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Contributed Paper

Application of Smartphone as a Digital Image Colorimetric Detector for Batch and Flow-based Acid-Base Titration

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ABSTRACT

In this research, we have developed the batch and flow-based system of titrimetric analysis by using a mobile phone as a detector. The digital image colorimetric detection system was set up with economic devices and to be easy to use by taking photograph with mobile phone camera, then the RGB signals were read from the RGB color picker application to calculate the RGB-based value and plot titration curve for evaluating the equivalence point. This method was applied to analyze samples of acid-base on daily basis, compared with the potentiometric and photometric titrations that using pH meter and spectrophotometer as a detector, respectively. The method was highly reproducible with the relative standard deviation of 1.14 % (n=11) for 0.5 %w/v of acetic acid standard solution. The proposed method was applied to the determination of acetic acid in vinegar and titratable acidity in fruit juices. Concentrations of acetic acid were found to be in a range of 5.23-5.35 %w/v. Concentrations of titratable acidity in the juice samples were found to be in a range of 0.27-0.50 %w/v. Thereafter, an analytical application involving the determination of the total alkalinity in mineral waters was performed, and it was found in the range of 11.50-18.50 mg/L of $CaCO_3$ which were in good agreement with the results obtained from the standard method at the 95 % confidence level.

Keywords: titration, flow-based analysis, smartphone, RGB color system, application RGB color picker

1. INTRODUCTION

Titration is a powerful quantitative chemical analysis that based upon the measurement of the reagent volume with observing a suddenly physical change in a solution that so-called endpoint. Indicators are often used for this noticeable transformation including the appearance or disappearance of color; a change in color, or the occurrence or vanishment of turbidity. Therefore, the accuracy in change observation with bare eyes could also subsequently affect the reliability of the analytical results. Apart from the change in color of the indicator, using of an electrode to measure the change in potential or a spectrophotometer to observe the absorbance that responded to a reagent or analyte concentration in order to construct a titration curve is an alternative way to obtain the endpoint. However, the higher expense of the instruments including the maintenance cost, comprised of its sophistication, should be considered.

A digital image-based method served for the quantitative chemical analysis is now popularly used as has been proposed in many pieces of literature. Digital imaging becomes an interesting alternative way as a detector for the various analytical measurements to many analytes due to its rapid, cheap and direct determinations as exemplified in Table 1.

A digital image which is an array of points or pixels (the smallest color unit), could be captured via the digital camera, webcam, or flatbed scanner that those based upon the use of charge-coupled devices (CCD) or

Table 1. The examples of the application of digital image method for the various analytical measurements.

Analytes	Samples	Analytical techniques	Digital imaging devices	References
Al(III) and Fe(III)	Synthetic alloys	Colorimetry using the chrome azurol S as a chromogenic reagent	Digital camera	[1]
HCl, H_3PO_4 and total alkalinity	Aqueous solution, mineral and tap water	Titration using phenol red, bromocresol green, and methyl orange as indicators	Webcam	[2]
Li, Na and Ca	Anti-depressive drug, physiological serum, and water	Flame emission spectrometry	Webcam	[3]
Ti(IV)	Plastics	Colorimetry using H_2O_2 and H_2SO_4 to form an orange complex	Digital camera	[4]
Total acidity	Red wines	Titration (without indicator)	Webcam	[5]
Ca hardness	City net, mineral, and natural water	Colorimetry using GBHA in alkaline media as a chromogenic reagent	Digital camera	[6]
Food dyes	Commercial product	Spotted the dyes on filter paper and subsequently measured the RGB value	Flatbed scanner	[7]
Al(III) and Cr(VI)	Natural water	Colorimetry using CTAB and DPC as the chromogenic reagent for Al(III) and Cr(VI), respectively	Webcam	[8]
Various organic compounds	-	Colorimetry by the reaction of the azo coupling of diazotized polyurethane foams (PUFs) with organic substances	Digital camera	[9]
Estrone, 1-Naphthylamine, 4-Aminophenol	-	Colorimetry by the reaction of the azo coupling of diazotized PUFs with organic substances	An eye-one pro mini-spectrometer and a monitor calibrator	[10]

