



## Method of analysis for determination of the chromium (Cr) species in water samples by spectrophotometry with diphenylcarbazine

Adam Wiryawan<sup>1\*</sup>, Retno Suntari<sup>2</sup>, Zaenal Kusuma<sup>2</sup>, Rurini Retnowati<sup>1</sup>,  
R.Y.Perry Burhan<sup>3</sup>, Syekhfani<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Sciences, Brawijaya University, Malang, East Java 65145, Indonesia

<sup>2</sup>Department of Soil Sciences, Faculty of Agriculture, Brawijaya University, Malang, East Java 65145, Indonesia

<sup>3</sup>Department of Chemistry, Faculty of Sciences, Institut Teknologi Sepuluh November (ITS), Surabaya, East Java 60122, Indonesia

**Abstract :** Speciation of Chromium (Cr) is very important because of the toxicity of these metals depending on the oxidation number and its concentration is very low in the water system. Chromium occurs in the environment primarily in two valence states, trivalent Cr(III) and hexavalent Cr(VI). Chromium(III) is an essential micro-nutrient for the human body, while the Cr(VI) is highly toxic and carcinogenic. Chromium(VI) in the water can be analyzed by spectrophotometry with diphenylcarbazine as reagent on pH=1 at maximum wavelength of 540 nm. The experimental result show that Cr(VI) can be analyzed using diphenylcarbazine in the concentration of 0.0015% and H<sub>3</sub>PO<sub>4</sub> solution as acidic in 0.03 mol/L. The absorbance was measured at minutes 5 after preparation. There is interference from ion Fe(III) at least 6.0 ppm and this interference can be overcome by using 0.3% NaF solution. The limit of detection of this method is 0.1959 ppm. Chromium(VI) in the artificial samples, mix of Cr(III) and Cr(VI), can be analyzed by using this method without oxidation by KMnO<sub>4</sub> solution. While Cr(III) in the artificial samples, mix of Cr(III) and Cr(VI), can be analyzed by using this method via oxidation by KMnO<sub>4</sub> solution in the acidic media (H<sub>2</sub>SO<sub>4</sub>), the result of this analysis is the total concentration of Chromium. The concentration of Cr(III) can be calculate via subtract the total of Cr concentration by concentration of Cr(VI).

**Keywords :** speciation, Cr(III), Cr(VI), spectrophotometry, diphenylcarbazine, Fe(III), interference

### Introduction

Speciation of Chromium (Cr) is very important in the field of environmental study, clinical, biology, agriculture and in controlling the quality of waste water, natural water, and drinking water because of the toxicity of these metals depending on the oxidation number. Chromium is one of the most frequently detected contaminants in groundwater<sup>1</sup>.

Toxic chromium enters into the water system, derived from nature and from waste or industrial waste such as metal industrial waste water, electroplating, wood preservation, fertilizers, leather preservation

industry<sup>2</sup>. In the marine environment, species Cr(VI) are in the form of  $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$ . While Cr(III) is in the form of hydroxide compounds as  $\text{Cr}(\text{OH})_n^{(3-n)+}$ . The average concentration of total chromium in the sea water and rainwater row by 0.2 to 1 g/L and 0.04 to 0.5 mg/L. Total chromium concentrations in surface water of 0.5 to 2 g/L, where the dissolved chromium in the form of 0.02 to 0.3 mg/L<sup>3,4</sup>.

Chromium is an element that is abundant on the order of 21 in the earth's crust at an average concentration of 100 ppm.<sup>5</sup> Chromium compounds found in the environment, because of the erosion of rocks containing chromium and may come from volcanic eruptions. The range of concentration in the soil is between 1 - 3000 mg/kg, and in rivers and lakes 26  $\mu\text{g/L}$  to 5.2 mg/L<sup>6</sup>.

