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Reaction Stability Test of Hexavalent Chromium Complex with 1,5-Diphenylcarbazide in Analysis using UV Visible Spectrophotometer

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Abstract

A reaction stability test of hexavalent chromium complex with 1,5-diphenyl carbazide in analysis using a UV Visible Spectrophotometer has been done in this study. This study aims to find out the colored complex stability for the reaction of chromium hexavalent and diphenyl carbazide in the analysis of hexavalent chromium using a UV Vis spectrophotometer in terms of time. The sample was measured in 540 nm of wavelength with 10, 30, 60, 90, 120, and 180-minute time intervals. Each interval was carried out with two times replications. There were no significant differences in the colored complex until the 180-minute time interval, and the measurement of Cr(VI) concentration showed similar results. This analysis exhibits a level of precision and accuracy, evident from the RPD values below 10 % and the recovery values falling within the range of 90 – 110 %. It means that the reaction of hexavalent chromium complex with 1,5-diphenyl carbazide in analysis using a UV Visible Spectrophotometer is stable.

Keywords: Colored complex, Diphenyl carbazide, Hexavalent chromium, Reaction stability, UV Visible Spectrophotometer

INTRODUCTION

Spectrophotometry is a common method usually used to determine the concentration of hexavalent chromium in a sample. The UV Visible Spectrophotometer is used in this method. The working principle of a UV-Vis spectrophotometer is based on the absorption of electromagnetic radiation by a substance in the UV and visible light range. It involves passing light through the sample and measuring the intensity of light transmitted. The sample absorbs specific wavelengths of light depending on its chemical components. By comparing the absorption spectrum of the sample with reference spectra, the spectrophotometer can identify substances and determine their concentration (Kafle, 2020). The analysis of hexavalent chromium is conducted utilizing a visible spectrophotometer, which takes advantage of the capability of chromium ions to generate a colored complex when combined with a chromogenic reagent (McCarroll et al., 2010).

The chromogenic reagent usually used in the method is 1,5-diphenyl carbazide which can form a reddish-purple-colored complex. This method has some advantages, such as faster reaction, higher stability, cheaper, and easier to perform than other methods (Suryati et al., 2015). On the other hand, the complex formed exhibits only a short-term stability, lasting for approximately 15 minutes (Sanchez-Hachair & Hofmann, 2018). Sometimes, the samples that have formed a colored complex are not immediately analyzed due to limited instruments or waiting for sample queues. This condition causes samples to change in color before analysis, making the result obtained is not valid.

This study aims to find out the colored complex stability for the reaction of chromium hexavalent and diphenyl carbazide in the analysis of hexavalent chromium using a UV Vis spectrophotometer in terms of time.

METHODOLOGY

Materials and Instrumentals

The instrument was used are Perkin Elmer Lambda 25 UV Vis Spectrophotometer, analytical balance (Ohauss), oven (Memmert 1060), and glassware. The materials used are potassium dichromate, phosphoric acid, sulfuric acid, 0.5 % 1,5-diphenyl carbazide soluted in the acetone, and distilled water.

Methods

This study refers to SNI 6989. 71: 2009 describes chromium hexavalent analysis in a sample using the

spectrophotometry method. This standard includes making reagents, sample preparation, calibration curves, sample analysis, calculation, and data analysis.

Figure 1. UV Visible Spectrophotometer

Preparation of standard series solution for Cr^{6+}

Sample Cr^{6+} (10 mg/L) as much as 2.0, 5.0, 10.0, 20.0, and 30.0 mL were piped into 100 mL of the volumetric flask for each concentration, then added 5 drops of phosphoric acid, and adjusted the pH to 2±0.5 with 0.2 N sulphuric acid. The next step was to add some distilled water until ¾ part of the volumetric flask. Then poured as much as 2 mL of 0.5 % diphenyl carbazide solution. A reddish-purple-colored complex would form. The last step is adding distilled water and make it homogenous.

Preparation of calibration curve

The standard series solutions were analyzed using an optimized UV Vis spectrophotometer in 540 nm of wavelength. The absorbance values were used to make a calibration curve. The coefficient of linear regression was accepted if the value was ≥ 0.995. Sample concentration is determined using Equation 1 (y: absorbance value, b: Slope, x: sample concentration, a: intercept)

$$y = bx + a \quad (1)$$

Sample preparation

The volume of the 10 mL sample was poured into a 100 mL volumetric flask, then 5 drops of phosphoric acid, and the pH was 2±0.5 with 0.2N sulphuric acid. The next step was to add some distilled water until ¾ part of the volumetric flask. After that, pour 2 mL of 0.5 % diphenyl carbazide solution. A reddish-purple-colored complex would form. The last step was to add more distilled water and make it homogenous.

Sample analysis

The sample was measured in 540 nm of wavelength with 10, 30, 60, 90, 120, and 180-minute time intervals. Each interval was carried out with two times replications.

