



## Full Length Research Article

### QUANTITATIVE DETERMINATION OF Cr (VI) BY DIPHENYLCARBAZIDE REAGENT

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#### ABSTRACT

A quantitative method of Cr (VI) - determination by using diphenylcarbazide reagent was studied in detail. This method exhibits a very high sensitivity in analyzing Cr(VI) in water samples. The optimal condition for the determination of Cr (VI) was established. If in the samples, the much excess of Cr (VI) compared with DPC the maximum absorbance of color complex would be reduced. This is very important problem when use of the method in practice.

#### INTRODUCTION

Chromium is a chemical element which is widely used for manufacturing materials such as steel iron, chromium alloy and refractory products. The most stable form, Cr (III), occurs naturally in environment, while Cr (VI) and Cr<sup>(0)</sup> are generally produced by industrial manufacture. Chromium is very useful for industry, however, against human body, chromium ions are toxic (Davies, Braver, Infante *et al* 1985). The toxicity of chromium depends on the oxidative state. The Cr (III) and Cr (VI) ions are most biologically significant (Kumpulainen, 1992). Cr (III) ion in biologic tissues helps to maintain the normal metabolism of glucose, protein and fat (D.G. Barceloux 1999, W. Merts, 1998). However, Cr (III) may be harmful if ingested in large amounts (thousands of micrograms per day). Cr(VI) ion is a strong oxidizing agent and highly toxic due to its carcinogenic and mutagenic properties (Cotton and *et al* 1999, Katzand and Salem, 1993, (Zhang and Li, 1987). For this reason chromium requires careful handling quantitative determination. There are many selective methods for determination of chromium such as ICP-MS, ICP-AES, UV-VIs, AAS, spectrophotometer (Sivanidlo da Silva and *et al.*, 1993, Wróbel and *et al.*, 1983; Tayone, 2015).

In this paper chromium is determined by spectrophotometric method using diphenylcarbazide reagent. Here, the paper was focused on the determination of the suitable experimental conditions for the formation of color complex between Cr(VI) with diphenylcarbazide reagent.

#### Experimental part

##### Chemicals

- Stock solution Cr(VI), this solution was prepared from K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with analytical grade (Merck): K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was dried at 150°C for one hour and left in a desiccator. In a 1000 mL-volumetric glass flask, the 2.828 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> were dissolved in distilled water and then diluted to mark. The stock solution concentration is 1.0 g/L
- Solution of diphenylcarbazide, (DPC) In a 50 mL-volumetric glass flask, the 25 mg of DPC were dissolved in acetone and then diluted to mark. The DPC solution concentration is 2.1mM kept at 4°C in a refrigerator. The solution was prepared weekly.
- Other solutions such as NaOH (2M), AgNO<sub>3</sub> (0.1 M), H<sub>2</sub>SO<sub>4</sub> (98%), H<sub>3</sub>PO<sub>4</sub> (80%), H<sub>2</sub>O<sub>2</sub>(30%), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.01M) were used with the analytical grade.

##### Equipments

- Spectrophotometer UV-VIs Biochrom S60, (2013) USA.

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- pH-meter TOA DDK HM-25R, (2010) Japan.

### Experimental procedure

#### Determination of maximum absorbance wavelength of color complex formed by the interaction between Cr(VI) and DPC

A set of three solutions was prepared as follows:

- The solution consists of  $K_2Cr_2O_7$  (0.2 mg/L), 0.5 mL  $H_3PO_4$  (80%) and distilled water in a 25 mL- measuring glass flask, denoted DD1.
- The solution consists of 0.5 mL  $H_3PO_4$  (80%) and distilled water in a 25 mL- measuring glass flask, denoted DD2.
- The solution consists of  $K_2Cr_2O_7$  (0.2 mg/L), 0.5 mL  $H_3PO_4$  (80%), 0.5 mL DPC and distilled water in a 25 mL- measuring glass flask, denoted DD3.

All solutions were kept for 5min before measuring absorbance. The absorbance was taken from 400 to 700 nanometer (nm) using distilled water as reference

#### Surveying factors influence on the maximum absorbance of the color complex

##### • pH influence

A set of 7 of 25 mL- glass flasks was prepared, numbered from No.1 to No.7. Every flask includes  $K_2Cr_2O_7$  (0.4mg/L), DPC (101.75 mM), distilled water, pH varying from 0.2 to 3.0 by  $H_3PO_4$  and the adding distilled water to mark. The flask was kept for 5 min before measuring absorbance using distilled water as reference.

##### • Influence of the initial concentration of DPC

A set of 7 measuring glass flasks was prepared. In each flask contains Cr (VI), 1mg/L or 0.019 mM; the DPC amount varying from 0.042 to 1.01 mM. The pH of sample was adjusted to be the optimal value before measuring absorbance. The dependence of the absorbance of color complex vs. DPC concentrations will be present by a plot.

