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Short Communication

Natural Indicators

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Abstract

Colours of substances make the world a wonderful place. Because of the colours and structures; flowers, plants, animals and minerals show their unique characters. There are various organic and inorganic compounds responsible for natural colours. Many researchers adopted the suitable techniques under different conditions for the isolation of compounds from flowers and used as indicators. Most of these indicators are organic dye and are of synthetic origin. Indicators used in titration show well marked changes of color in certain intervals of pH depending on whether they donate or accept proton. Therefore pH indicators are themselves acids or bases. Due to environmental pollution, availability and cost of synthetic indicators, the search for natural compounds as an acid-base indicator was started. In the present work acid base titration has been performed by using natural indicators. The natural indicator is prepared from the most commonly occurring flowers of *Lantana camara* L, *Crossandra infundibuliformis* Nees, *Hibiscus syriacus, Tagetes erecta.* Extracts of flowers were used as natural indicator. The results obtained by the natural indicators are almost similar to the results given by the synthetic indicator. These indicators were found to be useful in all type of acid-base titrations.

Keywords: Natural indicators, *Lantana camara* L, *Crossandra infundibuliformis* Nees, *Hibiscus syriacus, Tagetes erecta.*

Introduction

The method of wet chemistry such as titrimetric analysis and gravimetry still has an important role in modern analytical chemistry. There are many areas in which titrimetirc procedures are valuable. The term titrimetric analysis refer to quantitative chemical analysis carried out by determining volume of solution of accurately known concentration which is required to react quantitatively measured volume of solution of substance to be determined.[1] The point at which equivalent quantities of reagents are present is detected using indicators. Hence indicators are used to locate the equivalent point of a titrations.[2] Indicators are dyes or pigments that can be isolated from a variety of sources, including plants, fungi, and algae. Almost any flower, for example, that is red, blue, or purple in color contains a class of organic pigments called anthocyanins that change color with pH.

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The use of natural dyes as acid-base indicators was first reported in 1664 by Sir Robert Boyle in his collection of essays Experimental History of Colors. Indeed, Boyle made an important contribution to the early theory of acids and bases by using indicators for the experimental classification of these substances.[3] Many researchers adopted the suitable techniques under different conditions for the isolation of compounds from flowers and used as dye.[4] There are various organic and inorganic compounds responsible for natural colours. Some of the organic compounds i.e. flavonoids, flavonols, acylated flavonoids, anthocyanins, glucosylated acylated anthocyanin, quinines, imines, polymethines, napthaquinones, anthraquinonoids, indigoids; dihydropyrans diarylmethanes carotene, etc. imparts colours to the flower. Among them anthocyanidins and flavones are main.[5] The advantage of natural indicators is that they are biodegradable thus helps in minimizing the use of synthetic non degradable dyes. Hence in this work, we described the use of flower extracts as an indicator for titration.

