A Novel Method to Measure the Concentration of EG with COD and Its Application to Alkali Wastewater of Polyester Textile

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Abstract: A novel method to accurately determine the concentration of ethylene glycol (EG) in the wastewater discharged from the alkali weight-reduction process of polyester textile by measuring the chemical oxygen demand (COD) via the oxidation with permanganate has been developed. There is a linear relationship between the COD value and the concentration of EG in the range of 0.5 ~ 6.0 mmol-EG/l, and the presence of other impurities such as terephthalic acid (TPA) and sodium hydroxide (NaOH) was found to have little effect on the COD value. In particular, the COD value remains almost unchanged in the pH range 2 ~ 14. Therefore, this new method could be very useful for the analysis of effluents from the alkali weight-reduction process where EG exists typically at a high concentration level.

Keywords: quantitative analysis of ethylene glycol (EG), alkali weight-reduction wastewater, COD, periodate method

Introduction

Ethylene glycol (EG, HOCH₂CH₂OH) is one of the most important raw materials in chemical industries. For example, the simplest diol is currently used in enormous volume as a coolant in automobiles, solar air conditioning, heating system, and a feed stock in the textile industry. EG is colorless, odorless and completely soluble in water due to the hydrogen bonding between EG and water. Under normal atmospheric pressure, the boiling point of EG is 192 °C. However, it is difficult to separate EG and water from the mixture by general methods such as distillation and reverse osmosis. Furthermore, EG itself is biologically degradable (BOD₅=0.6 g-O₂/g) [1]. Thus, the discharge into the sewage system is not allowed because of water pollution. On the other hand, a tremendous volume of alkali wastewater is discharged from the weight-reduction stage of polyester textile which is composed of equal molar compositions of TPA and EG [2-5]. Thus, a large amount of depolymerized EG exits through this wastewater. Typically, the pH of alkali wastewater is higher than 11 due to the presence of NaOH and disodium terephthalate (TPA-2Na).

Generally in the case of high concentration of EG in water, the quantitative analysis is accompanied by gas or liquid chromatography containing the pretreatment of solvent extraction and in the low concentration, by indirect determination of 1,2-diols, or α-glycol using periodate based on the redox reaction [6-8]. The first method has some deviations because of the deactivation of column due to the water content in the pretreated sample. The second is suitable for the range of 3.2 × 10⁴ ~ 3.2 × 10⁵ mmol/L of EG. The reaction between periodate and diol group is well known as the Malaprade reaction [9]:

\[
\text{HOCH}_2\text{CH}_2\text{OH} + \text{IO}_3^- \rightarrow 2 \text{HCHO} + \text{IO}_3^- + \text{H}_2\text{O}
\]

and is used for the indirect determination of 1,2-diols. The reaction must be proceeded by redox reaction through several steps, and finally monitored by measuring the decrease in absorbance of the reaction mixture at λmax. However, to obtain the more accurate data it is inconvenient that the reagent concentrations and reaction conditions must be optimized in acidic atmosphere. Moreover, this method is subject to interference from

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matrix and is used in the small calibration range.

In this study we report a new method that is simple but enables the fast and accurate determination of EG in aqueous media by simply measuring COD via the oxidation with permanganate. The proposed method is compared with the conventional periodic method for the determination of EG concentration in alkali weight-reduction wastewater of polyester textile.

**Experimental**

Alkali wastewater was obtained from DYECEN Complex, which was generated from the alkali weight-reduction process of polyester fiber [10-13]. The amount of NaOH and TPA contained in alkali wastewater was calculated from the following equations:

\[
\text{NaOH(\%)} = \frac{A \times N \times F \times 40}{\text{Sample Weight}} \times 100
\]

\[
\text{TPA(\%)} = \frac{(B - A) \times N \times F \times 88}{\text{Sample Weight}} \times 100
\]

where A is the volume (mL) of phenolphthalein at 1st break point, B is the volume (mL) of methyl orange at 2nd break point, N is the normality of HCl standard solution, and F is the factor of HCl standard solution.

