Direct Spectroscopic Determination of Aqueous Phase Hexavalent Chromium

David Kim¹, Joon Om²,*

¹Lambert High School, Suwanee, 30024, Georgia, United States
²Department of Civil Engineering Faculty, Polytechnic University of NYU, Brooklyn, 11201, New York, United States
*Corresponding Author:jom@poly.edu

Abstract  Hexavalent chromium concentration in solutions was determined directly at 363 nm with a path length of 1 cm using quartz cuvettes. The validity of the proposed method was evaluated by comparing it with the commonly accepted diphenylcarbazide colorimetric assay. According to Student’s t-test comparison, one of three trials was accepted without statistical differences. Comparing the % recovery observation with Cr(VI)-spiked samples, higher accuracy was obtained with the direct spectroscopic method while better precision was found with the diphenylcarbazide colorimetric method. It was also shown that the direct spectroscopic method is in tolerance with common ions, such as Al³⁺, Na⁺, K⁺, Mg²⁺, Cl⁻, NO₃⁻, CO₃²⁻, SO₄²⁻, in different degrees of effectiveness.

Keywords  Hexavalent Chromium, Direct Spectroscopic Determination, Student’s T-Test

1. Introduction  Chromium has a long history of use in various human activities. In nature, two common oxidation states of chromium are found, including hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). While trivalent chromium compounds are insoluble and essential nutrition for human beings, hexavalent chromium compounds are soluble and potential carcinogens. With these two distinct physical and chemical properties and toxicity, scientists have developed various dissolved Cr(VI) determination methods, such as graphite furnace atomic absorption spectrometry (GFAAS) [1], high-performance liquid chromatography inductively coupled plasma atomic emission spectrometry (ICP-AES) [2], inductive coupled plasma mass spectroscopy (ICP-MS) [3], spectrofluorometric spectrometry [4], speciated isotope dilution mass spectrometry (SIDMS) [5], and various colorimetric spectrometries using different color development processes [6–10]. Among various Cr(VI) determination methods, the diphenylcarbazide (DPC) complex colorimetric method has been considered as a trustworthy assay and has been applied to various samples [11, 12]. While accuracy and precision are critical factors to develop a Cr(VI) determination assay, considering the potential transformation between these two different oxidation states, the development of a reliable and quick Cr(VI) determination method is needed. The present study aims to evaluate the potential application of a simple direct spectroscopic determination of Cr(VI) in solution in comparison with the current reliable DPC colorimetric method.

2. Materials and Methods  The amount of Cr(VI) in the spiked solutions was determined using both direct spectroscopic and DPC colorimetric methods with a UV-Vis spectrophotometer (Cary 50, Varian Inc.) with 1.0 cm quartz cuvettes. The 1,000 mg/L of hexavalent chromium stock solution was prepared with potassium dichromate (K₂Cr₂O₇) and the prepared stock solution was stored in an amber bottle. A fresh 20–100 mg/L Cr(VI) solution was prepared for each experiment using the stock solution. The pH of the freshly prepared solution was controlled by either 0.1M HCl or 0.1M NaOH solution. All chemicals used for the research were ACS grade or higher, and water prepared through reverse osmosis processes (Water Pro/RO, Labconco Inc.) was used to prepare all solutions.

In order to identify the most responsive wavelength, 100 mg/L of Cr(VI) was scanned in the wavelength range of 250–700 nm. Quartz cuvettes and polymethyl methacrylate (PMMA) cuvettes were used for direct spectroscopic method and DPC colorimetric method, respectively. The effect of common ions on the direct spectroscopic method was studied by mixing various sodium or potassium salt solutions with the freshly prepared Cr(VI) solution. Three
different Cr(VI)-spiked solutions (9, 13, 23 mg/L Cr(VI)) were prepared, and the % recovery was determined by both direct spectroscopic and DPC colorimetric methods, which were compared statistically for the validity of the proposed direct spectroscopic method. All the experiments were performed at least triplicated, and Student’s t-test methodology was used for comparison between two different Cr(VI) determination methods.

3. Results and Discussion

The wavelength for the application of the direct spectroscopic method was identified based on the sensitivity of absorbance as a function of wavelength. Figure 1 shows the absorbance data at various wavelengths for the 100 mg/L Cr(VI) solution. As shown in figure 1, Cr(VI) shows high spectral response at 363 nm, and the selected wavelength was used for the rest of the research in the direct spectroscopic determination method. Absorbance for freshly prepared standard solutions was determined using the direct spectroscopic and DPC colorimetric methods, and the obtained standard curves are shown in figures 2.

