni^{2+}, Co^{2+}, and Ca^{2+} and ions deriving from lanthanides. The complex's color depends on the pH and the nature of metallic ions. Murexide permits Ca^{2+} titration with EDTA at pH = 11. The color turns red from violet blue.

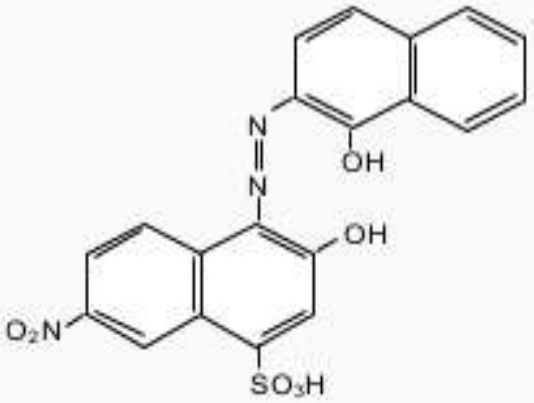


Red-violet pH < 9;
Violet pH = 9,2 - 10,3;
Blue-vilolet pH > 10,3

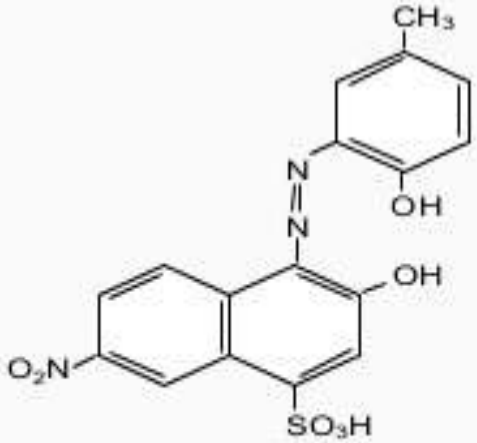
Murexide binds to metal ions to give a red color. Upon release of the metal to EDTA, it becomes violet

Solutions of free murexide are red-violet until pH = 9, violet in the range 9–11, and blue beyond. Murexide forms complexes with numerous metal cations such as Cu^{2+}, Ni^{2+}, Co^{2+}, and Ca^{2+} and ions deriving from lanthanides. The complex's color depends on the pH and the nature of metallic ions. Murexide permits Ca^{2+} titration with EDTA at pH = 11.

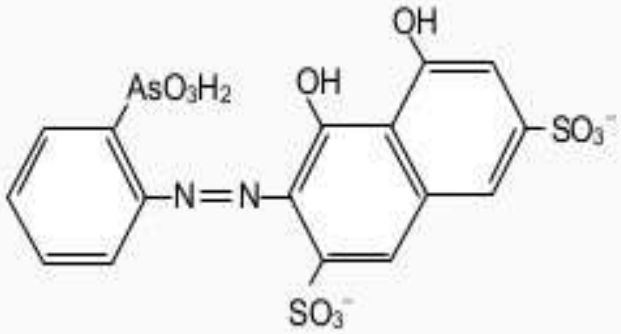
Common indicators for complexometric titrations