complementary metal-oxide semiconductors (CMOS) to provide RGB color data [6, 11-12]. The RGB color system consists of three primary color components; red (R), green (G), and blue (B), of which the mixing of these colors in each pixel is utilized in a display or computer graphic applications [12-13]. The RGB colors are combined in different intensities with values from sensor reading vary from 0 to 255 (8 bits) per color [2, 14-15]. Thus, the total number of possible colors from the primary color combination is $2^8 \times 2^8 \times 2^8 = 16,777,216$ colors [6, 13]. With these numerous values, the construction of analytical curves from RBG-based signal that response to the change in analytical measurements, e.g., calibration curve [16-18] and titration curve, is feasible.

Hence, in this work, the digital image-based colorimetric method is applied to the acid-base titration by using the RGB-based values obtained from a smartphone camera to build a titration curve. The capture of the digital image of indicator change including to the RGB data assessment is achieved via a high-resolution camera coupled with a costless downloadable application which installed in multipurpose, easily portable, and daily usage devices, i.e., smartphone. Moreover, a flow-based technique is also applied to this work in order to decrease the chemical consumption, increase the sample throughput, as well as to facilitate higher automation in detection procedure. Therefore, the requirement of the previous complicated instrumental techniques seems to be reduced by the novel proposed method.

2. Materials and Methods

2.1 Chemicals

All solutions were freshly prepared with de-ionized water (DI water) and analytical grade chemicals.

Primary standard solutions of $KHC_8H_4O_4$ or KHP (RFCL) and Na_2CO_3 (Labscan) were prepared for the standardization procedure. About 0.1 M NaOH (Labscan) was standardized before use as the titrant for the titration of strong acid of HCl (Merck) and weak acid of CH_3COOH (Labscan) to build a titration curve, including the determination of CH_3COOH in vinegar and acidity in juice. The titration curve of the strong acid-weak basic titration was also done using the exact concentration of HCl and NH_3 solution (Labscan). Total alkalinity in natural water samples was determined by using a standardized H_2SO_4 as the titrant.

About 1.0 %w/v of bromothymol blue (Ajax), methyl orange (Labscan), methyl red (Labscan) and phenolphthalein (Labscan) were used as indicators in the titration.

Buffer solutions at each pH used for observation of color change of indicators were prepared by mixing these solutions of different volumes as follow; 0.2 M KCl (Ajax) and 0.2 M HCl (pH 1 and 2), 0.1 M KHP and 0.1 M HCl (pH 3 and 4), 0.1 M KHP and 0.1 M NaOH (pH 5-7), 0.1 M KH_2PO_4 and 0.1 M NaOH (pH 8), 0.1 M HCl and 0.0025 M $Na_2B_4O_7$ (Ajax) or borax (pH 9), 0.1 M NaOH and 0.0025 M borax (pH 10), 0.1 M NaOH and 0.05 M Na_2HPO_4 (Ajax) (pH 11 and 12), and 0.2 M KCl and 0.2 M NaOH (pH 13)

2.2 Apparatus and Detection Procedure

2.2.1 RGB-detection box for a conventional titration setup and detection procedure

First, a manual conventional titration setup was built. Titrant was released from burette with the defined volume into a beaker which contained titrand and indicator that were being continuously stirred by a magnetic stirrer (Dragon Laboratory). Then, a portion of 2.00 mL of mixed solution in the beaker was pipetted and discharged into a test tube. An RGB-detection box (10 cm×11 cm×17 cm) was made of balsa wood as illustrated in Figure 1 in order to place test tube and also avoid the interfering of ambient light while metering the RGB additive color. A light bulb

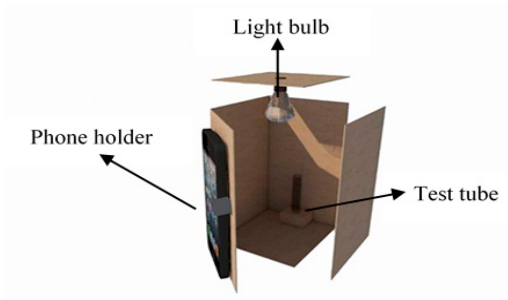

Figure 1. A schematic of RGB-detection box for a conventional titration setup.

