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A SIMPLE 3D TOOLBOX-BASED SMARTPHONE COLORIMETER: THE ABILITY TO DETECT THE STOICHIOMETRIC EQUIVALENT OF A CHEMICAL REACTION

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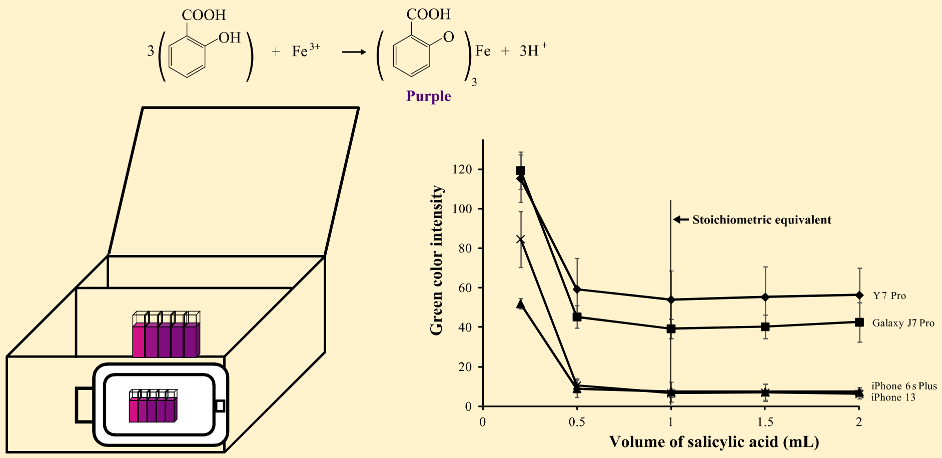
Abstract: The simple 3D toolbox is constructed and utilized with a smartphone to detect the stoichiometric equivalent of chemical reactions. The reaction chosen for this purpose involves salicylic acid and iron(III) ions, forming a purple complex. An image of the resultant purple product is captured and analyzed for RGB color intensities. These color intensities are contingent upon the concentration of the colored product, and a consistent color intensity is observed once the reaction reaches its stoichiometric point. Numerous smartphones were tested for image capture and color intensity measurement. It was discovered that all smartphones are suitable, although tuning the white balance mode is necessary to obtain clear images for accurate color intensity measurement. This smartphone-based spectrometer yields results comparable to those obtained from a commercial ultraviolet-visible spectrometer. This endeavor can serve as a blueprint for developing portable devices in chemical analysis using smartphones. Furthermore, the device and methodology developed herein can be effectively replicated in chemistry laboratory classes to impart a practical understanding of stoichiometry and chemical reactions through smartphone-based experimentation.



Keywords: *Colorimetry, iron(III) ion, salicylic acid, smartphone, stoichiometric equivalent*

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1. Introduction

Nowadays, a smartphone can be used not only for human communication and entertainment but also for sensing and chemical analysis (Crocombe, 2018). The important feature is the smartphone's camera, which can capture an image and discriminate the color under controlled illuminance (Nixon et al., 2020). Based on the colorimetric method, pictures of standard solutions with different colors were taken and read for RGB color intensities to create a calibration graph for analyzing samples. The advantages of this method are portability, simplicity, low cost, and ease of operation. The achievements of these smartphone-based spectrophotometric methods have been widely reported in various fields, such as agriculture (Jin et al., 2021; Qi et al., 2020), education (Kajornklin et al., 2020; Santos et al., 2020), the environment (Koohkan et al., 2020; Sargazi & Kaykhaii, 2020), food (Peamaroon et al., 2021; Ko et al., 2021), forensic science (Li et al., 2020; Jackson et al., 2020), industry (Moonrungsee et al., 2020; Shahvar et al., 2020), medical diagnostics (Samacoits et al., 2021; Kap et al., 2021), and pharmaceuticals (Phadungcharoen et al., 2020; Lantam et al., 2020).

