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The Application of the HSV Color Model for Accurate Digital Colorimetric Analysis of Fluoride Detection Using a Thiourea Receptor

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Abstract. Color analysis using colorimetric detection has shown significant advancements, although it still faces challenges when capturing color images under varying illumination conditions. This study explores the utilization of the HSV (hue, saturation, value) color model for precise color analysis, enabling the differentiation of colors based on their type, intensity, and brightness without being affected by illumination. The HSV model, measured by the Euclidean Distance (ΔE) value, is employed to investigate the impact of fluoride solution pH and concentration on the colorimetric detection process of fluoride ions using a thiourea receptor. The colorimetric detection of fluoride ions at low and high pH levels decreases ΔE values and notable color changes. Additionally, the HSV model elucidates the color variations induced by fluoride concentration and demonstrates a linear relationship up to 0.9809.

Introduction

Color analysis using the visual colorimetry method, which measures analyte concentration by observing the color change with the naked eye, has been developed to distinguish the color produced during detection. The development of color analysis also aims to avoid subjective factors from naked eye analysis so that insignificant color changes can be precisely distinguished [1]. Moreover, in modern society, color analysis development in colorimetric detection requires more facile, convenient, and digitalization. Hence, color analysis using digital images has been developed by employing color models such as RGB, CMYK, and HSV to represent the produced colors and to identify the colors more precisely [2].

The RGB model is the most common color model used in digital analysis, which describes the colors in a cube, with each coordinate indicating red, green, and blue colors [3,4]. This model has been used mainly in the initial digital analysis of colorimetric detection because of its simplicity in describing and converting colors. However, it also means that merely based on the red, green, and blue colors will be distinguished. In addition, there is an interference in the actual condition when applying the RGB model from ambient illumination, which affects the intensity of the identified color [5].

The HSV model used in digital analysis defines color in three components: hue means color type, saturation or intensity of the color, and value means color brightness [6]. This model is also a mathematical transformation or conversion from the RGB model. Therefore, using the HSV model, color identification can be more comprehensive, not only from simple color combinations. Saturation components in the HSV model identify the color more flexibly towards the ambient illumination factor and make the color difference more accurate [5,7]. Moreover, suppose the HSV model is adapted with photoelectric colorimetry analysis like spectrophotometry. In that case, the Hue component is well-fitted to be compared with spectrophotometer wavelength because it represents the color using a single numerical value [8]. The application of the HSV model for color analysis in colorimetric detection has been reported, such as in PhCs gel sensor synthesis [9]. The sensor response to temperature and organic solvent showed linearity up to 0.95 between the Hue component and various influencing parameters, which was higher than that obtained using the RGB model.

Furthermore, high linearity was produced up to 0.993 between the Hue component and spectrophotometry usage for color analysis of pH detection by an inverse opal photogenic gel (IOPG) sensor [8].

The colorimetric detection of fluoride ions with the thiourea receptor produces a specific color from the detection process, which is also influenced by the pH and concentration of the fluoride ion solution. The color resulting from the colorimetric detection of fluoride ions can be analyzed digitally to identify color changes more efficiently and accurately [10]. Therefore, this study employed the HSV color model for digital analysis of the color produced by fluoride ion colorimetric detection using a thiourea receptor.

Experimental

Materials used in this research were acetonitrile, 1,1'-(1,4-phenylene)bis(3-(4-nitrophenyl)thiourea), tetra-n-butylammonium fluoride, NaOH crystals, HCl (37%) solution. This research was conducted by adding specific amounts of tetra-n-butylammonium fluoride into a thiourea solution in acetonitrile. Afterward, the color that had been produced from the fluoride detection was performed digitally by placing the test solution in a cuvette on a lightbox illuminated with a fixed LED lamp on the top side of the box. The OPPO Reno smartphone was placed in a holder at a fixed distance (20 cm) from the colorimetric solution. Photographs of the solution cuvette were captured using the smartphone's built-in camera with 48 Megapixel resolution. The ColorGrab application was used to convert the HSV value from the image. The Euclidean Distance (ΔE) value represents the distance between the hue, saturation, and value component, which is proportional to the fluoride concentration used for quantitative analysis. The ΔE was determined using the following equation:

$$\Delta E = \sqrt{(Ri - R0)^2 + (Gi - G0)^2 + (Bi - B0)^2}$$

Results and Discussion

The colorimetric detection of fluoride ion with thiourea receptor resulted in a color change from colorless to orange. The color change occurred because of the interaction between the NH active site on the thiourea receptor and fluoride ion, as shown in Figure 1. The positive partial of hydrogen in the NH group enabled the formation of a bond with fluoride ion, which has high electronegativity. In addition, the acidity of the thiourea receptor was strengthened with the electron-withdrawing group, NO_2, on its structure so that the NH group could donate hydrogen more efficiently [11]. A significant color change from fluoride ion detection may also be caused by thiourea receptor usage with more than two chromophore groups on its structure, which makes the surrounding electrons more delocalized.

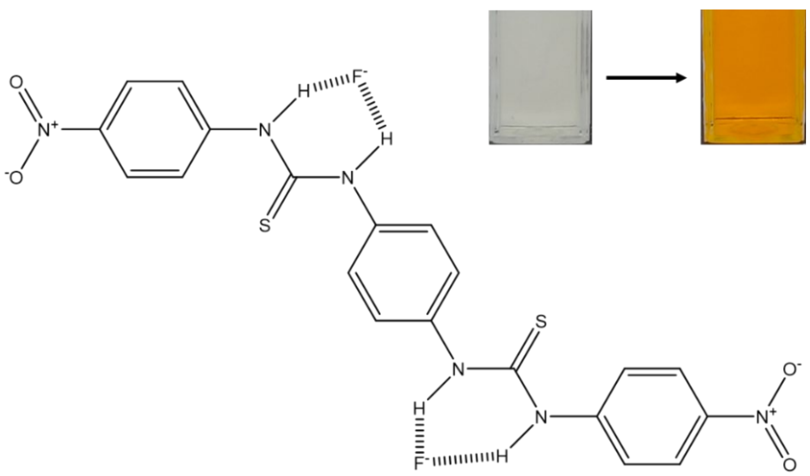

Fig. 1. Interaction between fluoride ion with thiourea receptor resulted in color change

Color analysis was performed using the HSV model to observe the influence of pH and concentration on the fluoride ion detection process. All the components used in the HSV model were combined to Euclidean Distance (ΔE) value, which represents the distance between components and is proportional to the fluoride concentration for quantitative analysis [12]. The Euclidean distance value shows a significant reduction in the influence of acidic pH on the fluoride ion detection process with thiourea, as shown in Figure 2.