3 W (Lumax) was attached at the top of the box. The internal walls of the box were all covered with white paper to provide uniform illumination. At the front of the box, opposite to the position of the test tube, was circularly drilled with a radius of 2.0 cm. A plastic clamp was also adhered on outside wall for holding a smartphone (Asus ZenFone 2) by placed the camera lens onto the hole to focus the solution in the test tube and then captured a picture to obtain R/G/B values. After monitoring RGB values, the measured solution in the test tube was transferred back to the titration beaker prior addition of the next portion of the titrant.

2.2.2 RGB-detection box for a flow-based titration setup and detection procedure

In order to avoid the leakage of the chemical during transferred from beaker to test tube, and to reduce time in R/G/B value detection procedure, a flow-based technique was applied to a titration setup as illustrated in Figure 2.

After a portion of a defined titrant volume was added to the titrand in a beaker which was continuously stirred, a mixed solution was drawn up through PTFE tubing (i.d. 0.795 mm) with a flow rate of 5 mL/min using a peristaltic pump (Ismatec, Switzerland). Three-way valve was employed for controlling a flow

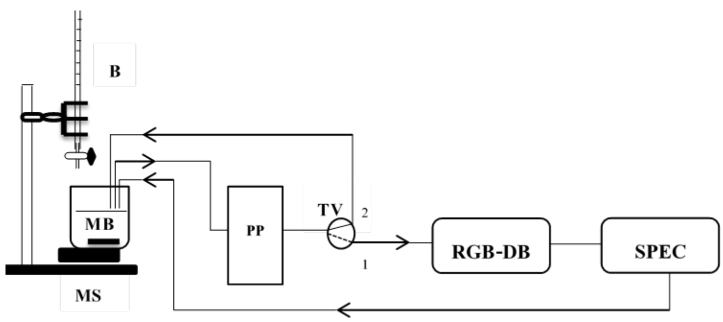

Figure 2. Schematic diagram of a flow-based titration setup with RGB-detection box, B = burette, PP = peristaltic pump, MB = magnetic bar, MS = magnetic stirrer, TV = three-way value, RGB-DB = RGB-detection box, and SPEC = UV-Vis spectrophotometer.

direction. Solution was propelled through a valve at position 1, RGB-detection box and spectrophotometer, respectively, before flow back to beaker by spending the circulation time of 45 seconds. The detection step was carried out by switching three-way value to position 2 in order to stop the flow in the detection box and spectrophotometer for recording RGB-based values and an absorbance, respectively.

More robust RGB-detection box was built employing the black opaque acrylic sheet (thickness of 3.00 mm) replacing to the balsa wood. The internal of the box was also covered with a white paper and attached a 3W light bulb on the top. The box was drilled for two small-size holes at the right side to insert PTFE tubing for flow inlet and outlet, respectively. A glass flow cell with an inner volume of 715 μL as shown in Figure 3(a) was put into the box at the same position of the test tube. The hole with a radius of 2.0 cm was drilled at the opposite to the flow cell. A smartphone was held on the box with a plastic clamp by placing the lens on the detection hole. The RGB-detection box for the flow-based titration setup was illustrated in Figure 3(b).

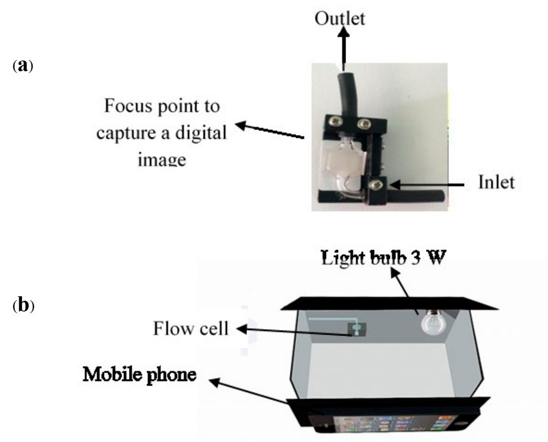

Figure 3. A schematic of (a) flow cell and (b) RGB-detection box for a flow-based titration setup.

