Concentration measurement of chromium passivation solutions by an optical method

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Abstract. Chromium passivation solutions are widely used in the last step of plating process for improving metal surfaces. The appearance as well as corrosion resistance of the treated surface depend on the thickness of chrome layer which is controlled by many factors including the concentration of the solution. In this research, we study the relation of the light absorption and the concentrations of a chromium passivation solution. We prepare the solutions with five different concentrations and measure their absorbance by using an ultraviolet-visible spectrometer. The absorption spectrum non-monotonously changes with the wavelength of the incident light. However, the absorbance always linearly increases with the concentration at all wavelengths. We construct several calibration equations at different wavelengths and test them by using solution samples with other concentrations. The results show that the concentration of chromium passivation solution should be measured at wavelengths in the range of 420-700 nm because the errors are less than 5%.

1. Introduction
Chromium passivation solutions are widely used in metal plating industry. Decorative chrome is typically the last layer in plating process and is applied on engine systems, automotive trims, hardware and appliances. The chrome layer provides colour and hue and improves corrosion resistance, abrasion resistance, tarnish resistance and weather resistance. The thickness of chrome layer affects the property of chromium layer and depends on many factors including the concentration of the chromium passivation solution [1-3].

The concentration of chromium in different samples can be measured using many methods as the following examples. The concentration of hazardous hexavalent chromium (VI) in river sediments of industrially exposed sites is determined by using inductively coupled plasma mass spectrometry [4]. A potentiometric flow titration with titrant iron (II) solution is used to determine chromium (VI) in a sample solution [5]. A study shows that rhodamine lactone exhibits higher colorimetric and fluorescence selectivity and sensitivity to chromium (III) in aqueous medium than other metal ions and a rapid detection using filter papers is demonstrated [6]. Digital imaging has been proposed as a fast and low-cost method for quantitative analysis of chromium (VI) in aquatic samples by using colorimetric reagent of diphenylcarbazide [7].

In this article, we investigate examining the concentration of chromium passivation solutions based on the Beer-Lambert law [8] by using a spectrometer. The relations between the standard concentration and
the absorbance of the solutions are established as calibration equations. Finally, chromium passivation samples are used to test the calibration equations.

2. Methods

A commercially high concentrated chromium passivation solution is received from Okuno-Auromex (Thailand) Co., Ltd. The passivation solution is diluted in deionizing water to create five solutions with concentrations of 1.750, 2.625, 3.500, 4.375, and 5.250 g/L (standard concentrations). The solutions are placed in 1-cm spectrophotometric cells and the absorbance spectra are investigated in LAMBDA 365 UV/Vis Spectrophotometer (Perkin Elmer). For a given wavelength, we construct a calibration equation which is a linear fit between the absorbance and the five concentrations as

\[ y = ax + b \]  

(1)

where \( x \) and \( y \) stand for the absorbance and the concentration, respectively.

To search for appropriate wavelengths for concentration measurements of the chromium passivation solution, we prepare other eight solution samples at concentrations in the same range of the five standard concentrations and measure the absorbance using the same spectrophotometer. The absorbance is used as the input of the calibration equations to calculate the concentration of the samples and the percentage error of the concentration from the calibration equations is determined. Using the method in [9], the absorbances of blank and a very diluted solution (0.175 g/L) are measured 20 times to estimate the resolution and the limit of detection (LoD) of the measurement method.

3. Results and discussion

![Figure 1. Chromium passivation solutions with five standard concentrations: 1.750, 2.625, 3.500, 4.375, and 5.250 g/L from left to right.](image)

In 1-cm spectrophotometric cells, the five diluted passivation solutions with standard concentrations appear as blue color and the higher concentration, the darker the color, as shown in figure 1. The image shows that the visible-light absorption of these solutions depend on the concentration.

The absorption spectra of the five diluted passivation solutions are illustrated in figure 2. Each spectrum shows two peaks at 420 nm and 565 nm and a local minimum at 485 nm located between the peaks. Even more, All curves do not cross each other and the absorbance increases with the concentration.

Regressions of the absorbance and the concentration as in equation (1) result in calibration equations with different parameters \( a \) and \( b \), as shown in table 1. Even though the the maximum absorption occurs at the wavelength of 565 nm, we construct many calibration equations for different wavelengths: the wavelengths at two peaks (420 nm and 565 nm), the local minimum (485 nm), and others in order to study the error of measurement. The parameters \( a \) and \( b \) are different for the tested wavelengths. The R-
Square is very close to the unity for all cases of tested wavelengths. This implies that the data fit very well to the linear regression as two examples in figure 3.