Chromium speciation analysis methods developed rapidly not only because of the impact of its toxicity but because its concentration is very low in the water system. Chromium(III) is an essential micro-nutrient for the human body, and play an important role in the metabolism of glucose and some fat. While the Cr(VI) is highly toxic and carcinogenic<sup>7</sup>.

Chromium occurs in the environment primarily in two valence states, trivalent Cr(III) and hexavalent Cr(VI). Chromium(III) is much less toxic than Cr(VI) and occurs naturally in the environment and is the most stable in nature and in biological systems<sup>8</sup>.

The Government of Indonesia through government regulation no.20 of 1990, has determined that the threshold of chromium(VI) is allowed in drinking water, raw materials of drinking water, water for fisheries and animal husbandry, the maximum is 0.05 mg/L<sup>9</sup>. While Cr(III) and Cr(VI) can be transformed to one another in the environment and during storage.

Chromium(VI) in the water can be analyzed with methods diphenylcarbazide<sup>10</sup>. Iron(III) can interfere to the analysis of Cr(VI) due to Fe(III) can form complexes with diphenylcarbazide<sup>11,12</sup>. By using magnesium sulfate/ phosphate buffer, interference of the metal can be deposited primarily of Fe(III)<sup>13</sup>.

Spectrophotometric methods can be used for selective determination of the different chromium species using reagents to form absorbing species that present selectivity in the response. The most common method for determining Cr(VI) in aqueous solutions is based on the reaction of diphenylcarbazide (DPC) with Cr(VI) at a pH of 1.0<sup>14-17</sup>. Spectrophotometric analysis of the magenta chromagen ( $\lambda_{\text{max}} \sim 540 \text{ nm}$ ) which is formed by the reaction of Cr(VI) with 1,5-diphenylcarbazide (DPC) in strongly acidic solution<sup>18</sup>. Because of that, the development of analytical methods for speciation of Cr(III) and Cr(VI) is important compared to methods of determining these metals in total.

## Experimental

### Material

Stock solution of Cr(III) 1000 mg/L was prepared by dissolving Chromium nitrate nonahidrat,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in a nitric acid solution of 0.01 mol L<sup>-1</sup>. Stock solution of Cr(VI) 1000 mg/L was prepared by dissolving Sodium chromate tetrahydrate ( $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ ) in a solution of nitric acid of 0.01 mol/L. A solution of 1,5-diphenylcarbazide (DPC) 0.05% dissolved in acetone. Phosphoric acid solution ( $\text{H}_3\text{PO}_4$ ) 1 M. A series of standard solutions of Cr(III) and Cr(VI) with a small concentration, prepared daily by diluting accurately from stock solutions.

### Instruments and glassware

Spectrophotometer UV-vis, Shimadzu, UV-160 type: for measuring absorbance of Cr (VI) to Cr (III). For all the glassware to be used soaked with a solution of 0.1 M  $\text{HNO}_3$  for 24 hours.

### Procedure for chromium(VI)

#### Optimum concentration of diphenylcarbazide (DPC)

Prepared 5 (five) series each solution: 0.5 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 3 mL  $\text{H}_3\text{PO}_4$  1 M. Each solution coupled with a solution DPC with variations: 1.0; 2.0; 3.0; 4.0;

5.0 mL DPC solution of 0.05%. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### **Optimum volume solution of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)**

Prepared 6 (six) series each solution: 2.0 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 1 M H<sub>3</sub>PO<sub>4</sub> solution with different volume: 0.0; 1.0; 3.0; 5.0; 7.0; 9.0 mL. Each solution was added with a solution of 0.05% DPC as 3.0 mL. Each solution was with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### **The influence of the absorbance measurement time after preparation**

Prepared 2.0 ml of Cr(VI) 100 ppm in a 100 mL volumetric flask. Plus 3.0 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and DPC solution plus as much as 3.0 mL of 0.05%. Further diluted with distilled water to 100 ml and shaken. Then the absorbance was measured at maximum wavelength of 540 nm with a UV-vis spectrophotometer with variation of time: 5, 15, 45, 75, 105, 135 minutes after preparation.