2.2.3 Acquisition of RGB-based value

The RGB-based values were assessed via a costless downloadable application, namely "RGB color picker", which could be downloaded from the "Play Store" application. The application provided a multipurpose utility by the caption of color at real time with the phone camera and flash. The main screen of this application is a small window (1.7 cm×2.5 cm) which could be manually adjusted on the touchscreen to select the suitable area for the picture caption. The color was displayed with the most common color models; i.e., CYMK, HSL, HSV, RGB and YUV, and even gave a name to the color. The captured color data were also available for the SD card.

In this work, after the application was standby, the color capture was done when placed/flowed the solution to the marked position in the box. Then selected RGB mode, each of values of R, G, and B were immediately shown without any assessment by the operator. The values of R, G, and B were reported with the number in the range of 000-255. To gain RGB-based value, all data of R, G, and B were multiplied to enhance the resolution of the total number of possible colors from the primary color combination. However, because the value of zero of R, G or B might be obtained in some cases, and then affected in multiplication step to gain the zero at last, every displayed values of R, G, and B must be plus by one before multiplying.

2.3 Preliminary Test of R/G/B Value of the Color Change of Indicators

The preliminary estimation of R/G/B values was monitored by observing the change in color of the indicator at the various pH. Three types of indicator; phenolphthalein, bromothymol blue, and methyl red were added three drops into 10 mL of different buffer solution medium at each pH from 1-13. The portions were contained in test tubes before manually detected the R/G/B values using a balsa wood RGB-detection box. The obtained values were plotted versus the pH to obtain characteristic graphs for each of the indicators.

2.4 Acid-base Titration Based on RGB-Based Value Detection

2.4.1 Accuracy evaluation of RGB detection for titrimetric analysis

From the preliminary test to observe the relationship between the change in color of each indicator and RGB-based value, the analyzer was then applied to acid-base titrations. However, the accuracy of RGB detection should be investigated to ensure that it is appropriate to both of the batch and flow-based titration setups. Three categories of titration were done consisted of; strong acid-strong base, weak acid-strong base, and strong acid-weak base, by using the known concentration of standard acidic and basic solutions as the titrant and titrand as summarized in Table 2. In case of NaOH and HCl which used as the titrant, NaOH was standardized with KHP and then used as the titrant to standardize HCl, respectively. The titrand of 25.00 mL was pipetted into a beaker (100 mL) and mixed with three drops of indicator. R/G/B value detection procedure was carried out as mentioned in the previous subject of RGB-detection box for a conventional titration setup and detection procedure. The titration curves were constructed by plotting the titrant volume versus RGB-based value to gain the equivalent point from the inflection point. Concentrations found of titrand were compared to the known concentrations. Moreover, all results were compared with those of potentiometric titration method by the monitoring with a pH meter (Vernier Software & Technology).

Table 2. Standard solutions used for the accuracy evaluation of RGB detection.

Categories of titration	Titrant	Titrand	Indicator
Strong acid-strong base	0.1045 M NaOH	HCl	Bromothymol blue
Strong acid-weak base	0.1032 M HCl	NH_4OH	Methyl red
Weak acid-strong base	0.1045 M NaOH	CH_3COOH	Phenolphthalein

2.4.2 Determination of acetic acid and total titratable acidity

Three brands of distilled vinegar and four brands of fruit juice (guava and orange) were bought from a convenience store in Chiang Mai. The known volume (1.00 mL) of vinegar was pipetted to make a ten-fold dilution. The juices were filtered through a filter paper (Whatman No.5) before pipetted at 10.00 mL of sample for titration. Three drops of phenolphthalein were added to all prepared samples and then titrated with a standardized NaOH (0.1060 M) [14]. R/G/B value detection procedure was carried out as mentioned in the previous subject of RGB-detection box for a flow-based titration setup and detection procedure. The titration of these samples was also compared with those methods that using a pH meter and a spectrophotometer as detectors to indicate the accuracy of the proposed method.

2.4.3 Determination of total alkalinity

Three brands of mineral water were also obtained from a convenience store. Three drops of methyl orange were added to 100.0 mL of each sample. Standard solution of 0.0100 N H_2SO_4 was used as the titrant [15]. RGB detection procedure was also carried out as done in the determination of titratable acidity. The results were also compared to that be obtained from a photometric titration using spectrophotometer as the detector.

