

Storage modeling standard Cr(VI) solution based on comparison of time regression value with UV-Vis spectrophotometry

Elfiwani and Fachrurrazie*

Received: [21 September 2022] Revision: [21 October 2022] Accepted: [30 October 2022]

ABSTRACT: Chromium (Cr) compounds are found in nature in two forms, Cr (III) and Cr (VI). Analysis of Cr (VI) was determined using spectrophotometer UV-vis. A standard solution must be fresh as a standard that is usually not used repeatedly in the measurement. This study aims to determine whether the standard solution of Cr (VI) be used for a certain period until it must be disposed of. This idea is based on Cr (VI) compounds that were categorized as hazardous and toxic materials. In this study, the shelf life of standard Cr (VI) was carried out with controlled temperature and humidity in a refrigerator at 4 °C during the test period of two days. In this study, there was found that every hour of storage of standard Cr (VI) will observe a change in the gradient value of the regression. The model then compared with p-value resulted in only up to 7 hours of storage with a deviation of regression slope and intercept compared with initial time (T_0-T_7) is 0.0062 and 0.0019 which and its increases over time. From the result, it can be concluded that standard regression can be used as a model for determining the maximum storage time by comparing the regression values each time so that the seven hours storage time is the limit where the Cr (VI) that can no longer be used as a measurement standard. It concerned that standard regression could be used as a model for determining the maximum storage time by comparing the regression values each time. Keywords: Cr (VI), Modeling, Regression, Spectrophotometry UV-vis, T-Test.

INTRODUCTION

Chromium (Cr) is one of the mineral metals whose existence is contained in the layers of the earth. It is found at minuscule concentrations in ores, animals, plants, volcanic ashes, and fumes. Hexavalent Cr is a globally distinguished environmental pollutant with potential as carcinogenic, teratogenic, and mutagenic consequences [1].

Epidemiological studies show that inhalation of Cr (VI) in particulate matter (PM) causes lung and nasal cancer. Induced nasal carcinoma and DNA damage have also been reported in workers exposed to Cr (VI) after roughly eight years of exposure in electroplating processes. On the other hand, oral exposure studies report serious reproductive effects, such as alteration of semen which decreases sperm count [2].

As an outgrowth of anthropogenic activities, there occurs a significant hastening in the release of Cr to the environment. An excessive amount of wastewater contains Cr (VI) formed by the various activities [3]. Depending on its valence, Cr can be unless poisonous or advantageous. Industrial effluents carry significant amounts of Cr. Cr (VI) is one of the prominent polluting elements in the environment, the forms of Cr (VI) chromate and dichromate are extremely soluble under all pH conditions, but they could precipitate with divalent cations [4].

Experimental work has shown that aqueous Cr (VI) production rates are primarily controlled by the solubility and dissolution rates of Cr (III) from host minerals as well as the solution pH. When manganese-iron oxides co-exist with Cr (III)-bearing minerals, Cr

(III) oxidation by Mn(V)-oxides can occur on the mineral surface, yielding Mn (II) and Cr (VI), which may then be mobilized into the aquatic phase [5].

Due to the extensively varying toxicity of Cr, total Cr measurement offends to be used to circumscribe the actual environmental impact. Thus, chemical speciation of Cr in environmental samples expect precisely assess pollution levels [6]. Accordingly, the determination of Cr (VI) at trace levels accurately has received considerable attention. In this study, we modelled the stability of Cr standard solution to define when the precision of the standard was diminishing over time.

RESULT AND DISCUSSION

Standard solution of Cr (VI) regression comparison for modeling storage time was conducted by time intervals 0, 4, 7, 25, 29, and 32 hours. The standard Cr (VI) was measured with the Visible Spectrophotometry method. Measurement was based on the colour of the purple complex due to the complexation reaction between Cr (VI) ions and 1,5-diphenylcarbazide.