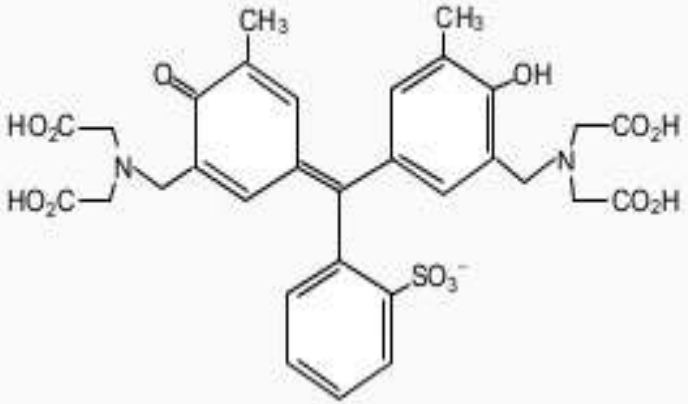
Eriochrome Black T



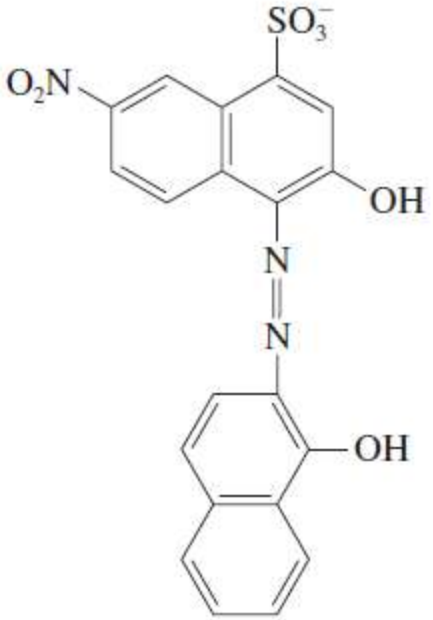
Calgamite

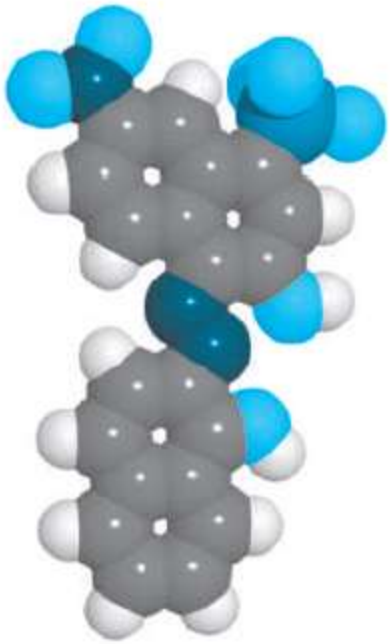


Arsenazo I



Xylenol Orange





Structure and molecular model of Eriochrome Black T. The compound contains a sulfonic acid group that completely dissociates in water and two phenolic groups that only partially dissociate.

The metal complexes of ***Eriochrome Black T*** are generally red, as is H_2In^-. Thus, for metal-ion detection, it is necessary to adjust the pH to 7 or above so that the blue form of the species, HIn^{2-}, predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is ***red***. With the first slight excess of EDTA, the solution turns ***blue*** as a result of the reaction:

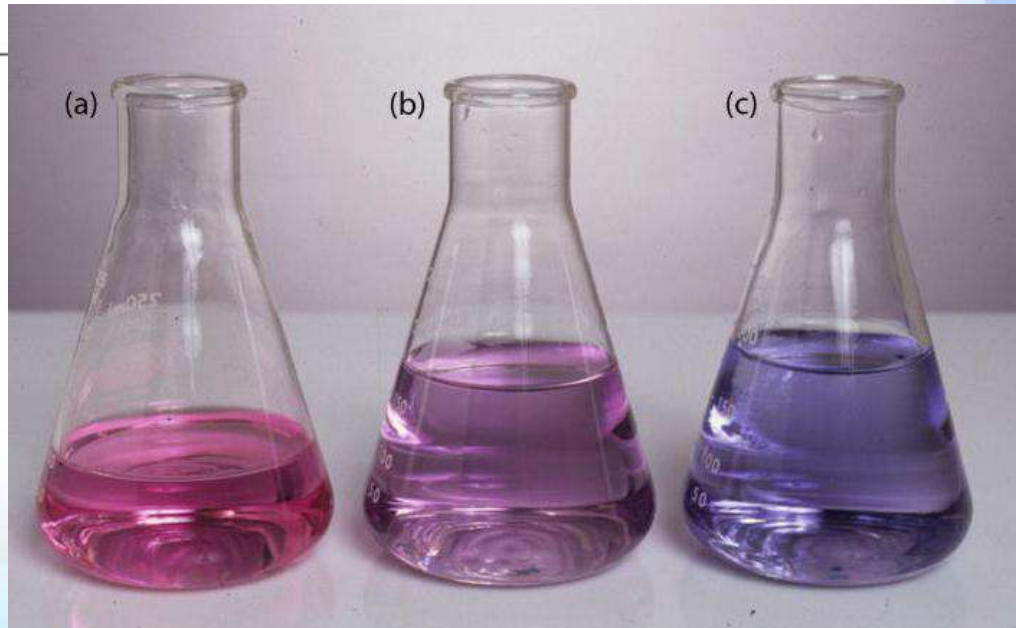
$$\underset{\text{red}}{MIn^-} + HY^{3-} \rightleftharpoons \underset{\text{blue}}{HIn^{2-}} + MY^{2-}$$

$$\underset{\text{(red)}}{MgIn^-} + \underset{\text{(colorless)}}{H_2Y^{2-}} \rightarrow \underset{\text{(colorless)}}{MgY^{2-}} + \underset{\text{(blue)}}{HIn^{2-}} + H^+$$

Eriochrome black T
Red pH < 6,3
Blue pH = 6,3 - 11,3
Yellow pH > 11,3.

A limitation of Eriochrome Black T is that its solutions decompose slowly with standing. Solutions of Calmagite**, an indicator that for all practical** purposes is identical in behavior to Eriochrome Black T.

Indicator	Colour of free indicator	Colour of metal-ion complex
Murexide		
< pH 9 (H_4In^-)	Red–violet	orange (Cu^{2+}), yellow (Ni^{2+} and Co^{2+}) and red (Ca^{2+})
pH 9–11 (H_3In^{2-})	Violet	
> pH 11 (H_2In^{3-})	Blue	
Solochrome black		
< pH 5 (H_2In^-)	Red	In pH range 7–11 colour change is blue–red (Mg, Mn, Zn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni and Pt metals)
pH 7–11 (HIn^{2-})	Blue	
> pH 11.5 (In^{3-})	Orange	
Calmagite		
<pH 5 (H_2In^-)	Red	Same colour change as solochrome black but clearer and sharper
pH 7–9 (HIn^{2-})	Blue	
>pH 11.4 (In^{3-})	Red–orange	
Pyrocatechol violet		
< pH 1.5 (H_4In)	Red	In pH range 2–6, yellow to blue (Bi and Th); pH 7 violet to blue (Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+})
pH 2–6 (H_3In^-)	Yellow	
pH 7 (H_2In^{2-})	Violet	
>pH 10 (In^{4-})	Blue	



