ANALYTICAL CHEMISTRY

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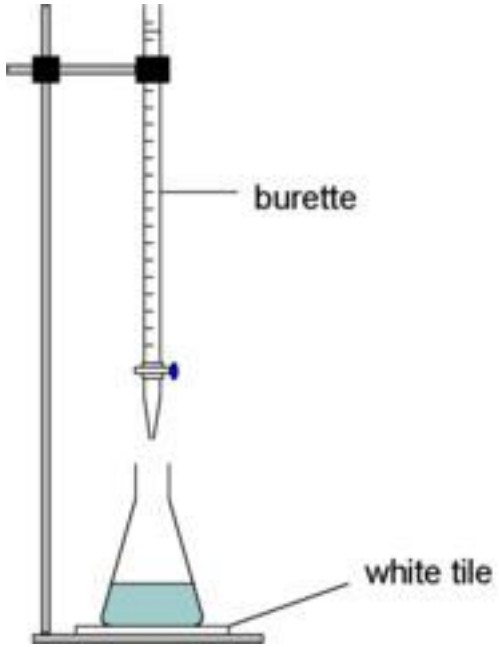
Volumetric analysis



Volumetric or titrimetric analysis

- measurement of volume of a solution of known concentration which is used to determine the concentration of the analyte

- **standard solution** is a solution of accurately known concentration prepared from a primary standard

- **Titration** is the process carried out to determine the conc. of analyte solution by adding standard solution in small quantities to measured volume of analyte solution

Volumetric or titrimetric analysis

- **equivalence point** is the point in a titration where the reacting solutions are used up in their exact stoichiometric proportions

- theoretical point

- Cannot be determined exactly experimentally

Volumetric or titrimetric analysis

- **Indicator** – substance used to indicate the completion of reaction
- **End point** – point of completion of reaction determined using indicator
- **Titer value** – volume of one of the reagents required to react completely with the known volume of other

Volumetric or titrimetric analysis

- Standard solution –accurately known comc.

- Ideal standard
  - Conc. Does not change with time
  - Quick to react – minimum time between additions
  - Selective reaction with analyte
  - Completely reacts
  - Simple balanced equation

Primary standard

- Compound of sufficient purity from which std. solution can be made by direct weighting followed by dilution

- Characteristics
  - Easy to obtain, purify, dry & preserve
  - Not hygroscopic or deliquescent
  - Composition unaltered on storage
  - High mol. Mass
  - Readily soluble in water or titration medium

- Anhy. Sodium carbonate(Na_2CO_3), Pot. Dichromate ($K_2Cr_2O_7$), Mohr's salt ($FeSO_4.(NH_4)2SO_4.6H_2O$, crystalline oxalic acid ($H_2C_2O_4.2H_2O$)

Secondary standard

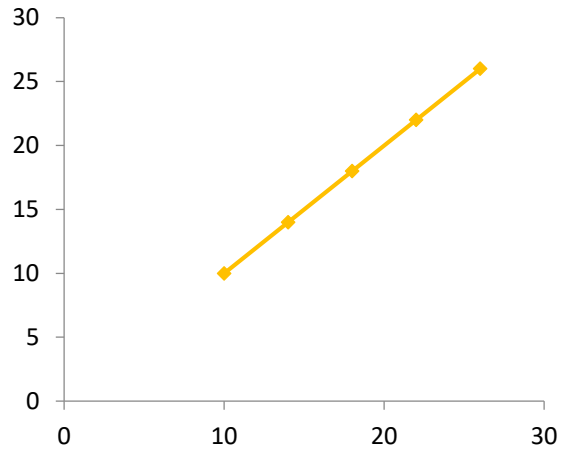
- Substance from which std, solution cannot be prepared directly but whose solution can be determined accurately using a standard solution

- Process – standardization

- NaOH, H_2SO_4, HCl, HNO_3, $KMNO_4$ etc

Double burette method

- excludes any mouth pipetting
- both titer and titrant are taken in two burettes
- Saves chemicals
- Minimizes use of indicator
- Reduces time
- Improves accuracy



Acid base or neutralization titration

- **Acidimetry** – titration of free base or those formed from salts of weak acid by hydrolysis against std. acid solution