The achievements of these smartphone-based spectrophotometers depended on the light-controlled box. The illuminance must be controlled to spread constantly around the samples. The sample blank is also required to be set, following the manner of the spectrophotometric method. In our previous works, many versions of light-controlled boxes have been fabricated using low-cost materials such as plastic and paper sheets for chemical analysis, including phosphorus (Moonrungsee et al., 2015), iron(III) (Moonrungsee et al., 2016), tyrosinase inhibitory activity (Moonrungsee[1] et al., 2018), salicylic acid (Moonrungsee[2] et al., 2018), copper(II) (Moonrungsee et al., 2020), and iodine number (Peamaroon et al., 2021), with a smartphone or a digital camera.

This work constructed the latest version of our designed box using a 3D printer. Another aspect of the smartphone spectrometer as a color measurement device is presented. A simple toolbox incorporated with a smartphone was employed to detect the stoichiometric equivalent of a chemical reaction. This work can serve as a guideline for creating a simple and low-cost smartphone-based spectrometer used for specific purposes.

2. Experimental

2.1 Chemicals and Solutions Preparation

All chemicals were of analytical reagent grade. All solutions were prepared using distilled water. A 3.0 mM iron(III) chloride solution ($FeCl_3.6H_2O$, Honeywell International Inc., Switzerland) was freshly prepared by dissolving 0.0203 g of iron(III) chloride in 25.00 mL of water. A 1.5 mM iron(III) chloride solution was prepared by diluting the 3.0 mM iron(III) chloride solution. A 4.5 mM salicylic acid solution ($C_7H_6O_3$, Ajax Finechem, Australia) was prepared by dissolving 0.0156 g of salicylic acid in a small volume of ethanol (C_2H_5OH, Ajax Finechem, Australia) and adjusted to the volume of 25.00 mL with water. A 0.1 M chromium(III) nitrate solution ($Cr(NO_3)_3.9H_2O$, Honeywell International Inc., Switzerland) and a 0.1 M ammonium sulphate solution ($(NH_4)_2SO_4$, Ajax Finechem, Australia) were prepared by dissolving 1.0004 g and 0.3304 g of solids in 25.00 mL of water, respectively. Finally, a 3.0 mM potassium thiocyanate solution (KSCN, Ajax Finechem, Australia) was prepared by dissolving 0.0073 g of potassium thiocyanate in 25.00 mL of water.

2.2 Device Fabrication and Color Intensity Analysis

A simple 3D toolbox was designed using the Tinkercad program, a free and user-friendly web application. The dimensions of the box were set at 15 cm × 15 cm × 9 cm (width × length × height), and the cover measured 15 cm × 15 cm (width × length). The designed models were then exported to STL format for compatibility with a 3D printer (XYZ Printing, da Vinci 1.0 Pro, Taiwan). The box was constructed using white polylactic acid (PLA) plastic as the printing filament. The box's exterior was covered with a black sticker sheet to create a controlled environment, as shown in **Figure 1(a).** Illumination inside the box was regulated by a strip of white light-emitting diode (LED) lamps affixed to the inner wall at the back end of the box, as depicted in **Figure 1(b).** The LED lamps were powered by a 12-volt direct current (DC) power supply. A white acrylic screen with a thickness of 1 mm was positioned 4 cm away from the lamps. Plastic cuvettes with a 1 cm optical path, serving as sample holders (up to 6 cuvettes), were positioned in front of the white acrylic screen. White plastic fins were inserted between the sample cuvettes to prevent color interference. A window measuring 3 cm × 3 cm on the front of the box allowed for the attachment of a smartphone to capture images of the color products.

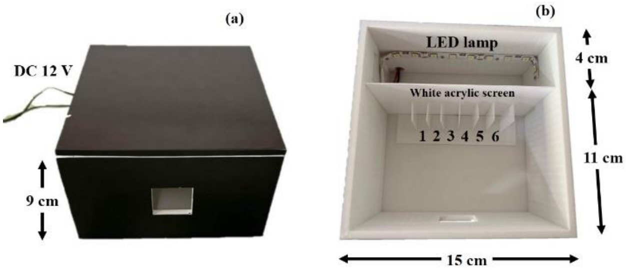

Figure 1. Dimensions and details of a simple 3D toolbox (a) outside (b) inside

A smartphone equipped with a fixed-focus camera, disabled flash, automatic white balance, and single image mode was positioned in front of the box to capture images of cuvettes containing the colored products resulting from reactions. The cuvettes were placed at the front of the white acrylic screen to minimize shadow effects and ensure optimal image capture. Each captured image was then analyzed using the Color Grab or Color Picker application, both available for free download and compatible with Android and iOS smartphones. These applications allowed the images stored in the smartphone's memory to be imported into the program for analysis. To determine color intensities, a screen touch was used to pinpoint the center of each cuvette, and the intensities of the red (R), green (G), and blue (B) colors were measured. The resulting color intensity values were displayed on the smartphone screen in the