II. Finding the End Point by Monitoring Absorbance.

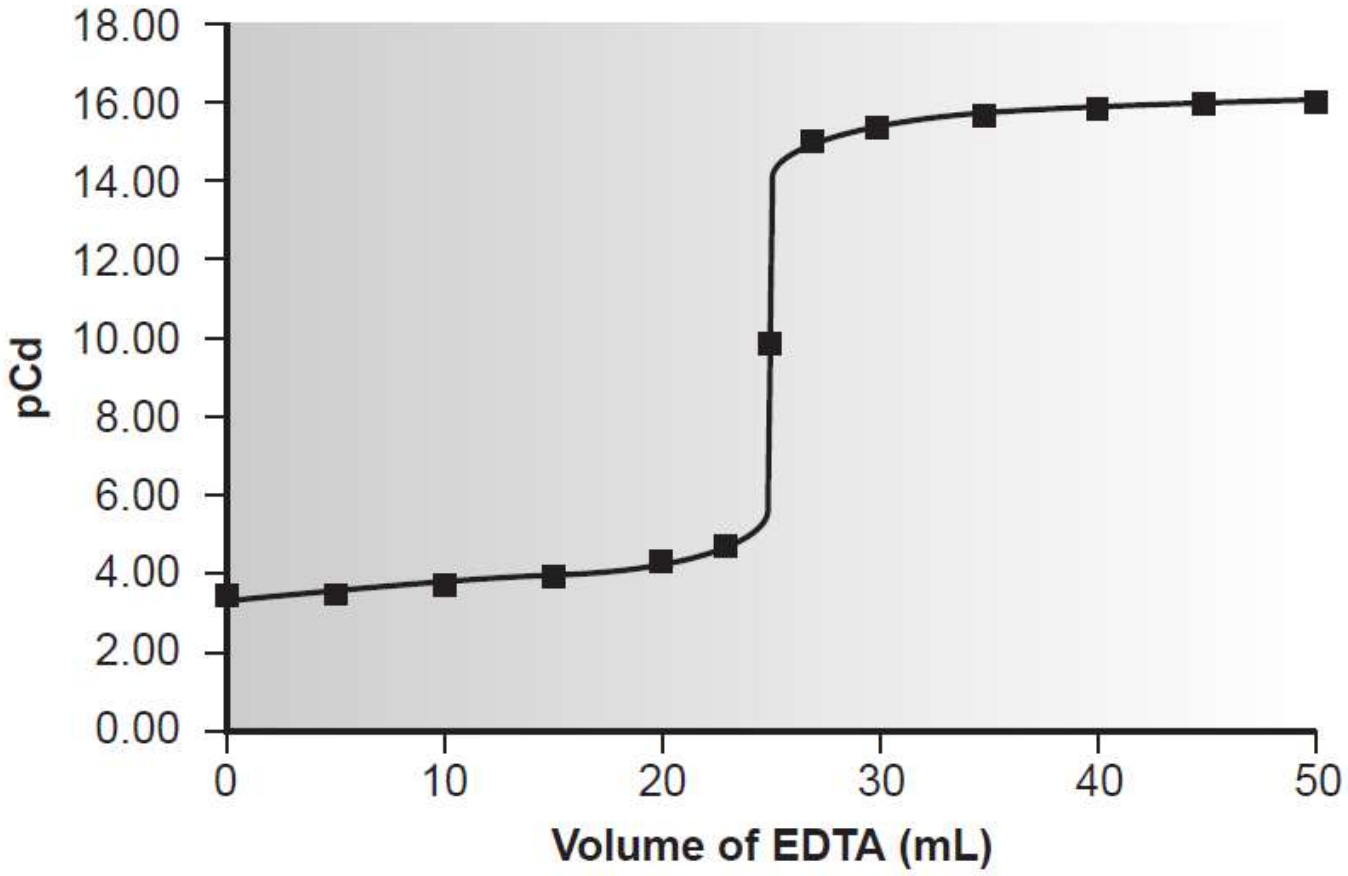
As long as at least one species in a complexation titration absorbs electromagnetic radiation, the equivalence point can be located by monitoring the absorbance of the analytical solution at a carefully selected wavelength. For example, the equivalence point for the titration of Cu^{2+} with EDTA, in the presence of NH_3, can be located by monitoring the absorbance at a wavelength of 745 nm, where the $Cu(NH_3)_4^{2+}$ complex absorbs strongly. At the beginning of the titration the absorbance is at a maximum. As EDTA is added, however, the reaction

$$Cu(NH_3)_4^{2+}(aq) + Y^{4-}(aq) \rightarrow CuY^{2-}(aq) + 4NH_3(aq)$$

occurs, decreasing both the concentration of $Cu(NH_3)_4^{2+}$ and the absorbance. The absorbance reaches a minimum at the equivalence point and remains essentially unchanged as EDTA is added in excess.

