

pH Indicators: A Valuable Gift for Analytical Chemistry

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Abstract

Analytical chemistry plays a major role in the quality control of various industrial chemical products. The quality and purity of the products are calculated and confined by applying various principles of chemistry. Thus analytical procedures are regarded to be the outcome of the fundamental principles of chemistry and related sciences. Neutralization titrations are common in establishing the quality of various industrial products taking account of the fact that industrial chemicals and products are mainly acids or bases. The results for the titrations performed on sample require sharp and distinct equivalence points that are identified by the use of suitable acid – base indicators. The present work is a review on common pH indicators used for the neutralization titrations in analytical chemistry.

Keywords: pH indicators, Neutralization Titrations, Analytical Chemistry.

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INTRODUCTION

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. Such substances which can be used to determine the pH of a solution are called acid-base indicators [1]. Acid-base indicators are either weak organic acids or weak organic bases [2].

An acid-base indicator is either a weak acid or weak base that exhibits a color change as the concentration of hydrogen (H⁺) or hydroxide (OH⁻) ions changes in an aqueous solution. Acid-base indicators are most often used in a titration to identify the endpoint of an acid-base reaction [3]. They are also used to gauge pH values and for interesting color-change science demonstrations [4].

Acid – Base titrations

Titrimetric analysis remains an important technique in analytical chemistry [5]. Origin of the titrimetric method of analysis goes back to the middle of the 18th century. It was introduced for the first time by Gay – lussac, who described it to be Volumetry, which was later termed as Titration [6]. Although the assay method is very old, there are signs of some modernization like potentiometric end point detection improving the precision of the methods. The detection of end – points in titrations, particularly acid – base titrations is of utmost importance and hence

identification of an indicator that can give a sharp color change upon reach of the point is very much important in titrimetric analysis.

What is pH?

It is important to know the concentration of hydrogen ions [H⁺] in chemistry. The concentration of Hydrogen ions [H⁺] are typically quite small numbers, therefore they are reported in terms of pH. It is defined as negative of the base 10 logarithm of Hydrogen ion concentration [7]

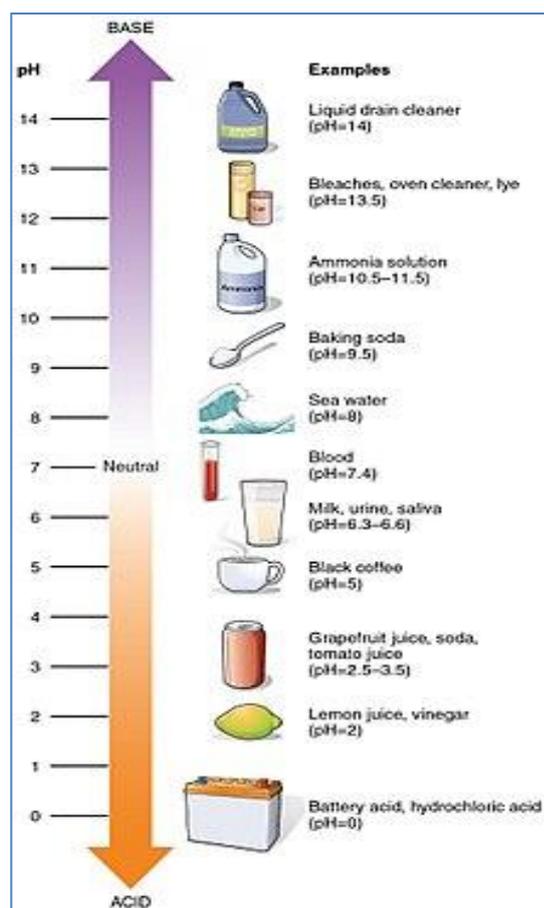
$$\text{pH} = -\log_{10} [\text{H}^+]$$



The concept of pH is very convenient for expressing hydrogen ion concentration. It was introduced by Sorenson in 1909[8]. It is now used as a general way of expressing other quantities also Sorenson.

pH scale

pH scale was introduced in order to express the hydrogen ion concentration or acidity of a solution [9]. The hydrogen ion concentration of different acidic solutions was determined experimentally, they were then converted to pH values using the mathematical relations. Then this pH values were computed on a scale with water as reference substance. The scale on which pH values are computer is called as the pH scale.