2.5 Precision of the RGB Detection

One of vinegar sample was random to the 11 replicated titrations as the procedure of the conventional and the flow-based method with the standardized solution of NaOH using phenolphthalein as the indicator. Percent relative standard deviation (%RSD) was calculated to estimate the precision.

3. RESULTS AND DISCUSSION

3.1 R/G/B Value Assessment of Color Change of Indicators

Bromothymol blue, phenolphthalein and methyl red were chosen due to the difference of color change at the different transition ranges of pH. From the experiment, based on using the RGB detection using the smartphone for a conventional titration setup (a static measurement), the change of R/G/B and RGB-based values of each indicator in the range of pH 1-13 were plotted as shown in Figure 4 (a-f).

As suggested from the theoretical aspect, the pH transition range and the color change of bromothymol blue, phenolphthalein and methyl red were 6.2-7.6 (yellow to blue), 8.2-

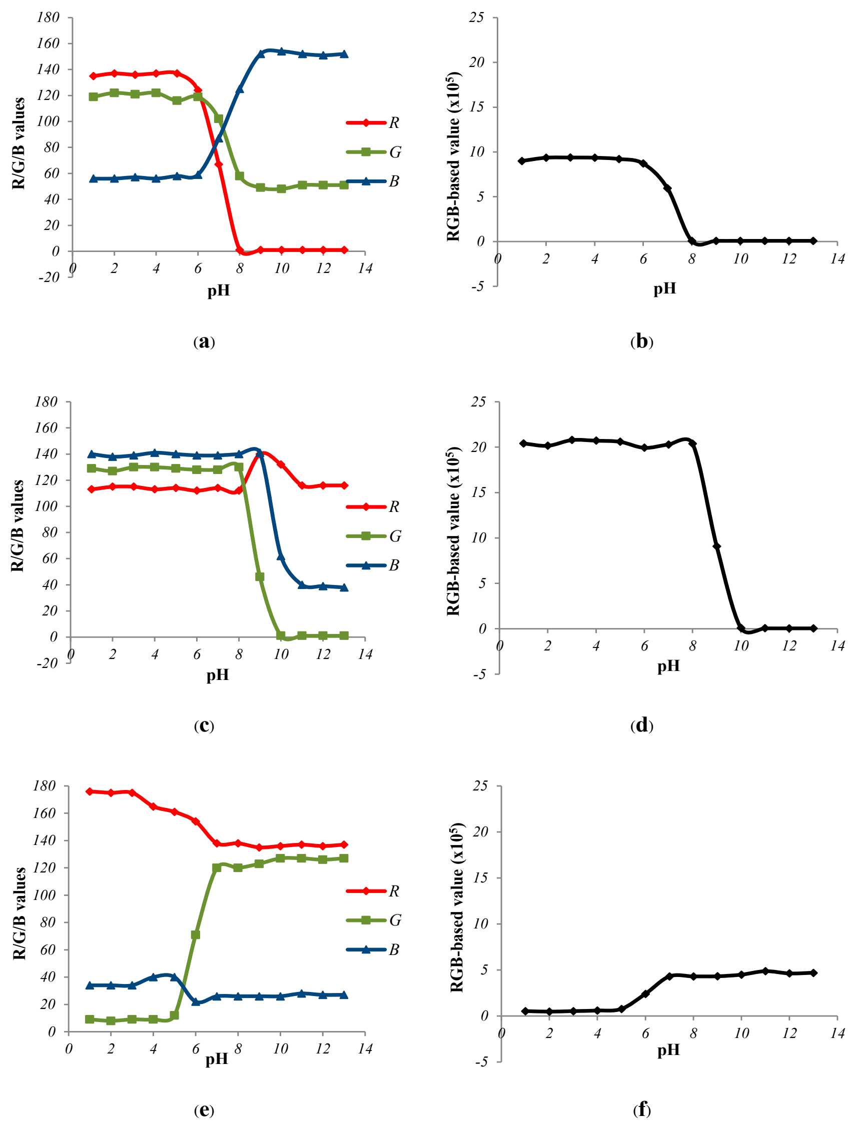

Figure 4. The change of R/G/B values and RGB-based value in the range of pH 1-13 of each indicator, (a-b) bromothymol blue, (c-d) phenolphthalein and (e-f) methyl red.

