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Studies of red cabbage (*Brassica oleracea*) and henna (*Lawsonia inermis*) leaves extracts as greener indicators in acid-base titrimetry

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Abstract
The work considered studies of BOI (*Brassica oleracea* extract indicator) and LII (*Lawsonia Inermis* leaves extract indicator) as green indicators versus some synthetic indicators in acid – base titration involving HCl- NaOH, CH3COOH-NaOH, CH3COOH -NH4OH, and HCl-NH4OH. About 10 mL of each base respectively, with three drops of the BOI, LII, MO (methyl orange), and PL (phenolphthalein) were used. Prior to the titrations, the extracts of *Brassica oleracea* and *Lawsonia Inermis* 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 pink (for BOI) and yellow (for LII) in acid; and green (for BOI) and brown (for LII) in base media. Both LII and BOI absorbed substantially in the UV-Visible region. The titre values of 12.10 ±0.70 mL (SA-SB), 14.95±0.15 mL (WA-SB), 2.05±0.35 mL (WA-WB), 1.40±0.28mL (SA-WB) and 12.50±0.42 mL (SA-SB), 34.90±0.57 mL (WA-SB), 35.90±0.28 mL (WA-WB), 2.75±0.21mL (SA-WB) were obtained for BOI and LII, 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, except with LII (for WA-SB and WA-WB). Hence LII is unsuitable for use as in indicator for the titrations of WA-SB and WA-WB, unlike BOI and PL. It will be beneficial to us to replace the use of MO and PL as indicators with BOI and LII as much as practicable, 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, *Brassica oleracea, Lawsonia Inermis*

Introduction

There is lack 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]. Burungale and Mali [15] also used positively *Euphorbia mili*, *Erythrina varigata*, and *Nelumbo nucifera* methanolic and aqueous extract 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 – 0.1 M 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 the use of red cabbage (*Brassica oleracea*) and henna (*Lawsonia Inermis*) leaves extracts as Greener Indicator in acid-base titrimetry. The results have importance in teaching of chemistry and science at large. It would also aid teachers' interest toward improvisation of teaching / learning material and learners' capacity for solving problems.

Materials and Methods 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.

Methods

Sample Collection and Identification

Purple cabbage (*Brassica oleracea*) and henna (*Lawsonia Inermis*) leaves (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.

Fig 1: Red cabbage (*Brassica oleracea*) and henna (*Lawsonia inermis)*

Sample Preparation and Extraction

About 30 g of the purple cabbage and henna leaves were washed and rinsed with distilled water to remove dirt.

Thereafter, the samples 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].

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.

Results and Discussion

Results for the BOI and LII in Different Media

The extracts of *Brassica oleracea* and *Lawsonia Inermis* leaves were found to show different colours in acidic and basic solutions. The products, BOI gave different sharp colours in acid (pink) and base (green). Whereas, LII produced brownish colour in base and yellow colour in acid (see Figure 2). This then become a potential as previously demonstrated, for their ability as indicators in acid-base titration.

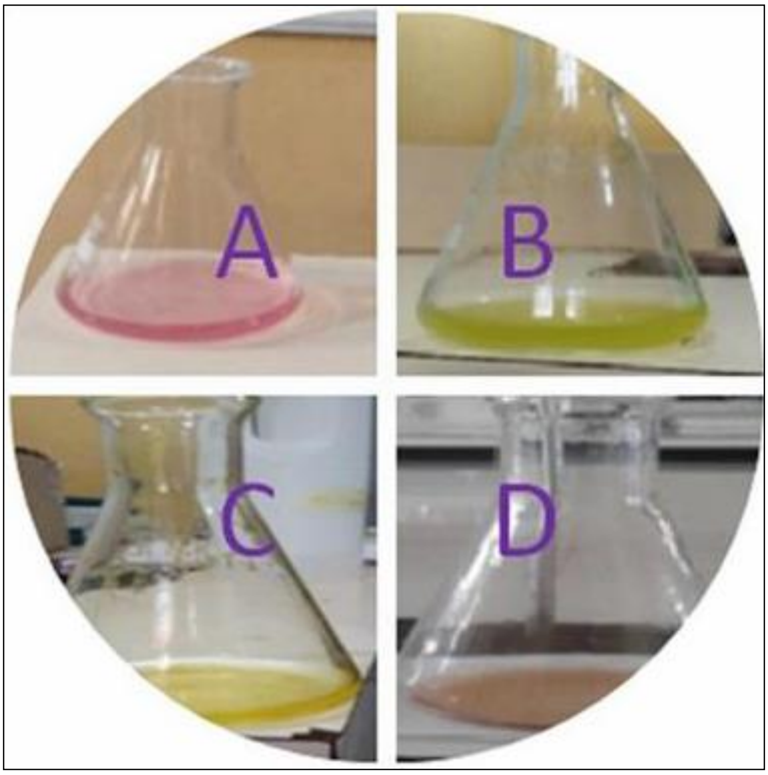

Fig 2: Colour change of the indicators in acidic and basic solution (A = BOI in acid (pink); B = BOI in base (green); C = LII in acid (yellow); and D = LII in base (brown))

Burungale and Mali [15] also 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 LII was found at 400-650 nm with absorbance of >0.04. For BOI, the wavelength range for its effective absorption was between 400 – 600 nm; however, beyond this range the absorbance became < 0.1. It has been also observed that BOI gave higher absorption than the LII biomaterial. Compounds that can absorbed in this region of the UV-visible 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].

