Report
on
Minor Research Project
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# Development of Eco-friendly Green Indicator for Volumetric Titration Methods


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# Development of eco-friendly green indicator for volumetric titration methods

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**Abstract**

Number of synthetic indicators are available to determine the equivalence point and understand the chemistry of acid-base titrations as well as determination of strength of acid and base. This is due to its sharp color change as response to the change in pH. Generally, these indicators are highly volatile, costly and non-ecofriendly. These indicators are also used to determine the content of different metal ions in water samples to check the quality of water. Easily available and cost effective natural indicators are thus being explored in last few decades to overcome the environmental pollution. Usage of natural indicators as an alternative to synthetic indicators, can help in reduction of the soil and water pollution up to a great extent. Today various plants' extracts are used as a natural acid-base indicator. They are also capable of giving comparable results with synthetic indicators. In this project, investigators have thus developed a natural indicator prepared from the flowers extract of Plumeria Rubara f. Rubra and proposed applications of this new indicator in acid-base titration as well as in the determination of percentage assay content for copper salts, which is very useful in laboratories.

*Keywords:* Plumeria rubra f. rubra, natural indicators, copper salts, acid-base titrations

## Introduction

Volumetric titration is one of the most commonly used quantitative techniques in chemical analysis in industries, academic institutions and wide range of fields.[1] Indicators are the substances used to determine the end point in volumetric titrations due to their color changing properties with different pH.[2] They are usually weak acid or base; which generally exist in two tautomeric forms in which at least one is colored. They may be used as external (added during the titration) or internal (self-indicator) analysis tool. Number of indicators are used in different types of titrations such as acid-base titration, redox titration, precipitation titration, complexation titration, non-aqueous titration etc. Different indicators work on the basis of diverse mechanisms. Phenolphthalein, Methyl orange, Crystal violet, Methylene blue and Methyl red are the most commonly used synthetic indicators for volumetric titrations in laboratories. These indicators are used due to their ability to give sharp color change at different pH. Due to the consideration towards the safety of the users and the environment, the continuous use of synthetic indicators has become questionable. Moreover, the cost of proper chemical disposal strategies is lacking in place and can easily contaminate the drinking water from the public water supply system.[3]–[5]

Natural indicators used in volumetric titrations are various types of dyes or pigments, which can be extracted from different sources including flower petals, fruits, vegetables, plants, fungi and algae.[6] Work on diverse types of natural indicators is being carried out as they serve as the best substitutes of synthetic indicators. Apart from being non-hazardous, low-cost and easily available, they also give almost accurate results as compared to the synthetic indicators. Hence it is interesting to discover different types of natural indicators for the titrimetric analysis and their isolation and characterization. Many researchers have reported the practical efficiency and usefulness of natural indicators extracted from various plants and other natural sources in acid- base titrations.[4], [7]–[10]

Many flowers are used as natural indicator for acid base titration due to their ability to change the colour in acidic and basic medium because if the presence of natural pigments.[11] These pigments can also act as a ligand and can lead to the formation of a complex compound with different transition metal ions. Out of all these, Plumeria rubra flowers are well known for their medicinal properties [12]–[15] but it is very less discovered for its properties as an indicator. Four different forms are available of Plumeria rubra (Champa) flower (Fig 1):[16]

- Plumeria rubra f. acutifolia
- Plumeria rubra f. lutea
- Plumeria rubra f. rubra
- Plumeria rubra f. tricolor