Lantana camara L (Verbenaceae) is an invasive species and has covered large areas in India, Australia and much of Africa.[6] Lantana camera is a rugged evergreen shrub growing to 1.8 m high. Stems are square in profile, with small prickles. The leaves are arranged in opposite pairs. They are broadly oval, rough with short hairs, with finely toothed edges. When crushed they have a strong smell. Flowers are a mixture of cream, pink or orange numerous small rounded heads, often in two colours, yellow and red. Fruits are fleshy berries in clusters, green ripening to black. *Lantana* species are widely spread weeds in warm climates.[7] It contains Triterpenes (lantadene A and lantadene B); Monoterpenoids; sesquiterpenoids; Iridoid glycoside (theveside) umuhengerin, Verbascoside, Flavonoids (camaraside), Phenylpropanoids (lantanaside).[7,8,9] It is used in treatment of sepsis; vermifuge; tetanus, rheumatism, malaria; diarrhoea; carminative, spasms, tumours, toothache, cold, uterine haemorrhage, chicken pox, eye injuries, whooping cough, asthma, bronchitis, ulcers, leprosy and scabies.[7] *Crossandra infundibuliformis* Nees (Acanthaceae) is an evergreen plant, native to North and South Karnataka and Maharashtra. It is best known and cultivated for flowers.[10] In India, the plant is considered an aphrodisiac; it is ornamental and bears red flowers which have high value in the Indian flower market.[11] It contains saponins, phytosterols, phenolic compounds, flavanoids, tannins, carbohydrates, terpenoids, oils and fats.[12] It is used as antibacterial, antifungal, anticanadial, aphrodisiac.[12,13] *Hibiscus syriacus* (Malvaceae) is a species of flowering plant, native to Asia.[14] *Hibiscus syriacus* is a hardy deciduous shrub. It is upright and vase-shaped, reaching 2–4 m (7–13 ft) in height, bearing large trumpet-shaped dark pink flowers with prominent yellow-tipped white stamens.[15] The bark contains several medically active constituents, including mucilage, carotenoids, sesquiterpenes and anthocyanidins. The leaves are diuretic, expectorant and stomachic.[16] A decoction of the flowers is diuretic, ophthalmic and stomachic. It is also used in the treatment of itch and other skin diseases.[17] A decoction of the root bark is antiphlogistic, demulcent, emollient, febrifuge, haemostatic and vermifuge. It is used in the treatment of diarrhoea, dysentery, abdominal pain, leucorrhoea, dysmenorrhoea and dermaphytosis.[17] *Tagetes erecta (*Asteraceae) is Mexican marigold, also called Aztec marigold, is native to Mexico and Central America. It is commonly known as aromatic annual herb reaches 0.4-1 m height. It is very popular as a garden plant and yields a strongly aromatic essential oil (tagetes oil), which is mainly used for the compounding of high-grade perfumes.[18] The plant *Tagetes erecta* has been shown to contain quercetagetin, a glucoside of quercetagetin, phenolics, syringic acid, methyl-3, 5-dihydroxy-4- methoxy benzoate, quercetin, thienyl and ethyl gallate.[18,19] The leaves are reported to be effective against piles, kidney troubles, muscular pains, ulcers, and wounds. The pounded leaves are used as an external application to boils and carbuncles. It is reported to have antioxidant, antimycotic, analgesic activity.[20,21] The flower is useful in fevers, epileptic fits (Ayurveda), astringent, carminative, stomachic, scabies and liver complaints and is also employed in diseases of the eyes. They are said to purify blood and flower juice is given as a remedy for bleeding piles and also used in rheumatism, colds and bronchitis.[22,23] The advantage of natural indicators is that they are biodegradable thus helps in minimizing the use of synthetic non degradable dyes. Hence in this work, we described the used of flower extracts as an indicator for titration.

Experimental

Fresh flowers were collected from the local gardens of satara regions, Maharashtra, and they were authenticated from Yashavant rao chavan science college botany department, Satara. All other ingredients were of analytical grade and purchased from Loba Chemie Pvt Ltd, Mumbai.

Method

The flowers were cleaned by using distilled water and cut into small pieces and macerated for 20 mins in 25ml of 90% ethanol. The extract was preserved in tight closed container and stored away from direct sun light. The experiment was carried 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 flowers extract, the reagents were not calibrated. The equimolar titrations were performed using 10 ml of titrant with three drops of indicator. A set of four experiments each for all the types of acid base titrations were carried out.

The mean and standard deviation for each type of acid base titrations were calculated from results obtained for Strong acid-strong base (HCl - NaOH), strong acid- weak base (HCl – NH_4OH), weak acid-strong base (CH_3COOH - NaOH) and weak acid-weak base (CH_3 COOH - NH_4OH) are listed. Each titration is carried out three times by using 1N, 0.1N, 0.5N strength of acid and alkali and results were recorded as mean ± SEM.[24]

Results and Discussion

Table 1: Acid-Base titrations using Standard Indicators.

