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An application of spectrophotometer for ADMI color measurement

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Abstract. The ADMI color scale is developed to measure the color of wastewater as an indicator of water quality. ADMI color is a metric quantity based on the Adams Nickerson color difference between the APHA/Pt-Co/Hazen liquid standards and distilled water. The Adams Nickelson color formula is obtained by transforming CIE tristimulus color indices into a uniform metric color scale that is independent of hue. If two colors of different hues are different to the same degree from the reference colorless water, then the difference will be the same. For a general purpose spectrophotometer with a measuring range of 360 nm to 830 nm and the wavelength resolution of 1 nm, we developed an ADMI color application based on APHA 2120F weighted-ordinate spectrophotometric method for measuring the color of wastewater in the range of 0 ADMI to 500 ADMI.

1. Introduction

The color of water caused by organic and inorganic substances both dissolve and non-dissolve in water. Before discharging of wastewater, the color has to be treated to an acceptable value [1-2]. There are two method types based on visual and spectrophotometric methods for color measurement in wastewater [3]. APHA/Pt-Co/Hazen is a popular visual method [4] while the ADMI (American Dye Manufacturers' Institute) is a standard spectrophotometric method [5-6]. The ADMI color is a metric quantity for color measurement of wastewater to determine the contamination of dye and pigment in water. In Thailand, the color of wastewater regulation is limited to 300 ADMI.

The ADMI scale is adopted the APHA/Pt-Co/Hazen liquid color standards as a set of reference standards which the dye effluent is rated using a total color difference correlation based on the Adams Nickelson color formula [7-8]. The ADMI unit is independent of hue. For instance, if a red dye effluent is observed to differ from pure water to the same magnitude as a yellow APHA/Pt-Co/Hazen standard solution, then the red effluent is assigned to the same value as the yellow standard color.

The APHA/Pt-Co/Hazen method can measure the yellow color of water that is suitable for natural water while the ADMI method can measure every color of water that is suitable for the dye effluent of industries. There were two ADMI submethods proposed [1]. The first ADMI method was APHA 2120E tristimulus filter method that based on tristimulus values of *X*, *Y* and *Z* via transmittance values of three filters. The second ADMI method was APHA 2120F weighted-ordinate spectrophotometric method.

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In this work, we developed an application of the ADMI color measurement for a general purpose spectrophotometer based on the APHA 2120F method.

2. Experiment

The ADMI method is applicable to any hue and sensitive to small color differences. The method requires generating CIE tristimulus values of a sample. We selected a UV-Vis spectrophotometer, T60 of PG Instruments. The CIE 1931 standard observer matching function with the spectrum range of 360 nm to 830 nm and the wavelength steps of 1 nm was selected as shown in Figure 1. The CIE-XYZ values can be calculated by

$$X = k \sum_{\lambda} \phi(\lambda)\bar{x}(\lambda)\Delta\lambda \quad (1)$$

$$Y = k \sum_{\lambda} \phi(\lambda)\bar{y}(\lambda)\Delta\lambda \quad (2)$$

$$Z = k \sum_{\lambda} \phi(\lambda)\bar{z}(\lambda)\Delta\lambda \quad (3)$$

where $\phi(\lambda)$ is the color stimulus function, k is a constant, and $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ are the color matching function of the CIE 1931 standard observer [9].

The tristimulus values of X, Y and Z are converted to Munsell values V_X, V_Y and V_Z respectively by solving the fifth-degree polynomial functions as

$$1.1913V_X - 0.22533V_X^2 + 0.23352V_X^3 - 0.020484V_X^4 + 0.0008194V_X^5 = X \quad (4)$$

$$1.1913V_Y - 0.22533V_Y^2 + 0.23352V_Y^3 - 0.020484V_Y^4 + 0.0008194V_Y^5 = Y \quad (5)$$

$$1.1913V_Z - 0.22533V_Z^2 + 0.23352V_Z^3 - 0.020484V_Z^4 + 0.0008194V_Z^5 = Z \quad (6)$$

The Adams-Nickerson color difference (DE) between the color of water intended to measure and distilled water as the reference color is calculated by

$$\mathrm{DE} = [(0.23\Delta V_Y)^2 + \left(\Delta(V_X - V_Y)\right)^2 + \left(0.4\Delta(V_Y - V_Z)\right)^2]^{1/2} \quad (7)$$

Then the DE value can be converted to ADMI by a calibration curve obtained by a set of color standards.

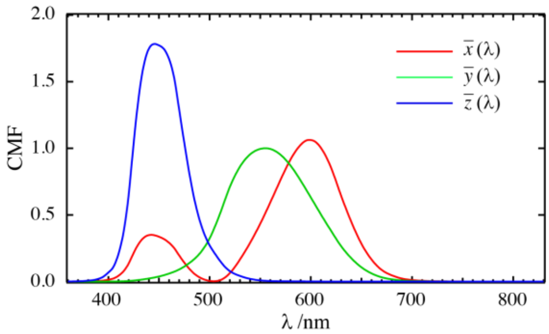

Figure 1. The CIE 1931 standard (2˚) observer matching functions.

The color standards based on ASTM D1209 [10] were prepared from a commercial APHA/Pt-Co/Hazen stock solution with the value of 500 units. Distilled water was measured as the baseline for the zero ADMI calculation. The stock solution was diluted as (25, 50, 100, 150, 200, 250) ADMI. The stock solution was used to measure a spectrum of the value of 500 ADMI. The cell path of 5.0 cm was used for the color calibration of the spectrophotometer.