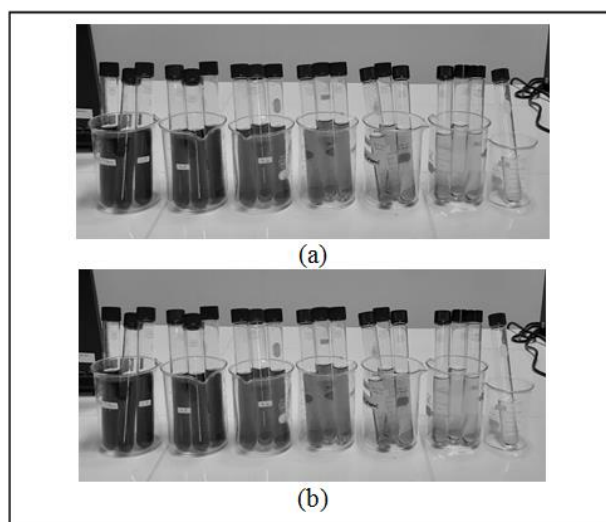


Figure 1. Cr (VI) standard (a) 0 hour and (b) 32 hours.

Based on the visual colour, we found that no significant difference in the visual appearance of the Cr (VI) day 0 standard with the 32 hours storage at 40C standards as shown in Figure 1. Nonetheless, this interpretation cannot conclude as a reference. From this finding, we needed a statistical method for the test to find when there was a distinct value between initial time measurement (T_0) with storage one. The biasness of the models was need to be tested using t-test, Root mean square error (RMSE) is also a good measure of how accurately the model predicts the response. RMSE is also most important criterion for fitness of model, if the main purpose of the model is predicting [7].

The investigation between the two regression models was conducted according to the last paper [8]. The two regression was compared in a two-step, first, we find where the p-value of the two-regression model with a parallel hypothesis or not, which mean the slope of the two-regression model was not different enough with a significant error of 5%. second, finding the p-value of two regression models that match each other, which is after passing

the first hypothesis the two regression intercepts are also not different enough with a significant error of 5%.

Figure 2 shows the standard Cr regression graph (VI) from 0 to 32 hours storage, there was a slight difference in the slope of each resulting regression but from the correlation coefficient (R^2), there was no distinction. The R^2 value of the measurement still produces a value of >0.9998 this condition means all of the regression still produce valid data. the intercept also shows a slight fluctuation there is no significant fluctuation in the regression equation and the deviation of regression slope and intercept compared with initial time (T_0 – T_7) is 0.0062 and 0.0019 respectively.