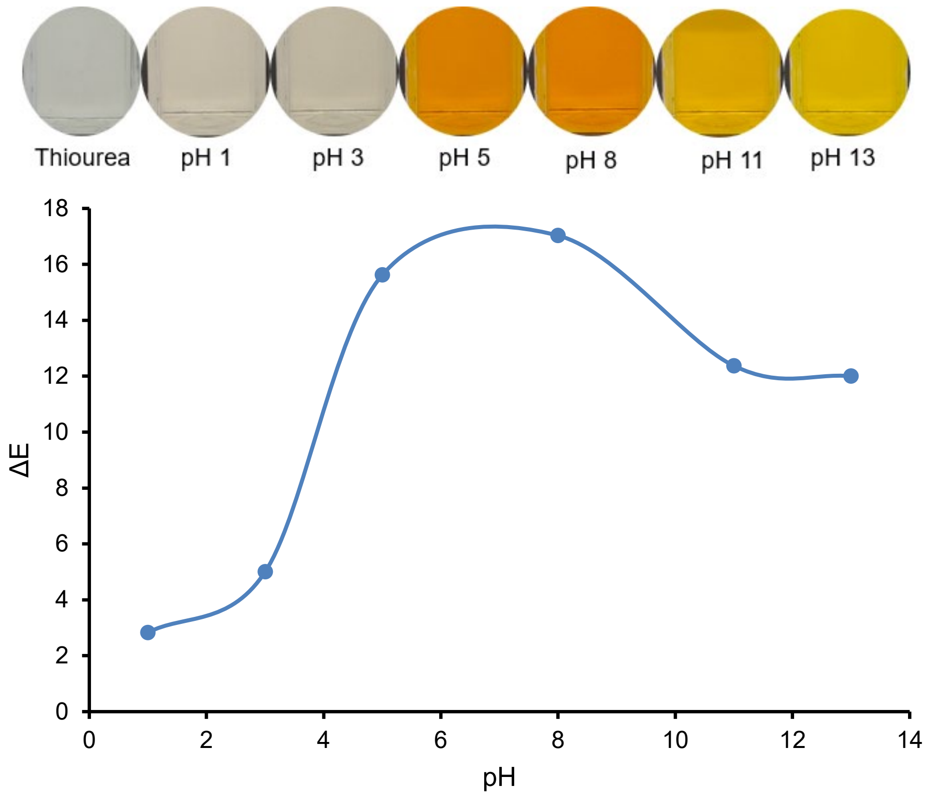

Fig. 2. Color changes and ΔE value of different fluoride solution pH condition

The reduction of the Euclidean distance value is caused by the formation of fluoride acid (HF), which is dominantly formed with excess hydrogen ions in solution [13]. The effect of acidic pH on the detection process does not produce a color change, so comparing HSV values at pH 5 (control) with acidic pH can be easily distinguished. The Euclidean distance value between the control and acidic pH (pH 1 and 3) experienced a significant difference because all three components of the HSV model from both pH ranges result in different values that are characteristic for each produced color.

On the other hand, under basic conditions, the fluoride ion detection process with thiourea still produces color even though the Euclidean distance value decreases. The different Euclidean distance values can be dominated by Hue or color type values, which differ from orange (control pH) to yellow (alkaline pH). The decrease in the value of ΔE at alkaline pH, which is not as large as that at acidic pH, is probably due to the presence of OH^- ions that bind to thiourea and reduce the acidity of its structure, thereby reducing the thiourea response to fluoride ions.

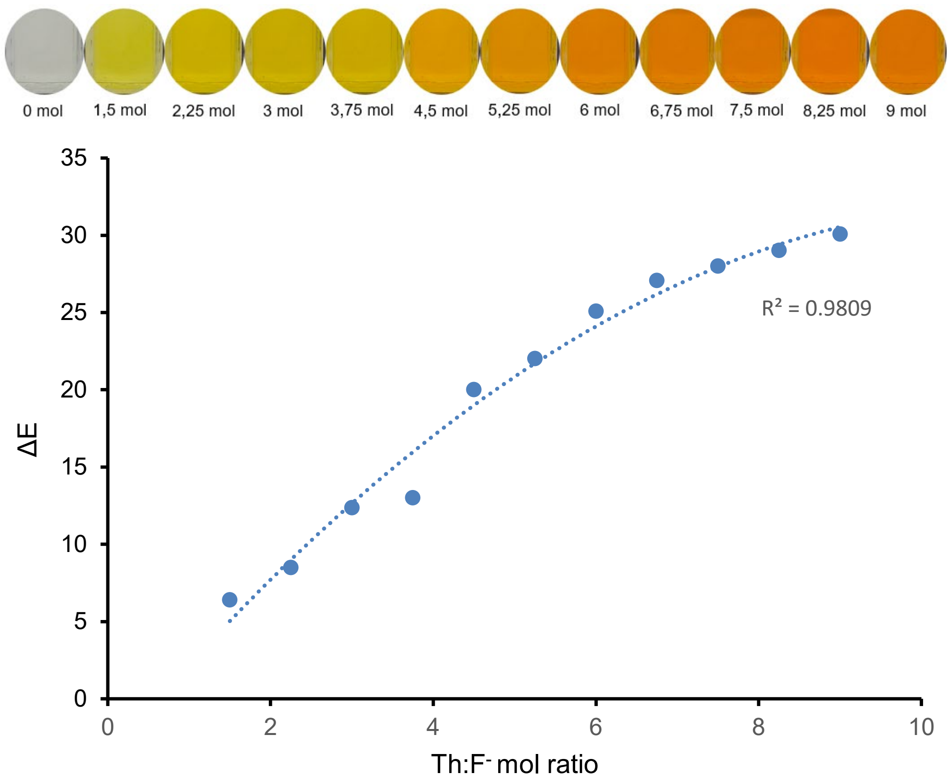

Fig. 3. Color changes and ΔE values of different fluoride solution concentrations

