Using a Smart Phone Camera as a Color Detector for Ethanol Estimation based on Time Analysis in Mixed Alcoholic Drinks

Narong Kotchabhakdi[1]*

[1]Department of Chemistry, Faculty of Science, Lampang Rajabhat Lampang University
* E-mail: kotchabhak_n@hotmail.com

Abstract

The colorimetric method for ethanol estimation was developed based on the redox reaction of chromium using a smartphone camera as a color detector. Time-Based Analysis (TBA) was employed for color signal evaluation. The Red Green Blue (RGB), Cyan Magenta Yellow (CMY) and Hue saturation Value (HSV) color models were used for monitoring a color change from Orange (Cr(VI)) to Blue (Cr (III)) in a reaction plate-form. The reaction time of ethanol and dichromate ion depended on the concentration of ethanol in which the stop time of each color model was selected and recorded in the second unit and employed for signal processing in log scale. The results showed a linear range of 1.0-5.0 %w/v ethanol, r^2= 0.991-0.998, % recovery of 82-118% and %RSD less than 10% of analysis performance test with mixed alcoholic drink samples. The proposed method was successfully applied for determination ethanol in real samples with less complicated, rapid, low cost and portable.

Keywords: Ethanol estimation, RGB HSV CMY color system, Time based Analysis (TBA), Smart phone camera, mixed alcoholic drinks

Introduction

The traditional methods for ethanol determination in alcoholic beverage samples involving distillation and mass determination are known to show less accuracy due to the presence of interfering volatile or other components in samples (Zimmerman, 1963). In the volumetric method, the determination of ethanol by titration with potassium dichromate in an acid condition that the color change of redox reaction was observed as the endpoint (Semichon & Flanzy, 1929). The spectrophotometric method had been developed using the reaction of potassium dichromate in concentrated acid and ethanol to produce chromium (III) and acetic acid and then was spectrometrically measured. The reaction is completed in 15 min at room temperature and the

chromium (VI) consumed can be determined by the decrease of absorbance at 267 nm (Williams & Darwin, 1950). However, the problem of the potassium dichromate method is a reaction rate of color change that affects the accuracy and precision of analysis. The drawbacks of this method are non-rapid, complicated, high cost and high waste.

Several methods have been used for the determination of ethanol concentration. The widely used method is a chromatography, especially gas chromatographic methods (Li et al., 2009; Zhang et al., 2015), gas chromatography-mass spectrometry (Nascimento, Cardoso & Franco, 2008), gas chromatography combustion isotope ratio mass spectrometry (Neves et al., 2015), and liquid chromatograph-mass spectrometry (Cabanero, Recio & Ruperez, 2010; Li et al., 2013). The gas or liquid chromatographic methods require expensive instruments and are time-consuming, so they cannot be widely used for portable and field tests.

Nowadays, colorimetric detection for chemical analysis was reported as an alternative method for a spectrophotometer. Using Charge Coupled Device (CCD) and Complementary Metal Oxide Semiconductor (CMOS) devices from a digital camera (Songjaroen et al., 2011), web camera (Diaz et al.,2012), smartphone camera (Devadhasan & Kim, 2015; Moonrungsee, Pencharee & Jakmunee, 2015) and scanner (Klasner et al., 2010; Jayawardane et al., 2014) were achieved with RGB color model for signal processing in RGB intensity.

The Interesting technique was reported by Wongwilai, Lapanantnoppakhun & Grudpan (2010) which employed a Time-based Analysis (TBA) with a webcam camera for a detector in a simple lab-on-chip reactor. The diffusion of acidic solution into the basic solution zone was recorded as the change of red, blue and green colors (%RBG.) The change was related to acid concentration. This work focused on using the colorimetric method by a redox reaction between ethanol and dichromate and detection of a color change by a smartphone camera and image processing.

Objectives

The objectives of this work were to develop less complicated, rapid, inexpensive, simple, low waste, high accuracy, and portable method for ethanol estimation in colorless alcoholic beverage samples. According to the problem for color monitoring of dichromate reaction with ethanol is complicated to directly detect. So, this experiment interested in a time-based analysis by monitoring a color change (RGB, HSV, and CMY) and recording a time of reaction. The results and plotting graphs for calibration equations were simultaneously evaluated by using Color Grab application, calculator application and regression line application in a smartphone.