- **Alkalimetry -** titration of free acid or those formed from salts of weak base by hydrolysis against std. base solution

- $NaOH + HCl \longrightarrow NaCl + H_2O$

End point Detection

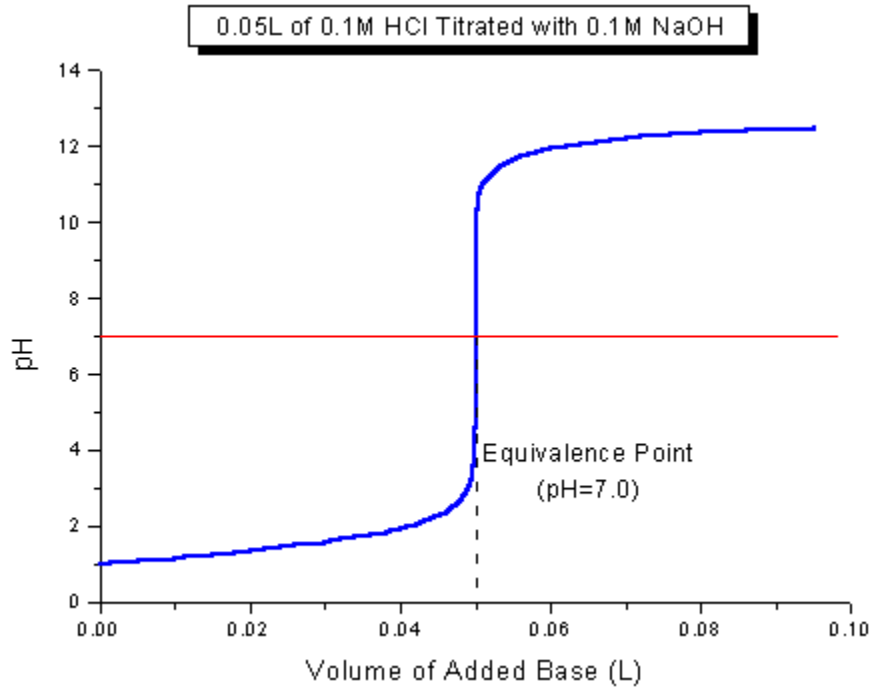
- Conductometry
- Potentiometry
- Acid base indicators

Acid Base indicator

- Substance employed for visual detection of end point in acid base titration as they change colour with pH change that occurs in the vicinity of end point

Indicator	pH Range	Acid	Base
Thymol Blue	1.2-2.8	red	yellow
2,4-Dinitrophenol	2.4-4.0	colorless	yellow
Methyl yellow	2.9-4.0	red	yellow
Methyl orange	3.1-4.4	red	orange
Bromphenol blue	3.0-4.6	yellow	blue-violet
Methyl red	4.4-6.2	red	yellow
***p*-Nitrophenol**	5.0-7.0	colorless	yellow
Phenol red	6.4-8.0	yellow	red
Thymol blue	8.0-9.6	yellow	blue
Phenolphthalein	8.0-10.0	colorless	red
Alizarin yellow	10.0-12.0	yellow	lilac
Salicyl yellow	10.0-12.0	yellow	orange-brown
Trinitrobenzoic acid	12.0-13.4	colorless	orange-red