![Figure 2](image)

**Figure 2.** The absorbance spectra of the five diluted chromium passivation solutions. Bottom to top curves correspond to the solution with concentrations of 1.750, 2.625, 3.500, 4.375, and 5.250 g/L, respectively.

![Figure 3](image)

**Figure 3.** Example of calibration curves of chromium passivation solutions at (a) 565 nm and (b) 725 nm. Squares and lines indicate the measured values and the linear fits, respectively.

| Wavelength (nm) | a     | b    | R-square |
|-----------------|-------|------|----------|
| 350             | 17.093| 0.0135| 0.9998   |
| 420             | 2.2896| 0.0720| 0.9999   |
| 453             | 3.8078| 0.0537| 0.9999   |
| 485             | 7.0150| 0.0381| 0.9999   |
| 525             | 3.0949| 0.0268| 0.9999   |
| 565             | 1.9424| 0.0762| 0.9999   |
| 633             | 4.7456| 0.0876| 0.9999   |
| 700             | 32.797| 0.1021| 0.9998   |
| 725             | 104.88| 0.0962| 0.9997   |

**Table 1.** Parameters a, b and R-square of linear regressions at different wavelengths.
To specify proper wavelengths for the concentration measurements of chromium passivation solutions, we measure absorbance of other eight passivation samples and insert it into the calibration equations with difference parameters $a$ and $b$ in table 1 so that the measured concentrations ($c_{\text{mea}}$) are obtained. The percentage error of $c_{\text{mea}}$ at different wavelengths is calculated as $\%\text{error} = \left( \frac{c_{\text{mea}} - c_{\text{ref}}}{c_{\text{ref}}} \right) \times 100$ where $c_{\text{ref}}$ represents the concentration of the prepared samples. The minimal and maximal errors for each wavelength are shown in table 2. The results indicate that when the accuracy of 5% is acceptable, the wavelengths 420 - 700 nm are suitable for the concentration measurement of chromium passivation solutions. For these wavelengths, the resolution and the LoD of the method are between 0.48 - 31.22 mg/L and 1.45 - 93.65 mg/L, respectively.

Table 2. Minimum and maximum percentage errors of the measured concentration of samples, resolution and LoD of the measurement method at different wavelengths.

| Wavelength (nm) | 350  | 420  | 453  | 485  | 525  | 565  | 633  | 700  | 725  |
|-----------------|------|------|------|------|------|------|------|------|------|
| Minimum error (%) | 0.21 | 0.04 | 0.04 | 0.03 | 0.01 | 0.01 | 0.01 | 0.06 | 0.01 |
| Maximum error (%) | 7.14 | 0.66 | 0.69 | 1.12 | 0.68 | 0.59 | 0.61 | 4.05 | 14.06 |
| Resolution (mg/L) | 18.65 | 0.63 | 1.21 | 1.85 | 0.96 | 0.48 | 1.28 | 9.63 | 31.22 |
| LoD (mg/L) | 55.97 | 1.90 | 3.64 | 5.56 | 2.88 | 1.45 | 3.85 | 28.89 | 93.65 |

4. Conclusion
We have presented an investigation of concentration measurements of chromium passivation solutions by an optical method. The absorption spectrum has two peaks and a local minimum and the absorbance increases with the concentration for all wavelengths. Calibration equations of the absorbance and the concentration constructed from linear regressions. Measurements of testing samples show that the wavelength of 565 nm result in the best accuracy and this approach is appropriate for the wavelengths of 420 – 700 nm if the acceptable error is less than 5%.

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References
[1] Dennis J K and Such T E 1993 Nickel and Chromium Plating (Cambridge: Woodhead Publishing)
[2] Lasheras F S, Vilán J A V, Nieto P J G and Diaz J J C 2010 Math. Comput. Model. 52 1169
[3] Lasheras F S, Nieto P J G, Juez F J C and Vilán J A V 2014 Appl. Math. Comput. 227 164
[4] Drinčič A, Zuliani T, Ščančar J and Milačič R 2018 Sci. Total Environ. 637-38 1286
[5] Katsumata H, Teshima N, Kurihara M and Kawashima T 1999 Talanta 48 135
[6] Kaewtong C, Kampaengsri S, Tuntulani T and Pulpoka B 2018 New J. Chem. 42 9930
[7] Firdaus M L et al 2014 Procedia Environ. Sci. 20 298
[8] Atkins P and Paula J 2011 Physical Chemistry for the Life Sciences (New York: W.H. Freeman and Company)
[9] Armbruster D A and Pry T 2008 Clin. Biochem Rev. 29 S49