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form of three-number series (R, G, B), such as 0, 0, 0, and 255, 255, 255 for black and white colors, respectively.

2.3 Reaction to Form the Colored Products

Three distinct colored products, namely purple, green, and red, were prepared to detect their respective stoichiometric equivalents. To generate the purple product, salicylic acid was reacted with iron(III) ions in a mole ratio of 3:1. The green product, on the other hand, was produced by the reaction between chromium(III) ions and ammonium sulfate in a mole ratio of 1:1. Lastly, the red product was obtained through the reaction between 1 mole of potassium thiocyanate and 1 mole of iron(III) ions. The stoichiometry of these reactions is illustrated in **Figure 2.** To enable accurate measurement using smartphones, the proportions of reactants were adjusted to achieve distinct and vibrant colors. The optimized formulas and comprehensive reaction details are outlined in a step-by-step manner as follows:

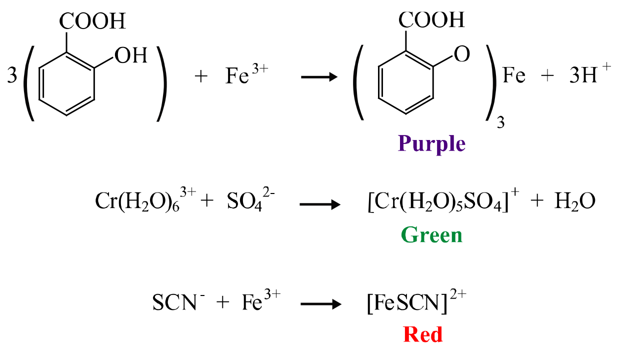

Figure 2. Chemical reaction for producing three colored products (purple, green, and red)

2.3.1 Reaction between Salicylic Acid and Iron(III) Ion

A volume of 1 mL of 1.5 mM iron(III) chloride solution, designated as the limiting reagent, was transferred to five cuvettes. Subsequently, 4.5 mM salicylic acid solution was added to the cuvettes in volumes of 0.2, 0.5, 1.0, 1.5, and 2.0 mL, respectively. Distilled water was added to achieve a final volume of 3 mL in all cuvettes.

2.3.2 Reaction between Chromium(III) Ion and Ammonium Sulphate

A volume of 1 mL of 0.1 M chromium(III) nitrate solution, designated as the limiting reagent, was transferred to five test tubes. Then, 0.1 M ammonium sulphate solution was added to the test tubes in volumes of 0.2, 0.5, 1.0, 1.5, and 2 mL, respectively. Afterward, distilled water was added to reach a final volume of 3 mL in all test tubes. Subsequently, all test tubes were heated in hot water (80-90°C) for 5-10 minutes.

2.3.3 Reaction between Potassium Thiocyanate and Iron(III) Ion

A volume of 1 mL of 3.0 mM iron(III) chloride solution, designated as the limiting reagent, was transferred to five cuvettes. Then, 3.0 mM potassium thiocyanate solution was added to the cuvettes in volumes of 0.2, 0.5, 1.0, 1.5, and 2.0 mL, respectively. Finally, distilled water was added to achieve a final volume of 3 mL in all cuvettes.