Strong acid strong base

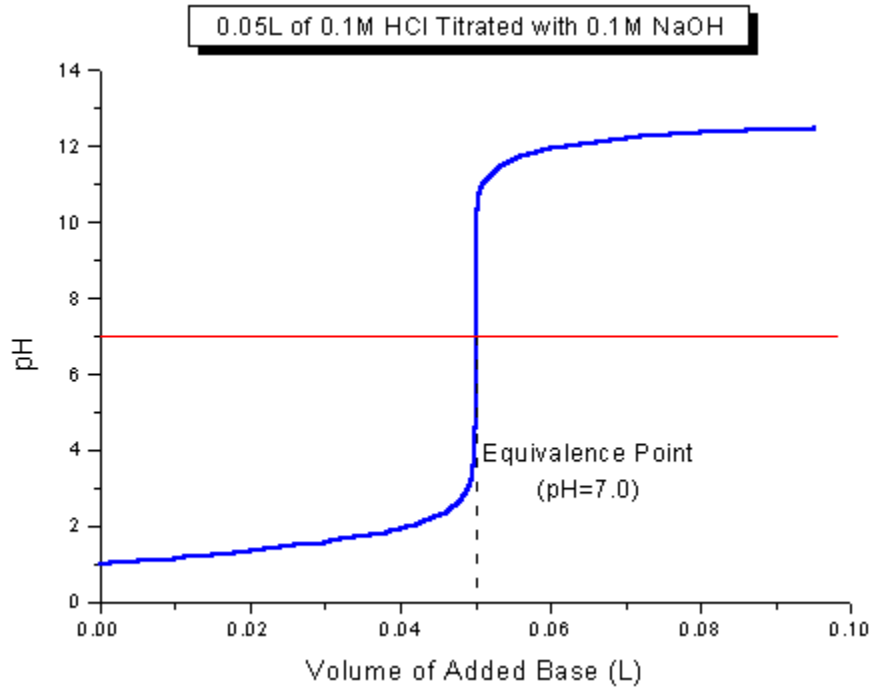


pH change	4 - 10

Methyl red	4.2-6.3
phenolphtalein	8-9.5
Methyl orange	3.1-4.4

Sigmoid curve

Strong acid strong base

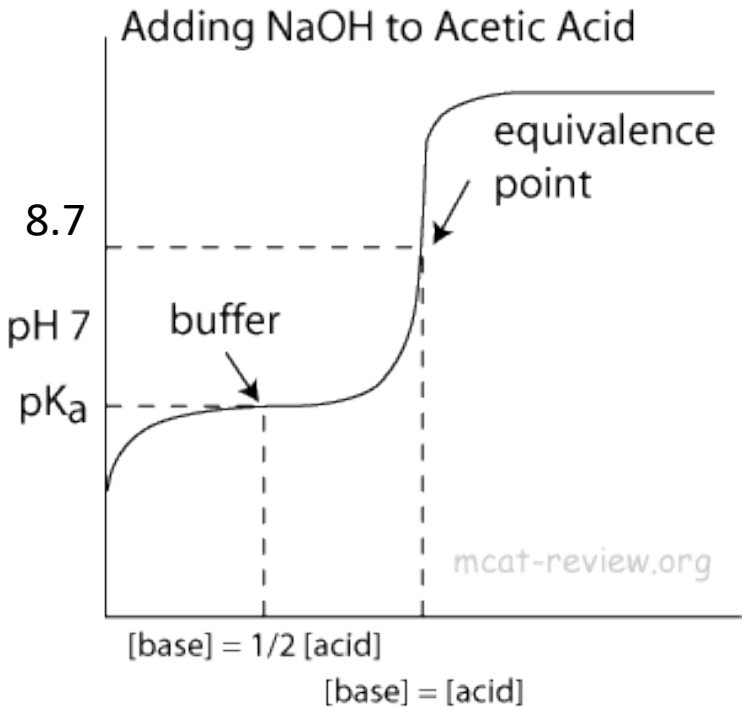


pH change	4 - 10

Methyl red	4.2-6.3
phenolphtalein	8-9.5
Methyl orange	3.1-4.4

Sigmoid curve

Weak acid strong base



pH change	6.5-10

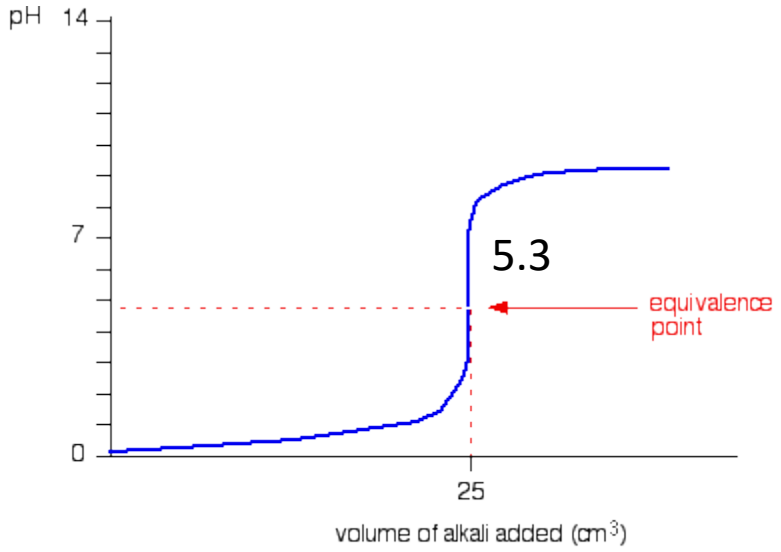
phenolphtalein	8-9.5

Do not choose

Methyl red	4.2-6.3
Methyl orange	3.1-4.4

Sigmoid curve

Strong acid Weak base



pH change	3 - 7

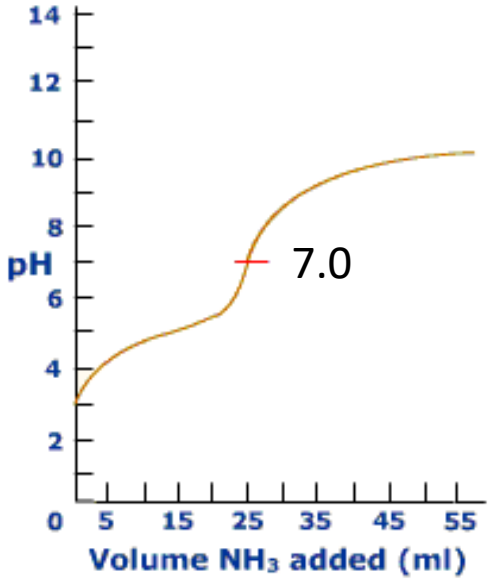
Methyl red	4.2-6.3
Methyl orange	3.1-4.4

Do not choose

phenolphtalein	8-9.5

Sigmoid curve

Weak acid Weak base



Titration curve of weak base (NH_4OH) and weak acid (CH_3COOH)

pH change	Gradual -

No sharp end point with simple I indicator

Conductometric method	prefered

Sigmoid curve

Ostwald theory