Titration (Titrant v/s Titrate)	Strength in moles	Indicator	Mean ±S.D.*	Color
1) Hcl v/s NaOH	1.0	Methyl orange	9.26±0.1528	Yellow to pink
	0.5	Methyl orange	9.066±0.1528	Yellow to pink
	0.1	Methyl orange	9.3±0.20	Yellow to pink
2) HCl v/s NH_4OH	1.0	Methyl red	9.1±0.10	Pink to yellow
	0.5	Methyl red	9.26±0.1155	Pink to yellow
	0.1	Methyl red	9.3±0.02	Pink to yellow
3) CH_3COOH v/s NaOH	1.0	Phenolphthalein	9.233±0.1155	Colorless to pink
	0.5	Phenolphthalein	9.186±0.08083	Colorless to pink
	0.1	Phenolphthalein	9.2466±0.01528	Colorless to pink
4) CH_3COOH v/s NH_4OH	1.0	Methyl Orange	10.226±0.02517	Orange to pink
	0.5	Methyl Orange	10.0566±0.05132	Orange to pink
	0.1	Methyl Orange	10.3433±0.0404	Orange to pink

*All values are mean ± S.D. for n=3

Table 2: Acid-Base titrations using *Latanta camara as* Indicators.

Titration (Titrant v/s Titrate)	Strength in moles	Indicator	Mean ±S.D.*	Color
1) Hcl v/s NaOH	1.0	*Latanta camara*	9.16±0.1155	Yellow-colorless
	0.5	*Latanta camara*	9.2±0.2000	Yellow-colorless
	0.1	*Latanta camara*	9.1±0.1000	Yellow-colorless
2) HCl v/s NH_4OH	1.0	*Latanta camara*	8.5±0.01528	Yellow-colorless
	0.5	*Latanta camara*	8.9±0.02	Yellow-colorless
	0.1	*Latanta camara*	8.7±0.1528	Yellow-colorless
3) CH_3COOH v/s NaOH	1.0	*Latanta camara*	8.6±0.2000	Yellow-colorless
	0.5	*Latanta camara*	9.4133±0.01528	Yellow-colorless
	0.1	*Latanta camara*	9.1066±0.08622	Yellow-colorless
4) CH_3COOH v/s NH_4OH	1.0	*Latanta camara*	9.556±0.05508	Yellow-colorless
	0.5	*Latanta camara*	9.863±0.03055	Yellow-colorless
	0.1	*Latanta camara*	9.2433±0.03215	Yellow-colorless

*All values are mean ± S.D. for n=3

Table 3: Acid-Base titrations using *Crossandra infundibuliformis as* Indicators.

Titration (Titrant v/s Titrate)	Strength in moles	Indicator	Mean ±S.D.*	Color
1) Hcl v/s NaOH	1.0	*Crossandra infundibuliformis*	9.9±0.1528	Yellow-colorless
	0.5	*Crossandra infundibuliformis*	6.3±0.1732	Yellow-colorless
	0.1	*Crossandra infundibuliformis*	6.63±0.2517	Yellow-colorless
2) HCl v/s NH_4OH	1.0	*Crossandra infundibuliformis*	9.3±0.1732	Yellow-colorless
	0.5	*Crossandra infundibuliformis*	9.63±0.2517	Yellow-colorless
	0.1	*Crossandra infundibuliformis*	9.1±0.100	Yellow-colorless
3) CH_3COOH v/s NaOH	1.0	*Crossandra infundibuliformis*	7.533±0.0577	Yellow-colorless
	0.5	*Crossandra infundibuliformis*	8.443±0.1106	Yellow-colorless
	0.1	*Crossandra infundibuliformis*	6.03±0.07000	Yellow-colorless
4) CH_3COOH v/s NH_4OH	1.0	*Crossandra infundibuliformis*	5.36±0.2516	Yellow-colorless
	0.5	*Crossandra infundibuliformis*	6.036±0.0404	Yellow-colorless
	0.1	*Crossandra infundibuliformis*	5.18±0.09165	Yellow-colorless

*All values are mean ± S.D. for n=3

Table 4: Acid-Base titrations using *Tagetes erecta as* Indicators.

