Measurements of tin-palladium catalyst concentration by an optical method

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Abstract. Electroless plating on plastics is a technology that changes the plastic surfaces to appear like metals for decoration as well as specific applications. The plastic surfaces are commonly treated in a catalysing process by using a tin-palladium catalyst whose concentration is in a specific range. Since the concentration of the tin-palladium catalyst strongly affects the catalysing process as well as the plating quality, its concentration is regularly monitored. We present a study on measurements of the concentration of the tin-palladium catalyst with red-brown color based on an optical method. Its absorption spectrum monotonously decreases when the wavelength of the incident light increases. For a given wavelength, the absorbance increases with the concentration. Five standard concentrations are used to construct several calibration equations between the absorbance and the concentration by linear fits for different wavelengths. The calibration equations are verified by eight tested solutions. The results show that wavelengths in the range of 310 – 500 nm are suitable for the concentration measurements of tin-palladium catalyst since the errors are less than 5%.

1. Introduction

The electroless plating on plastics is a technology that changes the plastic surfaces to appear like metals for decoration as well as specific applications. Surface preparation of plastic process requires a catalyst to change the surface of the plastic to be able to conduct electricity before entering the electroless plating process [1]. Tin-palladium catalyst is commonly used for this task and its concentration is very important for the plating quality. Therefore, the concentration of tin-palladium catalyst should be measured [2] and adjusted during the surface preparation process.

Palladium in samples can be determined by difference methods as follows. The concentration of palladium in synthetic mixture is measured by spectrophotometric method based on the complex formation of palladium (II) with cefixime in methanol-distilled water medium [3]. Palladium (II) ion in aqueous medium and live cell is detected by using fluorescent sensor that synthesized from coumarin oxime and 2-chloroethyl methyl sulfide [4]. A detection of palladium (II) in pure water is shown by using a “turn-on” fluorescent and colorimetric chemosensor method that synthesized through an introduction of sulfur as a ligand atom to Rhodamine B. and it can be made into test paper to detect palladium (II) [5]. In electroless plating industry, the inductively coupled plasma mass spectrometry is commonly used to measure the concentration of tin-palladium catalyst with high accuracy [6].

In this paper, we study measurements of tin-palladium catalyst concentration by an optical method base on the Beer-Lambert law [7]. We consider the absorption spectrum of a tin-palladium catalyst and
construct calibration equations from the catalyst with standard concentrations. Finally, we test the calibration equations using catalyst samples with different concentrations.

2. Methods
A commercial tin-palladium catalyst with a high concentration is obtained from Okuno-Auromex (Thailand) Co., Ltd. Appropriate volumes of the high concentrated solution are diluted in 22% v/v HCl to form the catalysts with five standard concentrations: 14, 18, 22, 26, and 30 ppm. Their absorbance is measured using a 1-cm spectrophotometric cell in a LAMBDA 365 UV/Vis spectrophotometer (Perkin Elmer). Calibration equations at different wavelengths are constructed by linear fits between the absorbance and the five concentrations.

To determine the suitability of each calibration equation, other eight catalyst samples are prepared at concentrations which are different from the five standard concentrations. Then their absorbance is measured using the same spectrophotometer. This absorbance is plug into the calibration equations in order to calculate the catalyst concentration. Finally, the percentage error of the concentration value obtained from the calibration equation is determined. The resolution and the limit of detection (LoD) are estimated from 20 absorption measurements of a blank and a very diluted solution (1.4 ppm) as in [8].

3. Results and discussion
As shown in figure 1, the diluted tin-palladium catalysts with five standard concentrations have similar a red-brown color. The catalysts with higher concentrations appear darker. This indicates that the optical absorption of this catalyst depends on the concentration, at least, in the wavelength range of the visible light.

Figure 2 shows the absorbance spectra of the five diluted tin-palladium catalysts (in figure 1). It can be clearly seen that the absorbance is monotonously decreases when the wavelength of the incident light increases from 310 nm to 1000 nm. For shorter wavelengths (< 310 nm), the absorbance reaches a high saturated value. For wavelengths > 310 nm, all five absorbance curves do not cross each other. At a given wavelength, the absorbance always increases with the catalyst concentration.