### **Effect of Fe(III) interference**

Prepared 8 (eight) series each solution: 2.0 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 1 M FeCl<sub>3</sub> solution with different volume: 0.0; 2.0; 4.0; 6.0; 10.0; 15.0; 20.0; 25.0 mL. Each mL of solution plus 3.0 mL of 1 M H<sub>3</sub>PO<sub>4</sub> solution and the solution DPC as much as 3.0 mL of 0.05%. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### **Overcoming the Effects of Fe(III) interference**

Prepared 6 (six) series each solution: 0.5 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 1 M FeCl<sub>3</sub> solution with a volume of 3.0 mL. Each solution plus 5% NaF solution with varying volumes, namely: 0.0; 4.0; 6.0; 10.0; 15.0 mL. Furthermore, each mixed solution plus 3.0 mL mL of 1 M H<sub>3</sub>PO<sub>4</sub> solution and 0.05% solution DPC as much as 3.0 mL. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### **Effect of Cu(II) interference**

Prepared 6 (six) series each solution: 2.0 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 100 ppm Cu(II) solution with different volume: 0.0; 2.0; 4.0; 6.0; 10.0; 20.0 mL. Each solution was added 3.0 mL of 1 M H<sub>3</sub>PO<sub>4</sub> solution and the solution DPC as much as 3.0 mL of 0.05%. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### **Effect of Zn(II) interference**

Prepared 6 (six) series each solution: 2.0 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 100 ppm Zn(II) solution with different volume: 0.0; 2.0; 4.0; 6.0; 10.0; 20.0 mL. Each solution was added 3.0 mL of 1 M H<sub>3</sub>PO<sub>4</sub> solution and the solution DPC as much as 3.0 mL of 0.05%. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectro-photometer.

### **Effect of Mn(II) interference.**

Prepared 6 (six) series each solution: 2.0 mL solution of Cr(VI) 100 ppm in a 100 mL volumetric flask. Each plus 100 ppm Mn(II) solution with different volume: 0.0; 2.0; 4.0; 6.0; 10.0; 20.0 mL. Each mL of solution plus 3.0 mL of 1 M H<sub>3</sub>PO<sub>4</sub> solution and the solution DPC as much as 3.0 mL of 0.05%. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### Selection of the range of concentrations of Cr(VI) which meets the Beer Lambert law

Prepared a series of solvent solution of Cr(VI) 100 ppm in a 100 mL volumetric flask, namely: 0.0; 0.15; 0.30; 0.45; 0.60; 0.75; 0.90; 1.05; 1.20; 1.35; 1.50 mL of Cr(VI) of 100 ppm. Each plus 3.0 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% solution DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### Detection limit of method of determination of Cr(VI).

Prepared a series of solvent solution of Cr(VI) 100 ppm in a 100 mL volumetric flask, namely: 0.0; 0.15; 0.30; 0.45; 0.60; 0.75; 0.90 mL of Cr(VI) of 100 ppm. Each plus 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% solution DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### Samples analysis of artificial (interference of Fe<sup>3+</sup>) and overcome this interference with NaF solution

For standard curve Cr (VI). Prepared a series of solvent solution of Cr(VI) 100 ppm in a 100 mL volumetric flask, namely: 0.0; 0.2; 0.4; 0.6; 0.60; 0.8 mL of Cr(VI) of 100 ppm. Each plus 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% solution of DPC. Each diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

For artificial sample of Cr(VI). Prepared three rows artificial sample solution of 0.5 ppm Cr(VI) with a volume of 100 mL, respectively coupled with NaF solution by volume: 6.0; 4.0; 2.0 mL (table 1.). Each diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. The absorbance of each solution were extrapolated to the standard curve of Cr(VI) and concentration can be known.