##### • Influence of the initial concentration of Cr (VI)

A set of 7 measuring glass flasks was prepared. In each flask contains DPC 10.18 mg/L or 0.042 mM; the Cr(VI) amount varying from 0.15 to 0.800 mM. The pH of sample was adjusted to be the optimal value before measuring absorbance. The dependence of the absorbance of color complex vs. Cr (VI) concentrations will be present by a plot.

- Surveying the stability of color complex

The experiment was implemented in a 25 mL-measuring flask consisting of Cr(VI), (0.4mg/L); DPC, (101 mg/L), pH=1.65. The absorbance of sample was measured in the time from 5 to 60 min, using distilled water as reference.

#### Establishment of calibration curve

A set of seven 25 mL-measuring glass flasks was prepared. In each flask there were DPC (1.05 mM) or 254.39 mg/L; pH =1.65 and Cr (VI) varying from 0.01 to 1.0 mg/L and distilled

water to mark. The absorbance was measured with the reference as distilled water.

## RESULTS AND DISCUSSION

#### Absorbance spectrogram of color complex formed by the interaction between Cr(VI) and DPC

The absorbance spectrogram of the color complex formed by the reaction between Cr(VI) and DPC was present in the Fig. 3.1.

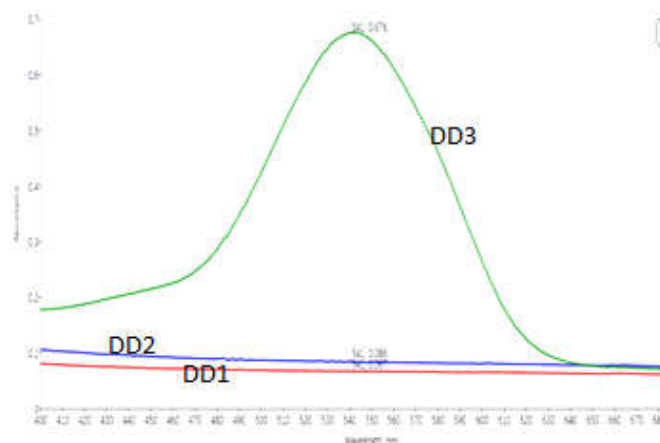


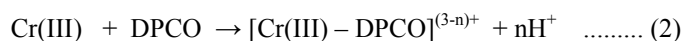
Fig. 3.1. Absorbance spectrogram of color complex of Cr(VI) with DPC

The result in Fig.3.1 showed that maximum absorbance at  $\lambda \sim 541$  nm for solution DD3 indicated the formation of a color complex between Cr (VI) and DPC. The appearance of the maximum absorbance of Cr (VI) with DPC has been explained by the formation of the complex compound in situ in the sample between Cr (III) and diphenylcarbazone (DPCO), (G.J.Wellems and *et al*). According these authors,

Under this condition, Cr (VI) was reduced by DPC to form Cr (III) and DPCO in the sample as follows:



Then a color complex was formed by the interaction between Cr(III) and DPCO as follows:



The overall reaction to form color complex can be written as follows:



Here n denoted the unknown number of protons released in the complex formation.

#### Influence factors on the maximum absorbance of the color complex

##### pH influence

The influence of pH on the maximum absorbance of the color complex was present in the Fig. 3.2 and 3.3.