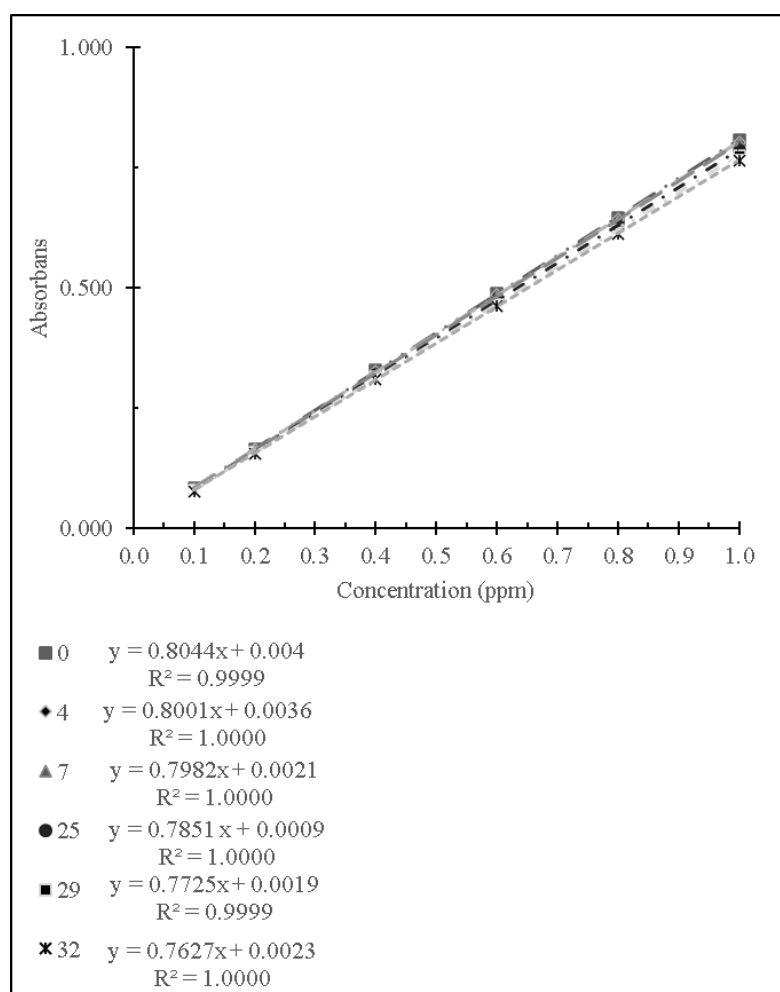


Figure 2. Cr (VI) Standard Regression Graph from 0 to 32 hours storage

This could be occurred by the instability complex between the Cr (VI) with 1,5-diphenylcarbazine. Interferences due to cationic and anionic species were could also be major problem for spectrophotometry technique, significant interferences were reported for iron (III), nevertheless, Cr (III), iron (III), copper (II) and mercury (II) did not interfere significantly up to their concentration of 10 mg l^{-1} the interference was considered significant if the observed change of Cr signal was higher than 5% [9].

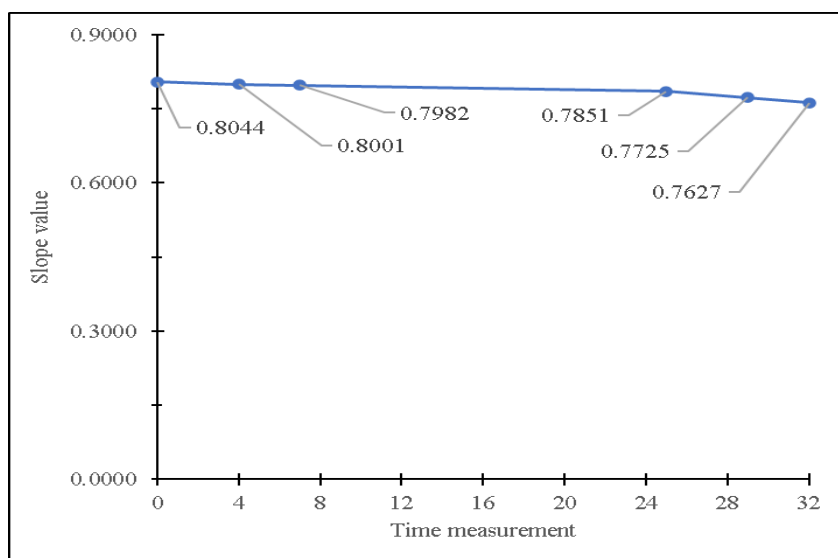


Figure 3. Cr (VI) Standard Regression Graph from 0 to 32 hours storage

Based on the regression results, we also compared the measurement results of the regression slope value vs time measurement (Figure 3). This could be seen from seven hours storage of standard solution there has been a decrease in the slope value of the standard regression curve, from 0.8044 to 0.7627 in only 32 hours. from that result, it would greatly affect measurement sensitivity thus accuracy would be affected too.

The pH of the acid complex formed so for the Cr (VI) was pH 1-1,5 and if it was not optimally coordinated, although the resulting absorbance showed a large absorbance, The optimum wavelength for the metal ion complex Cr (III) at pH 8 [10]. During analyses, the pH of samples analysis was adjusted to 9–9.5. At this pH Cr exists as CrO_4^{2-} species. The adjustment of pH of samples to 2 ensured that Cr exists as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ [11].