**Table 1. Composition of the solution**

No.	The solution is added to Cr(VI) before dilution
1.	6 mL NaF + 3 mL Fe(III) + 3 mL H <sub>3</sub> PO <sub>4</sub> + 3 mL DPC
2.	4 mL NaF + 3 mL Fe(III) + 3 mL H <sub>3</sub> PO <sub>4</sub> + 3 mL DPC
3.	2 mL NaF + 3 mL Fe(III) + 3 mL H <sub>3</sub> PO <sub>4</sub> + 3 mL DPC

### Procedure for chromium (III)

#### Determination of Cr (III) via oxidation of Cr(III) to Cr(VI)

For standard curve of Cr(VI), prepared a series of solvent solution of Cr(VI) 100 ppm in a 100 mL volumetric flask, namely: 0.0; 0.1; 0.2; 0.3; 0.4; 0.5 mL of Cr(VI) of 100 ppm. Each plus 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% solution DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

For selection of pH to oxidation Cr(III) to Cr(VI), prepared five series of artificial sample solution of 0.4 ppm Cr(III) in different test tubes and added with 1 mL of distilled water. Each test tube was acidified by adding a solution of H<sub>2</sub>SO<sub>4</sub> (1:3) is different, namely: 0.05; 0.10; 0.15; 0.20; 0.25 mL. Each one is oxidized with KMnO<sub>4</sub> solution drop wise in a test tube that is inserted in the beaker glass containing water that is heated on a hot plate. The addition of KMnO<sub>4</sub> solution is stopped when there is little excess KMnO<sub>4</sub> solution which marked the formation of a permanent red color. When it is cold, each solution was added with 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength is 540 nm with a UV-vis spectrophotometer. The absorbance of each solution were extrapolated to the standard curve of Cr(VI) and concentration can be known.

For artificial samples of Cr(III), prepared three rows of sample solution of : 0.2; 0.3; 0.4 ppm Cr(III) in a test tube and added with 1 mL of distilled water. Each test tube was acidified by adding 0.15 mL of a solution

of H<sub>2</sub>SO<sub>4</sub> (1:3). Each one is oxidized with KMnO<sub>4</sub> solution drop wise in a test tube that is inserted in the beaker glass containing water that is heated on a hot plate, as Figure 1. The addition of KMnO<sub>4</sub> solution is stopped when there is little excess KMnO<sub>4</sub> solution which marked the formation of a permanent pink color. When it is cold, each plussolution was added with 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. The absorbance of each solution were extrapolated to the standard curve of Cr(VI) and concentration can be known.

### Determination of Cr(VI) to Cr(III) in an artificial of water sample.

By using the optimum conditions (from the experiment c.2. and c.3.), concentration of Cr(VI) to Cr(III) in artificial samples were determined. For standard curve Cr (VI), prepared a series of solution of Cr(VI) 100 ppm in a 100 mL volumetric flask, namely: 0.0; 0.1; 0.2; 0.3; 0.4; 0.5 mL of Cr(VI) of 100 ppm. Each plus 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% solution DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. For mixing Cr(VI) and Cr(III) in a sample of artificial water, prepared a series of artificial sample solution, a mixture of 0.2 ppm Cr(III) and 0.2 ppm Cr(VI), then treated as table 2:

**Table 2. The solution added to mix of Cr(III) and Cr(VI)**

No.	Addition of Fe(III) and NaF solution	Oxidation with KMnO <sub>4</sub>	Cr measured as
1.	0 mL Fe(III) and 0 mL NaF	Without oxidation	Cr(VI) only
2.	3 mL Fe(III) and 0 mL NaF	Without oxidation	Cr(VI) only
3.	3 mL Fe(III) and 6 mL NaF	Without oxidation	Cr(VI) only
4.	0 mL Fe(III) and 0 mL NaF	Oxidation by KMnO <sub>4</sub>	Cr(VI) and Cr(III)
5.	3 mL Fe(III) and 0 mL NaF	Oxidation by KMnO <sub>4</sub>	Cr(VI) and Cr(III)
6.	3 mL Fe(III) and 6 mL NaF	Oxidation by KMnO <sub>4</sub>	Cr(VI) and Cr(III)