The reaction products, which exhibited the colors purple, green, and red, were initially analyzed using an ultraviolet-visible spectrophotometer (Thermo Scientific, model GENESYS 10S, USA) at wavelengths of 530 nm, 595 nm, and 545 nm, respectively. Following this, one of the reactions was chosen for analysis using the smartphone colorimeter. Images of the reaction products placed within the simple 3D toolbox were captured using a smartphone. These images were then analyzed for color intensity using freely available applications (such as Color Grab or Color Picker) installed on the smartphone, allowing for the inspection of stoichiometric equivalents. The intensities of the red, green, and blue (RGB) colors were assessed to determine the optimal color intensity. The point of constant color intensity, signifying the achievement of stoichiometry, was observed.

2.4 Evaluating Suitability of Various Smartphones

Four smartphone brands (Samsung, Vivo, Huawei, and Apple) with ten models were employed to detect stoichiometry using their default camera functions. All ten smartphones were set to fixed-focus camera mode without flash, automatic white balance, and single image mode. These smartphones were positioned in front of the box to capture images through the box window. The specifications of the smartphones utilized are presented in **Table 1.**

Table 1. Specifications of the 10 smartphones used for color measuring device

No.	Brand	Model	Operating system	Camera maximum resolution (megapixels)
1	Samsung	Galaxy J7 Pro	Android	13
2	Samsung	Galaxy A7	Android	24
3	Vivo	V11	Android	16
4	Huawei	Y7 Pro	Android	13
5	Apple	iPhone 6s Plus	iOS	12
6	Apple	iPhone XR	iOS	12
7	Apple	iPhone 12 Pro	iOS	12
8	Apple	iPhone 7	iOS	12
9	Apple	iPhone 12 Pro Max	iOS	12
10	Apple	iPhone 13	iOS	12

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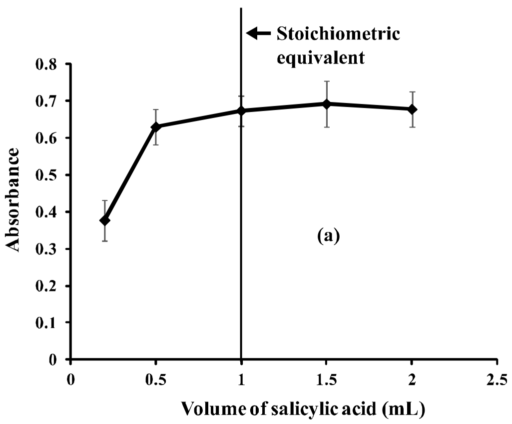
3. Results and Discussions

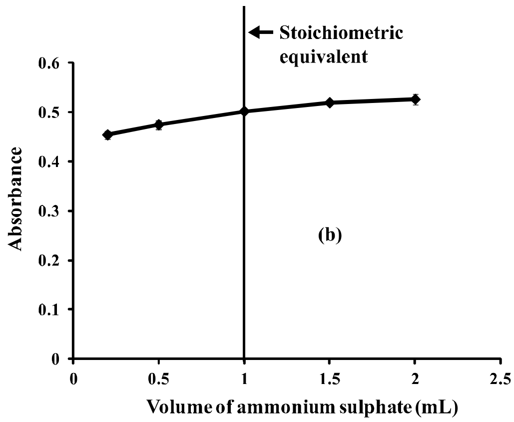
3.1 The Simple Toolbox Performance

The precision of the simple 3D toolbox was assessed by calculating the percentage of relative standard deviation (%RSD = (standard deviation of color intensity/mean of color intensity) × 100) of the measured color intensities. Food coloring solutions (red, green, and blue) at a concentration of 0.001% w/v were added to five cuvettes and measured using three smartphones with iOS and Android operating systems. This test aimed to evaluate the color intensities. The results indicated that the color intensities exhibited similar values across all five cuvettes for each tested color. The %RSD for each color solution was less than 10%, confirming the suitability of this toolbox for color intensity measurements.

3.2 Spectrophotometric Measurement

All the reactions were designed to use a constant volume of 1 mL for the limiting reagent. The other reactant was incrementally added to reach the equivalence point. After this point, a constant color intensity product could be achieved despite excess reactant. The absorbance of the purple, green, and red products was measured. The purple and green products displayed constant absorbance after reaching the equivalence points (**Figure 3(a)-(b)**), while the absorbance of the red product remained higher (**Figure 3(c)**). This could be attributed to the chemical equilibrium that influenced the color of the red product. The reaction between potassium thiocyanate and iron(III) ion could not be completed under our conditions. When comparing the reactions for forming the purple and green products, the reaction between chromium(III) ion and ammonium sulphate was more complex, likely due to the heating step involved. Additionally, the former reaction required a longer time to reach completion. Consequently, the reaction between salicylic acid and iron(III) ion (with iron(III) ion as the limiting reagent) to form the purple product was selected for smartphone-based measurement.