Materials and Methods

Concept and operating system

Chemical oxidation methods are based on the complete oxidation of ethanol by dichromate in the presence of sulfuric acid with the formation of acetic acid. This reaction is popular because potassium dichromate is easily available in high purity and the solution is indefinitely stable in air. The theoretical reaction stoichiometry is shown below:

$$2Cr_2O_7^- + 3C_2H_5OH + 16H^+ \longrightarrow 4Cr(III) + 3CH_3COOH + 11H_2O$$

yellowish   light blue

Dichromate (Cr(VI)) is in color and the reduced chromic product (Cr(III)) is intensely green. Because the absorption spectra of dichromate and chromic ions overlap significantly, Beer's law is not obeyed. Instead, the spectra of the solution of interest must be analyzed at multiple wavelengths to calculate the individual concentrations of dichromate and chromic ions in a mixture subject to the material balance that the total number of chromium atoms must be conserved (Williams & Darwin, 1950).

The operation of the method started in the reaction plate-form while acidic dichromate reagent with ethanol was mixed and then transferred into a protect lightbox (showed in figure 1). The yellowish color has changed to green (yellow/blue) and finally blue color in which mixed color of the solution was monitored (i.e. an RGB CMY HSV values) *via* a smartphone and recorded using Color Grab application (seen in figure 2).
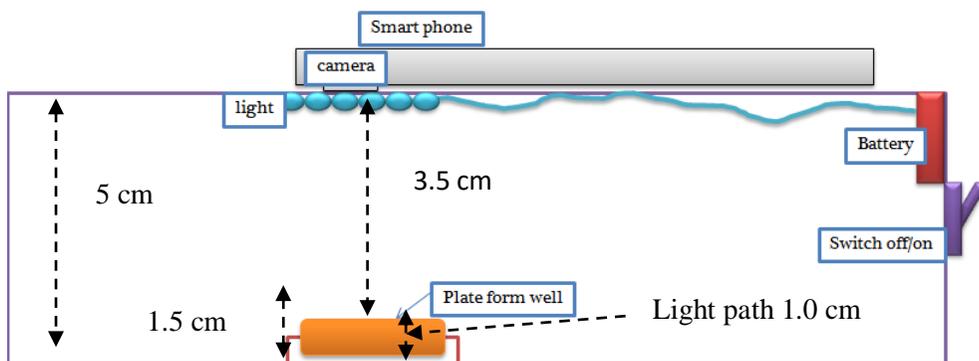

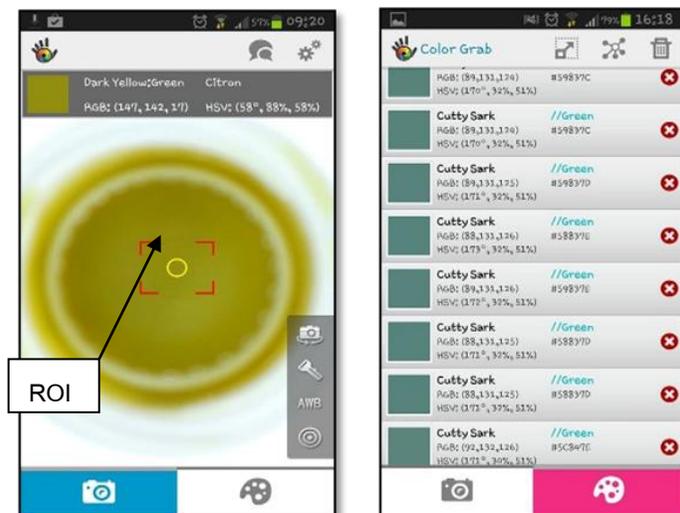**Figure 1** The diagram and photograph of protective light box

Figure 2 Color measurements *via* Color Grab application; (left) Region of interest (ROI) position
(right) recorded color value

Reagents, Solutions, and standard preparation

Potassium Dichromate Reagent Solution: Potassium dichromate (Merck, Germany): 1.0 g was added concentrated (6 M) sulfuric acid (Merck, Germany) to 100 ml and shake to dissolve; heat slightly if necessary. Standard Ethanol: Saturated 95%v/v ethanol (Merck, Germany) was diluted with DI water. The selected colorless mixed alcoholic drinks were purchased from commercials. The alcohol level of each drink was shown on the label. All samples were used for the performance test of the method. The criteria of optimum concentration for both potassium dichromate and sulfuric acid were optimized by considering the sensitivity, background, and linearity of ethanol standard range at 1.0-5.0 %w/w. The selected concentration of potassium dichromate and sulfuric acid was 1%w/v and 6 M, respectively.