No. 1, 2, 3 : each in a 100 mL volumetric flask, added 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% DPC. No. 4, 5, 6: oxidation carried out in a test tube and added with 1 mL of distilled water. Each test tube was acidified by adding 0.15 mL of a solution of H<sub>2</sub>SO<sub>4</sub> (1:3). Each one is oxidized with KMnO<sub>4</sub> solution drop wise in a test tube that is inserted in the glass beaker containing water that is heated in a hot plate, as Figure 1. The addition of KMnO<sub>4</sub> solution is stopped when there is little excess KMnO<sub>4</sub> solution which marked the formation of a permanent pink color. When it is cold, a solution of each test tube transferred to a different flask, added with 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% DPC.

Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength is 540 nm with a UV-vis spectrophotometer. The absorbance of each solution were extrapolated to the standard curve of Cr(VI) and concentration can be known.

### The use of NaClO and HClO<sub>4</sub> as oxidizing Cr(III)

The oxidation process of Cr(III) with NaClO and HClO<sub>4</sub> performed as a process of oxidation with KMnO<sub>4</sub>. Prepared two sample solution made in 0.2; 0.4 ppm Cr(III) in a test tube and added with 1 mL of distilled water. Each test tube was acidified by adding 3 drops of a solution of H<sub>2</sub>SO<sub>4</sub> (1: 3). Each one is oxidized with NaClO and HClO<sub>4</sub> solution dropwise in a test tube that is inserted in a glass beaker filled with water heated in the hot plate. When it is cold, each solution was added with 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### The use of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as oxidizing Cr(III)

For variations K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution. Five (5) series prepared solution of Cr (III) of 0.2 ppm in the test tube is different, each coupled K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution with different volumes, namely: 0.5; 1.0; 2.0; 4.0;10.0 mL. Each plus H<sub>2</sub>SO<sub>4</sub> solution (1: 3) as much as 0.2 mL. Solution in a test tube they will be placed in a glass beaker containing water and heated on a hot plate for about 10 minutes. When it is cold, each plus 3 mL of 1 M H<sub>3</sub>PO<sub>4</sub> and 3.0 mL of 0.05% DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

For the time variation of oxidation with  $K_2S_2O_8$ . Five (5) series prepared solution of Cr(III) of 0.2 ppm in the test tube is different, each  $K_2S_2O_8$  each solution coupled with the volume of 2.0 mL. Each plus  $H_2SO_4$  solution (1: 3) as much as 0.2 mL. Solution in different test tubes placed in a glass beaker filled with water and heated on a hot plate with variations in heating time: 2, 6, 10, 14, 20 minutes. When it is cold, each solution was added with 3 mL of 1 M  $H_3PO_4$  and 3.0 mL of 0.05% DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

For variations concentration  $H_2SO_4$  solution (1: 3). Five (5) series prepared solution of Cr(III) of 0.2 ppm in the test tube is different, each  $K_2S_2O_8$  each solution coupled with the volume of 2.0 mL. Each solution was added with  $H_2SO_4$  solution (1: 3) with different variations of volume, namely: 0.10; 0.15; 0.20; 0.25; 0.30 mL. Solution in different test tubes were placed in a glass beaker water heated on a hot plate 10 minutes. When it is cold, each solution was added with 3 mL of 1 M  $H_3PO_4$  and 3.0 mL of 0.05% DPC. Each solution was diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

### Mix of Cr(VI) to Cr(III) in a sample of artificial water.

Prepared two rows of artificial sample solution, a mixture of 0.2 ppm Cr(III) and 0.2 ppm Cr(VI). Then treated as table 3. Both are in the 100 mL volumetric flask, added 3 mL of 1 M  $H_3PO_4$  and 3.0 mL of 0.05% DFC. Each diluted with distilled water to 100 mL. Shaken and left for 5 minutes. Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer.