Classification of materials as Acids and Bases

The classification of reagents, solvents and chemicals based on their pH values leads to a broader concept of grouping namely Acids and bases [10]. The reagents or chemicals for which the pH value is found to be less than 07 are termed to be Acids. The chemicals for which it is measured to be above 07 are grouped under Bases.

Identification and measurement of pH

Identification of materials by their color was always an easy task. This serves to be one of the best and the easiest method in identifying materials.

The pH of a solution may also be identified by the color it produces on certain selected materials, which are mentioned to be pH indicators.

History

The use of a natural dye as acid-base indicators was first reported in 1664 by Sir Robert Boyle in his collection of essays, "Experimental History of Colors" [11]. Indeed, Boyle made an important contribution to the early theory of acids and bases by using indicators for the experimental classification of these substances.

Theory of Indicators

The theories leading to the working principle of acid – base indicators are mainly two and are named to be Ostwald theory and Quinonoid theory [12].

Ostwald theory

According to this theory, every acid – base indicator is either a weak acid or a weak base. They can undergo dissociation to the respective ions and are in equilibrium with the dissociated form. They follow the principle of Le Chatlier to adjust the stress felt during the addition of excess of acid or base and hence the equilibrium will be shifted to either of the sides making the indicator an ionized or unionized, causing to produce the color change.

Consider an acid – base indicator which is weakly acidic in nature, let it be represented as HIn.

This can undergo dissociation to H^+ and In^- .

This dissociation can be represented as follows:



In equilibrium,

$$pK_a = \frac{[H^+][In^-]}{[HIn]}$$

Similarly when the taken indicator is a weak base, it may be represented as InOH, which undergoes dissociation as follows:



In equilibrium,

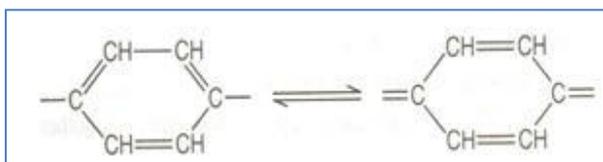
$$pK_b = \frac{[In^+][OH^-]}{[InOH]}$$

The indicators are possessing different colors in different pH.

The addition of acid or base to this equilibrium causes a stress to be felt by it. This tends the equilibrium to shift to a side that can reduce the stress. The side to which the equilibrium has shifted decides the color of indicator.

Quinonoid theory

This theory is helpful in identifying the structural changes taking place during the variations in pH felt by the acid – base indicator. It says that indicators are tautomers capable to exist in both benzenoid and quinonoid forms of a compound. The indicators are said to be in their light color in benzenoid form and in dark color in quinonoid form of existence which in turn is dependent on the pH of the medium.



The two forms have different colors. The color change is due to the inter conversion of one tautomeric form into other. One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the color change occurs.

Aim of the Work

The work intends to prepare a collection of information about the various research and review articles published in reputed journals, books etc to provide awareness about the acid base indicators. Even though there is a lot of information available on the

topic, these are found to be available in a manner that is distributed and the researcher may experience trouble in finding time to collect these data from the various distributed sources. The article serves to be an excellent source of information for a researcher who plans to carry out research work on acid – base indicators, preparation of such indicators and also introducing methods of titration protocol for the assay of drugs, chemicals and other reagents.

METHODOLOGY

The work shall make use of various available sources like books relevant to the topic, various Journals that publish novel research and review articles besides the internet which serves to be a quick and a major source of information that almost all the researchers depend on nowadays.

A thorough and extensive search for information regarding the various aspects of acid -base indicators was done, and a wealth of information was collected. The details obtained were then sorted and classified and arranged in manner easy for the reader to understand.

