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NATURAL INDICATORS AS ALTERNATIVE TO SYNTHETIC ACID BASE INDICATORS

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Abstract:

In acid-base titrations, indicators are used to show sharp color change at intervals of pH. Natural pigments in plants are highly colored substances and may show color change with variation of pH. An attempt has been made to investigate the indicator activity of flower pigments and to replace synthetic indicators as they have certain disadvantage like chemical pollution, availability problems and high cost. Alcoholic extract of Hibiscus rosasinensis, Calotropis gingantia, Brassica oleracea-capitata, Rosa chinensis, Brassica oleracea-italica, Ixora chinensis, Cantharanthus roseus gives sharp intense color change as compared to phenolphthalein and methyl orange. Herbal indicators are evaluated by using different titrations of acids versus bases. The flowers were cleaned by distilled water and cut into small pieces and macerated for two hours in 25 ml of 90% ethanol. The equimolar titrations were performed using 10ml of titrant with three drops of indicator. The mean and standard deviation for each type of acid base titrations were calculated from results the obtained.

In all these titrations, promising results were obtained when it was tested against standard synthetic indicators. Titration show sharp color change at the equivalence point and the extract was found to be very useful and accurate for indicating the neutralization point. Natural indicators employed in the acid base titrations was found economic, safe and an efficient alternative for traditional indicators.

Keywords: *Herbal indicator, economic, accurate indicator, efficient alternative, sharp end point*

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INTRODUCTION:

Indicators are dyes or pigments that can be isolated from a variety of sources, including plants, fungi, and algae. Almost any flower which is red, blue, or purple in color contains a class of organic pigments called anthocyanins that change color with pH. The use of natural dyes as acid-base indicators was first reported in 1664 by Sir Robert Boyle in his collection of assays "*Experimental History of Colours"*. Indeed, Boyle made an important contribution to the early theory of acids and bases by using indicators for the experimental classification of these substances.

An acid-base indicator is not always a synthetic chemical. Many plant pigments and other natural products are good indicators, and synthetic ones like phenolphthalein and methyl red are also available and widely used. Acid-base indicators are large organic molecules that behave as weak acids, they can donate hydrogen ions to water molecules to form conjugate bases. The distinguishing characteristic of indicator is that the acid and conjugate base forms are different colors. A good acid-base indicator will change its color as the concentration of hydrogen ions in a solution changes. Often an indicator will have one or more atoms that can gain or lose protons (H+) [1]. The color of an acid-base indicator depends on the concentration of H_3O^+ ions, which is most conveniently expressed using the pH scale. The mathematical relationship between pH and $[H_3O^+]$ is given below:

pH = -log{H3O+]

The present work highlights the use of the alcoholic extract of the flowers as indicator in acid-base titrations. Natural indicators are easy to extract as well as easily available.

Hibiscus rosa-sinensis **(Hawaiian Hibiscus)** belonging to family malvaceae. The original species usually has bright red flowers but there are many cultivars with colors ranging from white and yellow to orange, pink. Leaves have finely toothed edges and are ovate, glossy, dark green, up to 6 inches long. Large, showy, delicate blooms with five petals and distinctive long stamens reach up to 4 inches wide. From phytochemical investigation and qualitative chemical tests, shows presence of anthocyanins, which are pigmented flavanoids, which may be the reason for its activity as an indicator.

Calotropis gigantea belongs to the botanical family Asclepiadaceae. It is a tall shrub reaching 2.4-3 m high. Flowers of plant are inodorous, purplish or white, arranged in umbellate lateral cymes, peduncles from between the petioles. Pedicels are much longer than the flowers, calyx are divided to base, sepals 6 by 4 mm, ovate, acute, cottony, corolla 2 cm long or more. The flowers are used as sweet, bitter, anthelmintic, analgesics, astringent, anti-inflammatory, anti-tumor, kapha, rat bite, good in ascites.

Catharanthus roseus is a renowned medicinal plant, belonging to the family apocynaceae; and is a rich source of alkaloids, which are distributed in all parts of the plant. The alkaloid content of *C. roseus* varies considerably in various parts..

Wild *Brassica oleracea* is a tall biennial plant, forming a stout rosette of large leaves in the first year, the leaves being fleshier and thicker than those of other species of *Brassica.* In its second year, the stored nutrients are used to produce a flower spike 1 to 2 metres (3–7 ft) tall bearing numerous yellow flowers. There are various cultivar group of the species: [2]

Brassica oleracea **var. *capitata*** is a sort of cabbage. Its leaves are colored dark red/purple. Red cabbage juice contains anthocyanin and can be used as a pH indicator. It is red, pink, or magenta in acids, (pH < 7), purple in neutral solutions (pH ~ 7), and ranges from blue to green to yellow in alkaline solutions (pH > 7).