Results of Titration Analysis

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

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

Acid- base	Titre value for PL or MO/ mL	Colour change for PL/ MO	Titre value for LII/ mL	Colour change for LII	Titre value for BOI/ mL	Colour change for BOI	Literature titre values mL [16]
SA- SB	12.25±0.15(PL)	Pink to colourless	12.50±0.42	Brown to yellow	12.10±0.70	Green to colourless	8.97 ± 0.0577* 8.87 ± 0.0577 (PL) *
WA-	13.90±0.7 (PL)	Pink to	34.90±0.57	Brown to	14.95±0.07	Green to	12.23 ± 0.0577*
SB		colourless		yellow		colourless	12.07 ± 0.0577 (PL)*
WA- WB	2.10±0.2 (PL)	Pink to colourless	35.90±0.28	Brown to yellow	2.05±0.35	Green to pink	- -
SA- WB	3.00±0.6 (MO)	Yellow to red	2.75±0.21	Brown to yellow	1.40±0.28	Green to pink	15.17 ± 0.0577* 14.57 ± 0.0577(PL) *

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, BOI = *Brassica Oleracea* extract indicator; LII = *Lawsonia Inermis* leaves extract indicator. The titre values are mean of triplicate titrations the standard deviations. * literature titre

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values for *Bougainvillea glabra* in [16]. For the titration involving HCl-NaOH, it was found that the titre values of 12.50±0.42 mL and 12.10±0.70 mL for LII and BOI, 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 LII in the titration, brown to yellow colouration change was observed. Meanwhile, green to colourless change in colour was shown during the titration of the SA-SB with the usage of BOI.

Similarly, in the titration of WA-SB, the titre values of 34.90±0.57 mL, 13.90±0.7 mL, and 14.95±0.07 mL were obtained for LII, PL, and BOI, respectively. LII gave titre value that is above those of PL and BOI. LII changed from brown to yellow; whereas the BOI indicator showed green colour that changed into colourless during the WA-SB titration. Then PL produced colouration change of pink to colourless (find the details in Table 1). It was also reported by Patil *et al* [13]. that turmeric and PL produced endpoint values of 8.0 ±0.2 mL and 7.5 ± 0.02 mL in the course of titration of HCl -NaOH [13]. In this work again, it can be seen that in WA-WB titration, LII showed brown colour that turned into yellow at the end of the titration with the titre value of 35.90±0.28 mL. This titre value was dissimilar to that of 2.10±0.2 mL (in PL) and 2.05±0.35 mL (in BOI). The titrimetric colour change of BOI was from green to pink, while PL colour change was still pink to colourless. It has been observed that LII again has given titre value that is above BOI and PL, hence LII is unsuitable for use as in indicator for the titrations of WA-SB and WA-WB, unlike BOI.

Furthermore, the titre values obtained for the titrations of SA-WB were 3.00±0.6 mL, 2.75±0.21 mL, and 1.40±0.28 mL for MO, LII, and BOI, 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 LII; whereas, BOI was from green to pink as shown in Table 1 and Figure 2. The results have shown that the bioderived materials, LII and BOI are efficient and effective for use as acid-base indicators in comparison to MO and PL. Beside the challenge due to misjudgement of the colour change common in titrimetry, we can conspicuously assert that these biomaterials are effective. More so, 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, 17]. For instances, the titrimetric titre values obtained by Kapilraj *et al* [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, Mahadi and Abubakar [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 vs NaOH. According to Kokil S. U. *et al* [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 vs NaOH titration. Meanwhile, in the HCl-NH4OH titration, 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 by Garg *et al* [12] for the natural indicator, *Tagetes erecta* in HCl – NaOH and CH3COOH-NH4OH titrations; 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 LII and BOI 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].

Conclusion

The work considered the studies of *Brassica oleracea* and *Lawsonia Inermis* as natural indicators against some synthetic indicators in acid – base titration. Prior to the titration experiments, LII and BOI were tested for their peculiar colours in acidic and basic media. Therefore, sharp colours of pink (for BOI) and yellow (for LII) in acid; and green (for BOI) and brown (for LII) 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 and so on in these natural materials, LII and BOI. The titre values of LII and those of BOI were similar to their synthetic ones, PL and MO in most cases. However, in the titrations of WA- SB and WA-WB, the titre values found using LII were substantially above the corresponding titre values in BOI and the synthetic indicators. This implied that LII is only suitable as indicator for SA-SB and SA-WB titrations, unlike BOI that is suitable in all cases. 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 chemistry laboratories with BOI and LII as much as possible. This will also facilitate the eradication of environmental toxicity accruing from synthetic indicators.

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