Literature survey

The search of literature was successful in collecting a vast and detailed set of information of ten popular reagents used as indicators in neutralization titrations and shall be summarized as in the table: 1.0

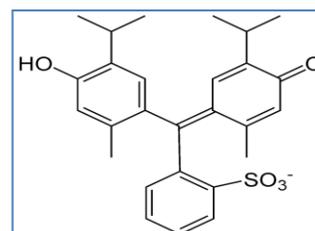
Table-1.0: Indicators, pH ranges and color changes.

Sl. No	Indicator	Ideal range (acid) pH		Color	
				Acid	base
1	Thymol Blue	1.2	2.8	Red	Blue
2	Congo Red	3.0	5.0	Blue	Red
3	Methyl Orange	3.0	6.3	Red	Yellow
4	Bromocresol Green	4.0	5.6	Yellow	Blue
5	Methyl Red	4.2	6.2	Pink	Yellow
6	Bromothymol Blue	6.0	7.6	Yellow	Blue
7	Phenol Red	6.8	8.2	Yellow	Red
8	Phenolphthalein	8.0	10	Colorless	Pink
9	Thymolphthalein	8.8	10.5	Colorless	Blue
10	Neutral red	6.8	8.0	Red	yellow

Thymol blue

IUPAC name:

(4-[9-(4-hydroxy-2-methyl-5-propan- 2-yl-phenyl) -7,7-dioxo-8-oxa- 7λ6 thiabicyclo[4.3.0]nona-1,3,5-trien-9-yl]- 5-methyl-2-propan-2-yl-phenol)

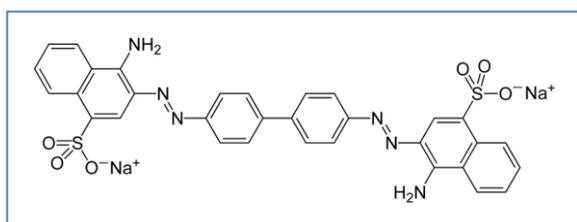


It is also known as thymolsulphonaphthalein. It is synthesized from Thymol. It is used as a solid pH sensor [13].



Fig-1: Color change of Thymol blue in acid (red) and alkaline (blue) medium.

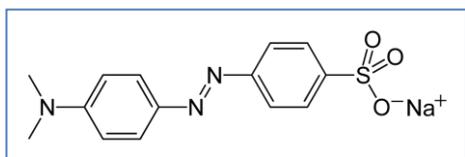
CONGO RED



IUPAC name:

Disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl) diazenylphenyl]phenyl]diazenyl-naphthalene -1-sulfonate

It is prepared by azo coupling of the bis(diazonium) derivative of benzidine with naphthionic acid. Besides its use in analytical chemistry, it serves to be a useful reagent in microbiology also [14]. Congo red is used for staining in amyloidosis, and for the cell walls of plants and fungi, and for the outer membrane of Gram-negative bacteria. The dye can also be used in flow cytometry experiments for the detection of Acanthamoeba, Naegleria and other amoebal cysts.



METHYL ORANGE

IUPAC name:

Sodium 4-[[4-(dimethylamino) phenyl]diazenyl] benzene-1-sulfonate

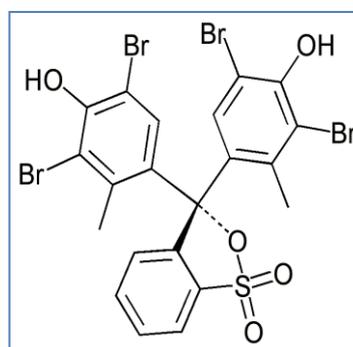
Methyl orange is a pH indicator frequently used in titration because of its clear and distinct color variance at different pH values. Methyl orange shows red color in acidic medium and yellow color in basic medium. Because it changes color at the pH of a mid-strength acid, it is usually used in titration for acids.

Methyl orange has mutagenic properties [15]. Direct contact should be avoided. It is a hazardous substance.



Fig-2: Color change observed, (acid to base).

BROMOCRESOL GREEN



IUPAC name:

2,6-Dibromo-4-[7-(3,5-dibromo-4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9λ6-thiabicyclo[4.3.0]nona-1,3,5-trien-7-yl]-3-methyl-phenol.