Indicator is a weak organic acid or a weak organic base whose unionized molecule has one colour and ions produced by ionization another colour

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

Acid colour — Base colour

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

$$In + H_2O \rightleftharpoons InH^+ + OH^-$$

Base colour — Acid colour

$$K_{In} = \frac{[OH^-][InH^+]}{[HIn]}$$

Ostwald theory - phenolphthalein

- Action of phenolphthalein

$$HPh + H_2O \leftrightarrow H_3O^+ + Ph^-$$

Colourless Pink

Common ion effect

Acidic solution - unionised - colourless

Basic solution - ionised - pink colour

Ostwald theory - methyl orange

- $MeOH \rightleftharpoons Me^{+} + OH^{-}$

Yellow red

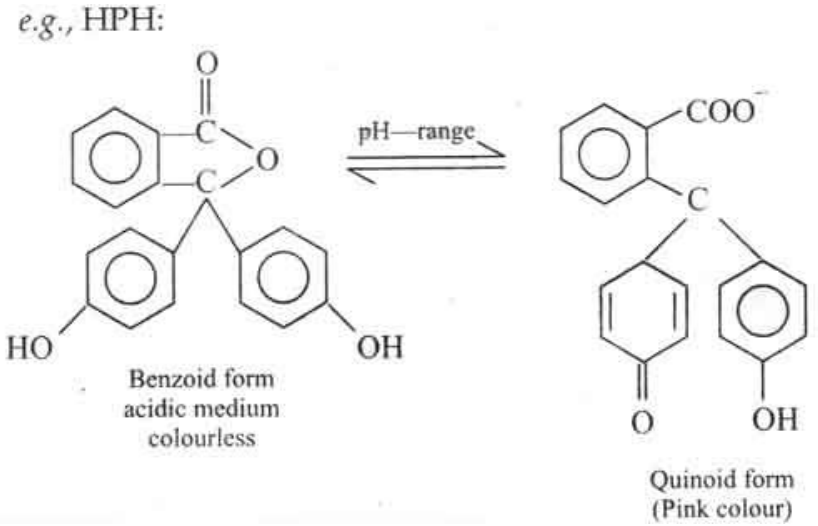
Alkaline solution – unionized – yellow

Acidic solution – ionised - red

Quinonoid theory

- Acid base indicator is a equilibrium mixture of two tautomeric form
- light coloured benzenoid form
- Dark coloured Quinonoid form