Calculation of Cr(VI) concentration

The Cr(VI) concentration is calculated by Equation 2 (C: The Cr (VI) concentration from analysis (mg/L), Df: Dilution factor).

$$C\ Cr(VI) = C\ x\ Df \quad (2)$$

Relative Percent Difference (RPD)

In this study, a Duplo analysis was conducted to calculate the Relative Percent Difference (RPD) (Equation 3) as a measure of analytical precision. The %RPD value was utilized as a control for accuracy in the analysis (X_1: first measurement result X_2: second measurement result) (Taylor, 2018).

$$\%RPD = \left| \frac{X_1 - X_2}{\frac{(X_1 + X_2)}{2}} \right| x\ 100 \quad (3)$$

Spike (Recovery percentage)

In addition to measuring standards and samples, spike measurements were also performed to assess the accuracy of the UV-Vis spectrophotometer instruments (Equation 4). This involved adding known concentration standard samples to the analysis (%R: recovery (%), A: spike sample concentration (mg/L), B: sample concentration (mg/L), C: added standard concentration (mg/L)).

$$\%R = \frac{A-B}{C}\ x\ 100 \quad (4)$$

Data analysis

One-way ANOVA is used in the statistical calculation. This statistical technique involves analyzing variance with one dependent variable. It is used to determine if there are any significant differences between the means of two or more groups. This analysis method is an expansion of the t–test for comparing the means of two samples (Muhid, 2019)

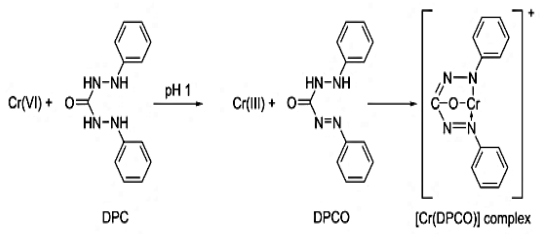

Figure 3. The reaction of Cr(VI) and DPC (Duffy et al., 2018)

RESULTS AND DISCUSSION

Diphenyl carbazide ($C_{13}H_{14}N_4O$) is a ligand compound used in analytical chemistry for the colorimetric determination of chromium and serves as a sensitive reagent for detecting metal ions (El-Kabbany, Taha, & Hafez, 2014). The principle of hexavalent chromium determination is based on the reaction between Cr(VI) ions and diphenyl carbazide in an acidic environment. In this process, diphenyl carbazide (DPC) is oxidized by Cr(VI) to form diphenyl carbazone (DPCO), while Cr(VI) is reduced to Cr(III) (Figure 3). As a result, the reddish-purple-colored complex, Cr(III)-DPCO is formed, which absorbs visible light at a maximum wavelength of 540 nm (Baalamurugan, Kumar, Senthilkumar, Govindaraju, & Dhas, 2021; Duffy et al., 2018)

The addition of acid to the solution serves to maintain the solution in an acidic environment, leading to the formation of complex anions of Cr^{6+}. The Cr^{6+} ions in the solution will combine with H^+ ions, resulting in the formation of dichromic acid (Equation 5).

$$Cr_2O_7^{2-}(aq) + 2H^+(aq) \leftrightarrow H_2Cr_2O_7(aq) \quad (5)$$

Figure 2. Standard Series Solution

Then, the sample is treated with a solution of diphenyl carbazide to form a purple-colored complex of (Cr-VI) diphenyl carbazide caused by an electronic transition in the Cr(VI) compound. The d orbitals of the Cr atom are not filled with electrons, so the electronic transition that occurs is not a d-d orbital transition but rather a charge transfer reaction within the molecule, resulting in the formation of the color (Ashley, Howe, Demange, & Nygren, 2003; Yanti, 2022). The research result showed that as the Cr(VI) concentration increases, the intensity of the color produced also increases. Table 1 below shows the result of standard series absorbance.

Table 1 shows that higher Cr(VI) concentrations produce higher absorbance values, according to the Lambert-Beer's (Firnanelty, Chadijah, Adawiah, Firdaus, & Nugraha, 2022; Ikhsan, Sekewael, & Hasanela, 2022). It means that the concentration and absorbance are directly proportional.

Table 1. Standard series absorbance

Concentration (mg/L)	Absorbance
0.2	0.017
0.5	0.041
1.0	0.084
2.0	0.164
3.0	0.247

Based on the standard calibration curve above, the linear regression coefficient value (R^2) is 0.9999 (Figure 4). This value meets the requirement of acceptable value for R^2, which is 0.995. It means that there is a strong correlation between absorbance (y) and concentration (x). The derived regression equation is y = 0.0821 x + 0.0006 with slope = 0.0821 and intercept value = 0.0006. The intercept value represents the influence of the matrix, so the larger the intercept value, the greater the matrix's impact on the sample measurement. Ideally, the intercept value should be zero (Sri, Dan, & Nurbayanti, 2019). This study resulted in an intercept value of 0.0006. On the other hand, the slope value indicates the sensitivity of a method (Frontmatter, 2004; Muhaimin et al., 2021). The regression equation is used to determine Cr(VI) concentration in the sample.

