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Comparative Analysis of *Curcuma longa* Rhizome and *Tectona* grandis Leaves Extracts as Green Indicators versus some Synthetic Indictors in Acid-Base Titration

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ABSTRACT: The work considered comparative analysis of CRI (Curcuma longa rhizome extract indicator) and TLI (Tectona grandis leaves extract indicator) as green indicators versus some synthetic indicators in acid – base titration involving HCl-NaOH, CH3COOH-NaOH, CH3COOH -NH4OH, and HCl-NH4OH. The codes used were SA (strong acid), SB (strong base), WA (weak acid) and WB (weak base). 10 mL of the base with three drops of the CRI, TLI, MO (methyl orange), and PL (phenolphthalein) were used. Prior to the titrations, the extracts of Curcuma longa rhizome and Tectona grandis leaves were tested for their colours in acidic and basic media. Also, the UV-visible absorptions of the extracts were determined. There were sharp colours of yellow (for CRI) and red (for TLI) in acid and brown (for CRI) and black (for TLI) in base media. Meanwhile, CRI absorbed (absorbance of 0.83-0.85) substantially at 400-450 nm, but gave lesser absorption at 500-800 nm with absorbance of 0.55-0.24. On the other hand, TLI was found with higher absorbance (0.09) at 400 nm and lesser absorption (absorbance ~0.04) at 720 nm. The titre values of 10.95±0.95 mL (SA-SB), 13.75±0.15 mL (WA-SB), 2.15±0.15 mL (WA-WB), 1.85±0.05 mL (SA-WB) and 11.70±0.3 mL (SA-SB), 13.45±0.45 mL (WA-SB), 2.15±0.05 mL (WA-WB), 2.20±0 mL (SA-WB) were obtained for CRI and TLI, respectively. The results matched with the values 12.25±0.15 mL (SA-SB), 13.90±0.7 mL (WA-SB), 2.10±0.2 mL (WA-WB), and 3.00±0.6 mL (SA-WB) of PL and MO, respectively. It will be beneficial to us to replace the use of MO and PL as indicators with CRI and TLI, because these green indicators are more benign and also effective. This will facilitate the eradication of toxicity accruing from synthetic indicators, MO and PL. In the future, we are looking out to determining the pKa and stability of these natural indicators.

KEYWORDS: Green acid-base indicators, Synthetic indicators, Toxicity, *Curcuma longa*, *Tectona grandis*

1. Introduction

This There is dearth of basic science teaching materials in most undeveloped worlds because of high cost of such reagents and chemicals. Thus, it has become imperative that ardent scientists look out for possible improvisation of science teaching materials and reagents so as to maintain science knowledge dissemination for overall growth and development of mankind [1]. Furthermore, the natural resources, plants are ever thought to be vast and viable reservoir from which human can derived arrays of feedstock in addition to food for numerous in institutions of human facet. In such a manner, the overdependence on petroleum (a finite resource) for myriads of raw materials for our industries and allied purposes can be substantially shifted to renewable source. In view of this, there has been high quantum of surge about sourcing/ deriving chemicals from plant-based origin [2–9]. More recently, Green Chemistry has also underscored the need for sustainable development, which partly provides the use of benign and renewable materials instead petrochemicals [10]. In a nutshell, the derivation of



products from biomass entails overall reduction in environmental pollution for better wellbeing of humanity.

Now, one important classical reagent used in acid-base titrations is indicator. Indicators are usually added in small quantity to a solution to determine the acidity or alkalinity of the solutions [11]. Most of the pH indicators are weak organic acids or bases, which have tendency to accept or donate electrons. They are supposed to exhibit distinct coloration in acid, base, or neutral medium. In that way they will be effective for the detection of end point in acid-base titration [1,11]. Unfortunately, nowadays commonly used indicators are expensive and shows some toxic and hazardous effect [12 - 13]. Thus, we need to look out for indicators from natural sources in order to avoid unwanted deleterious effects of synthetic indicators. In fact, commonly used synthetic indicators have some harmful effects which are oftentimes ignored. For example, a commonly used indicator phenolphthalein has carcinogenic properties which may cause ovarian cancer. Methyl orange causes local skin destruction or dermatitis. Also, the repeated exposure of the methyl orange will impart lung damage and also eye irritation. Methyl red is capable of causing cancer and neurological disorder. Therefore, these indicate the harmful effects of the synthetic indicators to human, and the environment in general. More so, because of these unwanted and toxic effects of synthetic indicators, there has been high advocacy for natural/ green acid-base indicators [12]. These natural indicators should be easily available, easy to prepare, simple to extract out, less toxic, inexpensive, and eco-friendly [12 - 13]. Again, coloured flower/ plants have potentials as natural indicators due to the presence of anthocyanin, quinine, flavones, flavonoid etc [12]. Besides, intense/sharp colour is desirable so that very little quantity of indicator is used; the volume of the indicator itself should not affect the pH of the solution [11 - 12].