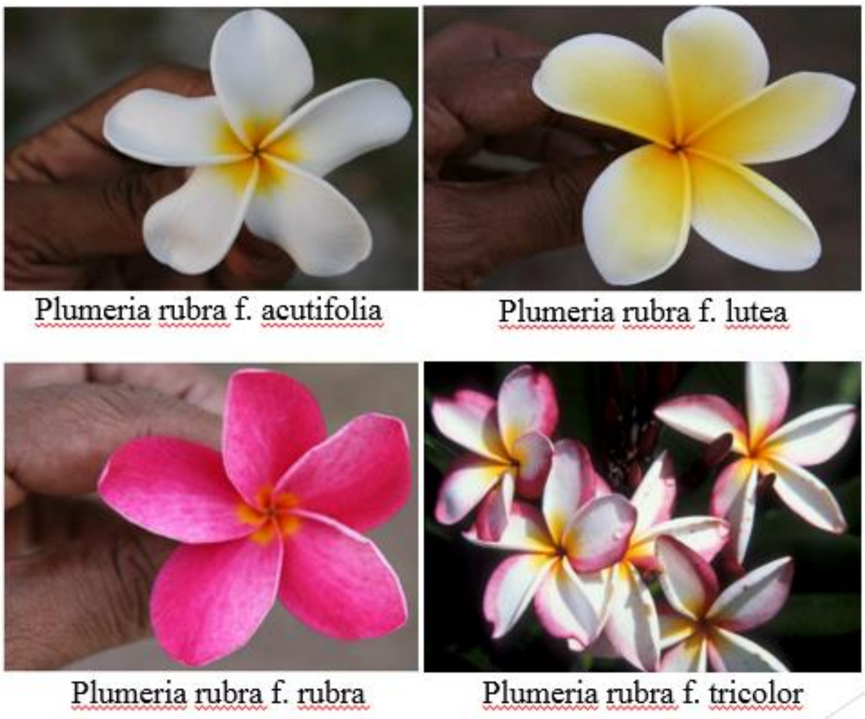


**Fig 1.** Different forms of of Plumeria rubra (Champa) flower

In this MRP, the investigators have discovered the properties of pink colored Plumeria Rubara f. Rubra flower petals extract as an indicator for acid-base titration. Moreover, it has been studied as an indicator for the determination of percentage assay content for different copper salts by titrimetric method.

## Materials and method

Plumeria rubra f. rubra flowers petals collected from Nirma University camputs. AR grade methanol was used to prepare the extract of flower petals. LR grade NaOH, KOH, HCl, $H_2SO_4$, $HNO_3$ and $CH_3COOH$ were used for the acid-base titration. Double distilled water was used to clean the apparatus and preparation and dilution of the solutions. Different LR hydrated copper salts and LR grade EDTA were used for the calculation of percentage assay. such as Cupric sulphate pentahydrate ($CuSO_4.5H_2O$), Cupric chloride dihydrate ($CuCl_2.2H_2O$), Cupric acetate monohydrate ($Cu(CH_3COO)_2.H_2O$), Cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$). For the uniform dissolution of salts in double distilled water, Sonicator was used and for the filtration of solutions, vacuum filtration assembly was used. Analysis has been performed by standard titrimetric and spectrophotometric methods. The method of flower petal extract preparation has been depicted in Fig 2. The flower extract was used for different titration purpose directly without any further dilution. The stock solutions of 2000 ppm of different copper salts prepared in double distilled water and diluted as and when required.