The standard solutions with different EG concentrations (0 ~ 7 mmol-EG/L) used in this study were prepared by combining EG (99.5%, Junsei), TPA (99.9%, Samsung), and NaOH (99%, Dongyang). The matrix effects were examined using the standard solution prepared by adding 6 mmol TPA with 100 mmol NaOH. The solutions used in determining the concentration of EG in aqueous media via the periodate method [8] are as follows: 0.02 M periodic acid (HIO₄) solution containing 2.5 g potassium iodide (KI) and 17.5 g sodium thiosulfate (Na₂S₂O₃), and 2,4-pentanedione (CH₃COCH₂COCH₃) solution prepared by mixing 150 g of ammonium acetate (CH₃COONH₄), 3 mL of acetic acid (CH₃COOH), and 2 mL of 2,4-pentanediene. These solutions were further diluted if required. In a typical analysis a given amount of EG-containing solution was transferred into a 100 mL erlenmeyer flask, and 10 mL of 0.02 M periodic acid solution were dropwise added to initiate the oxidation of EG. After adding 10 mL of potassium iodide/sodium thiosulfate solution to the above solution, 40 mL of acetylacetone solution was then mixed. Finally, a portion of solution was transferred into a UV cell within 20 s to measure the absorbance for every 5 min. The absorbance measurements continued until diacetylidyhydroxylutidine (DDL) having a yellow color was completely formed.

The concentration of EG in aqueous solution was determined by measuring their absorbance at 470 nm using a Spectronics 20D+ UV spectrophotometer [16]. COD value in alkali wastewater was analyzed by a Central Kagaku HC-407 digital COD meter, using JIS method [14,15]. The concentration of EG was calculated by the differences in the measured COD value.

**Results and Discussion**

**Composition of Alkali Wastewater**

The typical composition of alkali wastewater used in this study was shown in Table 1. Because alkali hydrolysis using NaOH, the weight-reduction process was proceeded to improve physical properties of polyester surface and alkali wastewater was mainly composed of TPA-2Na, EG and NaOH in aqueous medium. And it has been predicted that inorganics such as Fe, Ca, Mg, Si, etc. and organics such as benzoquinone, anthraquinone, and etc. have coexisted as minor components. The TPA content in alkali wastewater used in this study was 47.0 mmol/L. Accordingly, this result indicates that EG concentration also is identical with the following equation:

\[
\text{EOH}_{n} + \text{H}_2\text{O} \rightarrow \text{HO}_{n-1} + \text{HO}_n\text{O} + n \text{HO}_n\text{OH}
\]

**The Periodate Method**

The effect of colorizing time, namely oxidation time, after the initiation of reaction in standard solutions (0.24, 0.48, 0.72 mmol-EG/L, respectively) is shown in Figure 1. Absorbance and the difference of absorbance between the standard solutions increased as the colorizing time increased. These results indicate that oxidation reaction between EG and periodate is very slow at the high concentration. Figure 2 shows the effect of temperature variation on absorbance measured at 5 min after initiation of oxidation. Continuous increase of absorbance was observed as the room temperature and the colorizing time increased. Change of pH due to the temperature variation may be affected, however it is not adequate to this tendency because the pH is adjusted to the neutral region with a buffer solution after the oxidation reaction. This result indicates that this method is very sensitive to the surrounding conditions.
Figure 1. The effect of colorizing time on the absorbance measured at 24°C in the periodate method.

Figure 2. The effect of temperature variation on the absorbance measured at 5 min colorizing time in the periodate method.