Therefore, natural fruits, vegetable, and flower indicators; apple skin, beets, blueberries, cabbage (red), cherries, cranberries, red or purple grapes, onions red, peaches, plums, radish skin, rhubarb skin, strawberries, tomato leaves, turnip skin dahlias, daylilies, geraniums, hibiscus, hollyhocks, hydrangeas, blue iris, morning glories, mums (purple), pansies, peonies, petunias, poppies, roses (red, pink), violets etc [14] have come onboard. Turmeric has also been demonstrated in the past as natural indicator. Main indicator characteristic compound of turmeric is curcumin. In acidic solution (pH < 7.4) it turns yellow, whereas in basic (pH >8.6) solution it shows bright red [13]. Other constituent present are volatile oils including turmerone, atlantone and zingiberone, sugars, proteins, and resins [13]. In [15], Euphorbia mili, Erythrina varigata, and Nelumbo nucifera methanolic and aqueous extract were positively used as acid-base indicator in titrations [15]. These green indicators were attested to be a very useful, economical, simple, accurate, and eco-friendly [15]. According to the results obtained from acid-base titrimetric analysis with plant (Tagetes Erecta, Impatiens Balsamina, and Tecoma stans) indicators, the tire values of these green indicators were insignificantly different from the synthetic counterparts [12]. However, rosa double delight flower did not give colour change for neither SA-SB nor WA-WB titration [12]. Other plants too, such as; daffodils, daisies, dandelions, marigolds, and mums (yellow) do not effectively give indicator properties [14]. In the titration of 0.1 M HCl - 0.1M NaOH; 24.75±0.16 mL, 24.60 ± 0.32 mL, 24.70 ±0.23 mL, 24.55 ±0.21 mL, 24.65±0.18 mL, 24.60±0.17 mL, and 24.70±0.14 mL titre values were obtained for Bougainvillea, Oleander, Flamboyant, Chinese rose, Pumpkin, Dutchman's pipe, and phenolphthalein, respectively [1]. In this study we report comparative analysis of CRI (Curcuma longa rhizome extract indicator) and TLI (Tectona grandis leaves extract indicator) as natural/ green indicators versus some synthetic indicators in acid-base titration. The results have importance in teaching of chemistry and science at large. It would also facilitate teachers' interest toward improvisation of teaching / learning material and learners' capacity for solving problems.

2. Materials and Methods

2.1. Materials/ Apparatus/ Reagents

100 mL beakers, mortar and pestle, measuring cylinder, 50 mL burette, 20 mL pipette, 100 mL conical flask, 1000 mL volumetric flask, funnel, white tile, clamp. Distilled water, 0.1 M hydrochloric acid, 0.1 M acetic acid, 0.1 M sodium hydroxide, 0.1 M ammonium hydroxide, UV-1800 Shimadzu UV-Visible spectrophotometer.

In addition, 5.748 mL (CH₃COOH), 5.86 mL (NH₄OH), and 8.7 6 mL (HCl) were separately transferred into 1000 mL volumetric flask and enough distilled water was added to mark to give a stock solution of 0.1 M CH₃COOH, 0.1 M NH₄OH, and 0.1 M HCl, respectively. Whereas 0.1 M NaOH was prepared by dissolving 4 g of NaOH pellets in 500 mL beaker using distilled water and was transferred in 1000 mL volumetric flask and enough distilled water was added to mark.

2.2. Methods

2.2.1. Sample Collection and Identification

Curcuma longa (turmeric) rhizome and *Tectona grandis* (teak) (see Figure 1 below) were collected from Makurdi municipal area of Benue State -Nigeria. The samples were subsequently identified by Mr. J. I. Wenga of the Dept. Biological Science, Benue State University, Makurdi - Nigeria.





Figure 1: Curcuma longa rhizome and Tectona grandis leaves

2.2.2. Sample Preparation and Extraction

About 30 g of the *Curcuma longa rhizome* and *Tectona grandis* leaves were washed and rinsed with distilled water to remove dirt. The rhizome of *Curcuma longa* and *Tectona grandis* leaves were separately triturated in mortar and about 5 g each transferred into 100 mL beakers. 20 mL of distilled water was added into each sample and left for 4 h for effective extraction. Thereafter, the mixture was filtered using whatman filter paper No.41 and the filtrates then collected into indicator bottles for the research work as similarly reported [1, 13].

2.2.3. Titration Procedure

0.1 M acid was titrated against 10 mL 0.1 M base using 3 drops of the indicator (synthetic and natural). Different acid-base combinations (HCl/NaOH, CH₃COOH/NaOH, CH₃COOH/NH₄OH and HCl/NH₄OH) were adopted.