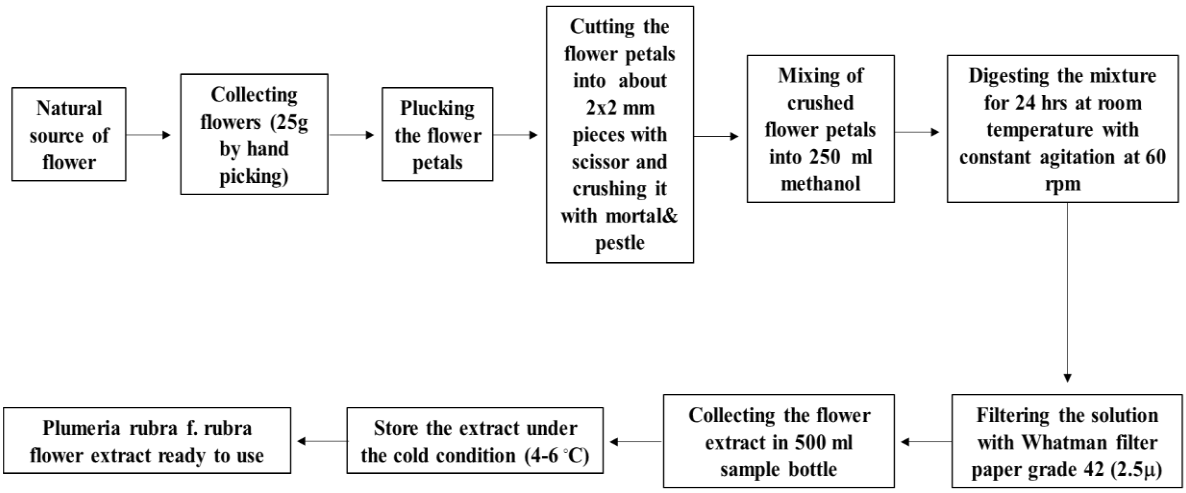


**Fig 1.** Method for the preparation of of Plumeria rubra f. rubra flower petal extract

## Results and discussion

### *As an acid-base indicator*

Plumeria rubra f. rubra flower extract was directly used as an indicator in acid base titration similarly as we are using other synthetic indicator such as phenolphthalein, methyl orange etc. but in little more quantity compared to the synthetic indicators as it is a natural indicator but it gave very sharp and distinct color change at the end point. The original color of flower petal extract is dark pink. In acidic medium it gives light pink color but in basic medium it gives brownish green color at the end point; which is very sharp and distinct to confirm the completion of titration and it is in agreement with the standard method using synthetic indicators.

### *As a complexometric indicator*

The extract of Plumeria rubra f. rubra flower extract has been studied as an indicator for the titrimetric method for the calculation of assay content of different copper salts listed in the materials and method section. It gave green color with different copper salts depending upon the anion attached with copper and also the number of water molecules associated with it. Colors of different copper salts and their complexes with newly developed indicator have been shown in Fig. 3.

Results for the acid-base titration with newly developed indicator has been summarized in Table 1 (A & B) and The calculation of assay content of different copper salt has been shown in Table 2. The calculation of percentage assay on as is basis as well as on anhydrous basis for all copper salts has been done with the help of formula given below.[17]

$$\%\ Assay\ (as\ is\ basis) = \frac{(Burette\ reading\ (ml) x\ Normality\ of\ EDTA\ x\ Formula\ weight\ factor\ x\ 100)}{Weight\ of\ copper\ salt\ in\ mg}$$

$$\%\ Assay\ (on\ anhydrous\ basis) = \frac{(Assay\ on\ as\ is\ basis\ x\ 100)}{(100 - \%\ water\ content)}$$

The results in Table 1 show that the end point obtained with newly developed indicator and with synthetic indicators are almost equal, comparable and well in agreement. On the other hand, the results in Table 2 show that the experimental values of the percentage assay of different copper salts are also well in agreement with the standard limit of specifications for the titrimetric analysis i.e. between 98-102 %w/w on anhydrous basis.

Spectrophotometric analysis of different copper salts and their complexes with newly developed indicator was performed using micro spectrophotometer. The analysis confirms the conversion of copper salts into their copper complexes with the change in color of salts. All the copper salts were of sky blue color and after the conversion into the complex, they turned into green color. This feature of the color change can be used as an identification method in qualitative analysis to check the presence of copper ion in any sample solution. This was confirmed by shifting of their wavelengths from lower to higher side i.e. with the help of spectrum Red Shift. All copper salts have single maximum of wavelength at 465 nm, which was then shifted to 410 nm (major) and 576 nm (minor) after the complex formation. After the titration with standard EDTA solution, this maximum of wavelength further shifted at 395 nm (major) and 529 nm (minor).

The titrations of copper salts were performed using standard EDTA solution and it regain the original sky blue color of copper salt. This is due to the green colored complex formation between copper and newly developed indicator followed by the breaking this complex and a new sky blue colored complex formation with copper and EDTA; but with different wavelengths, which shows that the product is again a new complex which is probably due to the complex formation of copper salt with EDTA. The mechanism may be proposed for two different coordination number 4 (Mechanism A) and 6 (Mechanism B) shown in Fig. 4.

### *Semi validation of newly developed methods*

The semi validation of both the methods for acid-base as well as percentage assay with a newly developed natural indicator has been conducted with different criteria of validation such as specificity, reproducibility, accuracy and precision, linearity, robustness, stability study at different temperature. The indicator is stable up to 12 weeks at normal room temperature and stable up to 24 weeks if stored in refrigerator at about 5-10 ˚C, provided it should be stored in air tight bottle due to the volatility of methanol. The photostability was also checked by exposing the indicator in sunlight for 72 hrs and found that it is not getting affected by the sun light radiation even up to 72 hrs which shows the photostability of the indicator. This newly developed natural indicator meets all the criteria in a specified limit, which indicates that this method is ready to use in laboratory with eco-friendly aspects.

