Field Project

INDICATORS

First year, Department of Chemistry

By

23521100001	ADITYA A J
23521100002	AJNA SAKEENSHA
23521100003	AMRITHA M K
23521100004	ANJALI SUNNY
23521100005	ANJALI SURESH S
23521100006	ANJITHA A S
23521100007	APARNA HARI G
23521100008	ARCHA P R
23521100009	ARYA R S
23521100010	ASHMITHA D G

ALL SAINTS' COLLEGE

UNIVERSITY OF KERALA, THIRUVANANTHAPURAM

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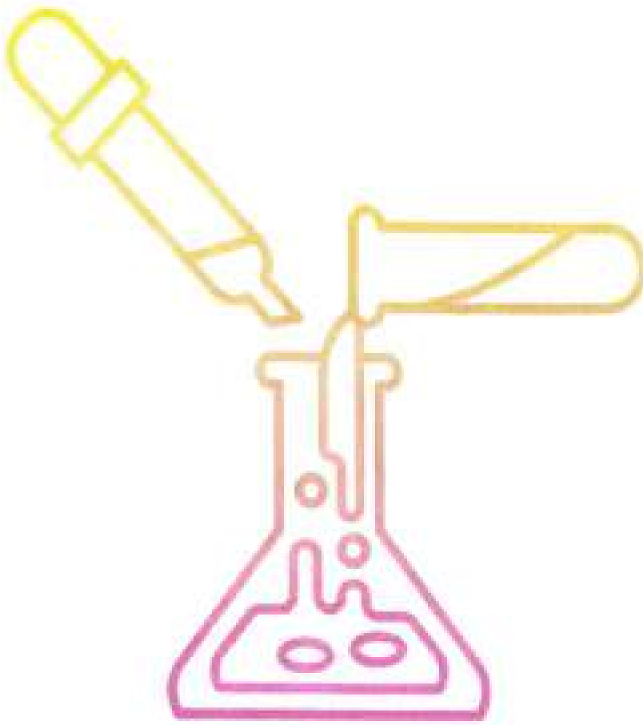
Teacher in charge

DEPARTMENT OF CHEMISTRY THIRUVANANTHAPURAM ALL SAINTS' COLLEGE

Head of the Department



INDICATORS

CERTIFICATE

This is to certify that this project report titled " INDICATORS " Submitted by Aditya A J, Ajna Sakeensha, Amritha MK, Anjali Sunny, Anjali Suresh S, Anjitha AS, Aparna Hari G, Archa PR, Arya RS and Ashmitha DG is a bonafide record of the project work carried out by them under my supervision and guidance.

Thiruvananthapuram

30.03.2022

Sunita K

Dr. Sunita Kurur
Supervising Teacher
Head of Department
Department of Chemistry
All Saints' College
Thiruvananthapuram

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Last but not the least, we owe our sincere grattitude to our friends, family and well wishers for their moral support.

Aditya. A J Ajna Sakeensha Amritha. MK Anjali Sunny
Anjali Suresh S Anjitha AS Aparna Hari G Archa PR
Ashmitha DG

CONTENTS

OBJECTIVE –

To Study The Characteristics Of Different Types Of Indicators

THEORY

* Chemical indicator, any substance that give a visible sign, usually by a colour change, of the presence or absence of a thershold concentration of a chemical species, such as an acid or an alkali in a solution.

* The colour of an indicator alters when the acidity or the oxidising strength of the solution, or the concentration of the certain chemical species, reaches a critical range of values.

* Indicators are therefore classified as acid-base, oxidation-reduction, or specific-substance indicators, every indicator in each class having a characteristic transition range.

TYPES OF INDICATOR

1) Natural Indicators

A natural indicator is a natural substance that can be used to determine the pH of another substance
For example: turmeric, beetroot, onion, red cabbage etc.

2) Synthetic Indicators

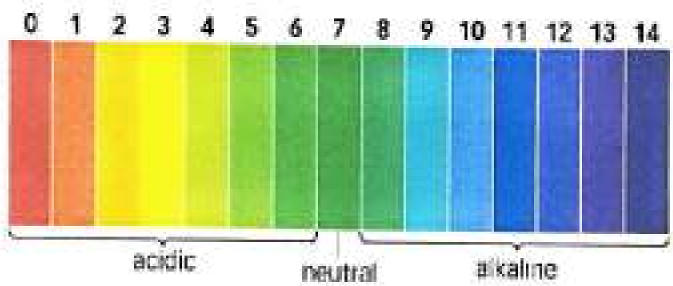
A synthetic indicator is a man made chemical substance used to determine pH.
For example: phenolphalein, methyl orange, litmus, etc.