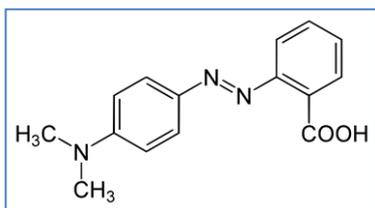
It belongs to a class of dyes called sulfonephthaleins. It is used as a pH indicator in applications such as growth mediums for microorganisms and titrations. In clinical practice, it is commonly used as a diagnostic technique. The most common use of Bromocresol green is to measure serum albumin concentration within mammalian blood samples in possible cases of kidney failure and liver disease [16].

It is used as a pH indicator and as a tracking dye for DNA agarose gel electrophoresis. It can be used in its free acid form (light brown solid), or as a sodium salt (dark green solid). It is also an inhibitor of the prostaglandin E2 transport protein. Additional applications include use in sol-gel matrices, the detection of ammonia, and the measurement of albumin in human plasma and serum.

Bromocresol green may cause irritation. Skin and eye contact should be avoided.

METHYL RED

IUPAC name:

2-[[4-(Dimethylamino) phenyl]diazanyl]benzoic acid

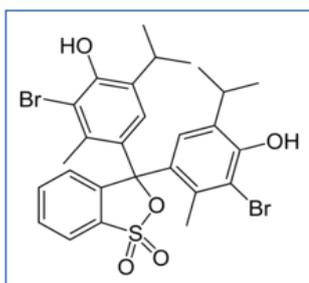
Methyl red is an indicator dye that turns red in acidic solutions. It is an azo dye, and is a dark red crystalline powder. Methyl red is a pH indicator; it is red in pH under 4.4, yellow in pH over 6.2.

BROMOTHYMOLO BLUE

IUPAC name:

4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3,3-diyl) bis(2-bromo-6-isopropyl-3-methylphenol)

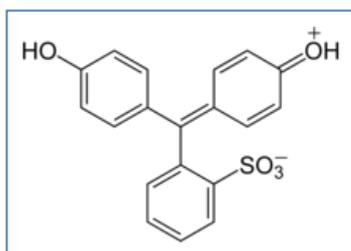
Bromothymol blue acts as a weak acid in a solution. It is mostly used in applications that require measuring substances that would have a relatively neutral pH. A common use is for measuring the presence of carbonic acid in a liquid. It is useful in treatment of respiratory disorders [17]. It is yellow in acidic pH and blue in alkaline pH.

**PHENOL RED**

IUPAC name:

4,4'-(1,1-Dioxido-3H-2,1-benzoxathiole-3,3-diyl) diphenol

Phenol red is yellow in acidic pH and red in alkaline pH. Above pH 8.2, phenol red turns a bright pink color. Phenol red exists as a red crystal that is stable. In air a solution of phenol red is used as a pH indicator, often in cell culture. Phenol red was used to estimate the overall blood flow through the kidney [18]. But this test is not common nowadays.

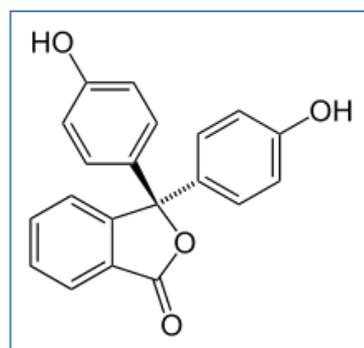
**PHENOLPHTHALEIN**

IUPAC name:

3,3-Bis(4-hydroxyphenyl)-2-benzofuran-1(3H)-one

Phenolphthalein is a chemical compound with the formula $C_{20}H_{14}O_4$. Phenolphthalein is often used as an indicator in acid-base titrations. It belongs to the class of dyes known as Phthalein dyes. It turns colorless in acidic solutions and pink in basic solutions.

Phenolphthalein's common use is as an indicator in acid-base titrations. It also serves as a component of universal indicator, together with methyl red, bromothymol blue, and thymol blue [19].