Apparatus and Software

Equipment of system

A Samsung Galaxy S IV smartphone was used as a color detector. The specification of the smartphone is Android OS, v4.0.4 (Ice Cream Sandwich) or v4.3 (Jelly Bean), and the resolution spatial of its camera is 8 MP, 3264 x 2448 pixels, autofocus, and LED flash. A protective lightbox was constructed with white opaque plastic for the size of 18 cm x 22 cm x 5 cm. The box was fitted with white light LED array source on top with 2 AA-type batteries and reaction plate-form on the bottom as showed in figure1. The light path of the media solution was 1.0 cm (volume for 2.0 ml of solution). The distance between the camera and the surface of the solution is 3.5 cm.

RGB CMY HSV value acquisition

For the average RGB reflectance value from a smartphone, an application Color Grab algorithm version 2.5.5 ©loomatix Ltd. for RGB real-time reader was used. It can be automatically focused on the surface of the solution at a distance of 3.5 cm. The Region of interest (ROI) of monitoring was the middle position of the reaction plate form as illustrated in figure 2. All color models were recorded only touch screen on ROI position as shown in figure 2.

Results and Discussion

Color models studies for time based analysis

Time-Based Analysis (TBA) for signal detection necessary to evaluate the suitable color model for the time recorder. The change of yellowish color to light blue color was monitored by Color Grab Application for the RGB, HSV, CMY color models. Three color models were selected by recording the time (second unit) and monitoring color values. The second unit of recording time was plotted versus the color value of each model. Change of reaction rate depended on the concentration of ethanol which a high concentration level occurs at fast change and, in contrast, at a low concentration level shows a slow change. Then, the time of color change for signal processing can be used to evaluate the stop time *via* color monitoring. The evaluation of suitable color models for stop time was studied with the dynamic graph as showed in figure 3. It was found that a Hue 50, Red 70 and magenta15 were selected as stop time. The criteria of selection were considered by the analytical curve between time recorded (Log of the second unit) versus the concentration of ethanol (%w/v). The sensitivity (slope and intercept) and correlation of determination (R^2) were considered.

Analytical characteristics

A dominant of each color model was selected for constructing the calibration curve by using stop time such as (Red channel = 70, Hue = 50 and Magenta = 15). All color model was studied for linearity evaluation with an ethanol standard solution in a range 1.0-5.0 %w/v which is a suitable concentration for color change monitoring and time recording because concentration affects the rate of reaction. The recording time is defined as a time when the color of each dominant color model runs to stop time after mixing of reagent and ethanol standard. The delay time of recording time was set at 5 seconds to ensure absolute mixing. The concentration of ethanol was plotted with a log of the second unit of reaction time that showed good results of linearity and an effective determination curve (see in figure 4). The results showed no difference in sensitivity for both 3 color models. The calibration graph were obtained (y = -0.166x + 2.416, R² = 0.998), (y = -0.159x + 2.760, R² = 0.991) and (y = -0.181x + 2.989, R² = 0.992) of Red channel,