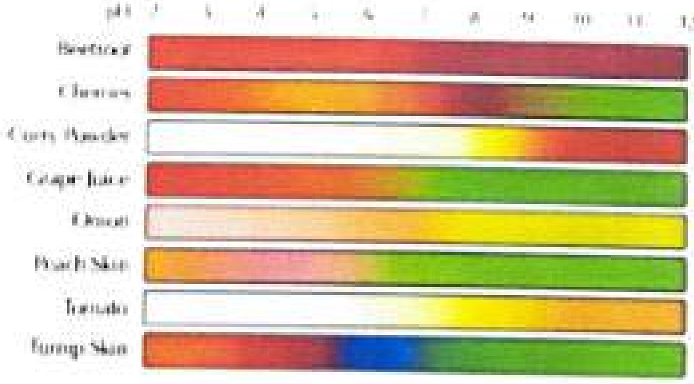
WHAT IS pH ?

pH is a measure of the hydrogen ion activity, in aqueous solution.

Acidic solution have pH<7, pH values lower than 0 are possible.

Basic solutions have pH >7, pH values greater than 14 are possible.



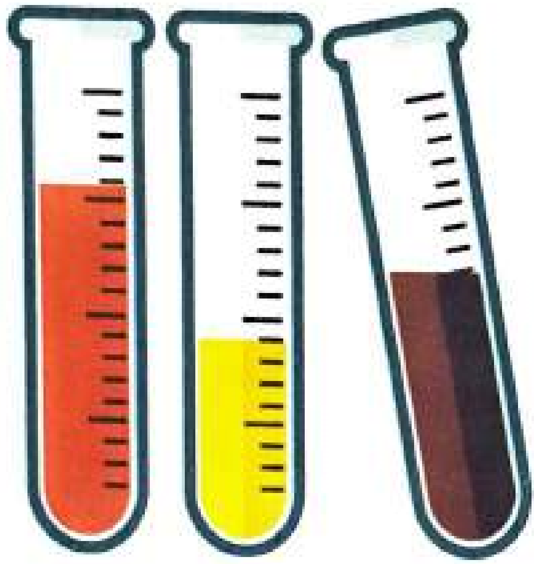


Volumetric Analysis : It involves determining the quantities of a substance present in a given solution to react quantitatively with a solution of another substance of known concentration.

Titration : Titration is a process in which a fixed volume of solution is taken in a conical flask, another solution of known concentration is added to it with the help of a burette to bring about a definite reaction to completion by reacting with the acid.

Acidity of a base : It is the number of OH ions produced in aqueous solution.

Basicity of an acid : It is the number of replaceable H+ ions present in an acid.



NATURAL INDICATORS

Experiment No : 1

Litmus As An Indicator

Materials Required:

Blue and red litmus paper, lemon juice and washing soda solution.

Procedure:

1. Mix some water with lemon juice in a plastic cup.
2. Put a drop of the above solution on a strip of the red litmus paper.
3. Repeat the same exerise with the blue litmus paper.
4. Perform the same activity with the washing soda solution.

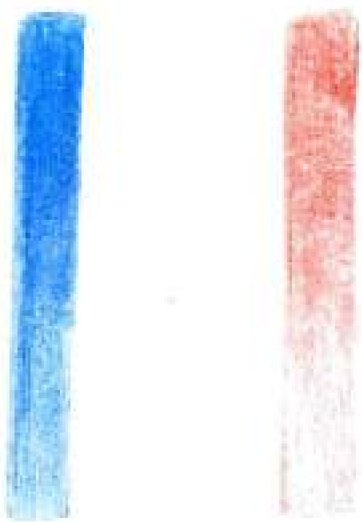
Result:

S.No	Test Solution	Effect on red litmus paper	Effect on blue litmus paper	Inference
1.	Lemon juice	colourless	red	Acidic in nature
2.	Washing soda Solution	blue	colourless	basic in nature

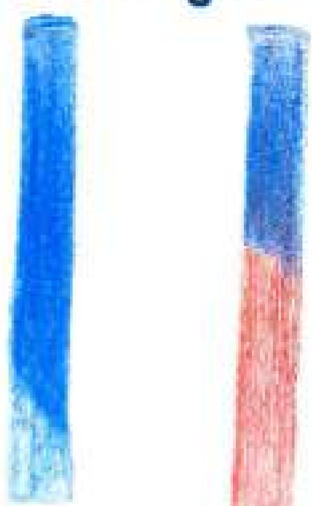
Therefore, If the solution is acidic the blue litmus paper turns red. If the solution is basic or alkaline, the red litmus paper turns blue.

Lemon juice

water



Washing Soda



Experiment No : 2

Turmeric As An Indicator

Materials Required:

Turmeric Powder, a lemon, a white paper, detergent, a glass of water.

Procedure :

1. Make turmeric paste by adding few drops of water
2. Now apply this turmeric paste on the white paper.
3. Now apply drops of lemon juice on the paper.
4. Now apply drops of detergent solution on the paper

Result :

1. When drops of lemon juice applied on the turmeric paper - no colour change is observed.
2. Whene drops of detergent solution is applied on the turmeric paper - yellow to red colour change is observed.

Therefore, The active ingredient present in turmeric is curcumin as an acid - base indicator that is yellow in acidic and neutral Solutions and orange or reddish brown in basic solutions

1. When drops of lemon juice is applied on the turmeric paper - no colour change is observed.

2. When drops of detergent solution is applied on the turmeric paper - red colour change is observed.

Experiment No : 3

Hibiscus As An Indicator

Materials Required :

Hibiscus, detergent, a lemon, a white paper, sugar solution.