10.0 (colorless to pink) and 4.4-6.2 (red to yellow), respectively. Figure 4(a) showed that R and G values were similar in the range of pH of 1-6 while B value was much lower. It could be described that the mixture between the additive color of red (R) and green (G) provided the yellow in accordance with the color of bromothymol blue at the pH lower than 6. After pH raised over 7, the color turn to blue, B value then obviously increased that was opposite to the change of R and G values.

In the case of phenolphthalein (Figure 4(c)), because of the clear solution at pH lower than 8, then the captured color was the white color of the covered paper in the detection box and affected to the similar values of R/G/B. After the color turn to pink at pH higher than 8, R value showed a constant while G and B values decreased suddenly.

For the change of R/G/B values of methyl red as shown in Figure 4(e), R value was higher than the other at pH less than 7. When pH surpassed 7, G value also increased due to the color transformation to yellow in the same way of the change in bromothymol blue [19]. Additionally, as Figure 4(b, d, f), the change of RGB-based values of each indicator provided the inflection point of the graph that corresponded to the indicator color transformation. The more numerous values from multiplying of R/G/B colors, the more resolutions of analytical signal contribute to the higher responsibility in analytical measurements. Therefore, the monitoring of RGB-based value during titrimetric process could be applied to construct the titration curve as well.

3.2 Acid-base Titration Curve Using RGB-Based Value

From the application of smartphone to detect RGB values using a batch setup in real titration of; strong acid-strong base (NaOH as titrant), weak acid-strong base (NaOH as titrant), and strong acid-weak base (HCl as titrant), a collection of points of added titrant volumes with the observed signals from both in the RGB-based and in the pH measurement values were recorded. The previously mentioned indicators, i.e., bromothymol blue, phenolphthalein, and methyl red, were used in the titration of the strong acid-strong base, weak acid-strong base, and strong acid-weak base, respectively, due to the appropriate color transformation at endpoint for each titration. Second derivatives of both data were further calculated. Two categories of titration curve, normal and second derivative were also constructed to observe the equivalence point as illustrated in Figure 5-7.

From the results, even if these titrations involved different changed patterns of pH, provided different pH at equivalence point and used different indicators, but it was found that the abrupt change of RGB-based value of all normal titration curves corresponded to the abrupt change in pH. These affected to localize the similar equivalence point in the second derivative titration curve. Therefore, the RGB detection using a smartphone could be effectively used for acid-base titration and be further applied to real sample analysis.

3.3 Application of RGB Detection Using the Smartphone in Real Sample Analysis

3.3.1 Determination of acetic acid in vinegars and total titratable acidity in juice

RGB detection using a smartphone for a flow-based titration setup was applied to real sample analysis by comparing the analytical results with the titration using of pH meter and spectrophotometer. The volumes at equivalence point from second derivative titration curve of each titrimetric method were calculated in order to assay the amounts of acetic acid in vinegars and total titratable acidity in juices as shown in Table 3. The analytical results from RGB detection using a smartphone were statistically compared by paired t-test to the assay of pH meter (t_{stat} = 1.48, $t_{critical}$ = 2.45)