Phenolphthalein



Redox indicator

- Reactions involving oxidation & reduction
- Permanganometry – $KMNO_4$
- Dichrometry – $K_2Cr_2O_7$
- Cerimetry - $Ce(SO_4)_2$

Permanganometry

- Titration of $KMNO_4$ as oxidant against reductant

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O \qquad E^o = +1.52\ V$

$2\ KMnO_4 + 5\ (COOH)_2 + 3\ H_2SO_4 \longrightarrow 2\ MnSO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 \longrightarrow 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$

To maintain acidity **only dil H_2SO_4**

- **Conc. H_2SO_4 & HNO_3** (both conc. & dilute)– can not be used -oxidizing agent
- **HCl** – KMNO4 oxidizes Cl^- to Cl_2 - positive error - permanganate is consumed
- KMNO4 – secondary standard – traces of MnO2
- standardized using Oxalic acid or Mohrs salt $\{(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O\}$
- Self indicator – 0.01mL of 0.02 M of KMnO4 – pale pink colour

Dichrometry

Titration of K2Cr2O7 as oxidant against reductant

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$

$K_2Cr_2O_7 + 6FeSO_4 + 7\ H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O$

External indicator – **potassium ferricyanide**

- Ferrous ion give blue colour to ferricyanid
- Blue colour due to formation of Prussiun blue KFe[Fe(CN)6]
- no blue colour at end point – Fe^{2+} ion absent – completely converted to Fe^{3+}

Internal indicator – n- phenylanthranilic acid, diphenylamin

Redox indicator

Marks the end point of a redox titration by undergoing a colour change in response to sudden change in potential in the vicinity of equivalence point

$$E = E^{o} + \frac{2.303RT}{nF} \log \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$ (nernst equation)

Colour A $In_{ox} + ne^{-} \rightleftharpoons In_{red}$ **colour B**

$$E_{In} = E_{In}^{o} - \frac{0.059}{n} \log \frac{[In_{red}]}{[In_{ox}]}$$

Conditions

Change from one coloured form to another rapid & reversible

Should not undergo any side reactions

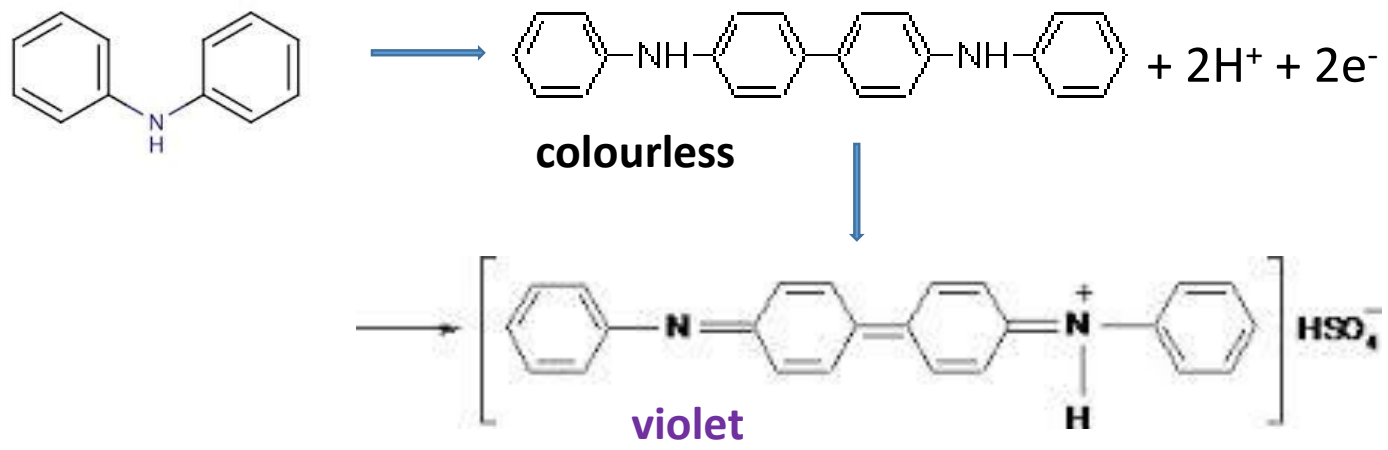
Should not begin to change colour until substrate reacted & colour change complete before appreciable excess of titrant appears