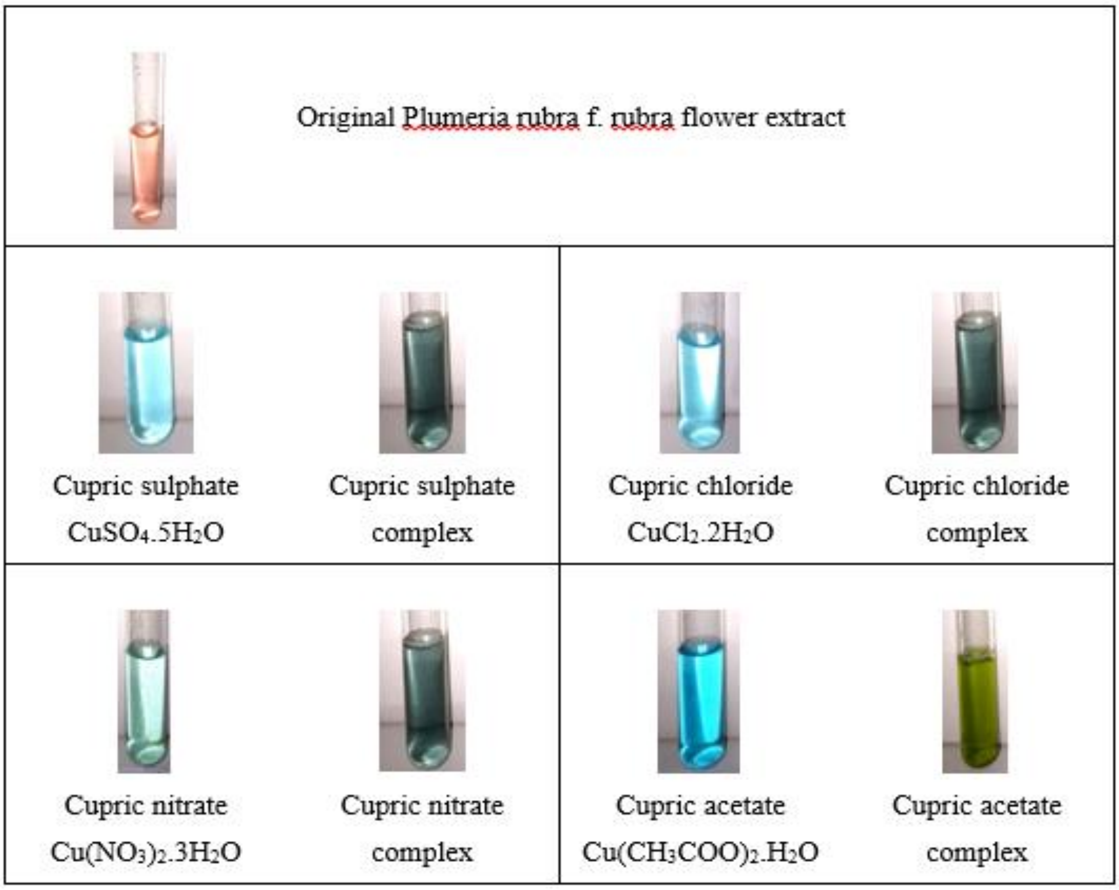


**Fig 3.** Colored complex formation with different copper salts

$$CuSO_4 + 4L \longrightarrow [Cu(L)_4]SO_4$$

$$CuCl_2 + 4L \longrightarrow [Cu(L)_4]Cl_2$$

$$Cu(OAc)_2 + 4L \longrightarrow [Cu(L)_4](OAc)_2$$

$$Cu(NO_3)_2 + 4L \longrightarrow [Cu(L)_4](NO_3)_2$$

**Mechanism A**

$$CuSO_4 + 6L \longrightarrow [Cu(L)_6]SO_4$$

$$CuCl_2 + 6L \longrightarrow [Cu(L)_6]Cl_2$$

$$Cu(OAc)_2 + 6L \longrightarrow [Cu(L)_6](OAc)_2$$

$$Cu(NO_3)_2 + 6L \longrightarrow [Cu(L)_6](NO_3)_2$$

**Mechanism B**

**Fig 4.** Proposed mechanism for the complex formation

**Table 1 (A)** Titration of acids with NaOH

| Name of Acid | Normality of acid | Volume of acid used in ml | Normality of NaOH | Burette reading with synthetic indicator in ml | Burette reading with new indicator in ml |
|---|---|---|---|---|---|
| Hydrochloric acid (HCl) | 0.1 | 10 | 0.1 | 9.9 | 9.8 |
| | | | | 9.9 | 9.8 |
| | | | | 10.0 | 9.9 |
| Sulfric acid ($H_2SO_4$) | 0.1 | 10 | 0.1 | 10.0 | 9.9 |
| | | | | 10.0 | 9.9 |
| | | | | 9.9 | 9.9 |
| Nitric acid ($HNO_3$) | 0.1 | 10 | 0.1 | 9.9 | 9.8 |
| | | | | 9.9 | 9.8 |
| | | | | 9.8 | 9.8 |
| Acetic acid ($CH_3COOH$) | 0.1 | 10 | 0.1 | 9.9 | 10.0 |
| | | | | 9.9 | 10.0 |
| | | | | 10.0 | 9.9 |

**Table 1 (B)** Titration of acids with KOH

| Name of Acid | Normality of acid | Volume of acid used in ml | Normality of KOH | Burette reading with synthetic indicator in ml | Burette reading with new indicator in ml |
|---|---|---|---|---|---|
| Hydrochloric acid (HCl) | 0.1 | 10 | 0.1 | 10.0<br>10.0<br>10.0 | 9.8<br>9.9<br>9.9 |
| Sulfric acid ($H_2SO_4$) | 0.1 | 10 | 0.1 | 10.0<br>9.9<br>9.9 | 10.0<br>10.0<br>9.9 |
| Nitric acid ($HNO_3$) | 0.1 | 10 | 0.1 | 9.8<br>9.8<br>9.8 | 9.7<br>9.7<br>9.7 |
| Acetic acid ($CH_3COOH$) | 0.1 | 10 | 0.1 | 9.9<br>10.0<br>10.0 | 9.8<br>9.8<br>9.9 |

**Table 2** Percentage assay calculation for different copper salts

| Compound | Burette Reading V ml | Normality of EDTA | Formula weight factor | Weight in mg | % Assay as such basis | % Water | % Assay on anhydrous basis | Avg. % Assay on anhydrous basis |