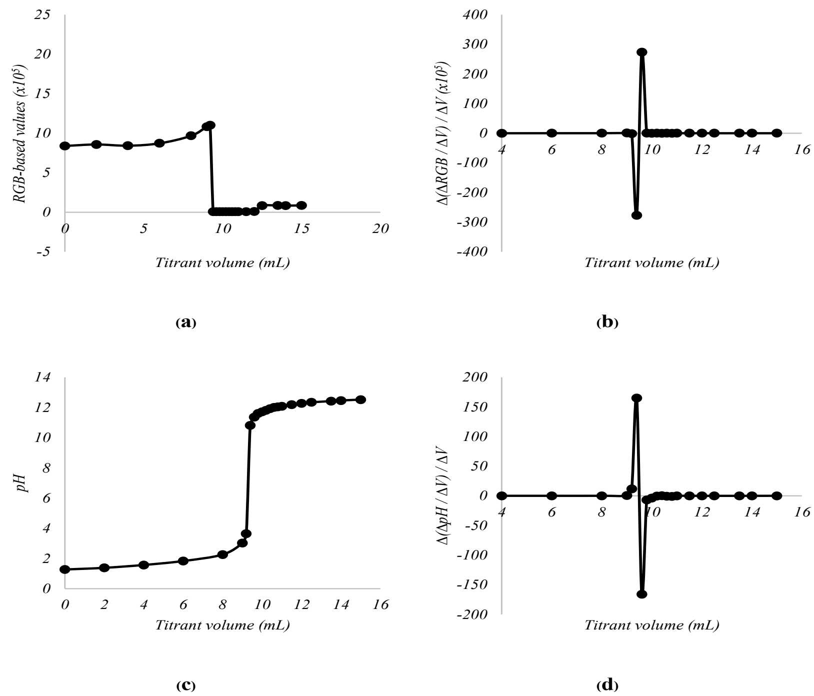

Figure 5. Normal and second derivative titration curves of strong acid-strong base model titration using (a-b) RGB-detection box (bromothymol blue as an indicator) and (c-d) pH meter.

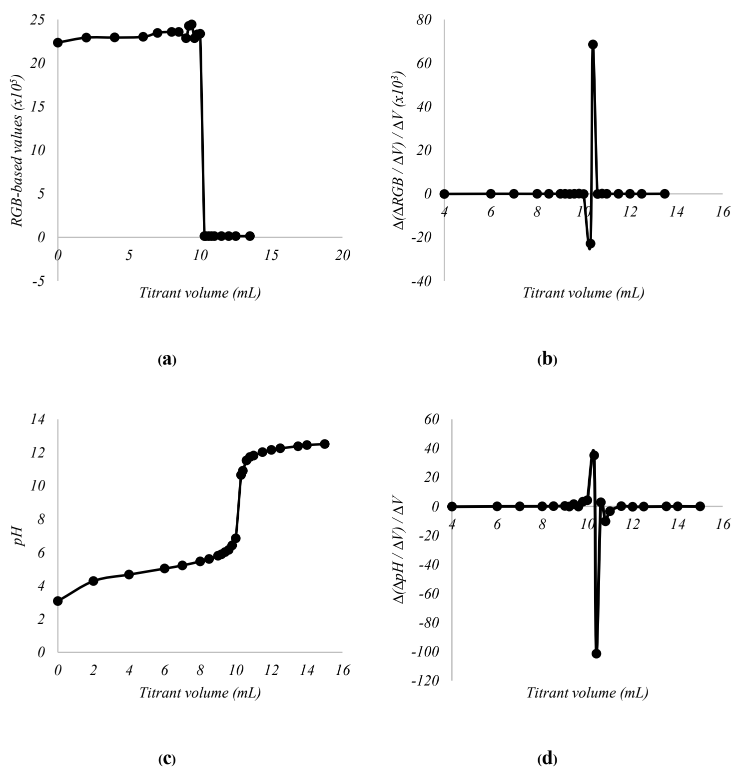

Figure 6. Normal and second derivative titration curves of weak acid-strong base model titration using (a-b) RGB-detection box (phenolphthalein as an indicator) and (c-d) pH meter.