For a perceptible colour change

$$\frac{[In_{red}]}{[In_{ox}]} = 1/10$$

$$E_{In} = E_{In}^{o} \pm \frac{0.059}{n} \quad [A \text{ to } B] \qquad \Delta E = \pm 2x\ 0.059/n = \pm 0.118/n \text{ Volt}$$

- Diphenylamine, N-phenylanthranilic acid



Low solubility in water: Tungstate & Mercuric ion interfere with action

sodium salt of diphenyl amine sulphonic acid used instead

Iodometry & Iodimetry

- Oxidising agent iodine - Iodimetry – standard solution of iodine

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

$$I_2 + I^- \rightarrow I^{3-} \quad (I_2 \text{ dissolved in KI solution})$$

$$I_3^- + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 3\ I^-$$

- Indicator -starch – added at end of titration

- Starch reacts with iodine in the presence of iodide to form a blue colour complex visible at low conc.

Iodimetry

- Iodine liberated from a chemical reaction

$$2KMnO_4 + 10KI + 8H_2SO_4 \longrightarrow 2Mn(SO_4) + 6K_2SO_4 + I2 + 8H_2O$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 3I_2 + 7H_2O$$

$$I2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S4O_6$$

$$CuSO_4 + 2KI \longrightarrow K_2SO_4 + CuI_2$$

$$2\ CuI_2 \longrightarrow Cu_2I_2 + I_2$$

Precipitation titeration

- Reaction accompanied by ppt formation
- **Argentometry**

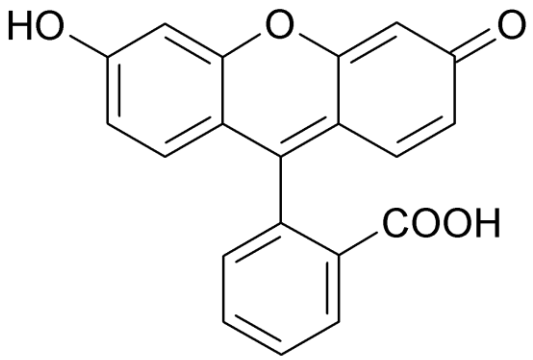
$AgNO_3$ + **NaCl** → AgCl↓ + $NaNO_3$

Indicator -potassium chromate (K2CrO4)

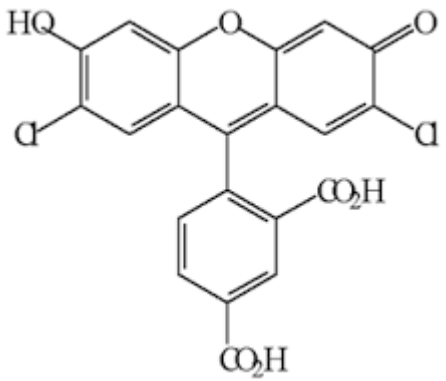
Yellow colour to chloride solution

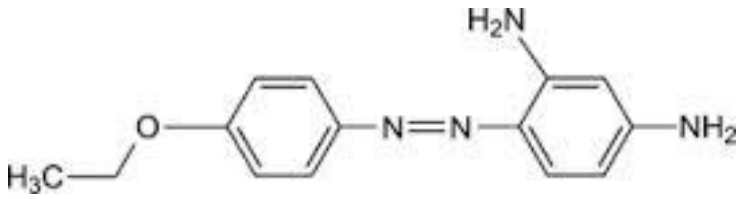
Reacts with silver ion to form **brick red** Ag_2CrO_4

Fluorescein



Dichlorofluorescein





P-Ethoxychrysodin

Mode of action of fluorescein

- $HFl + H_2O \longrightarrow H_3O^+ \ Fl^-$

Before end point – excess of Cl^- ion

$(AgCl).Cl \ | \ Ag^+$

.

Primary layer Sec Layer

After End Point – excess Ag+ ions

$(AgCl).Ag^+ \ | \ Cl^-$

. Primary layer Sec Layer

.