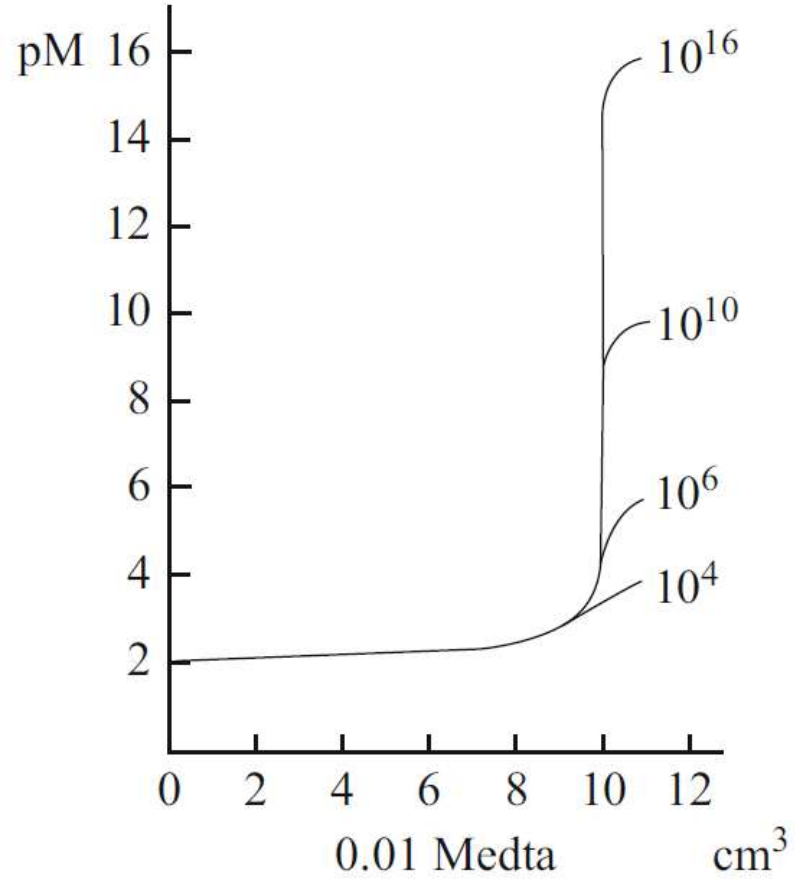
Typical examples of sensors include:
1) recording a potentiometric titration curve using an ion-selective electrode (analogous to measuring pH with a pH electrode),
2) monitoring the temperature of the titration mixture.

Metal–EDTA Titration Curves

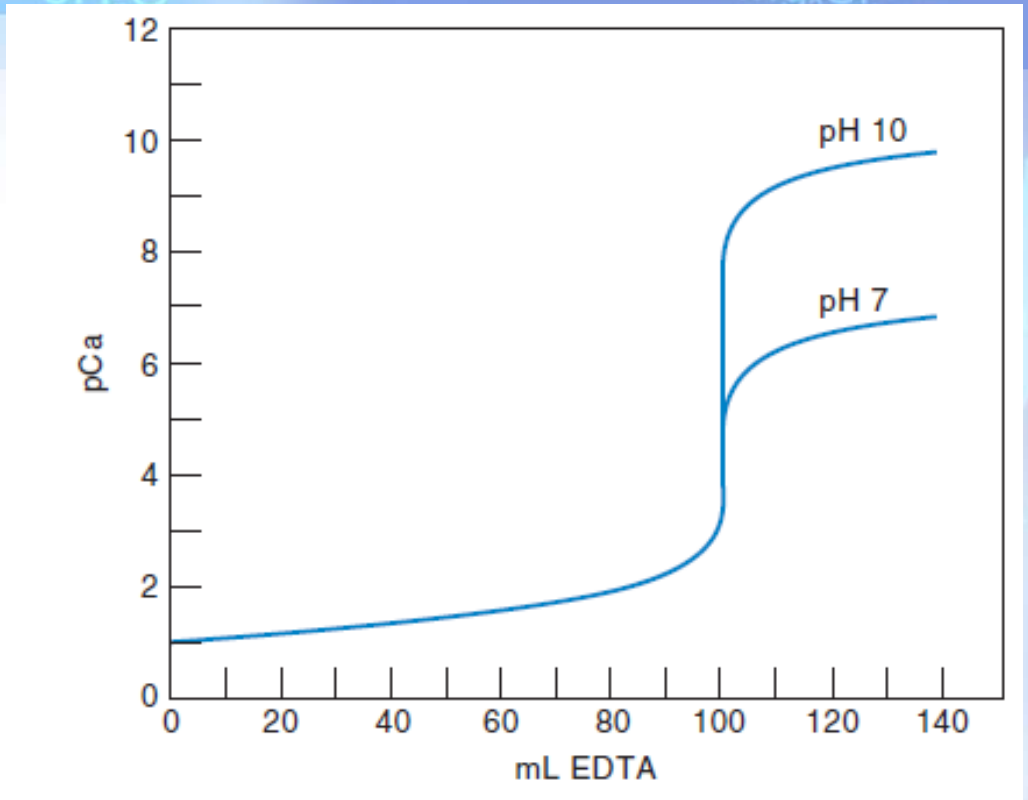


Complexometric titration curve for 50.0 mL of 5×10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10