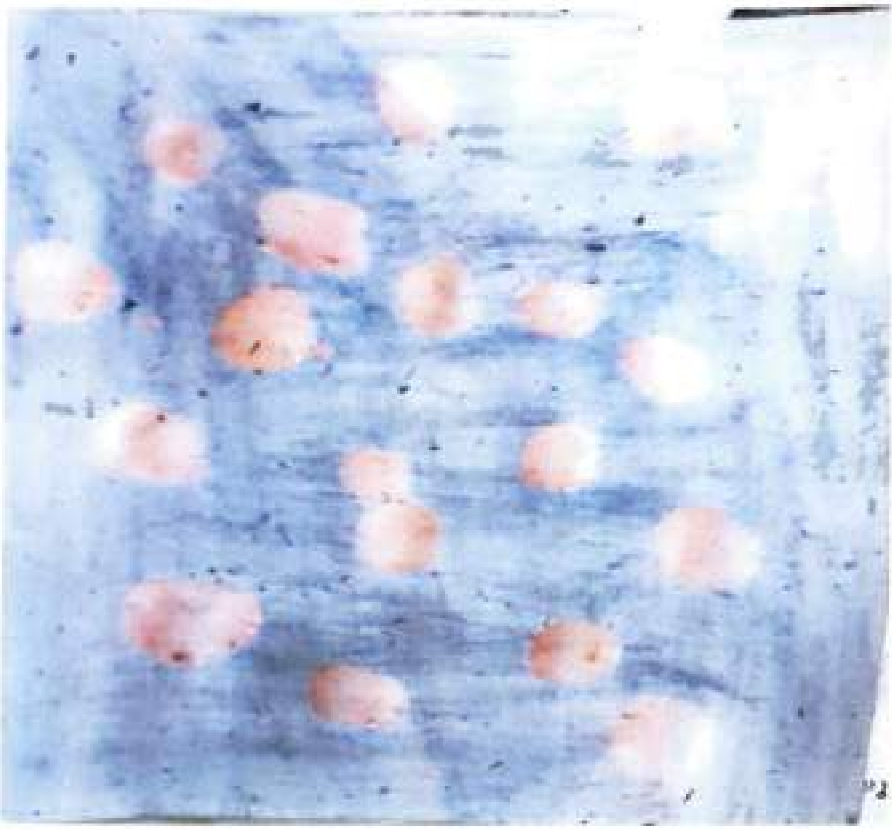
Procedure :

1. Rub the hibiscus on a paper.
2. Now apply drops of lemon juice on the paper.
3. Now apply drops of detergent solution on the paper.
4. Now apply drops of sugar solution on the paper.

Result :

1. Soap water
   Hibiscus paper changes to blue. It is a base.
2. Lemon juice
   Hibiscus indicator changes to pink. It is an acid.
3. Sugar
   No colour change in hibiscus paper. It is neutral.

Therefore, if the solution is acidic, the colour changes to pink. If the solution is basic or alkaline the colour changes to blue.



Lemon juice
Hibiscus indicator changes to pink

Soap water
Hibiscus paper changes to blue

Experiment No: 4

Beetroot As An Indicator

Materials Required :

Beetroot, Water, beaker, lemon juice, washing powder solution.

Procedure :

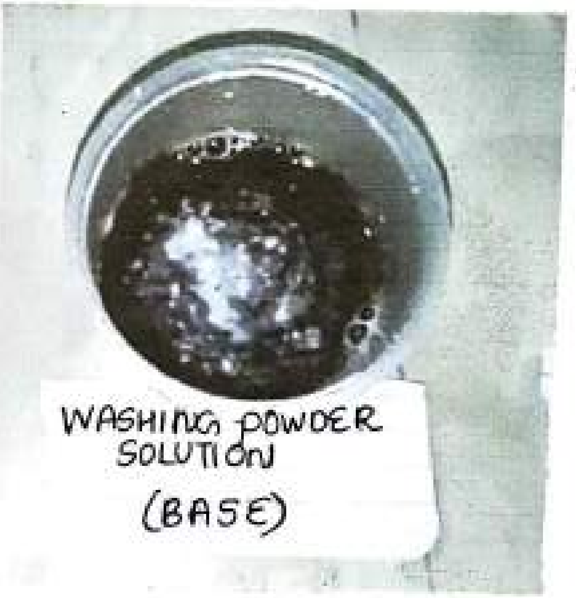
1) Take sufficient water in a beaker and boil it to obtain the extract.
2) Add beetroot extract to lemon juice
3) Add beetroot extract to washing powder solution

Result :

1) When drops of lemon juice are added on the beetroot extract - lighter brown colour is observed.
2) When drops of detergent solution are added on the beetroot extract - bluish red to bluish violet is observed.

Therefore, the active ingredient present in beetroot is Betanin as an acid-Base indicator that is bright bluish red in acidic solutions and yellow brown colour in basic solutions.