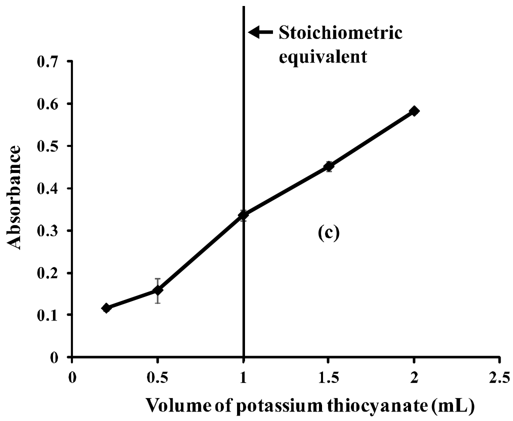


Figure 3. Absorbance of the products from the reaction between (a) salicylic acid (4.5 mM) and iron(III) ion (1.5 mM, 1 mL); (b) ammonium sulphate (0.1 M) and chromium(III) nitrate (0.1 M, 1 mL); (c) potassium thiocyanate (3.0 mM) and iron(III) ion (3.0 mM, 1 mL)

3.3 Smartphone Colorimetric Measurement

3.3.1 RGB Color Intensities

The smartphone (iPhone 6s Plus) captured an image of five cuvettes filled with the purple product. The intensities of the RGB colors for each cuvette were measured and plotted as a function of the volume of salicylic acid, as depicted in **Figure 4.** All colors exhibited a constant intensity after reaching the equivalence point at 1.0 mL of salicylic acid. However, the green color displayed the highest intensity difference between 0.5 and 1.0 mL of salicylic acid compared to the red and blue colors. This indicated that the green color provided better sensitivity than the red and blue colors. As a result, subsequent measurements were conducted using the intensity of the green color.

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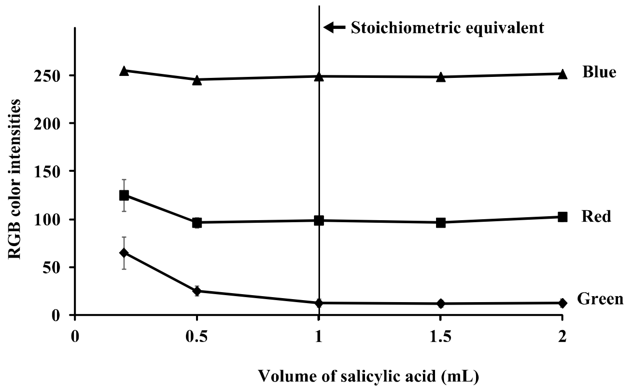

Figure 4. Intensities of RGB colors of the products from the reaction between salicylic acid (4.5 mM) and iron(III) ion (1.5 mM, 1 mL)

3.3.2 Effect of Smartphones Varieties

The image of the five cuvettes containing the purple products was captured using ten different smartphones (**Table 1**). **Figure 5** illustrates that the same image taken with various smartphones displayed different color intensity values due to differences in camera performance. This phenomenon was observed even when smartphones with the same camera resolution were used. Additionally, despite setting the automatic white balance mode on all smartphones, picture clarity and color variations were observed among both iOS and Android smartphones. These variations impacted the color intensities derived from the captured images.

The figure indicates that clear pictures obtained from smartphones such as Y7 Pro, Galaxy A7, Galaxy J7 Pro, iPhone 6s Plus, iPhone 13, and V11 yielded accurate results, showing the true colors of the samples. Following the equivalence point, a constant green color intensity was observed. On the other hand, the remaining smartphones (iPhone XR, iPhone 12 Pro, iPhone 7, and iPhone 12 Pro Max) produced light blue pictures and inaccurate results, with a green color intensity of zero at a volume of 0.5 mL of salicylic acid.