Brassica oleracea italica plant belonging to a family brassicaceae, is with dense clusters of tight green flower buds. The Italica cultivar group of the species *Brassica oleracea* is also known as broccoli. It has large flower heads, usually green in color, arranged in a tree-like structure on branches sprouting from a thick, edible stalk. The mass of flower heads is surrounded by leaves. Broccoli most closely resembles cauliflower, which is a different cultivar group of the same species.

Ixora coccinea is a species of flowering plant in the Rubiaceae family. A shrub with many stems, up to 2 m tall. Leaves obovate-oblong, coriaceous, base rounded, cordate or sometimes obtuse, apex obtuse, and petiole short, stipules long-awned. Flowers with corolla tube 3-3.5 cm long, lobes circular-obovate, broadly rounded at apex, 6 mm x 6 mm, orange-red or white.

Catharanthus roseus (**madagascar periwinkle**) is a species of *Catharanthus* native and endemic to Madagascar. Belonging to a family apocynaceae.

It is an evergreen subshrub or herbaceous plant growing to 1 m tall. The leaves are oval to oblong,

2.5–9 cm long and 1–3.5 cm broad, glossy green, hairless, with a pale midrib and a short petiole, arranged in opposite pairs. The flowers are white to dark pink with a darker red centre, with a basal tube with five petal-like lobes.[3]

MATERIALS AND METHODS:

Materials:

Fresh flowers were collected from the local market of Nashik region, Maharashtra and they were authenticated from department of botany. All chemicals and solvents used in the investigation were of analytical grade purchased from S.D. Fine Chemicals, Mumbai, India. Volumetric solutions were prepared as per Indian pharmacopoeia.

Method:

The flowers were cleaned by distilled water and cut into small pieces and macerated for two hours in 25 ml of 90% ethanol. Finally the extract was filtered and was preserved in tight closed container and stored away from direct sun light.

The experiment was carried out by using the same set of glassware's for all types of titrations. As the same aliquots were used for both titrations i.e. titrations by using standard indicators and flower extracts, the reagents were not calibrated. The equimolar titrations were performed using 10ml of titrant with three drops of indicator. All the parameters for experiment are given in the table [4,5]

A set of five experiments each for all types of acid base titrations were carried out. The mean and standard deviation for each type of acid base titrations were calculated from results the obtained.

RESULTS AND DISCUSSION:

The flower extract was screened for its use as an acid base indicator in various acid base titrations, and the results of this screening were compared with the results obtained by standard indicators methyl orange and phenolphthalein. The titrations of strong acid with strong base, strong acid with $NaHCO_3$, Na_2CO_3, strong base with tartaric and citric acid. [6,7].

Table 1: Mean (n=5) screening results of base *versus* acid titrations

Sr. No.	Indicators	pH Change	Titrant (NaOH) V/s HCl (titre)		Titrant (NaOH) titre (tartaric acid)		Titrant (NaOH) v/s titre (citric acid)		End point
			Burette reading (ml)		Burette reading (ml)		Burette reading (ml)		
			0.5M	1M	0.5M	1M	0.5M	1M	
	Standard indicator								
1	Phenolphthalein **(IP)**	8.0- 9.5	35.01 ± 0.51	17.22 ± 0.06	22.3 ± 0.10	9.27 ± 0.15	12.47 ± 0.06	6.4 ± 0.17	Colorless to pink
	Flower extract								
1	Hibiscus Rosa - sinensis	9.7-10.2	34.6 ± 0.38	17.06 ± 0.51	20.67 ± 0.05	9.43 ± 0.06	11.77 ± 0.05	6.37 ± 0.06	Orange to green
2	Calotropis gingantia	9.3- 9.7	35.17 ± 0.84	17.03 ± 0.80	21.63 ± 0.05	9.76 ± 0.15	12.55 ± 0.09	5.78 ± 0.03	Pink to green
3	Brassica Oleracea Capitata	9.2- 10.3	36.35 ± 0.99	18.07 ± 0.61	20.47 ± 0.06	10.0 ± 0.10	12.35 ± 0.09	6.47 ± 0.06	Pink to green
4	Rosa Chinensis	8.7- 10.6	37.13 ± 1.19	18.5 ± 0.56	21.36 ± 0.05	9.6 ± 0.1	12.77 ± 0.06	6.44 ± 0.05	Orange to yellow brown
5	Brassica Oleracea Italica	6.5- 8.5	30.2 ± 0.75	15.03 ± 0.85	21.03 ± 0.06	9.67 ± 0.05	12.48 ± 0.03	6.48 ± 0.07	Colorless to yellow
6	Ixora Chinensis	7.0- 8.2	35.07 ± 1.25	17.27 ± 0.46	21.73 ± 0.12	9.43 ± 0.15	12.59 ± 0.01	6.59 ± 0.02	Orange to yellow
7	Cantharanthus Roseus	8.6- 10.1	33.14 ± 0.85	16.73 ± 0.21	24.36 ± 0.06	9.36 ± 0.05	12.79 ± 0.08	6.37 ± 0.04	Pink to green