When drops of lemon juice are added on the beetroot extract - lighter brown colour is observed.



When drops of detergent solution are added on the beetroot extract - bluish red to bluish violet is observed.

EXPERIMENT No - 5

ONION AS AN INDICATOR

Materials Required

An onion, water, beaker, a lemon, washing soda

Procedure

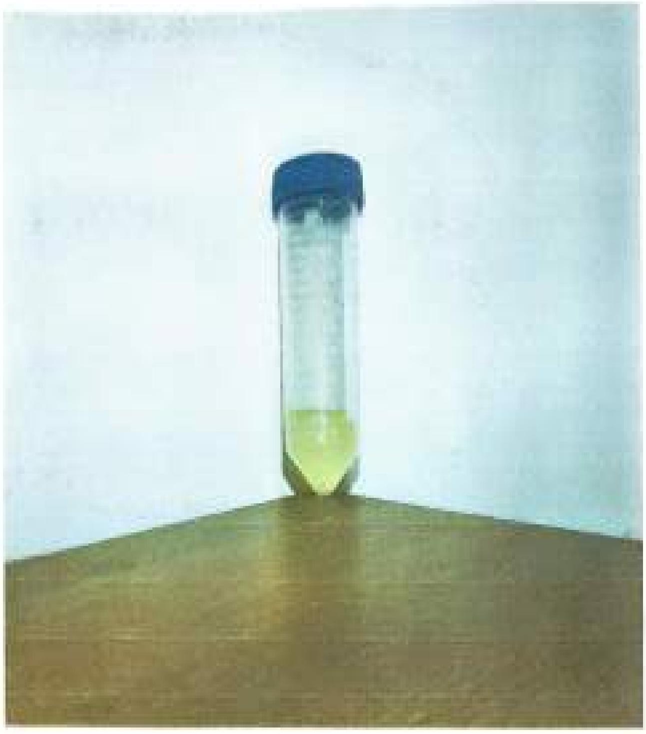
1. Take an onion and cut it into small pieces
2. Boil 250ml of water in a beaker and add onion pieces into it and boil again
3. Extract was cooled and filtered
4. Pour equal amount of onion extract into two transparent glasses
5. Add lemon juice into one glass and add washing soda into the other glass

Result

1. When lemon juice is added in to the onion extract, the colour of the extract changes to pale red

2. When washing soda solution is added in to the onion extract, the colour of the extract changes to green.

Therefore, the active ingredient present in onion is Anthocyanins as an acid-base indicator that is pale red in acidic solutions and green in basic solutions.



When washing soda solution is added into the onion extract, the colour of the extract changes to green.

When lemon juice is added into the onion extract, the colour of the extract changes to pale red.

Theory of Titration

→ Titrimetric analysis is the quantitative chemical analysis which is carried out to determine the volume of a standard Solution which is required to react quantitatively with a measured volume of another Solution of unknown concentration. A Solution of accurately known concentration is referred to as a Standard solution. The reagent of known concentration is called a titrant and the substance being titrated is called titrate.

→ During titration a standard Solution is added to an unknown Solution. The completion of titration is detected by some physical change produced by the standard Solution itself like the pink colour formed by $KMnO_4$ or usually by the addition of an indicator like methyl orange, Phenolphthalein etc. Immediately after the completion of reaction, the indicator will give a clear colour change in the liquid being titrated. The point at which this colour change occurs is known as the end point of titration.

SYNTHETIC INDICATORS

ACID-BASE INDICATORS

* In acid base titrations, solutions of acids are titrated against standard alkali solutions or vice versa.
* Acid base indicators are substances showing colour change according to hydrogen ion concentration of the solution.
* A suitable indicator for an acid base titration is the one which shows a distinct colour change at a pH close to the end point of titration.
* The first useful theory of acid base indicators was proposed by W. Ostwald based upon the concept that the indicators are very weak organic acids or bases.
* Consider a weak organic acid indicator with the general formula HIn.

$$\underset{\text{Colour A}}{HIn} \rightleftharpoons H^+ + \underset{\text{Colour B}}{In^-}$$

The equilibrium constant, $K_{in} = [H^+][In^-]/[HIn]$

K_{in} is the indicator constant.

* If the solution is acidic, with excess H^+ ions, in order to keep the value of Kin a constant, the ratio $[In^-]/[HIn]$ will become low.

* Otherwise in presence of excess H^+ ions the equilibrium will shift towards left and the indicator will show predominantly the acid colour A.

* On the other hand if the solution is alkaline, with excess OH^- ions, the H^+ ions in solution will be continuously removed by OH^- to form water. So the equilibrium will shift towards right and there will be a higher concentration of In^- ions. As a result the indicator mainly shows the basic colour B in solution.