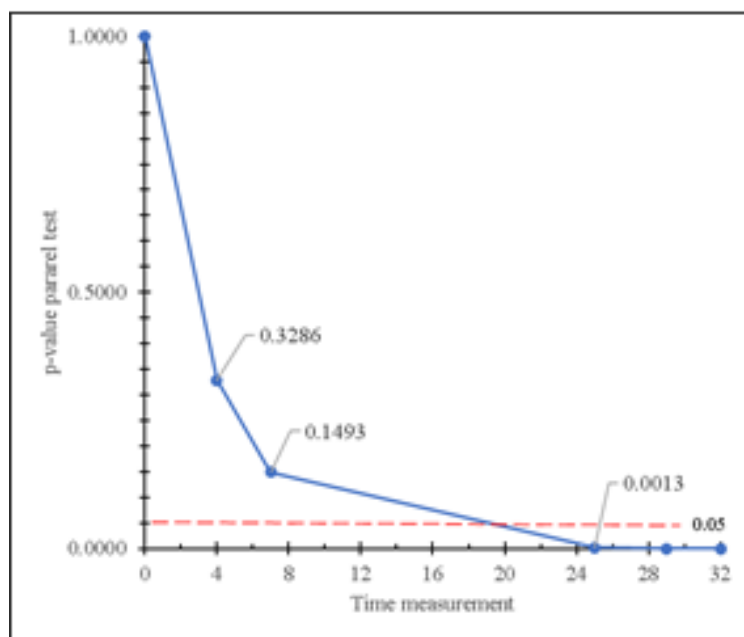


Figure 4. Cr (VI) Standard Regression p-value parallel test

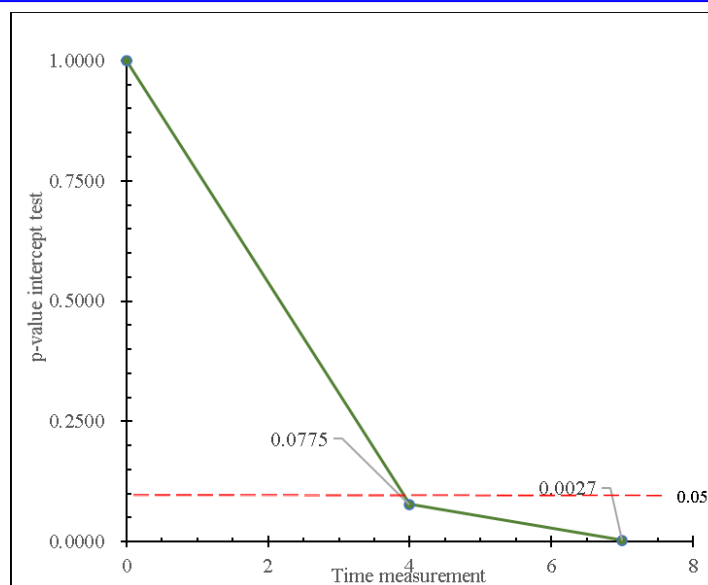


Figure 5. Cr (VI) Standard Regression p-value intercept test

Performing a regression comparison between fresh to 4, 7, 25, 29, and 32 hours storage, we modelled so we could know when the standard solution was different from fresh standards solution regression result. In Figure 4, we got the p-value of the regression parallel test the critical point of the probability of rejecting H_0 has occurred when we store the standard over seven hours. when H_0 is accepted it means the regression curve was parallel with the fresh standard solution. on the p-value intercept test (Figure 5), we found the p-value test was occurred not over four hours storage standard regression which was near the critical point probability of rejecting H_0 . eventually in four hours regression p-value which was $0.0775 > 0.05$ the H_0 was accepted in this test it means the regression curve was parallel and fit with fresh regression standard and not differ significantly. It also shows that in this test the measurement results from the standard test over four hours storage in 4°C cannot be used again as an standard.

CONCLUSION

This study concluded that the storage of the standard series of Cr (VI) for more than four hours after being prepared as a standard solution could cause decreasing slope value of the regression curve and affect the sensitivity of the measurement of Cr (VI). By modeling the p-value test vs time measurement, we could predict the critical point when the event that $p\text{-value} < 0.05$ was occurred and caused reject H_0 condition. There was a need for further studies that study the hourly changes in the regression slope of another unstable standard that could be determined when no longer be used from the time of its making.

MATERIAL AND METHOD

Reagents and materials

All chemicals and solvents used were of pro analysis (pa) reagent grade quality were used without further purification with brand Merck grade produced in Germany. Doubly deionized distilled water was used throughout. Standard $\text{K}_2\text{Cr}_2\text{O}_7$, 1,5-diphenylcarbazine, H_2SO_4 , and acetone were used.

Apparatus

Equipment used to comprise this study were a refrigerator, laboratory glassware, pH indicator paper, and Shimadzu analytical balance. Shimadzu UV-Vis Spectrophotometer UV-1800 type double beam UV-vis spectrophotometers with quartz cell used for the solution electronic spectra and the absorbance of the produced complex ion-associates in the organic solvent.