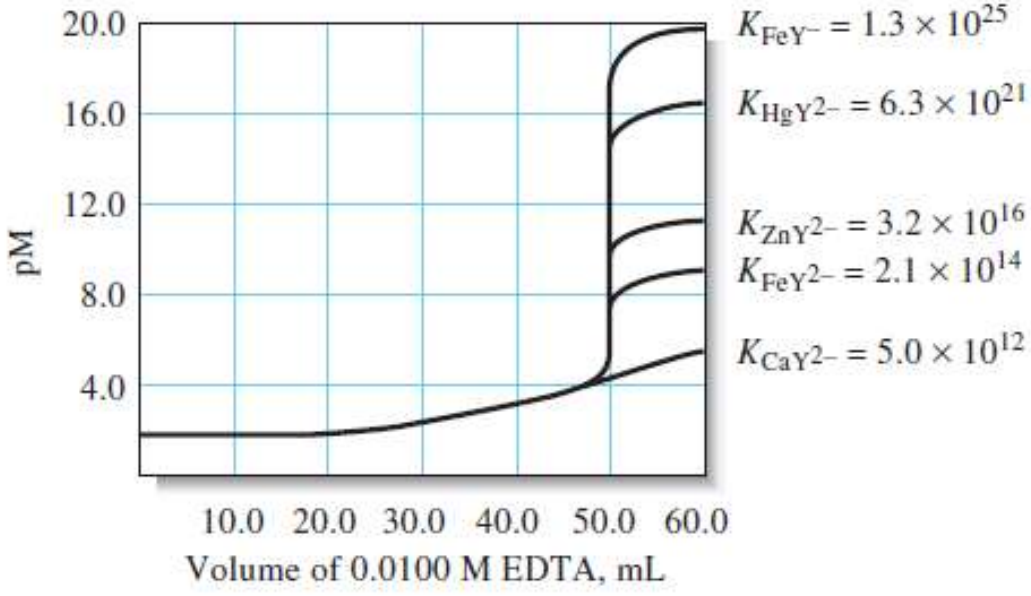
Before the equivalence point, the Cd^{2+} concentration is nearly equal to the amount of unchelated (unreacted) calcium since the dissociation of the chelate is slight (analogous to the amount of an unprecipitated ion). At the equivalence point and beyond, pCd is determined from the dissociation of the chelate at the given pH.



Shapes of the curves obtained during the titration of 10 ml of a 10^{-2} mol/L metal cation with 10^{-2} mol/L EDTA

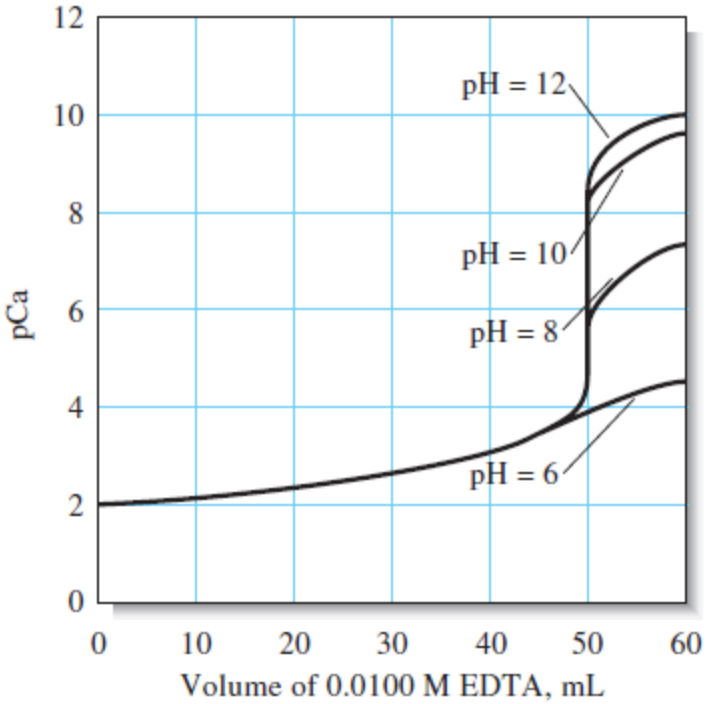


Titration curves for 100 mL 0.1 *M* Ca^{2+} *versus* *0.1 M* Na_2EDTA at pH 7 and pH 10.