Phenolphthalein As An Indicator

- Phenolphthalein is a colourless weak organic acid which can be represented as Hph. It dissolves in water and partially dissociates to give pink coloured anions ph. The equilibrium can be represented by :

$$HPh \rightleftharpoons H^+ + ph^-$$

Colourless   pink

- In acidic solutions the H^+ ions present in excess will Suppress the dissociation of phenolphthalein by shifting the equilibrium towards the left. So the acidic Solution remains colourless. On adding an alkali to this solution, the H^+ ions get removed by OH^- ions. As a result the equilibrium will shift towards right generating more ph^- ions and solution become pink in colour. Thus phenolphthalein indicator appear as Colourless in acidic solution and pink coloured in alkaline solution above pH 8.

- Even though phenolphthalein is a suitable indicator in strong acid strong base titrations, it is not preferred when the base is weak like ammonium hydroxide.

METHYL ORANGE AS INDICATOR

* Methyl Orange is a weak base and it can represent as In-OH. It dissolves in water and undergoes dissociation to a small extent. The dissociation of MeOH can be respresented as:

$$In\text{-}OH \rightleftharpoons In^+ + OH^-$$

Yellow Red Colourless

* The undissociated base molecule is yellow in colour while the In^+ ion show red colour.

* When methyl Orange is added to an acidic solution. the OH^- ions combine with H^+ ions in solution to form water.

As a result the equilibrium will shift towards right giving a higher concentration of In^+ and the solution becomes red.

* On adding alkali the OH ions suppress the dissociation of weak base by the common ion effect and the equilibrium will shift towards left. So the solution in alkaline medium becomes yellow in colour.

* Methyl orange is not a suitable indicator for titrating a weak acid like acetic acid against a strong base like NaOH.

Some commonly used indicators, their pH ranges and colour in acidic and alkaline medium are summarized in the following the table

Indicator	pH range	Colour in acidic solution	Colour in alkaline solution
Cresol red (acid)	1.2 - 1.8	Red	Yellow
Thymol blue (acid)	1.2 - 2.8	Red	Yellow
Bromophenol blue	3.1 - 4.6	Yellow	Purple
Methyl Orange	3.1 - 4.5	Red	Yellow
Methyl red	4.2 - 6.3	Red	Yellow
Bromothymol blue	6.0 - 7.6	Yellow	Blue
Phenol red	6.4 - 8.2	Yellow	Red
Cresol red (base)	7.0 - 8.1	Yellow	Red
Thymol blue (base)	8.1 - 9.6	Yellow	Blue
Phenolphthalein	8.0 - 9.8	Colourless	Pink
Thymolphthalein	9.3 - 10.5	Colourless	Blue
Alizarin yellow	10.1 - 12.1	Yellow	Lilac

REDOX INDICATORS

Titrations involving oxidising and reducing agents are known as titrations.

A redox indicator is a substance which shows different colours in oxidized and reduced forms.

$$In_{ox} + ne^- \rightleftharpoons In_{red}$$

The oxidation and reduction should be reversible. At a potential E, the ratio of the concentrations of the oxidized and reduced forms is given by the Nernst equation.

$$E = E^{\circ}_{in} + RT/nF \ln [In_{ox}]/[In_{red}]$$

For a sharp colour change at the end point, the standard potential of the indicators should lie in between the standard potentials of the oxidation - reduction systems being titrated aganist each other.

INTERNAL INDICATORS

N-phenoyl anthranilic acid ($C_{13}H_{11}O_2N$) can be used as an internal indicator. At the end point the colour changes from green to violet red.

One percent solution of diphenly amine in concentrated H_2SO_4 can also be used as internal indicator. When dipehnyl amine is the indicator is essential to add phosphoric acid. The indicator imparts a green colour to ferrous solution which turns bluish green just before the completion of the reaction. The end point of titration is characterized by the apperence of deep violet or blue violet colour.

EXTERNAL INDICATORS

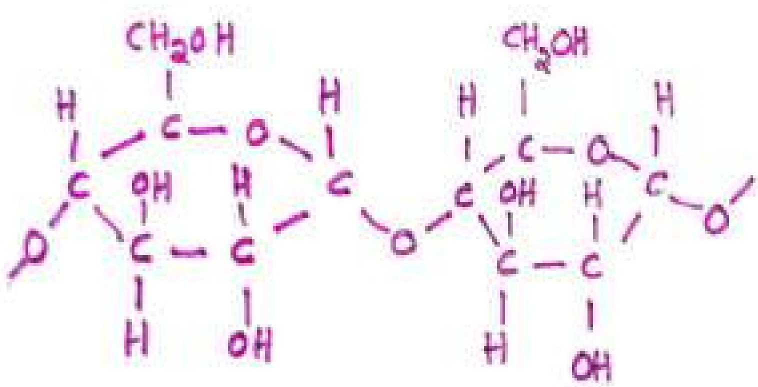
The reaction between $K_2Cr_2O_7$ and Ferrous iron can also be performed using external indicators like potassium hexacyanoferrate, $K_3[Fe(CN_6)]$. In contact with Fe^{2+} it gives a blue colour due to the formation of the complex $KFe[Fe(CN_6)]$.