3. Results and Discussion

3.1. Colour Results for CRI and TLI in different Media

The extracts from *Curcuma longa* rhizome and *Tectona grandis* leaves were found to show different colours in acidic and basic solutions. The products, CRI gave different sharp colours in acid (yellow) and base (brown). Whereas, TLI produced black colour in base and red colour in acid (see Figure 2). This then become a potential as previously demonstrated, for their ability as indicators in acid-base titration.

In [15], it was observed that many natural products around us like turmeric, mangosteen skin, and purple cabbage can be used as indicator of acid and base because these materials give a different color in acid, alkali, and neutral media. In addition, the UV-visible absorptions of the extracts were carried out between 300-800 nm. Higher absorption of UV-visible radiation for the CRI was found at 400-450 nm with absorbance of 0.83-0.85 and less absorption was found at 500-800 nm with absorbance of 0.55-0.24. For TLI, the λ max for the TLI was found at 400 nm with absorbance of 0.09 and lesser absorption was found at 720 nm with absorbance slightly above 0.04. Compounds that can absorbed in this region of the UVvisible radiation are conjugated and aromatic compounds. Hence, curcumin, flavonoids, flavonols, anthocyanins, quinines, quinones, and carotene are likely present in these extracts as previously established [12].

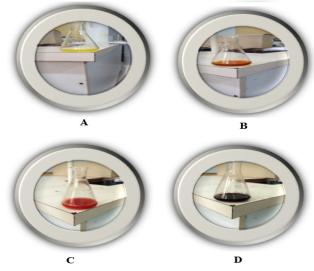


Figure 2: Colour change of the indicators in acidic and basic solution (A = CRI in acid (yellow); B = CRI in base (brown); C = TLI in acid (red); and D = TLI in base (black))

3.2. Results of the Acid- Base Titration Analysis

The titrimetry result using natural indicators (CRI and TLI) and some synthetic indicators are shown in the Table 1 as follows. The titre values obtained with the CRI and TLI were similar to those of the synthetic indicators. Different acid-base combinations (HCI-NaOH, CH₃COOH-NaOH, HCI-NH₄OH, and CH₃COOH-NaOH, NH₄OH) were employed during the titrations.

For the titration involving HCl-NaOH, it was found that the titre values of 10.95±0.95 mL and 11.70±0.3 mL for CRI and TLI, respectively were similar to that of PL (12.25±0.15 mL) as indicated in Table 1. In addition, for the SA -SB titration, there was colour change of the solution from pink to colourless for PL. Using CRI in the titration, brown to yellow colouration change was observed. Meanwhile, black to red change in colour was shown during the titration of the SA-SB with the usage of TLI.

Similarly, in the titration of WA-SB, the titre values of 13.75 \pm 0.15 mL, 13.90 \pm 0.7 mL, and 13.45 \pm 0.45 mL were obtained for CRI, PL, and TLI, respectively. All the indicators used (natural and synthetic) gave titre values that are absolutely comparative to one another. CRI changed from brown to yellow; whereas the TLI indicator showed black colour that changed into red during the WA-SB titration. Then PL produced colouration change of pink to colourless (find the details in Table 1). It was also reported in [13] that turmeric and PL produced endpoint values of 8.0 \pm 0.2 mL and 7.5 \pm 0.02 mL in the course of titration of HCl-NaOH [13].



Acid-	Titre value for	Colour	Titre value	Colour change	Titre value	Colour	Literature titre
base	PL or MO/ mL	change	for	for CRI	for TLI/ mL	change	values mL [16]
		for PL/ MO	CRI/ mL			for TLI	
SA-SB	12.25±0.15(PL)	Pink to colourless	10.95±0.95	Brown to yellow	11.70±0.3	Black to red	8.97 ± 0.0577* 8.87 ± 0.0577 (PL) *
WA-SB	13.90±0.7 (PL)	Pink to colourless	13.75±0.15	Brown to yellow	13.45±0.45	Black to red	12.23 ± 0.0577* 12.07 ± 0.0577 (PL)*
WA-WB	2.10±0.2 (PL)	Pink to colourless	2.15±0.15	Brown to yellow	2.15±0.05	Black to red	-
SA-WB	3.00±0.6 (MO)	Yellow to red	1.85±0.05	Brown to yellow	2.20±0	Black to red	15.17 ± 0.0577* 14.57 ± 0.0577(PL) *

Table 1: Comparison of the titrimetric titre values for some synthetic and natural indicators

SA-SB (strong acid -strong base) = HCl-NaOH, WA-SB (weak acid – strong base) = CH₃COOH-NaOH, WA-WB (weak acid – weak base) = CH₃COOH-NH₄OH, and SA-WB (strong acid – weak base) = HCl- NH₄OH; PL= phenolphthalein indicator, MO= methyl orange indicator, CRI = *Curcuma longa* Rhizome extract Indicator, and TLI = *Tectona grandis* Leaves extract Indicator. The titre values are mean of triplicate titrations ± the standard deviations. * literature titre values for *Bougainvillea glabra* green indicator in [16].