3. Results and discussion

To demonstrate the procedure, a spectrum of 150 ADMI is measured by the spectrophotometer. The spectrum range was 360 nm to 830 nm with the step of 1 nm. A color stimulus function can be shown as in Figure 2a and the corresponding results of multiplication between the stimulus function and the matching functions shown in Figure 2b.

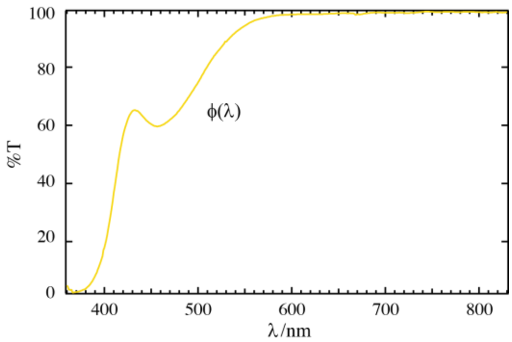

Figure 2a. A stimulus function of standard color solution that equivalent to the color value of 150 ADMI.

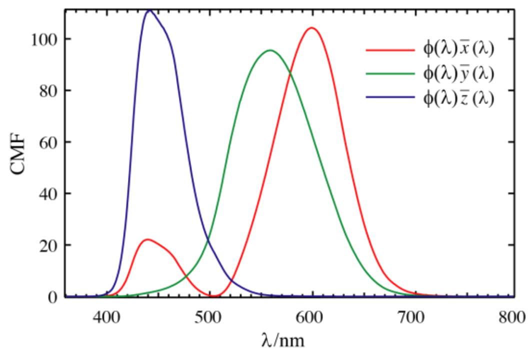

Figure 2b. The CIE-XYZ functions obtained by multiplications between the stimulus function and the standard (2˚) matching functions.

The calibration of the spectrophotometer was carried out to determine a calibration curve for the color measurement of wastewater by the mean of ADMI method. The calculated results are tabulated in Table 1. The calibration curve can be obtained by a third-degree polynomial fitting between the DE and the color values ADMI with R^2=0.9998 as shown in Figure 3.

Table 1. Calculated results of the CIE *X*, *Y*, *Z*, Munsell values V_X, V_Y, V_Z and the Adams-Nickerson color difference (DE)

ADMI	*X*	*Y*	*Z*	V_X	V_Y	V_Z	DE
0	10687.2	10686.3	10690.8	30.67725	30.67681	30.67918	0.00003
25	10492.6	10527.0	9869.12	30.57461	30.59287	30.23454	0.14676
50	10272.0	10326.3	9031.28	30.45627	30.48555	29.74813	0.30064
100	9920.05	10002.4	7666.48	30.26298	30.30872	28.86809	0.58520
150	9734.86	9819.94	6657.87	30.15898	30.20696	28.12857	0.84068
200	9417.77	9484.14	5607.11	29.97700	30.01551	27.24963	1.11837
250	8877.75	8984.40	4569.93	29.65494	29.71982	26.23206	1.41480
500	8795.92	8637.02	2439.26	29.60472	29.50606	23.28191	2.50704

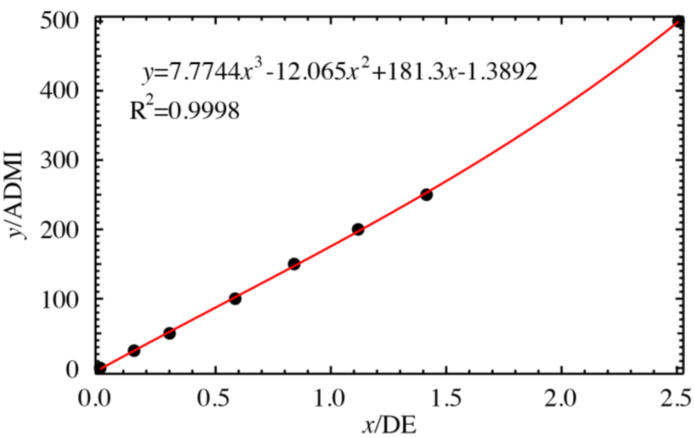

Figure 3. A calibration curve of the ADMI color measurement for the spectrophotometer.

The color of wastewater from a spectrum can be calculated by the third-degree polynomial equation in the unit of ADMI as

$$y = 7.7744x^3 - 12.065x^2 + 181.3x - 1.3892 \tag{8}$$

where x is the calculated DE.

The uncertainty of the measurement can be evaluated by

$$U(y) = t_{\propto/2,n-4} s_{y,x} \sqrt{\frac{1}{n} + \frac{(x-\bar{x})^2}{\sum_{i=1}^{n}(x_i-\bar{x})^2}} \tag{9}$$

where $t_{\propto/2,n-4}$ is the coverage factor according to Student's t distribution, n is the number of calibration points, $n-4$ is the degree of freedom, $s_{y,x}$ is the standard deviation of $y(x)$. The color values and uncertainties with 95 % degree of confidence at the calibration points can be shown in Table 2.

Table 2. Calculated results of the color values and uncertainties at the calibration points.

x/DE	color/ADMI	y/ADMI	$U(y)$/ADMI
0.00003	0	-1.4	4.6
0.14676	25	25.0	4.2
0.30064	50	52.2	3.8
0.58520	100	102.1	3.3
0.84068	150	147.1	3.1
1.11837	200	197.2	3.2
1.41480	250	253.0	3.8
2.50704	500	499.0	7.3

4. Conclusion

We developed an application of ADMI color measurement for a UV-Vis spectrophotometer. The color standards liquid were prepared for the values of (0, 25, 50, 100, 150, 200, 250, 500) ADMI. A third-degree polynomial calibration curve was obtained with an uncertainty equation. The application works well for the color measurement of wastewater in the range of 0 ADMI to 500 ADMI.

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