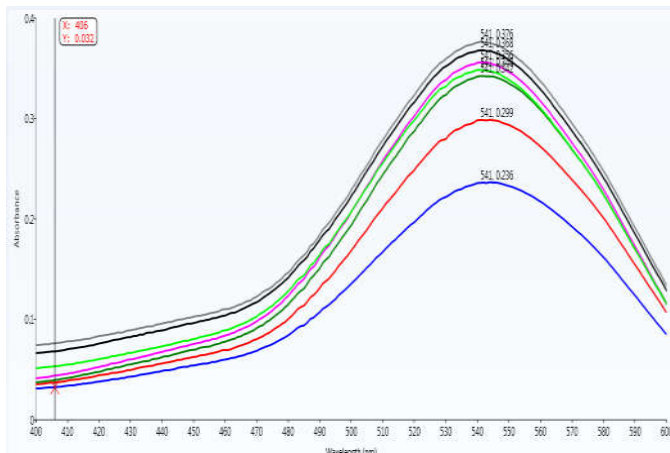


Fig. 3.2. Influence of pH on the maximum absorbance

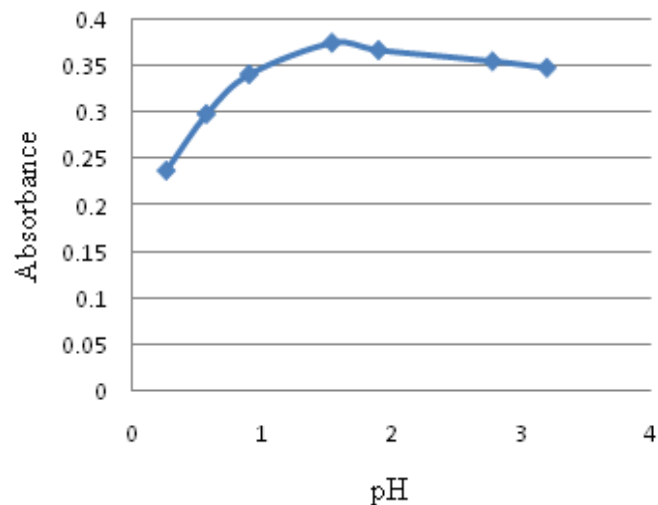


Fig. 3.3. Dependence of maximum absorbance on pH

The influence of the pH on the maximum absorbance indicated that the formation of color complex occurred in acid media. The maximum absorbance was increased. With pH increasing from 0.20 to 1.65 and then decreasing slowly. This phenomenon was consistent with the work (G.J. Wellem's and *et al*), due to the formation of Cr (H<sub>2</sub>O)<sub>x</sub> that could not react with DPCO to form color complex.

**Influence of the initial concentration of DPC**

The dependence of the absorbance of color complex vs. DPC concentrations will be present by a plot in Fig. 3.4.

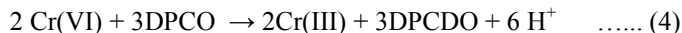
The Fig. 3.4. indicated that the suitable molar ratio of DPC/ Cr(VI) = 2.18 that be selected for the further experiments.

**3.2.3. Influence of the initial concentration of Cr(VI)**

The dependence of the absorbance of color complex vs. Cr (VI) concentrations will be present in the Fig.3.5.

The experimental data showed that the maximum absorbance increased from 0.1 to 0.5 mM of Cr(VI) and then decreased. This phenomenon can be explained in the work (G.J.Wellem's

and *et al*), due to the reaction of Cr (VI) with DPCO to producing diphenylcarbadizone ( DPCDO) as follows:



The Cr(III) could not react with DPCDO to producing color complex, therefore the absorbance reduced. This influence must be studied before its application in practice.

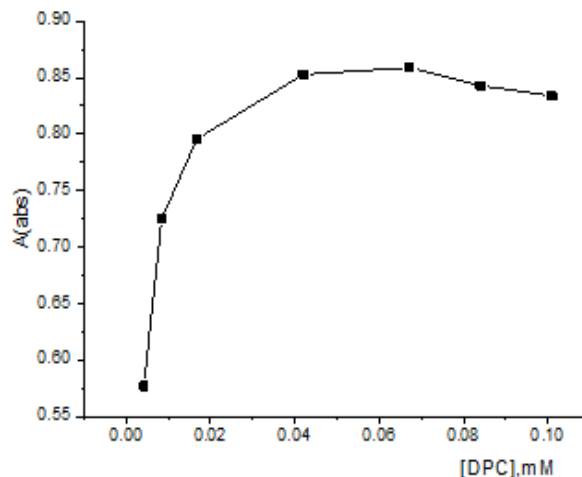


Fig. 3.4. Influence of DPC on maximum absorbance

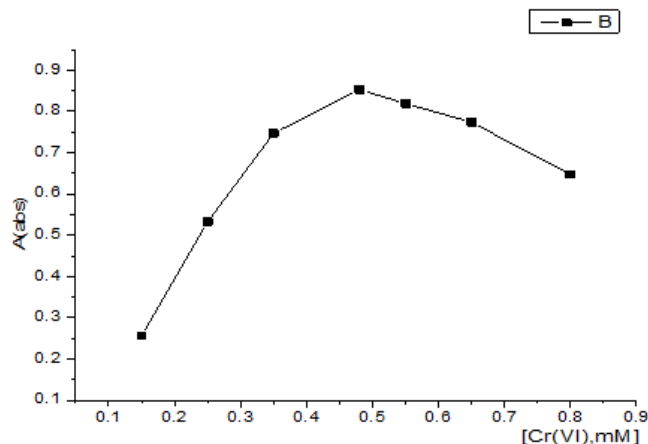


Fig. 3.5. Influence of the initial concentration of Cr(VI) on the maximum absorbance

**The complex stability versus the time**

The stability of the complex was presented in Fig. 3.6.

The experimental data showed that the complex Cr(III)-DPCO is very stable within 60 mn.