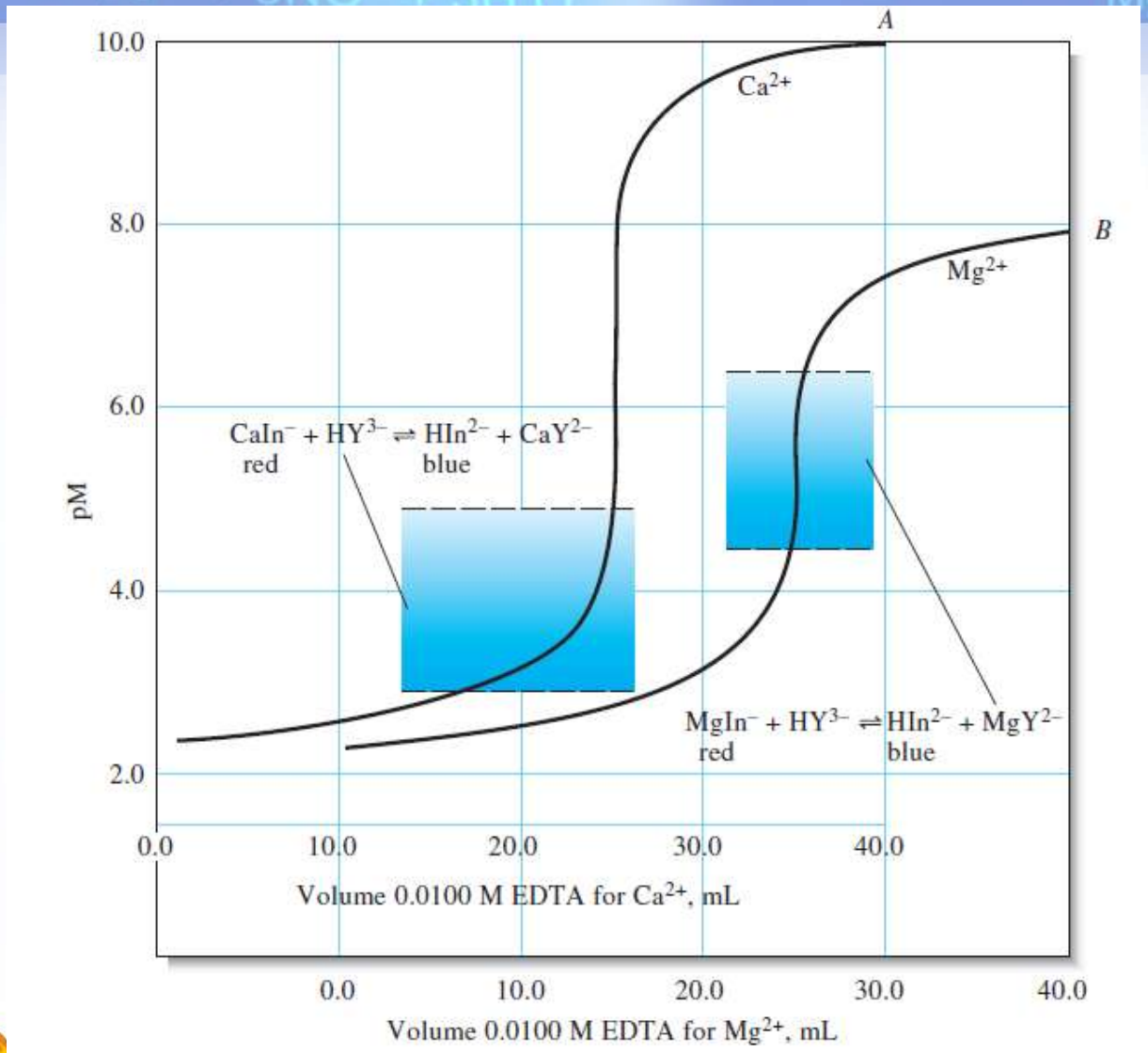
Titration curves for 50.0 mL of 0.0100 M solutions of various cations at pH 6.0.

Cations with ***larger formation constants provide sharp end points*** even in acidic media. If we assume that the conditional constant should be at least 10^6 to obtain a satisfactory end point with a 0.01 M solution of the metal ion, we can calculate the minimum pH needed.



Influence of pH on the titration of 0.0100 M Ca^{2+} with 0.0100 M EDTA. Note that ***the end point becomes less sharp as the pH decreases*** because the complex-formation reaction is less complete under these circumstances.

An adequate end point in the titration of calcium requires that the pH be greater than about 8.0.



EDTA titration curves for 50.0 mL of 0.00500 M Ca^{2+} ($K'_{CaY}=1.75\times10^{10}$) *and* Mg^{2+}($K'_{MgY}=1.72\times10^{8}$) *at pH 10.0.* Note that because of ***the larger formation constant, the reaction of calcium ion with EDTA is more complete, and a larger change occurs in the equivalence-point region***. The shaded areas show the transition range for the indicator Eriochrome Black T.

CONSTRUCTION A TITRATION CURVE

During a titration with EDTA, the metal ion (M) solution is in the flask and EDTA is added from the burette. At any point in the titration we can calculate the value of pM (= -log[Mn+]).

Let's consider the titration of 100 ml 0,05 M $CaCl_2$ solution with 0,05000 M EDTA.