$(AgCl).Ag+ \ | \ Fl^-$

Primary layer Sec Layer

Adsorbtion indicator

- Anionic indicator
    - Fluorescein
    - Dichlorofluorescein
    - Eosin

- Cationic Indicator
    - Methyl violet
    - Rhopdamine 6G
    - P- Ethoxychrysodin

Choise of proper indicator

- Adsorbability of ion being titrated higher than that of indicator ion

- AgCl adsorb Cl^- than Fl^-

Complexometric titration

Metal Chelate Complexes

- **Complexometric Titrations are based on the reaction of a metal ion with a chemical agent to form a metal-ligand complex**
- ***Chelating agent – multidentate ligand which combines with a metal to form a cyclic complex - chelate***

Metal Ligand Metal-Ligand Complex

Complexometric titration

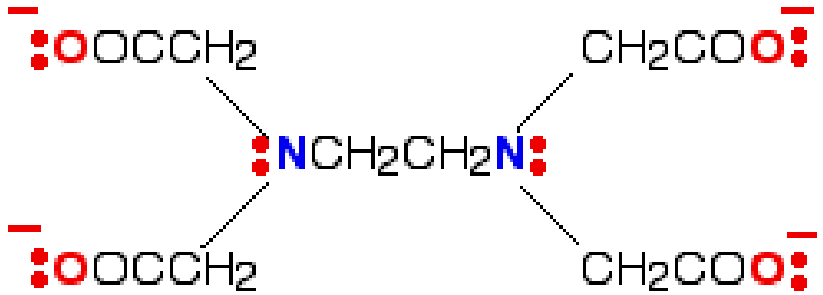
Chelating agents used as titrant

- React **completely** with metal ion
- Form **1:1 complex** with metal ion in a **single step**
- Sharp end point

Complexometric titration

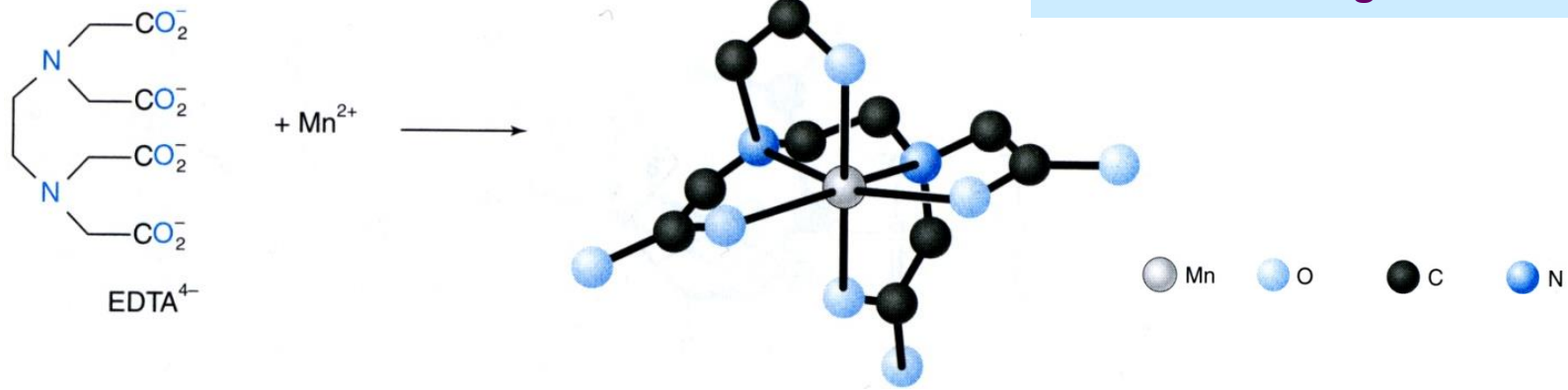
EDTA (Ethylenediaminetetraacetic acid)

- most common chelating agents used
- Tetraprotic acid – H4Y
- hexadentate – *6* free electron pairs it can donate to metal ions



the $EDTA^{4-}$ ion

Complexometric titration



Note: multiple atoms from EDTA are binding Mn^{2+}

$H_4Y + H_2O \rightarrow H_3Y^- + H_3O^+$

$H_3Y^- + H_2O \rightarrow H_2Y^{2-} + H_3O^+$

$H_2Y^{2-} + H_2O \rightarrow HY^{3-} + H_3O^+$

$HY^{3-} + H_2O \rightarrow Y^{4-} + H_3O^+$

pH >10 fully deprotonated

EDTA titrations

- The basic form of EDTA (Y^{4-}) reacts with most metal ions to form a 1:1 complex.