Although the maximum absorption occurs at the wavelength of 310 nm, we test the measurement at several wavelengths to search for appropriate wavelengths. For each tested wavelength, we construct calibration equation as a linear fit:

\[ y = ax + b \]  

between the absorbance \((x)\) and the concentration \((y)\) of the five diluted tin-palladium catalysts.

The detail of the calibration equations at various wavelengths is shown in table 1. The parameter \(a\) (the slope of the graph) increases with the wavelength. The parameter \(b\) also depends on the wavelength, but their relation is not clear. The R-square, which indicates the linearity of the data relation, is high for
the wavelength 310 – 500 nm and decreases when the wavelength increases from 500 nm to 800 nm. Figure 3 shows two examples of the graphs with different R-square values. It is clearly shown that the data at the wavelength of 350 nm (R-square = 0.9982) fit to the linear regression better than those at the wavelength 800 nm (R-square = 0.9834).

![Graph showing absorbance spectra of tin-palladium catalysts](image)

**Figure 2.** The absorbance spectra of the five diluted tin-palladium catalysts. Bottom to top curves correspond to the catalysts with concentrations of 14, 18, 22, 26, and 30 ppm, respectively.

![Calibration curves of tin-palladium catalyst](image)

**Figure 3.** Example of calibration curves of tin-palladium catalyst at (a) 350 nm and (b) 800 nm. Circles and lines indicate the measured values and the linear fits, respectively.

**Table 1.** Parameters a, b and R-square of linear regressions at different wavelengths.

| Wavelength (nm) | a    | b    | R-square |
|-----------------|------|------|----------|
| 310             | 10.866 | 3.5014 | 0.9855   |
| 350             | 21.061 | 0.5526 | 0.9982   |
| 400             | 28.201 | 0.0045 | 0.9987   |
| 500             | 50.863 | 0.3704 | 0.9987   |
| 600             | 89.29  | 0.8799 | 0.9978   |
| 700             | 145.76 | 1.8102 | 0.9943   |
| 800             | 221.88 | 2.8047 | 0.9834   |

To search for appropriate wavelengths as well as calibration equations in measurement of tin-palladium catalyst concentration, the measured absorbance of other eight catalyst samples is used to calculate the concentration by using the calibration equation with different parameters a and b in table **Table 1**.
1. The percentage error of the eight concentrations (c_{mea}) obtained from calibration equations at different wavelengths is calculated as 
\[ \% \text{error} = \left( \frac{c_{\text{mea}} - c_{\text{ref}}}{c_{\text{ref}}} \right) \times 100 \] 
while \( c_{\text{ref}} \) is the concentration of the prepared samples. Table 2 summarizes the range of percentage error at different wavelengths.

| wavelength (nm) | 310  | 350  | 400  | 500  | 600  | 700  | 800  |
|-----------------|------|------|------|------|------|------|------|
| %error          | 0.1-2.8 | 0.1-3.4 | 0.1-3.5 | 0.3-4.3 | 0.6-6.4 | 0.4-10 | 0.2-14 |
| Resolution (ppm)| 0.03 | 0.04 | 0.03 | 0.03 | 0.04 | 0.04 | 0.07 |
| LoD (ppm)       | 0.10 | 0.12 | 0.09 | 0.08 | 0.08 | 0.12 | 0.20 |

The results indicate that the maximum error increases with the wavelength. Therefore, shorter wavelengths give better accuracy of the concentration measurement than longer wavelengths. If the accuracy of 5% is acceptable, the wavelengths 310-500 nm are suitable for the measurement of tin-palladium catalyst concentration. For these suitable wavelengths, the resolution and the LoD of the method are between 0.03-0.04 ppm and 0.08-0.12 ppm, respectively.

4. Conclusion
We have presented a study on measurements of the concentration of the tin-palladium catalyst based on an optical method. Its absorption spectrum decreases monotonically as the wavelength increases and the absorbance increases with the concentration, for a given wavelength. The linear fits for different wavelengths construct several calibration equations using standard concentrations. Measurements of testing samples show that the wavelength 310 nm results in the highest sensitivity. Even more the wavelengths 310-500 nm are suitable when the acceptable error is less than 5%.

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