Magenta channel and Hue, respectively where Y is Log of recording time in second unit and X is concentration of ethanol % w/v.
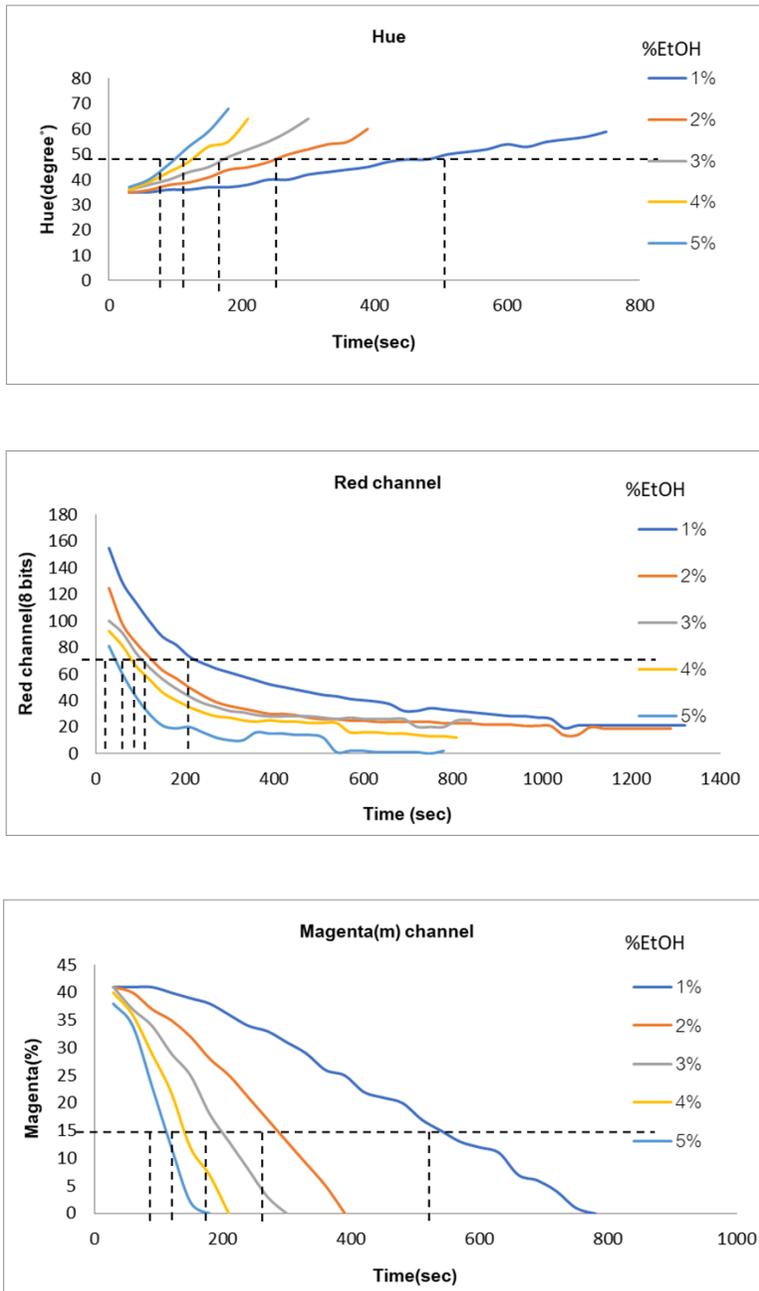