Figure 3. The matrix effect for the measurement of absorbance with the standard solution and mixed solution with 6 mmol TPA and 100 mmol NaOH for the periodate method.

were obtained as follows:

without TPA and NaOH;
Absorbance = 6.36 × 10⁻⁴°C (mmol-EG/L) + 5.43 × 10⁻³
with a regression coefficient r = 0.9996

with TPA and NaOH;
Absorbance = 6.32 × 10⁻⁴°C (mmol-EG/L) + 8.51 × 10⁻³
with a regression coefficient r = 0.8373

However, at the high concentration of EG in alkali wastewater containing 6 mmol TPA and 100 mmol NaOH, it was impossible to measure the stoichiometric amount of EG (Table 2). It appears that system is interfered by matrices such as TPA-2Na and NaOH in alkali wastewater. Therefore the standard solution with TPA and NaOH was applied for the determination of EG. The addition of TPA and NaOH resulted in the remarkable decrease of absorbance of solution comparing to that measured without TPA and NaOH in solution. This indicates that the determination of EG using the periodate method is unsatisfactory for alkali wastewater. Supposedly the pH of sample solution is very important factor in the periodate method. However, in this study it would be known that it is suitable to apply the periodate method on the higher concentration of EG contained in pure water.

The Proposed Method
Figure 4 shows the good correlation between the
Table 2. Analysis of EG in Alkali Wastewater by the Periodate and Proposed Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stoichiometric amount (mmol/L)</th>
<th>Amount of EG (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali wastewater</td>
<td>47.0</td>
<td>45.61 (46.22)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not detected</td>
</tr>
</tbody>
</table>

1 Alkali weight-reduction wastewater. 2 Standard solution treated with 6 mmol TPA and 100 mmol NaOH

concentration of EG and COD in the standard solution with or without 6 mmol TPA and 100 mmol NaOH. As can be seen, the concentration of EG was directly proportional to the value of COD in standard solution made of pure water. A calibration curve for a series of standard solution of EG (0.5 – 6.0 mmol-EG/L) is shown to be a typical line with the following regression feature:

COD (µg-O2/mL) = 13.62 × C (mmol-EG/L) — 0.15
with a regression coefficient r = 0.9995

As the matrix effect was existed in the periodate method with TPA-2Na and NaOH, standard solution has to be used with different concentrations of TPA-2Na and NaOH in pure water. However, this method measuring COD showed no difference with or without TPA and NaOH. Therefore this method can be utilized for the determination of EG in alkali wastewater including TPA-2Na and NaOH. However, in comparison with the periodate method, it can be seen that the proposed method is suitable for the concentration of 0.5 – 6.0 mmol-EG/L. Below this range the COD could not be detected because of detection limit. To evaluate the analytical applicability of the proposed method, the analysis of EG by measuring COD in alkali wastewater was compared with the periodate method, as shown in Table 2. The result is well agreed with the stoichiometric amount of EG calculated from the content of TPA in alkali wastewater.

Figure 4. The correlation between the concentration of EG and COD in the standard and mixed solution with or without 6 mmol TPA and 100 mmol NaOH.

Figure 5. The relationship between pH and COD value in the standard solution containing 4.83 mmol-EG/L.

The COD values remain almost unchanged in the pH range of 2 – 14. However, at pH < 2 it was impossible to measure COD. It indicates that the proposed method for the COD measurement could not be applied to the strong acidic solution. The determination of EG concentration by applying this COD measurement is very simple and adequate in the wide pH range for the quantitative analysis of samples including EG, TPA, NaOH and other impurities in aqueous media. The systematic investigations toward understanding the relationship of glycol structure and COD are being in progress.
Conclusions

It was found that the periodate method is not adequate for the determination of EG concentration in alkali wastewater, especially when the level of EG concentration and the pH of the analyzing solution are high. This can be attributed to the slow rate of the reaction of periodate with diol group, which required the long colorizing time to stabilize the solution. Furthermore, this method is very sensitive to the presence of TPA and NaOH in alkali wastewater, making it unreliable to determine the concentration of EG. In contrast, the method proposed in this study demonstrates a linear relationship between the measured COD value and the concentration of EG in alkali wastewater with a wide pH range even under conditions where TPA and NaOH exist at high concentration levels. This led us to believe that the simple measurement of COD can be successfully applied to analyzing the effluents with high concentration levels of EG, NaOH, and TPA.

References