Recommended procedures

Cr (VI) Standard Solution

The reagent was made by weighing 250 mg of 1,5-diphenylcarbazine and then dissolved in 50 mL of acetone with the dark container. Two litres of doubly deionized distilled water added a few drops of 4 N H₂SO₄ adjusted to pH of 1.5 with pH indicator paper. 0.0283 gram K₂Cr₂O₇ weighed and dissolved in 100 ml volumetric flask with doubly deionized distilled water. The standard series 0.1; 0.2; 0.4; 0.6; 0.8; and 1.0 ppm was allowed to stand for 5-10 minutes and then measure the absorbance with a UV-Vis Spectrophotometer at a wavelength of 543 nm.

Standard Cr (VI) measurement

The standard series was measured then stored in the refrigerator at 4°C. Absorbance measurements carried out with intervals 0, 4, 7, 25, 29, and 32 hours from the initial reading.

Regression Comparison [8] and p-value vs Time Model

Two statistical tests are needed to compare between two simple linear regression lines, namely:

1. Statistical test to determine whether $\beta_1 = \beta_2$ This test is to determine whether the two regression lines have the same slope value. If the slope values are the same, then you can be sure that the two lines are parallel.
2. Statistical test to determine whether $\alpha_1 = \alpha_2$ this test is to determine whether the two regression lines have the same intercept. Test this only done if the two regression lines have slope values that are not significantly different ($\beta_1 = \beta_2$). If the two regression lines have the slope and intercept values are the same ($\beta_1 = \beta_2$ and $\alpha_1 = \alpha_2$), then the two regression lines are the same or coincide.

There are four steps for statistical test to find out whether $\beta_1 = \beta_2$:

first determine the null hypothesis (H_0) and its alternative hypothesis (H_1):

$H_0: \beta_1 = \beta_2$

$H_1: \beta_1 \neq \beta_2$

second calculate the t-test statistics using the following formula:

$$t = \frac{(b_1 - b_2)}{\sqrt{\text{var}(b_1 - b_2)}} \quad (1)$$

where:

$$\text{var}(b_1 - b_2) = \frac{S_p^2}{\sum (x_1 - \bar{x}_1)^2} + \frac{S_p^2}{\sum (x_2 - \bar{x}_2)^2} \quad (2)$$

$$S_p^2 = \frac{JKS_1 + JK S_2}{(n_1 - 2) + (n_2 - 2)} \quad (3)$$

$$JKS_1 = \sum (Y_1 - \bar{Y}_1)^2 - \frac{\sum (X_1 - \bar{X}_1)(Y_1 - \bar{Y}_1)}{\sum (X_1 - \bar{X}_1)^2} \quad (4)$$

$$JKS_2 = \sum (Y_2 - \bar{Y}_2)^2 - \frac{(\sum (X_2 - \bar{X}_2)(Y_2 - \bar{Y}_2))^2}{\sum (X_2 - \bar{X}_2)^2} \quad (5)$$

third, calculate the value of the significance level from the absolute value of the test statistic $t = |t|$ using t distribution for two tails with degrees of freedom $df = n_1 + n_2 - 4$ the significance value is known as p-value, which is the critical point of the probability of rejecting H_0 . And fourth draw statistical conclusions with a significance value of 5%, so that if the p-value < 5% means that H_0 is rejected.

There are also five steps statistical test to find out whether $\alpha_1 = \alpha_2$: first determine the null hypothesis (H_0) and its alternative hypothesis (H_1):