In this work again, it can be seen that in WA-WB titration, TLI showed black colour that turned into red at the end of the titration with the titre value of 2.15±0.05 mL. This titre value was relatedly similar to that of 2.10±0.2 mL (in PL) and 2.15±0.15 mL (in CRI). The titrimetric colour change of CRI was from brown to yellow, while PL colour change was still pink to colourless.

Furthermore, the titre values obtained for the titrations of SA-WB were 3.00±0.6 mL, 1.85±0.05 mL, and 2.20±0 mL for MO, CRI, and TLI, respectively. The titre values of the natural indicators coincided to that of MO (synthetic and common indicator) yet again. The MO colour change was yellow to red. Brown to yellow change in colour was shown for CRI; whereas, TLI was from black to red as shown in Table 1 and Figure 2. The results have shown that the bioderived materials, CRI and TLI are efficient and effective for use as acid-base indicators in comparison to MO and PL. In comparison to other researchers, we have seen higher titre values for the titrations involving WA-WB and SA-WB than the ones found in this report. This is likely due to misjudgments of the colour change before the actual endpoint. However, most of previous studies also reported that both synthetic and natural/ green indicators can give similar results, hence green indicators are suitable enough to replace synthetic ones where applicable.

More so, the trend of our results agreed with other investigators that did work on natural/ green indicators [1, 11-12,16]. For instances, the titrimetric titre values obtained in [16] using *Bougainvillea glabra* extracts indicator in WA-SB titration was 12.23 ± 0.0577 mL; and 12.07 ± 0.0577 mL with PL in same experiment [16]. In another development, the findings in [1] obtained the endpoint value for flamboyant extract indicator as 24.70 ± 0.23 mL which was also similar to the PL (24.70 ± 0.14

mL) during the titration of HCl-NaOH. According to the report in [11], titre values of 11.0± 0.155 mL and 11.1±0.154 mL for MO and vinca flower extract indicators, respectively were observed for HCl-NaOH titration. Whereas, for HCl-NH4OH, the titre values were found as 4.2±0.118 mL and 4.2±0.106 mL for PL and vinca flower extract indicators, respectively [11]. In same vein, titre values obtained in [12] for the natural indicator from Tagetes erecta in HCl - NaOH and CH₃COOH-NH₄OH titration; 8.0 mL and 10.8mL, respectively; were quite same as those found with MO (8.2 mL and 11.2 mL, respectively) and PL (8.0 mL and 11.2mL, respectively) [12]. The results have shown that CRI and TLI can supplant MO and PL as indicators in acid-base titration. This is also in conformity to the pursuit of green chemistry advancement of the reduction of environmental pollution and use of renewable materials at least [10, 17–21].

4. Conclusion

The work considered the comparative analysis of CRI and TLI as natural/ green indicators versus some synthetic indicators in acid - base titration. Prior to the titration experiments, CRI and TLI were tested for their peculiar colours in acidic and basic media. Therefore, sharp colours of yellow (for CRI) and red (for TLI) in acid and brown (for CRI) and black (for TLI) in base media were obtained. More so, the substantial absorption in the UV-Visible region highly implicated the presence of curcumin, flavonoids, flavonols, anthocyanins, quinines, quinones, and carotene in these natural materials, CRI and TLI. Thus, the titre values of 10.95±0.95 mL (SA-SB), 13.75±0.15 mL (WA-SB), 2.15±0.15 mL (WA-WB), 1.85±0.05 mL (SA-WB); and 11.70±0.3 mL (SA-SB), 13.45±0.45 mL (WA-SB), 2.15±0.05 mL (WA-WB), 2.20±0 mL (SA-WB) were obtained using the natural indicators CRI and TLI, respectively. The results matched or coincided with the



titre values of 12.25±0.15 mL (SA-SB), 13.90±0.7 mL (WA-SB), 2.10±0.2 mL (WA-WB); and 3.00±0.6 mL (SA-WB) of the synthetic indicators PL and MO, respectively. Thus, since these green indicators are effective, easily available, easy to prepare, less toxic, inexpensive, and eco-friendly it would be possible to replace the MO and PL indicators in conventional laboratories with CRI and TLI as much as possible. This will also facilitate the eradication of environmental toxicity accruing from synthetic indicators.

5. Conflict of Interest

The authors declare no conflict of interest.

6. Acknowledgment

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