The equivalence points in titrations using phenolphthalein indicator is identified by the colour change from pink to colourless or vice-versa depending on the use of base or alkali respectively as the titrant.

Phenolphthalein is an indicator of choice in titrations of strong acids against strong bases. Having an ideal working range of pH between 8.0 to 10.0, it gives a distinct and sharp colour change marking the easy identification of equivalence point.



Fig-3: Color change observed, (base to acid).

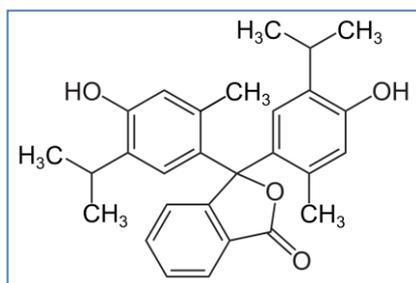
THYMOLPHTHALEIN

IUPAC name:

3,3-bis(4-hydroxy-2-methyl-5-propan-2-ylphenyl)-2-benzofuran-1-one

Thymolphthalein is a Phthalein dye used as an acid-base indicator. It is used in titrations involving poly protic systems like titration of Phosphoric acid

against standard basic solutions. It is colourless in acid pH and is blue in basic pH. The equivalence point determination is done by the colour change from colourless to blue and vice – versa depending on the use of base or alkali respectively as the titrant.

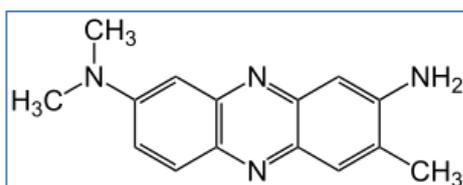


NEUTRAL RED

IUPAC name:

3-Amino-7-dimethylamino-2-methylphenazine hydrochloride

Neutral red acts as a pH indicator, changing from red to yellow between pH 6.8 and 8.0. Neutral red (toluyle is a eurhodin dye, commonly used for staining in histology. Neutral red has an affinity for the highly acidic storage granules in adrenal chromaffin cells.



Other common indicators

Besides the indicators discussed above, there are also a number of indicators that are used in the analysis of chemical compounds by titration processes. Some of them include.

Bromophenol blue Congo red Cresol purple Alizarin red Chlorophenol red Aniline blue Bromocresol purple Alizarin yellow R Crystal Violet

Choice of Indicators for Titrations

There is a need to choose an indicator which changes colour as close as possible to that equivalence point, this varies from titration to titration[20].

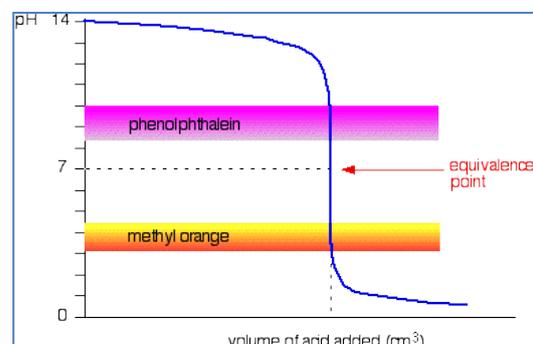
Titration curve

To impart a good knowledge on the indicators specific for titrations, titration curve needs to be considered. It is the plot of volume of titrant added against the pH value observed. The shape of the titration curve differs with the type of the titration. Every titration curve has a distinct vertical portion in its shape. This vertical region covers a range of definite value of pH, making it possible to select any indicator having effective pH value lying in the range.

Case 1

Titration of a strong acid against a strong base

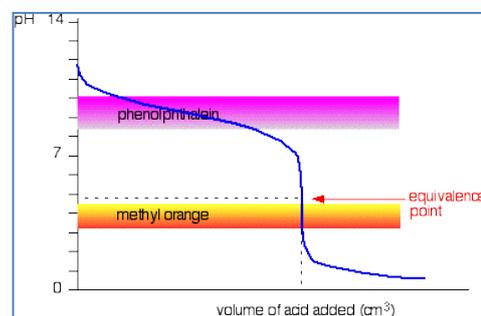
In this type of titration the vertical portion of the titration curve falls between 3.4 to 9.5, hence any any indicators whose effective pH range falls within range (preferably in the steep of the vertical) can be selected, eg: Methyl Orange and Phenolphthalein.