Figure 3 Analytical signals showing continuous changes of color changing time with the color model (Hue, Red, Magenta) of the ethanol at various concentrations.
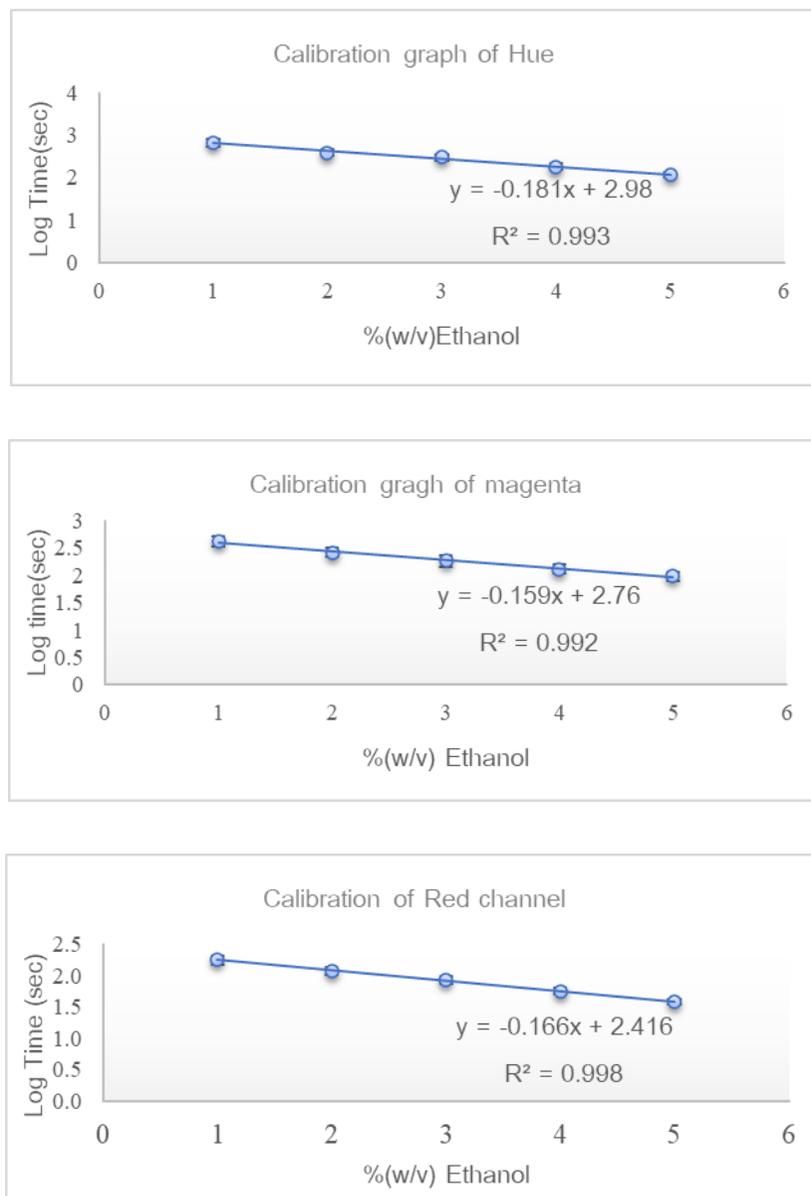
Calibration graph of Hue

$y = -0.181x + 2.98$

$R^2 = 0.993$

%(w/v)Ethanol

Calibration gragh of magenta

$y = -0.159x + 2.76$

$R^2 = 0.992$

%(w/v) Ethanol

Calibration of Red channel

$y = -0.166x + 2.416$

$R^2 = 0.998$

%(w/v) Ethanol

Figure 4 The time-based calibration graph obtained from the color measurement system at the selected dominant (Red, Hue and Magenta) color model for stop time.

Table 1 Accuracy and precision test of magenta dominant channel

Mixed alcoholic drinks (N=10)	% w/v Ethanol (labeled)	Measured value	% Recovery	% RSD
1	8	6.9 (±0.2)	86	2.7
2	5	5.5 (±0.5)	110	1.6
3	5	4.6 (±0.5)	93	1.3
4	5	5.4 (±0.5)	108	1.2
5	5	4.1 (±0.4)	83	1.9

Table 2 Accuracy and precision test of Hue dominant channel

Mixed alcoholic drinks (N=10)	% % w/v Ethanol (labeled)	Measured value	% Recovery	% RSD
1	8	7.1 (±0.1)	89	0.3
2	5	5.6 (±0.5)	112	1.5
3	5	4.7 (±0.5)	94	1.2
4	5	5.5 (±0.6)	110	1.6
5	5	4.2(±0.4)	82	1.8

Table 3 Accuracy and precision test of red dominant channel

Mixed alcoholic drinks (N=10)	% % w/v Ethanol (labeled)	Measured value	% Recovery	% RSD
1	8	6.7 (±0.8)	83	1.1
2	5	4.6 (±0.5)	92	1.2
3	5	5.6(±0.6)	112	1.1
4	5	5.2 (±0.4)	104	2.2
5	5	5.9 (±0.2)	118	4.2

* %Recovery = (measured/labeled) x 100

Conclusions

       An application of Time-Base Analysis (TBA) with color monitoring with the aids of application on a smartphone as a simple, rapid, portable and low-cost effective for a traditional complicated method in ethanol determination was demonstrated. The proposed method is an alternative of ethanol estimation and could be improved the disadvantage of the dichromate method from colorimetry. The proposed method could be developed into an automatic system and field test kit.

Acknowledgments

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