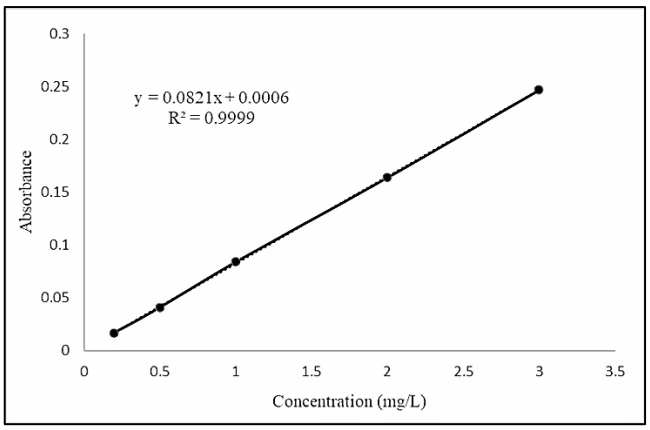

Figure 4. Standard Calibration Curve

In the sample analysis process, there are some variations in waiting time: 10, 30, 60, 90, 120, and 180 minutes. The measurements were done as duplos for each time interval. There were no significant differences in the colored complex until the 180-minute time interval, and the measurement of Cr(VI) concentration showed similar results. It means that the complex reaction is stable (Table 2).

Table 2. Sample measurement result

No	Time interval (Minutes)					
	10	30	60	90	120	180
1	0.7113	0.7235	0.7235	0.7236	0.7235	0.7113
2	0.7357	0.7235	0.7235	0.7236	0.7235	0.7235
Avg	0.7235	0.7235	0.7235	0.7236	0.7235	0.7174
Total	1.4470	1.4470	1.4470	1.4472	1.4470	1.4348

These data are analyzed using One-Way ANOVA or ANOVA single factor. This method is a variance analysis involving one dependent variable. It is used to check whether there is a significant difference between the means of two or more groups (Muhid, 2019). Table 3 below shows the results.

Table 3. ANOVA calculation

Groups	Count	Sum	Average	Variance
10	2	14.470	0.7235	0.00030
30	2	14.470	0.7235	0.00000
60	2	14.470	0.7235	0.00000
90	2	14.472	0.7236	0.00000
120	2	14.470	0.7235	0.00000
180	2	14.348	0.7174	0.00007
Source of Variation	SS	df	MS	F
Between Groups	0.000062	5	0.000013	0.200944
Within Groups	0.000372	6	0.000062	
Total	0.000434	11		

Based on Table 3, hypothesis evaluation can be carried out in two ways: firstly, by comparing the calculated F value with the F table, and secondly, by comparing the significance level (p-value) with the error. Firstly, if the calculated F value is bigger than the F table, Ho will be rejected. If the calculated F value is smaller than the F table, Ho will be accepted (Suherman, Milawonso, Morita, Mizuguchi, & Oki, 2020). This study produces a calculated F value of 0.200944, indicating that the calculated F value is smaller than the F table, which is 4.387374. It means that Ho is accepted. In the second way, if the p-value (95%) is smaller than 0.05, Ho will be rejected, and vice versa. Based on Table 3, the p-value is bigger than 0.05, so Ho is accepted. Hypothesis evaluation in 2 ways is accepted, thus proving that there is no significant difference in the variation of time interval in the hexavalent chromium analysis.

This study is carried out as a duplicate to calculate RPD value (Table 4). The value is used to control the accuracy of the analysis.

Table 4. The RPD value

Sample	C sample	% RPD
A 10	0.7113	3.3725
B 10	0.7357	
A 30	0.7235	0.0000
B 30	0.7235	
A 60	0.7235	0.0000
B 60	0.7235	
A 90	0.7357	0.0000
B 90	0.7357	
A 120	0.7235	0.0000
B 120	0.7235	

The result meets the requirement of the National Standard of Indonesia, which specifies a maximum error rate of 10 %. Therefore, this implies that the result has good accuracy. In addition to standards and sample measurement, spike measurement is also conducted to assess the accuracy of the UV-Vis spectrophotometer (Retnaningtyas et al., 2020). The result is shown in Table 5.

Table 5. Spike measurement

Spike	C Spike+spl (mg/L)	C spl (mg/L)	C spike (mg/L)	% Recovery
A	2.7211	0.7113	2	100.49
B	2.7211	0.7357	2	99.27

The percentage of recovery obtained meets the requirements specified in SNI 6989-71: 2009, where the acceptable range for the recovery of standards is between 90 % to 110 %. This result indicated accurate analytical findings.

CONCLUSION

The analysis of hexavalent chromium in this study shows that there is no significant difference when the analysis is conducted within the time variation range of measurement. This proves that when analysis is performed within the maximum time range of 180 minutes, the obtained results are still considered valid. This analysis exhibits a level of precision and accuracy, evident from the RPD values below 10 % and the recovery values falling within the range of 90-110 %.

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