Case 2

Titration of a strong acid against a weak base

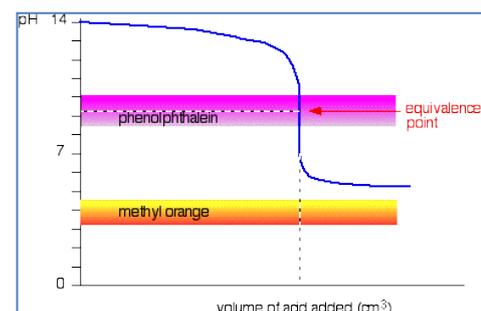
It is obvious for such titrations that Phenolphthalein won't suit for this type of titrations as the pH of phenolphthalein falls outside the limit of the vertical region. But methyl orange can be a choice in this type of titrations. Any other indicators whose pH falls on the steep bit of the curve may also used.



Case 3

Titration of a strong base against a weak acid

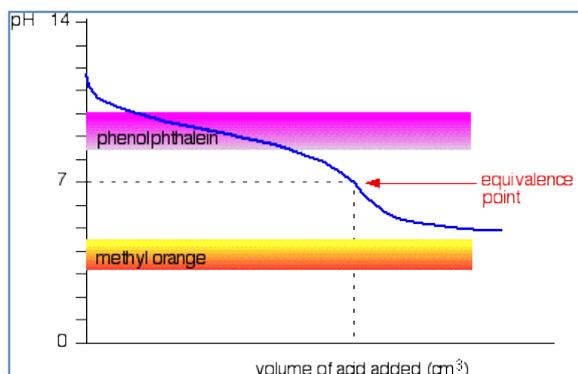
It is obvious for such titrations that methyl orange won't suit for this type of titrations as the pH of methyl orange falls outside the limit of the vertical region. But phenolphthalein can be a choice in this type of titrations. Any other indicators whose pH falls on the steep bit of the curve may also use.



Case 4

Titration of a weak base against a weak acid

Titration of weak acids against a weak base in the presence of a single indicator is practically not possible as there is no vertical region observed in the curve of such titrations. It is therefore advised to use better alternate methods like the use of mixed indicators or other electrochemical methods like potentiometry or conductometry.



DISCUSSION

Neutralization titrations play a major role in Analytical chemistry, particularly in the estimation of active ingredient in various samples. It is of utmost importance in certain selected areas of analytical chemistry like pharma industry for the determination of quantity of drug samples and expression of the estimated quantity as percentage of purity (assay). The results obtained for such estimations are to be documented for further verification as per the legal procedures. Therefore it is significant that the analytical method used for the estimation is perfect and that analyst is following highest grade of sincerity to arrive at results that are free from all possible sources of errors.

In this regard it becomes important for an analyst to take care that neutralization titrations which are still a mentioned procedure for assay of many drugs as per the monographs of various pharmacopeias, are carried out in a manner that produce results of maximum accuracy by eliminating all possibilities of errors. One of the major factors that contribute to the achievement of this is the use of appropriate acid – base indicator for the identification of equivalence point. The equivalence point appears sharp and distinct only when indicators that are specific for a given combination of titrant and analyte are used. Moreover the quantity of indicators also plays a role in identification of the end point.

The survey done on various common acid – base indicators used for the neutralization titrations was useful in identifying their general features and properties. It provided a good idea about the colour changes taking place in individual indicators and their

ideal range of working pH. The survey was helpful in identifying the suitable indicator of choice for a given type of neutralization process depending on the strength of the titrant and analyte used.

CONCLUSION

The review of literature done on the use of indicators for neutralization titrations was quite useful to gather information about reagents starting from their IUPAC name itself. The use of reagents as indicators for neutralization titrations and their choices for selected type of titrations was well understood. The study remained a good source of knowledge pertaining to the reagents that are used commonly in neutralization titrations as indicators for the identification of equivalence point.

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