For the direct spectroscopic method, two different cuvettes were examined such as quartz and polymethylmethacrylate (PMMA). As shown in figure 2, quartz cuvettes showed higher accuracy and stable data. Figure 2 also indicates that the pH values of the prepared standard solution decreased as the Cr(VI) concentration increased.

![Figure 1. Spectral responses of 100 mg/L hexavalent chromium solution in the range from 300 to 700 nm.](image)

![Figure 2. Standard curves prepared by both direct spectroscopic method at 363 nm, and diphenylcarbazaid colorimetric method at 540 nm. The pH values of various Cr(VI) standard solution were determined for direct spectroscopic method and the additional Y-axis was used.](image)
The preliminary experiments confirmed that no significant effect of the solution pH on the adsorption was observed in the pH range of 2.5–7.4, and all the experiments were performed in this pH range. The standard curve prepared using the DPC colorimetric method (figure 2) was obtained following the well-established Cr(VI) determination method under the slightly acidic condition controlled with phosphate buffer at 540 nm [7].

\[
\text{\textit{A}}_{\text{DPC}} - \text{\textit{A}}_{\text{DS}} = \frac{n_{\text{DPC}} + n_{\text{DS}}}{n_{\text{DPC}} \times n_{\text{DS}}} \times S_{\text{pooled}}
\]

Figure 3. The % recovery of various Cr(VI)-spiked solutions using both direct spectroscopic and diphenylcarbazide colorimetric methods.

Figure 3 shows the % recovery of various Cr(VI)-spiked solutions using two different determination methods. Error bars were prepared using a 95% confidence interval based on three-times and six-times replicated measurements for the DPC colorimetric and direct spectroscopic determination methods, respectively. The direct spectroscopic determination method showed approximately 1.2–1.4 times higher confidence intervals than those for the DPC colorimetric method, indicating that the direct spectroscopic method is slightly less precise than the DPC colorimetric method. The % recovery, however, demonstrated higher accuracy with the direct spectroscopic detection method.

3.1 Comparison of Two Cr(VI) Determination Methods

A null hypothesis indicating that both Cr(VI) determination methods adopted in this research relied on each other was evaluated by comparing both means with Student’s t-test. The t-test for the comparison of means was calculated through following the equation:

\[
t_{\text{calculated}} = \frac{\overline{\text{A}}_{\text{DPC}} - \overline{\text{A}}_{\text{DS}}}{S_{\text{pooled}}} \times \sqrt{\frac{n_{\text{DPC}} \times n_{\text{DS}}}{n_{\text{DPC}} + n_{\text{DS}}}}
\]

\[
S_{\text{pooled}} = \sqrt{\frac{(n_{\text{DPC}} - 1)(s_{\text{DPC}})^2 + (n_{\text{DS}} - 1)(s_{\text{DS}})^2}{n_{\text{DPC}} + n_{\text{DS}} - 2}}
\]

The calculated t values are 25.5, 2.3, and 17.0 for the 9, 13, and 23 mg/L Cr(VI) solutions, respectively. When the calculated t values were compared with the t-test value at a proper degree of freedom [13], the result showed that both methods are reliable for the 13 mg/L solution. For other spiked solutions, the other results indicated that two concentrations determined by both methods are different at the 95% confidence level.

3.2. Effects of Ions on the Direct Spectroscopic Method

Additional efforts were performed to investigate the effects of various common ions on the direct spectroscopic Cr(VI) determination method. For cations, no significant effects of Na⁺ and K⁺ were observed up to 1,000 mg/L of each ion. Aluminum (Al³⁺) and magnesium ions (Mg²⁺) may interfere with the Cr(VI) determination when the concentration is higher than 100 mg/L and 15 mg/L, respectively. Common anions, such as nitrate (NO₃⁻) and chloride (Cl⁻), did not affect up to 1,000 mg/L, and no effects were observed for sulfate (SO₄²⁻) and carbonate (CO₃²⁻) up to 200 mg/L.

4. Conclusion

Experimental studies have been performed to study the potential application of the direct spectroscopic determination of hexavalent chromium in solution. According to the experimental findings, aqueous phase hexavalent chromium showed significant spectral response at 363 nm following Beer’s law. The standard curve, which was obtained following the traditional least squares method, showed the linear regression with an r² value of 0.9917. In comparison with the diphenylcarbazide colorimetric method, the direct spectroscopic method showed higher accuracy than that of the DPC colorimetric method, which showed enhanced precision. The direct spectroscopic method is a convenient and rapid dissolved Cr(VI) determination method without adding additional chemicals which could be applied to Cr(VI) solutions with low ionic strength.

REFERENCES