$H_0: \alpha_1 = \alpha_2$

$H_1: \alpha_1 \neq \alpha_2$

second, calculate the combined slope value (b_g) according to the formula:

$$b_g = \frac{\sum (X_1 - \bar{X}_1)(Y_1 - \bar{Y}_1) + \sum (X_2 - \bar{X}_2)(Y_2 - \bar{Y}_2)}{\sum (X_1 - \bar{X}_1)^2 + \sum (X_2 - \bar{X}_2)^2} \quad (6)$$

third, calculate the t-test statistics using the following formula:

$$t = \frac{(\bar{Y}_1 - \bar{Y}_2) - b_g(\bar{X}_1 - \bar{X}_2)}{\sqrt{S_p^2 \left(\frac{1}{n_1} + \frac{1}{n_2} + \frac{(\bar{X}_1 - \bar{X}_2)^2}{\sum (X_1 - \bar{X}_1)^2 + \sum (X_2 - \bar{X}_2)^2} \right)}} \quad (7)$$

fourth, calculating the value of the significance level (p-value) from the absolute value of the t-test statistic $= |t|$ using Student's t distribution for two tails with degrees of freedom $df = n_1 + n_2 - 3$ the significance value is known as p-value, which is the critical point of the probability of rejecting H_0 , and fifth step, draw statistical conclusions with a significance value of 5%, so that if the p-value < 5% means that H_0 is rejected.

After statistical test between regression slope and intercept completed, we modelled the p-value the into a time frame of measurement with intervals 0, 4, 7, 25, 29, and 32 hours.

DECLARATION

There is no conflict of interest from authors for this research.

ACKNOWLEDGEMENT

Our research team expressed gratitude and sincere appreciation to AKA Polytechnic Bogor that accommodated the laboratory, equipment, and material to ensure this research was done great.

AUTHOR INFORMATION

Corresponding Author:

Fachrurrazie, fachrurrazie@gmail.com

Chemical Analysis Study Program, AKA Polytechnic Bogor, Jl. Pangeran Sogiri No. 283, Tanah Baru, Bogor 16158

Authors

Elfiwani and Fachrurrazie

Chemical Analysis Study Program, AKA Polytechnic Bogor, Jl. Pangeran Sogiri No. 283, Tanah Baru, Bogor 16158

REFERENCES

- [1] Wise, J.P. et al. (2022) *Current understanding of hexavalent chromium [Cr(VI)] neurotoxicity and new perspectives*. Environ. Int. **158**, 106877.
- [2] N A, C. et al. (2021) *Colorimetric detection of chromium (VI) using peroxidase mimetic IONPS with 4- Aminoantipyrene and 3-Aminophenol as a chromogen*. Environ. Nanotechnology, Monit. Manag. **16**, 100471.
- [3] Ramírez-Quesada, M.M. et al. (2021) *New advances in the method validation, extraction methods and measurement uncertainty for the determination of water-soluble hexavalent chromium in hydraulic cement*. Talanta **232**.
- [4] Oliveira, H. (2012) *Chromium as an Environmental Pollutant: Insights on Induced Plant Toxicity*. J. Bot. 2012, 1–8.
- [5] Coyte, R.M. et al. (2020) *Occurrence and distribution of hexavalent chromium in groundwater from North Carolina, USA*. Sci. Total Environ. **711**, 135135.
- [6] El-Shahawi, M.S. et al. (2005) *Chemical speciation of chromium(III,VI) employing extractive spectrophotometry and tetraphenylarsonium chloride or tetraphenylphosphonium bromide as ion-pair reagent*. Anal. Chim. Acta **534**, 319–326.
- [7] More, A.G. and Gupta, S.K. (2018) *Predictive modelling of chromium removal using multiple linear and nonlinear regression with special emphasis on operating parameters of bioelectrochemical reactor*. J. Biosci. Bioeng. **126**, 205–212.
- [8] Giyanto (2003) *Comparing Two Simple Linear Regression Equations*. Oseana **XXVIII**, 19–31.
- [9] Wróbel, K. et al. (1997) *Enhanced spectrophotometric determination of chromium (VI) with diphenylcarbazide using internal standard and derivative spectrophotometry*. Talanta **44**, 2129–2136.
- [10] Supriyanto, R. (2011) *Speciation Analysis Study of Cr (III) and Cr (VI) Metal Ions With Tannic Acid From Gambir Extract Using UV-VIS Spectrometry*. J. Sains MIPA **17**, 35–42.
- [11] Onchoke, K.K. and Sasu, S.A. (2016) *Determination of Hexavalent Chromium (Cr(VI)) Concentrations via Ion Chromatography and UV-Vis Spectrophotometry in Samples Collected from Nacogdoches Wastewater Treatment Plant, East Texas (USA)*. Adv. Environ. Chem. **1**–10.