Prior to the beginning of titration, spots of the indicators are applied on a white porcelain tile. During the titration drop of the reaction mixture is taken out using a glass rod at regular intervals and it is brought into contact with the indicators spot. Once the reaction is over, Fe^{2+} ions will be absent and so on applying the test solution the indicators will not give a blue colour.

STARCH

* Starch is a tasteless, fluffy white powder that is insoluble in cold water, alcohol and other solvents. Starch is a polysaccharide made up of 1,4 linkages between glucose monomers.

* The chemical formula of the starch molecule is $(C_6H_{10}O_5)_n$.



Simple Starch

* Starch is made up of long chains of sugar molecules that are connected together.

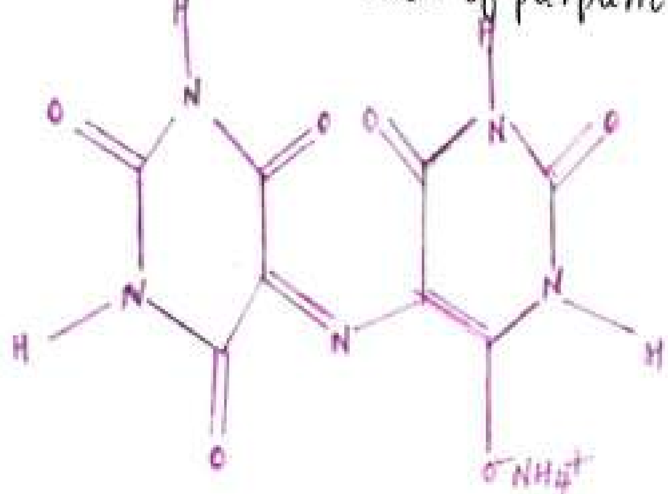
* In iodine titrations starch is used as an indicator. starch reacts with iodine in the presence of iodide to form an intensely blue coloured complex. At the end point the blue colour disappears.

METALLOCHROMIC INDICATORS

* The reactions involving complex ions or undissociated neutral molecules fall under the category of complexometric titration.
* These titration involve the complexation using mono dentate, bidentate or multidentate (polydentate) ligands.
* Metal ion determination can be made more convinient by titration with the polydentate ligand, EDTA (ethylene diamina tetra acetic acid)
* The indicators used in complexometric titration are called Metallochromic indicators.
* Substance like Eriochrome black T (solochrome black T), Murexide, Xylenol orange, patton and Reeder's indicator, Bromopyragallol red, Calcon (solochrome), Calmagite, Eriochrome red, Thymolphthalexone, Fast Sulphon Black F, pyrol catechol violet etc. are the most commonly used indicators.

1. MUREXIDE

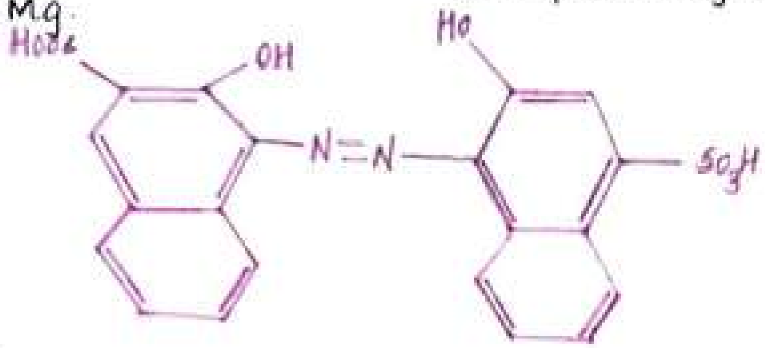
* This is ammonium salt of purpuric acid.



* Murexide solutions are reddish violet upto pH = 9 (H_4D^-), Violet from pH 9-11 (H_3D^{2-}) and blue violet (or blue) above pH 11 (H_2D^{3-}).
* The colour change are due to progressive displacement of protons from imido groups.
* Since there are four such groups, Murexide represents as H_4D^- in which two or four acidic hydrogens can be removed by adding an alkaline hydroxide group.
* Murexide form complexes with many metal ions, Cu, Ni, Co, Ca and Lanthanides which are sufficiently stable to find application in analysis.
* Their colours in alkaline solution are orange (Cu), Yellow (Ni or Co) and red (Ca) depending on pH.

2. PATTON AND REEDER'S INDICATOR

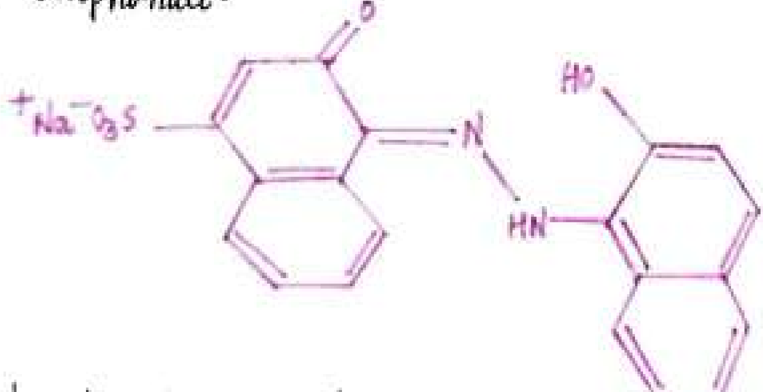
* The indicator is 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthyl azo)-3-naphthoic acid, abbreviated as HHSNNA.
* It's main use is in the direct titration of Ca particularly in presence of Mg.