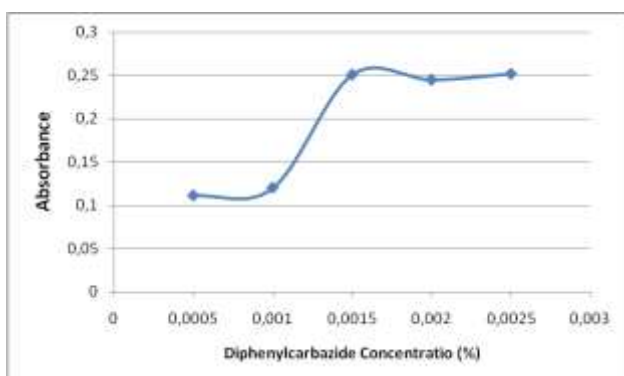
**Table 3. Combination Cr(III) and Cr(VI)**

No.	Mix of Cr(VI) + Cr(III)	Oxidation with $K_2S_2O_8$	Cr measured
1.	0.2 ppm Cr(III) + 0.2 ppm Cr(VI)	Without oxidation	Cr(VI) only
2.	0.2 ppm Cr(III) + 0.2 ppm Cr(VI)	With oxidation	Total Cr

## Result and Discussion

### Diphenyl carbazide (DPC) optimum concentration

Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. From Figure 1. taken 0.0015% DFC as the optimum concentration.



**Figure 1. The effect of DPC concentration to the absorbance.**

### Selection the optimum concentration of $H_3PO_4$ solution

Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. From the Figure 2. taken 0.03 M  $H_3PO_4$  as optimum concentration.

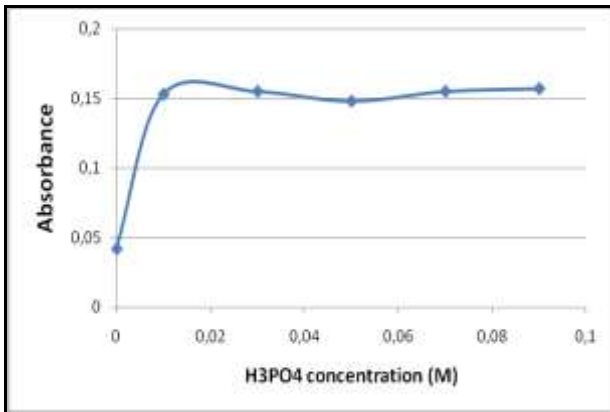


Figure 2. The effect of H<sub>3</sub>PO<sub>4</sub> concentration to the absorbance.

#### The influence of the absorbance measurement time after preparation

Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spektrofotometr with variation of time: 5, 15, 45, 75, 105, 135 minutes after preparation. From the Figure 3. the optimum time is 5 minutes after preparation.

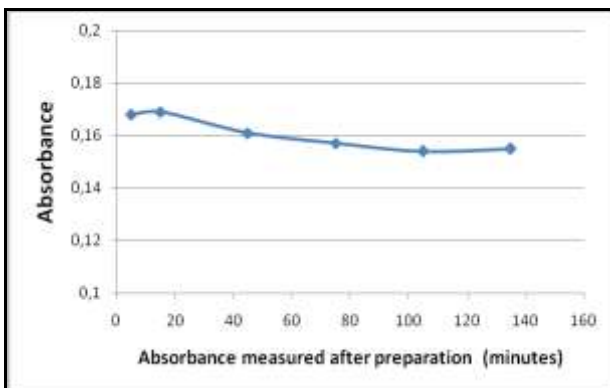


Figure 3. Measurement the absorbance in the variation time after preparation

#### Effect of Fe(III) interference

Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. From Figure 4. chosen concentration of 6.0 ppm Fe(III).