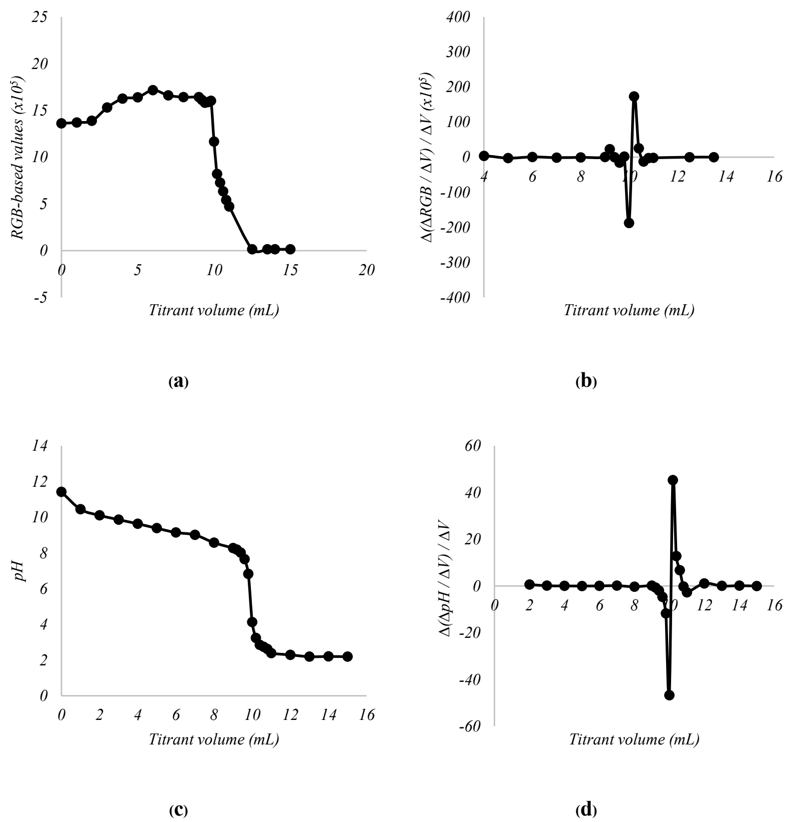

Figure 7. Normal and second derivative titration curves of strong acid-weak base model titration using (a-b) RGB-detection box (methyl red as an indicator) and (c-d) pH meter.

Table 3. Determination of acetic acid and total titratable acidity by titration using three detection instruments.

Sample	Found amount (%w/v)		
	RGB-detection box	pH meter	Spectrophotometer
1. Vinegars			
Sample A	5.23 ± 0.09	5.69 ± 0.07	5.17 ± 0.07
Sample B	5.35 ± 0.10	5.69 ± 0.07	5.29 ± 0.08
Sample C	5.23 ± 0.08	5.60 ± 0.06	5.17 ± 0.08
2. Juices			
Guava juice A	0.27 ± 0.01	0.26 ± 0.01	0.27 ± 0.01
Guava juice B	0.33 ± 0.02	0.31 ± 0.01	0.34 ± 0.01
Orange juice A	0.50 ± 0.02	0.48 ± 0.02	0.49 ± 0.02
Orange juice A	0.50 ± 0.03	0.50 ± 0.02	0.49 ± 0.02

and spectrophotometer (t_{stat} = 0.284, $t_{critical}$ = 2.45), respectively, and found that no significant difference by those methods. Therefore, it might be indicated that a smartphone could be effectively employed to the acid-base titration for the colored sample.

3.3.2 Determination of total alkalinity.

Apart from the acid determination in real samples, the assay of base in term of total alkalinity in mineral water samples have also succeeded with the statistically agreeable results (paired t-test at 95% confidence level; t_{stat} = 0.99, $t_{critical}$ = 4.30) using the same setup as proposed in Table 4 when comparing to the photometric titrimetric standard method.

3.3.3 Precision of the monitoring with RGB-detection box

From the study, 0.5 %w/v of CH_3COOH was evaluated for 11 replications for both of batch, and flow-based titration, the percent relative standard deviation (%RSD) values were 1.20% and 1.14%, respectively. The flow-based titration had a detection frequency about 80 cycles/h with a flow rate of 5 mL/min.

Table 4. Determination of total alkalinity by titration using two determination instruments.

Mineral water sample	Found amount (mg/L of $CaCO_3$)	
	RGB-detection box	Spectrophotometer
1	11.50 ± 0.55	12.00 ± 0.50
2	16.50 ± 0.30	16.00 ± 0.45
3	18.00 ± 0.50	18.75 ± 0.40

4. Conclusions

The experimental results indicated that the developed RGB detection using a smartphone could be applied for the batch and flow-based titration. RGB-based value could be successfully applied to build a titration curve which gave the agreeable results comparing to the use of pH value or absorbance. Moreover, the proposed analyzer showed obvious advantages, e.g., concise, portable, inexpensive, fast and cheap analysis, which should be appropriate for the determination of acid and base in various beverages despite the colored sample.

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