**Establishment of calibration curve**

The calibration curve with the Cr (VI) from 0.01 to 1.0 mg/L corresponding the equation  $A = (0.8324 \pm 0.00901).C_{Cr} + (0.0086 \pm 0.00506)$  was present in Fig.3.7

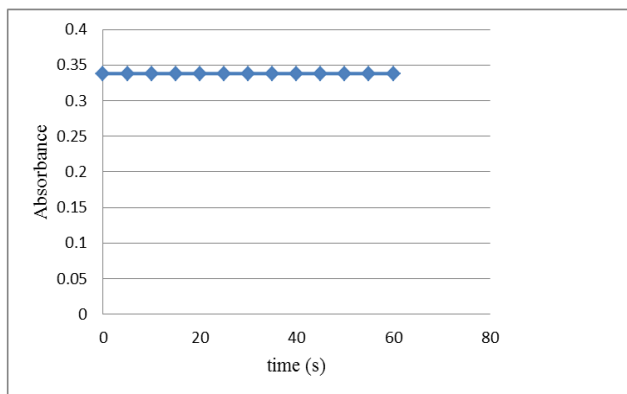


Fig. 3.6. The dependence of color complex vs. the time

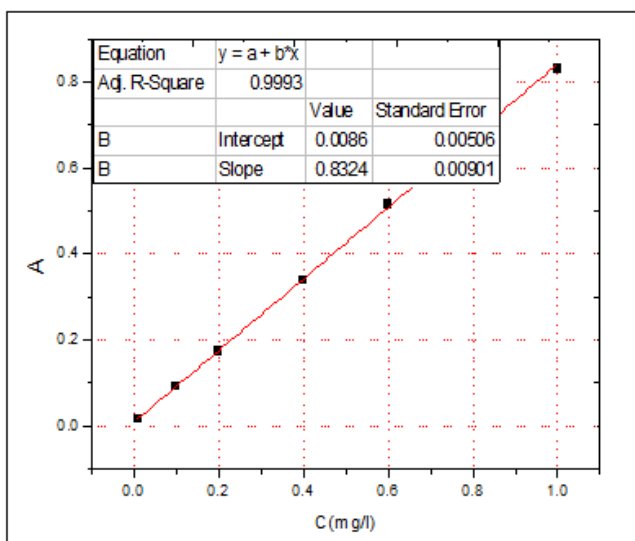


Fig. 3.7. The calibration determining Cr(VI) in sample

Table 3.1. The Cr(VI) in 10 times of analysis

Samples	A(541nm)	Cr(VI) mg/L	Samples	A(541nm)	Cr(VI) mg/L
M1	0.033	0.03913	M6	0.036	0.04231
M2	0.033	0.03944	M7	0.033	0.03965
M3	0.035	0.04157	M8	0.036	0.0426
M4	0.033	0.03875	M9	0.033	0.3865
M5	0.034	0.03971	M10	0.035	0.04112

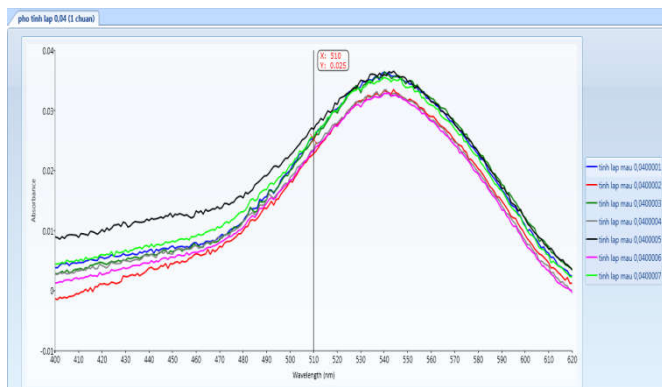


Fig. 3.8. UV-Vis spectrogram of Cr(VI) in 10 times analyzed

## Determination of LOD and LOQ

The limit of detection (LOD), and limit of quantification (LOQ) of this method was implemented using a sample in which the Cr(VI) was analyzed 10 times. The experimental data presented in Table 3.1 and Fig.3.8.

By these data, we have the standard derivation  $SD = 1.476 \times 10^{-3}$ , the  $LOD = 3 \times SD = 4.429 \times 10^{-3}$  mg/L;  $LOQ = 10 \times LOD = 1.476$  mg/L.

## Conclusion

Chromium is a chemical element existing in environment, in which Cr(VI) is very high toxic against human life. The determination of Cr(VI) in samples is very important. The analysis of Cr(VI) may be carried out using spectrophotometry with DPC reagent. The absorbance of color complex of Cr(VI) and DPC was measured at  $\lambda = 541$  nm. The factors influencing on the maximum absorbance of the color complex were studied in detail. The much excess of Cr(VI) compared with DPC concentration must be studied before its application in practice. The LOD and LOQ are  $4.429 \times 10^{-3}$  mg/L and 1.476 mg/L respectively.

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