- **Before the addition of EDTA**

$$c_0(Ca^{2+}) = c(CaCl_2) = 5 \cdot 10^{-2}\ M$$

$$pCa = -\lg c_0(Ca^{2+}) = -\lg(5 \cdot 10^{-2}) = 1.3$$

- **After the addition of 90.0 ml EDTA:**

Some of the Ca^{2+} will have reacted with the EDTA and we need to find the new $c(Ca^{2+})$:

$$c(Ca^{2+}) = \frac{c_0(CaCl_2) \cdot V(CaCl_2)_{left}}{V_{total}} = \frac{0{,}05 \cdot 10}{190} = 2{,}5 \cdot 10^{-3}\ M$$

$$pCa = -\lg c_0(Ca^{2+}) = -\lg(2{,}5 \cdot 10^{-3}) = 2.6$$

- **After the addition of 99.9 ml EDTA :**

$$c(Ca^{2+}) = \frac{c_0(CaCl_2) \cdot V(CaCl_2)_{left}}{V_{total}} = \frac{0{,}05 \cdot 0.1}{199.9} = 2{,}5 \cdot 10^{-5}\ M$$

$$pCa = -\lg c_0(Ca^{2+}) = -\lg(2{,}5 \cdot 10^{-5}) = 4.6$$

- **The equivalence point:**

How can we calculate the $c(Ca^{2+})$? All the Ca^{2+} has gone… We have to remember that the reaction is actually an equilibrium and some (very small amount) of the CaY^{2-} will dissociate to give some Ca^{2+} and we can find $c(Ca^{2+})$ by using:

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

$$\beta = \frac{c(CaY^{2-})}{c(Ca^{2+}) \cdot c(H_2Y^{2-})}$$

The only Ca^{2+} in the solution will have come from the dissociation of the CaY^{2-} and this will also be the only source of uncomplexed EDTA; therefore:

$$c(Ca^{2+}) = c(H_2Y^{2-})$$

$$c(Ca^{2+}) = \sqrt{\frac{c(CaY^{2-})}{\beta}} = \sqrt{\frac{0.025}{5 \cdot 10^{10}}} = 7 \cdot 10^{-7}\ M$$

$$\beta = \frac{c(CaY^{2-})}{c^2(Ca^{2+})}$$

$$pCa = -\lg c_0(Ca^{2+}) = -\lg(7 \cdot 10^{-7}) = 6.15$$

- **After the equivalence point:**

After the equivalence point, all the Ca^{2+} has been reacted and the only source of Ca^{2+} is again the dissociation of the CaY^{2-} complex. This time, however, we have excess EDTA in the solution, and we can determine c(EDTA) and $c(CaY^{2-})$ from the stoichiometric quantities.

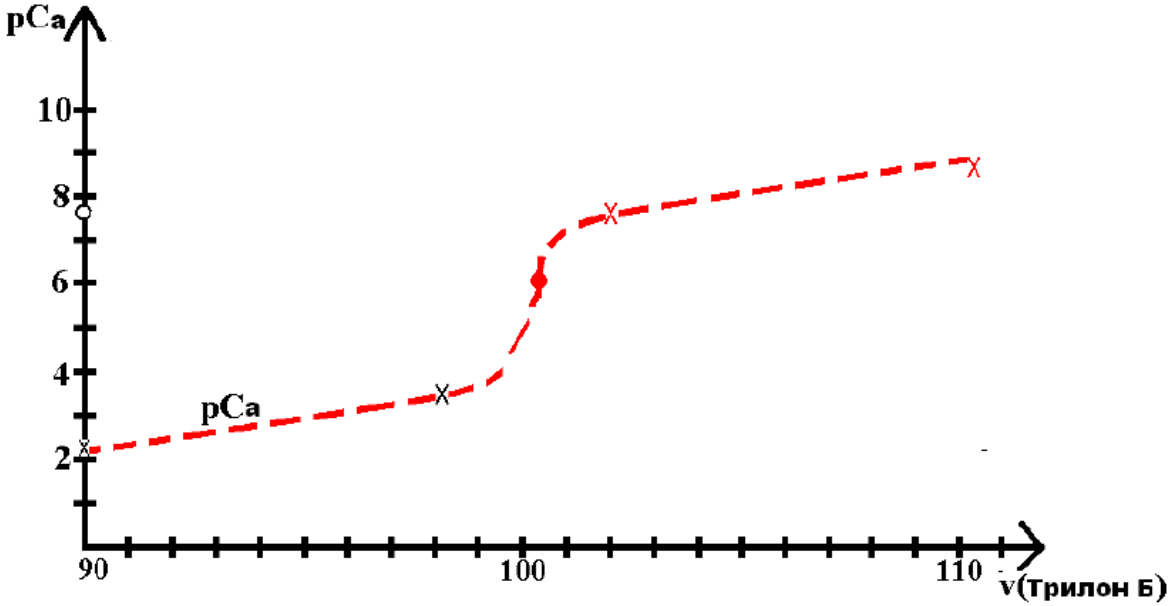
$$c(Ca^{2+}) \neq c(H_2Y^{2-})$$

- **After the addition of 100.1 ml EDTA :**

$$c(Ca^{2+}) = \frac{c(CaY^{2-})}{\beta \cdot c(H_2Y^{2-})} = \frac{0{,}025}{5 \cdot 10^{10} \cdot \frac{0{,}05 \cdot 0{,}1}{200{,}1}} = 2 \cdot 10^{-8}\ M$$

$$pCa = -\lg c_0(Ca^{2+}) = -\lg(2 \cdot 10^{-8}) = 7.7$$

№	$V(EDTA)$	pCa
1	0	1.3
2	90	2.6
3	99	3.6
4	99,9	4.6
5	100	6.15
6	100,1	7.4
7	101	8.4
8	110	9.4