* A sharp colour change from wine red to pure blue is obtained when Ca ions are titrated with EDTA at pH values between 12 and 14.
* This indicator may be used as an alternative to Murexide for the determination of Ca.
* This indicator is not very stable in alkaline solution.

3. SOLOCHROME DARK BLUE (CALCON)

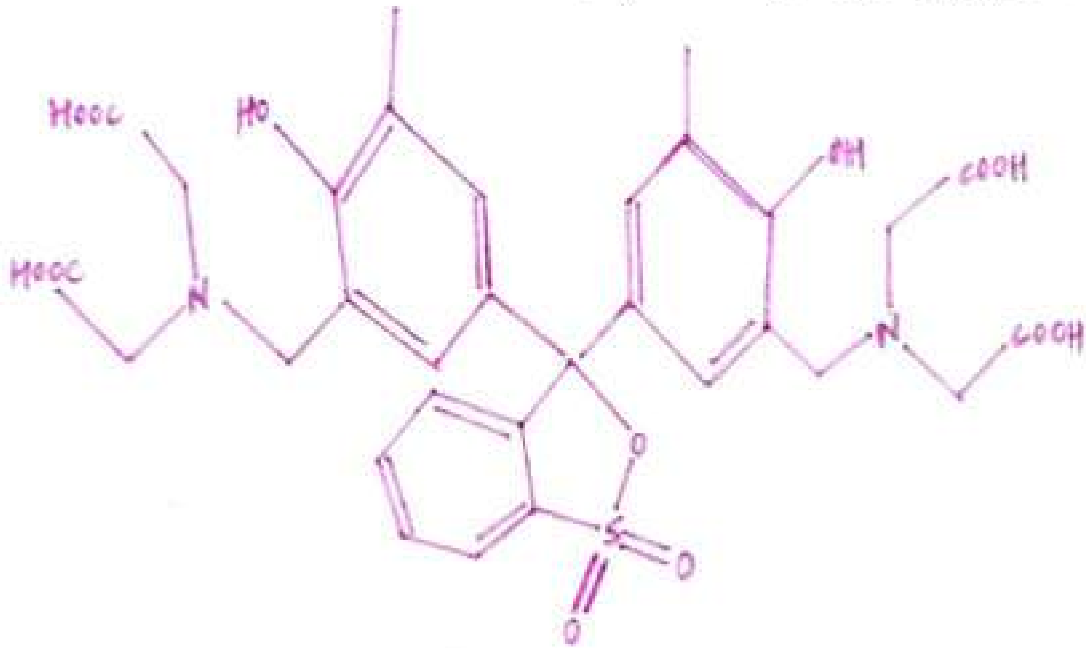
* This is also referred as Eriochrome blue black RC.
* It is infact sodium 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate.



* It has two ionisable phenolic hydrogen atoms.
* The important applications is the complexometric titration of Ca in presence of Mg at pH = 12.5

4. XYLENOL ORANGE

* This indicator is 3,3'-bis [N,N-di (carboxy methyl)]-ortho cresol sulphophthalein.
* It retains acid-base properties of cresol red and displays metal-indicator properties even in acid solution.

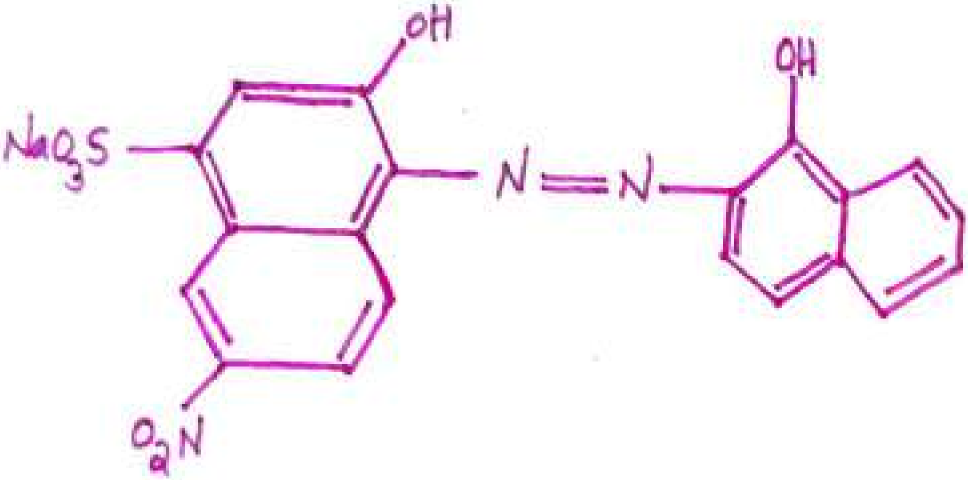


* Acid solutions (pH 3-5) of the indicator are coloured-lemon yellow and those of the metal complexes are intensely red.