|---|---|---|---|---|---|---|---|---|
| $CuSO_4.5H_2O$ | 6.55 | 0.0960 | 24.97 | 24.952 | 62.92 | 36.08 | 98.44 | 98.51 |
| | 6.55 | | | 24.981 | 62.85 | | 98.32 | |
| | 6.65 | | | 25.245 | 63.14 | | 98.78 | |
| $CuCl_2.2H_2O$ | 8.15 | 0.0960 | 17.05 | 17.112 | 77.95 | 21.14 | 98.84 | 98.54 |
| | 8.20 | | | 17.325 | 77.46 | | 98.23 | |
| | 8.05 | | | 16.952 | 77.72 | | 98.55 | |
| $Cu(NO_3)_2.3H_2O$ | 7.90 | 0.0960 | 24.16 | 24.025 | 76.27 | 22.37 | 98.25 | 98.41 |
| | 8.00 | | | 24.235 | 76.57 | | 98.63 | |
| | 8.15 | | | 24.756 | 76.36 | | 98.36 | |
| $Cu(CH_3COO)_2.H_2O$ | 9.35 | 0.0960 | 19.96 | 20.010 | 89.56 | 9.02 | 98.43 | 98.42 |
| | 9.20 | | | 19.710 | 89.46 | | 98.33 | |
| | 9.15 | | | 19.572 | 89.60 | | 98.49 | |

## Conclusion

From the study, it can be concluded that Plumeria rubra f. rubra flower petal extract in methanol is a very good acid-base indicator due to the presence of pigments and can be used instead of regular synthetic indicator to reduce the pollution. These pigments can also act as ligand and can lead to the complex formation with copper ion with different colours. It can be used for the identification and quantification of copper ions in waste water by EDTA complexometric titration method. It will be definitely a very easy and economic tool to minimize the water and soil pollution as it is a natural and biodegradable compound.

## Acknowledgement

PI and Co-PI are thankful to the management of Nirma Unviersity, Ahmedabad, Gujarat for providing us financial support under the Minor Research Project. They are also thankful to the laboratory staff Mr. Devendrabhai Patel, Mr. Manishbhai Patel and Mr. Dhavalbhai Oza for providing their valuable support during the purchase of chemicals, glassware, equipment and during the experimental work for this project.

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