Types of EDTA Titrations

- ***Direct Titrations***

  The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to pH = 10 with bufer,) and titrated directly with the standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal (or a basic salt) by the addition of some auxiliary complexing agent, such as tartrate or citrate or triethanolamine.

  At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in colour of a metal indicator or by amperometric, spectrophotometric, or potentiometric methods.

- ***Back Titrations***

  Many metals cannot, for various reasons, be titrated directly; thus they may precipitate from the solution in the pH range necessary for the titration, or they may form inert complexes, or a suitable metal indicator is not available. 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; a solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions introduced in the back-titration.

This procedure deserves further comments. First, the metal ion indicator must respond to the titrant ion, usually Zn^{2+} or Mg^{2+}. Second, the color change occurring at the endpoint is the inverse of that obtained in a direct titration. Before the endpoint of the back-titration reaction, the indicator is free; after it is complexed with the metallic ion (Zn^{2+} or Mg^{2+}), it is in excess.

- ***Replacement or Substitution Titrations***

Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. The metal cation Me^{n+} to be determined may be treated with the magnesium complex of EDTA, when the following reaction occurs:

$$Mn^{+2} + Mg\,EDTA^{-2} \longrightarrow Mg^{+2} + Mn\,EDTA^{-2}$$

Mn displaces Mg from Mn EDTA solution. The freed Mg metal is then directly titrated with a standard EDTA solution. In this method, excess quantity of Mg EDTA chelate is added to Mn solution. Mn quantitatively displaces Mg from Mg EDTA chelate. This displacement takes place because Mn forms a more stable complex with EDTA. By this method Ca, Pb, Hg may be determined using Eriochrome blackT indicator.

Fluoride may be determined by precipitation as lead chlorofluoride, the precipitate being dissolved in dilute nitric acid and, after adjusting the pH to 5-6, the lead is titrated with EDTA using xylenol orange indicator.

Sulphate may be determined by precipitation as barium sulphate or as lead sulphate. The precipitate is dissolved in an excess of standard EDTA solution, and the excess of EDTA is back-titrated with a standard magnesium or zinc solution using solochrome black as indicator.

Quantitative Applications

Inorganic Analysis Complexation titrimetry continues to be listed as a standard method for the determination of hardness, Ca^{2+}, CN^{-}, and Cl^{-} in water and wastewater analysis.

The determination of Ca^{2+} is complicated by the presence of Mg^{2+}, which also reacts with EDTA. To prevent an interference from Mg^{2+}, the pH is adjusted to 12–13, precipitating any Mg^{2+} as $Mg(OH)_2$. Titrating with EDTA using murexide or Eriochrome Blue Black T as a visual indicator gives the concentration of Ca^{2+}. Cyanide is determined at concentrations greater than 1 ppm by making the sample alkaline with NaOH and titrating with a standard solution of $AgNO_3$, forming the soluble $Ag(CN)_2^{-}$ complex. The end point is determined using *p-dimethylaminobenzolrhodamine as a visual indicator, with the solution turning* from yellow to a salmon color in the presence of excess Ag^{+}. Chloride is determined by titrating with $Hg(NO_3)_2$, forming soluble $HgCl_2$. The sample is acidified to within the pH range of 2.3–3.8 where diphenylcarbazone, which forms a colored complex with excess Hg^{2+}, serves as the visual indicator. Xylene cyanol FF is added as a pH indicator to ensure that the pH is within the desired range. The initial solution is a greenish blue, and the titration is carried out to a purple end point.

Titration Selectivity, Masking and Demasking Agents

EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations.

The following procedures will help to increase the selectivity:

- Use of masking and demasking agents
- pH control.
- Use of selective metal indicators.
- Classical separation
- Solvent extraction
- Removal of anions
- Kinetic masking

• It is 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. A small amount of iron may be masked by cyanide if it is first reduced to the iron(II) state by the addition of ascorbic acid. mercury with iodide ions; and aluminium, iron(III), titanium(IV), and tin(II) with ammonium fluoride (the cations of the alkaline-earth metals yield slightly soluble fluorides).

• Suitable control of the pH of the solution.

This, of course, makes use of the different stabilities of metal-EDTA complexes. Thus bismuth and thorium can be titrated in an acidic solution (pH = 2) with xylenol orange or methylthymol blue as indicator

and most divalent cations do not interfere. A mixture of bismuth and lead ions can be successfully titrated by first titrating the bismuth at pH 2 with xylenol orange as indicator, and then adding hexamine to raise the pH to about 5, and titrating the lead.