* Direct titration of Bi, Th, Zn, Cd, Pb, Co, etc are readily carried out and the colour change is sharp.

5. SOLOCHROME BLACK T [ERIOCHROME BLACK T]

* This substance is Sodium 1-(1-hydroxy 2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate.
  The structure is shown below:



* The sulphonic acid group gives up its proton before the pH range of 7-12 and hence only the dissociation of the two hydrogen atoms of the phenolic groups should be considered.
* Therefore the formula can be represented as H_2D. Below the pH 5.5, the Solution of Solochrome Black T is red in colour (due to H_2D).
* Between pH 7 and 11, it is blue (due to D^{2-}).

- Above p^H 11·5, It is yellowish orange (due to D^{3-}).

* In the p^H range 7-11, addition of metallic salt produces a brilliant change in colour from blue to red.

$$\underset{\text{blue}}{M^{2+} + HD^{2-}} \longrightarrow \underset{\text{red}}{MD} + H^{+}$$

* The colour change can be observed with ions of Mg, Zn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and Pt metals.

PROPERTIES OF METAL ION INDICATOR

The success of an EDTA titration depends on precise determination of the end point. For visual detection of end point, a metal ion indicator should satisfy the following criteria

- The colour reaction must be such that before the end point, when nearly all the metal ion is complexed with EDTA, the solution should be strongly coloured.

- The colour reaction should be specific at least

- The metal ion indicator complex must possess sufficient stability else because of dissociation a sharp colour change is not obtained. But metal indicator complex must be less stable than metal EDTA complex because at the end point EDTA removes the entire metal ion from metal indicator complex.

- The colour contrast between free indicator and metal indicator complex should be readily observable to metal ion so that the colour change occurs as near to the equivalence point as possible.

• The above all requirements must be fulfilled within the pH range at which the titration is performed.

The use of metal ion indicator in an EDTA titration maybe written as

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

This reaction will proceed if the M-In complex is less stable than M-EDTA complex. The former dissociates to a limited extend and 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 stability of M-In complex may be expressed in terms of formation constant or indicator constant k_{In}.

$$k_{In} = \frac{[M\text{-}In]}{[M][In]}$$

The indicator colour change is affected by the hydrogen ion concentration of the solution. thus Solochrome Black, which may be written as H_2In^{2-} exhibites the following behaviour.

$$\underset{(red)}{H_2In^{2-}} \underset{}{\overset{pH\ 5.3\ to\ 7.3}{\rightleftharpoons}} \underset{(blue)}{HIn^{2-}} \overset{pH\ 10.5\ to\ 12.5}{\rightleftharpoons} \underset{(yellow\ orange)}{In^{3-}}$$

In the pH range 7 to 11 in which the dye itself exhibits a blue colour, many metals ions form red complexes, these colours are extremely sensitive.

In EDTA metal ion indicator is used to detect change of p^M. p^M is negative logarithm of free metal ion concentration i.e;

$$p^M = -\log[M^{2+}]$$

With all the metal ion indicator used in complexometric titrations detection of the end point depends on recognizing a specified change in colour.

ADSORPTION INDICATORS

Adsorption indicators are usually dyes which are very sensitive and highly effective in dilute solutions. At the end point these indicators suddenly change the colour of precipitate, due to the adsorption of indicator on the precipitate.

Several precipitates separate in the colloidal state and due to selective adsorption of common ions they posses charge. For example the precipitate of AgCl can adsorb either silver or chloride ion depending on the condition of colloidal formation.

Consider the precipitation of AgCl. The charge developed on AgCl will depend on the availability of Ag^+ and Cl^- ions in solution. If the charge of precipitate is opposite to that of indicator, then there is adsorption of indicator ions on the precipitate and the change in colour. If the charge on the precipitate is same as that of indicator, adsorption will not take place and the dye will remain as such in solution.

Mechanism of indicator can be explained by taking the titration of silver nitrate with potassium chloride in which dichloro ~~fluoro~~ fluorescein is used as an indicator.

In this titration silver nitrate is added to potassium chloride solution in which indicator is present. A partial colloidal precipitate of AgCl is formed. The chloride ions which are present in excess in solution get adsorbed on the AgCl precipitate and impart a negative charge to the precipitate this known as primary adsorption surface. Oppositely charge Na^+ ions present in solution are adsorbed on the quantity of $AgNO_3$ solution is increased, the concentration of chloride ions decreases due to the formation of AgCl. At the equivalence point, the precipitate loses its charge because no more chloride ions are present in solution. When a single drop of $AgNO_3$ is added in excess, the Ag^+ ions ~~being~~ being in excess are adsorbed over AgCl. The negative ions of pink coloured dichlorofluorescein are absorbed over the positively charged silver chloride precipitate and give a pink coloured silver dichlorofluoresceinate.

Another example is the titration of silver nitrate with potassium bromide using eosin (tetrabromo fluorescein) as indicator.

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