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$$

$$Mg^{2+} + EDTA \rightleftharpoons Mg(EDTA)^{-2}$$

For a +1 cation: $Ag^{+} + Y^{4-} \rightarrow Ag\,Y^{3-}$

For a +2 cation: $Hg^{2+} + Y^{4-} \rightarrow Hg\,Y^{2-}$

For a +3 cation: $Fe^{3+} + Y^{4-} \rightarrow Fe\,Y^{-}$

For a + n ion: $M^{n+} + Y^{4-} \rightarrow MY^{(n-4)+}$

Complexometric indicator

- Metal ion sensitive
- Responsive to pM i.e – $\log[M^{n+}]$
- Exhibits different colour in presence – absence of metalion

Indicator - Essential characteristic

- Resonance system typical of dyes
- characteristic colour at pH range of titration
- Forms differently coloured chelate with metal ion
- Binds to metal ion less strongly than titrant chelating agent
- Sudden & observable colour change in going from complexed to uncomplexed form
- Sensitive to pM ; colour change near equivalence point

Indicator - action

$$M + In \rightleftharpoons M\text{-}In$$ (metal indicator complex)

On add. of EDTA

$$M + In \rightleftharpoons M\text{-}In$$ (metal indicator complex)

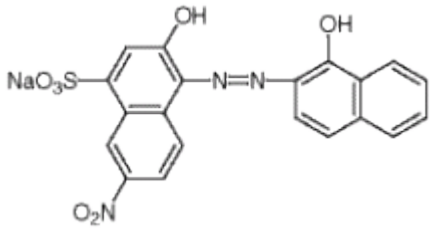
$$M + EDTA \rightleftharpoons M\text{-}EDTA$$ (metal EDTA complex)

After complexing with all free ion

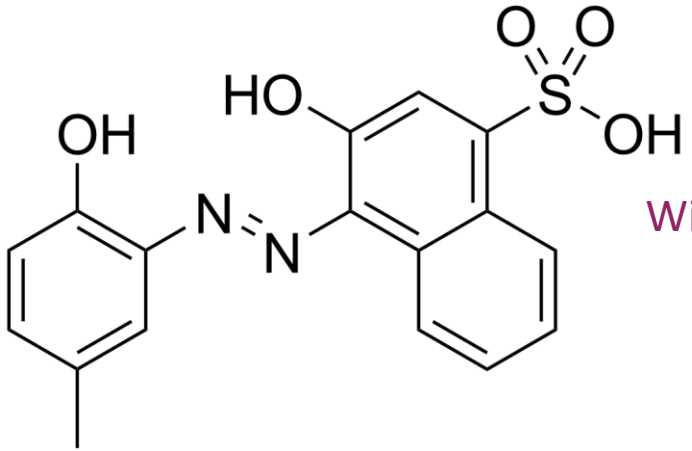
$$M\text{-}In + EDTA \rightleftharpoons M\text{-}EDTA + In$$

Erichrome Black T - wine red to blue

Complexometric titration

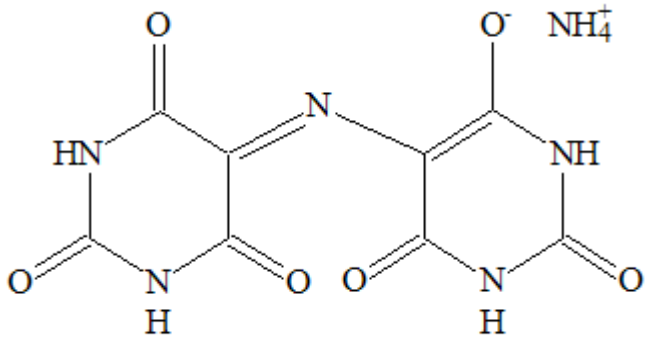


Erichrome Black T
Wine red to blue



Calmagite

Wine red to blue



Murexide
Violet to blue

Reference

- **Analytical chemistry - Skoog West Holler**
- **Principals of inorganic chemistry – Puri Sharma & Kaliya**


Thank
you