The current market offers a wide variety of smartphones, which presents challenges in maintaining control over this study. Color evaluation using different smartphones results in varying color intensities (Souza et al., 2018). It is necessary to adjust the white balance mode of the smartphone to obtain clear pictures before conducting measurements. Consequently, a fixed green color intensity cannot be universally applied to all smartphones. Determining the optimal RGB color for analysis is essential. For simplified operation, it is recommended to designate and use one smartphone per box for sample analysis.

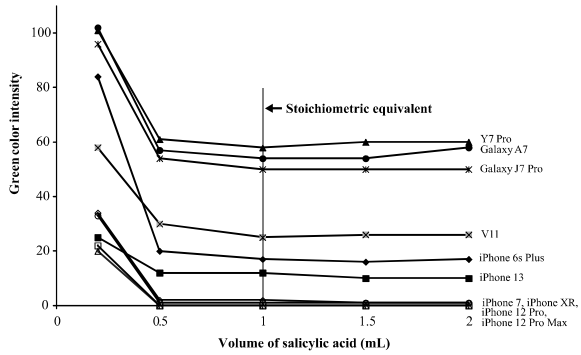

Figure 5. Intensity of green color from the ten smartphones in the range of 0.2-2.0 mL salicylic acid

Four smartphones were selected for the stoichiometric study: two Android devices (Y7 Pro, Galaxy J7 Pro) and two iOS devices (iPhone 6s Plus, iPhone 13). The study was repeated thrice (n=3), and the outcomes are presented in **Figure 6.** The green color intensity exhibited a consistent pattern following the equivalence point (1.0 mL of salicylic acid). This constant trend persisted even in excess reactant, indicating that the colored product remained unchanged. This consistent behavior of the curve was evident across all four smartphones.

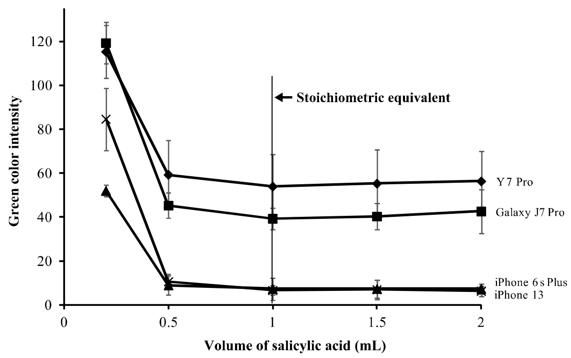

Figure 6. Intensity of green color from the four smartphones in the range of 0.2-2.0 mL salicylic acid.

In conclusion, this study presents a versatile approach that can be applied to monitor a wide range of chemicals, particularly hazardous substances like radioactive elements, pesticides, and heavy metals. The smartphone spectrometer demonstrated excellent performance in detecting colors across the visible light spectrum. In cases where the analyte lacks color or is present in low concentrations, a chemical reaction is employed to produce a colored product. By utilizing a selective color-forming reagent, this method allows for both qualitative and quantitative analysis. The excess reagent reacts with the analyte, forming a colored product whose intensity is linearly proportional to its concentration. For instance, salicylic acid can be determined using excess iron(III) ions as a coloring reagent (Moonrungsee[2] et al., 2018), and vice versa (Rajendraprasad & Basavaiah, 2016). The remaining unreacted reagent remains stable and

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does not interfere when mixed with the colored product. Furthermore, this approach has practical applications in educational settings, as it can be implemented in chemistry laboratory classes to teach concepts related to stoichiometry and chemical reactions using smartphones.

4. Conclusion

To summarize, this work demonstrates the adaptation of a smartphone for measuring RGB intensities of sample solutions within a specially designed light-controlled box referred to as the "simple 3D toolbox". The device successfully detected the stoichiometric equivalent of the reaction between salicylic acid and iron(III) ion. Notably, constant color intensities were observed once the reaction reached its stoichiometry. While all smartphones can be employed, it is important to note that fine-tuning the white balance mode may be necessary to ensure clear and accurate measurements.

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