Regarding the effect of fluoride ion concentration on the detection process presented in Figure 3, the Euclidean distance value of the HSV model increased as the concentration of fluoride ions increased. These increases could be caused by the greater the concentration of fluoride ions added and the more fluoride ions interact with thiourea. At the beginning of fluoride ion addition at a small concentration, the presence of fluoride ion induces an interaction between the NH groups on thiourea and the ion. The addition of fluoride ions at higher concentrations causes deprotonation of the thiourea structure, as shown in Figure 4, resulting in a sharper and more saturated color change [11].

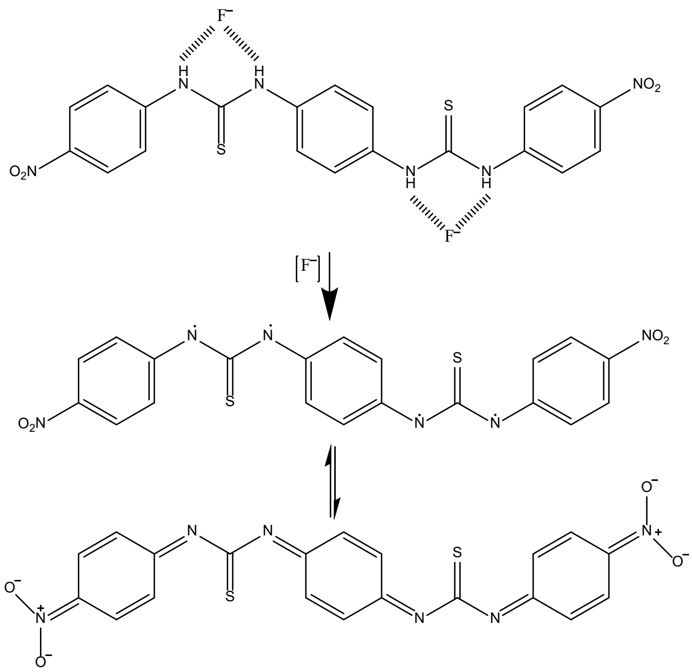

Fig. 4. Protonation and deprotonation structure of thiourea receptor toward fluoride addition

Based on the Euclidean distance value and the observed color shifts, the most influential component of the HSV model appears to be the Hue component. This is evident in the substantial color variations ranging from colorlessness to shades of green, yellow, and orange at various concentration points. A notable shift in color occurs between concentrations of 3.75 and 4.5, transitioning from yellow to orange. This transition is marked by a significant increase in the Euclidean distance value at both concentrations.

In contrast, at higher concentrations exceeding 7.5 mol, it is conceivable that the NH group in thiourea attains full occupancy, rendering it unresponsive to or unable to interact with fluoride ions. Consequently, the orange color observed loses its vibrancy to the naked eye. Nonetheless, the color shift remains discernible utilizing HSV analysis through the Euclidean distance.

The analysis of the HSV model indicates strong compatibility with different fluoride ion concentrations, showing a linearity of up to 0.9809. This compatibility suggests that the HSV model is highly effective in elucidating and distinguishing the color changes that occur during the fluoride ion detection process with thiourea.

Conclusion

The HSV color model has been used to analyze the color resulting from fluoride ion detection using the thiourea receptor, which produces a color change from colorless to orange. On the effect of pH in the detection process, the analysis was carried out using the HSV model, represented by the Euclidean distance (ΔE) value, and shows a decrease in both acidic and basic pH levels, corresponding to the resulting color change. Using the HSV model, the effect of fluoride ion concentration is also explained by increases in the ΔE value as the fluoride ion concentration increases with a linearity of 0.9809. Therefore, it can be concluded that the HSV color model can accurately describe the color change under the influence of pH and concentration. It shows the convenience in the colorimetric analysis of fluoride ion detection with the thiourea receptor.

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