Titration (Titrant v/s Titrate)	Strength in moles	Indicator	Mean ±S.D.*	Color
1) Hcl v/s NaOH	1.0	*Tagetes erecta*	7.56±0.1000	Yellow-colorless
	0.5	*Tagetes erecta*	9.86±0.05774	Yellow-colorless
	0.1	*Tagetes erecta*	9.86±0.1528	Yellow-colorless
2) HCl v/s NH_4OH	1.0	*Tagetes erecta*	7.26±0.1725	Yellow-colorless
	0.5	*Tagetes erecta*	8.1±0.100	Yellow-colorless
	0.1	*Tagetes erecta*	6.56±0.05667	Yellow-colorless
3) CH_3COOH v/s NaOH	1.0	*Tagetes erecta*	2.433±0.1528	Pink-colorless
	0.5	*Tagetes erecta*	2.486±0.06807	Pink-colorless
	0.1	*Tagetes erecta*	2.65±0.2170	Pink-colorless
4) CH_3COOH v/s NH_4OH	1.0	*Tagetes erecta*	2.28±0.02000	Pink-colorless
	0.5	*Tagetes erecta*	2.956±0.05132	Pink-colorless
	0.1	*Tagetes erecta*	2.04±0.03606	Pink-colorless

*All values are mean ± S.D. for n=3

Table 5: Acid-Base titrations using *Hibiscus syriacus as* Indicators.

Titration (Titrant v/s Titrate)	Strength in moles	Indicator	Mean ±S.D.*	Color
1) Hcl v/s NaOH	1.0	*Hibiscus syriacus*	7.36±0.1528	Yellow-colorless
	0.5	*Hibiscus syriacus*	5.66±0.152	Yellow-colorless
	0.1	*Hibiscus syriacus*	7.33±0.2082	Yellow-colorless
2) HCl v/s NH_4OH	1.0	*Hibiscus syriacus*	6.33±0.2082	Light green-Yellow
	0.5	*Hibiscus syriacus*	8.86±0.1582	Light green-Yellow
	0.1	*Hibiscus syriacus*	7.9±0.1465	Light green-Yellow
3) CH_3COOH v/s NaOH	1.0	*Hibiscus syriacus*	3.733±0.05774	Pink- colorless
	0.5	*Hibiscus syriacus*	1.863±0.2173	Pink- colorless
	0.1	*Hibiscus syriacus*	2.6966±0.09074	Pink- colorless
4) CH_3COOH v/s NH_4OH	1.0	*Hibiscus syriacus*	1.12±0.02646	Pink-Yellow
	0.5	*Hibiscus syriacus*	2.056±0.05132	Pink-Yellow
	0.1	*Hibiscus syriacus*	1.646±0.04509	Pink-Yellow

*All values are mean ± S.D. for n=3

The flower extracts were screened for its use as an acid base indicator in acid base titrations and the result of this screening were compared with the results obtained by standard indicators methyl red, phenolphthalein, methyl orange (Table No.1). The results of the screening of flower extracts for strong acid and strong base (HCL & NaOH), strong acid and weak base (HCL & NH_4OH), weak acid and strong base (CH_3COOH & NaOH) and weak acid and weak base (CH_3COOH & NH_4OH) are listed in Table No. 2, 3, 4, 5. The tables represents mean of three titrations and standard deviation. For all types of titrations equivalence point obtained by the flower extracts of *Crossandra infundibuliformis, Lantana camara* either exactly coincided or very closed with the equivalence point obtained by the standard indicators as compared to the equivalence point obtained for *Hibiscus syriacus, Tagetes erecta*. It may be due to presence of flavonoids and anthocynins in the flower extracts. This represent the usefulness of flower extracts as an indicator in acid base titrations. Its use in acid- base titrations was found to be more significant over standard indicator as it gives sharp colour change in a narrow pH range and chemical indicators were found more expensive and hazardous. The results obtained showed that the routinely used indicator can be replaced successfully by flower extracts.

Conclusion

The results obtained in all the types of acid base titrations lead us to conclude that it may be due to the presence of flavonoids and anthocynins sharp colour changes which occurred at end point of titrations showed that the routinely used indicators could be replaced successfully by flower extract as they are simple, accurate, economical and precise. Hence, we can also conclude that, it is always beneficial to use *Crossandra infundibuliformis, Lantana camara, Hibiscus syriacus, Tagetes erecta* flowers extracts as an indicator in all types of acid base titrations because of its economy, simplicity and wild availability.

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