Table 2: Mean (n=5) screening results of acid *versus* base titrations

Sr. No.	Indicators	pH Change	HCl (titrant) v/s $NaHCO_3$ (titre)		HCl (titrant) v/s Na_2CO_3 (titre)		End point
			Burette reading (ml)		Burette reading (ml)		
			0.5M	1M	0.5M	1M	
Standard indicator							
1	Methyl orange	3.0- 4.5	15.58 ± 0.03	9.17 ± 0.05	30.27 ± 0.11	15.60 ± 0.10	**Yellow to pink**
Flower extract							
1	Hibiscus Rosa -sinensis	9.7-10.2	15.27 ± 0.06	8.69 ± 0.02	32.03 ± 0.06	15.67± 0.06	Green to orange
2	Calotropis gingantia	9.3- 9.7	15.69 ± 0.02	9.07 ± 0.06	30.67 ± 0.05	15.87 ± 0.12	Green to pink
3	Brassica Oleracea Capitata	9.2- 10.3	15.58 ± 0.03	8.64 ± 0.07	31.57 ± 0.06	16.33 ± 0.11	Green to pink
4	Rosa Chinensis	8.7- 10.6	15.39 ± 0.01	9.17 ± 0.05	31.03 ± 0.06	15.43 ± 0.11	Yellow brown to orange
5	Brassica Oleracea Italica	6.5- 8.5	15.47 ± 0.06	8.67 ± 0.06	31.06 ± 0.11	16.23 ± 0.15	Yellow to colorless
6	Ixora Chinensis	7.0- 8.2	15.69 ± 0.03	8.86 ± 0.07	30.10 ± 0.10	16.47 ± 0.06	Yellow to orange
7	Cantharanthus Roseus	8.6- 10.1	16.04 ± 0.07	8.58 ± 0.03	30.13 ± 0.12	15.57± 0.15	Green to pink

The flower extract of *Hibiscus rosasinensis, Calotropis gingantia, Brassica oleracea-capitata, Rosa chinensis, Brassica oleracea-italica, Ixora chinensis, and Cantharanthus roseus* was found to have coloring matter poly-phenolic, flavonoids, and anthocyanins and is pH sensitive. For all types of titrations, the equivalence points obtained by the flower extract either exactly coincided or very closed with the equivalence point obtained by the standard indicators. This represent the usefulness of flower extract as an indicator in acid base titrations while in case of weak acid and weak base titration, the results obtained by the flower extract matched with the results obtained by standard indicator. But it was noted that if we decreased the strength of weak acid and weak base, the sharpness of color change was also deceased. Thus, the results obtained showed that the routinely used indicator can be replaced successfully by fruits extracts. Also the natural indicator employed in the acid base titrations was found economic, safe and an efficient alternative for traditional indicators. In comparison to this, chemical indicators were found more expensive and hazardous, which proves that the mentioned flower extracts as a natural indicator is more worthy.

Promising results were obtained when it was tested against standard synthetic indicators. Titration shows sharp color change at the equivalence point. This indicator was found to be useful in all type of acid-base titrations except weak acid and weak base titration. It was found very useful, economical, simple and accurate indicator for said titrations.

CONCLUSION:

The results obtained in all the types of acid-base titrations lead us to conclude that, it was due to the presence of flavonoids, sharp color changes occurred at end point of the titrations. At the end we can also state that, it is always beneficial to use *Hibiscus rosasinensis, Calotropis gingantia, Brassica oleracea-capitata, Rosa chinensis, Brassica oleracea-italica, Ixora chinensis, Cantharanthus roseus* flower extract as an natural indicator in all types of acid base titrations because of its economy, simplicity and wild availability.

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