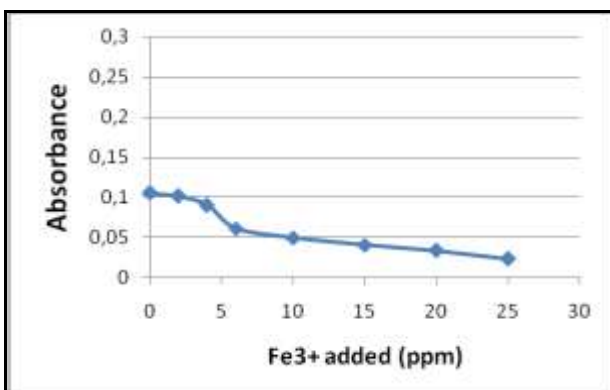


Figure 4. The effect of Fe(III) concentration to the absorbance

### Overcome Fe(III) interference using NaF solution

From this experiment as presented in Figure 5. NaF optimum concentration is 0.3%.

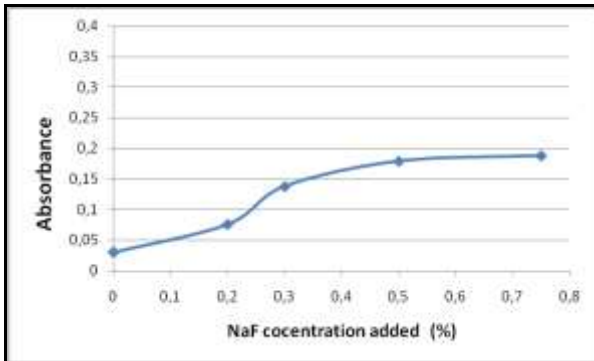


Figure 5. The effect of NaF solution addition the absorbance with Fe(III) interference.

### Selection of the range of concentrations of Cr (VI) which meets the Beer Lambert law

Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. So the range of concentrations of Cr(VI) which meets the Beer Lambert law is 0.1 to 0.9 ppm, because after 0.9 ppm not linier (Figure 6.).

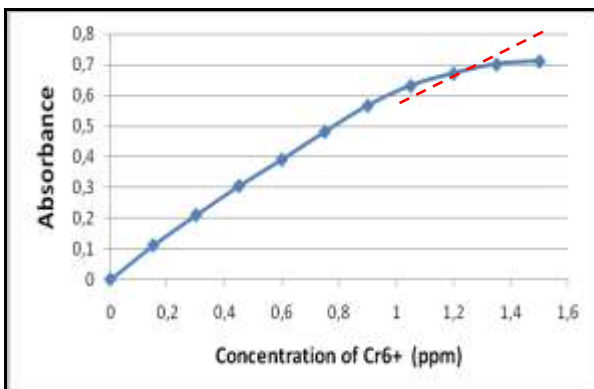


Figure 6. Standard curve of Cr(VI)-DPC for knowing the linierity

### Determination limit ditecton (19)

Making the standard curve Cr6+

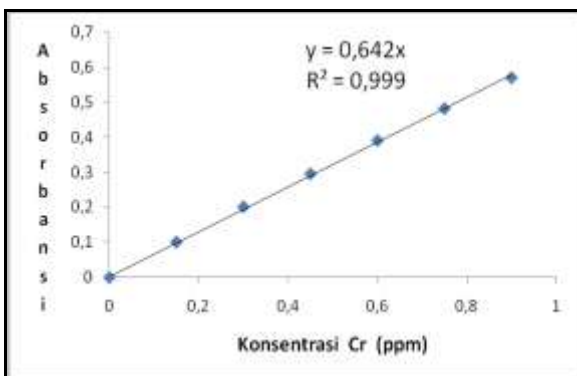


Figure 7. Standard curve of Cr(VI)-DPC



Making the curve for Determination Limit of detection.

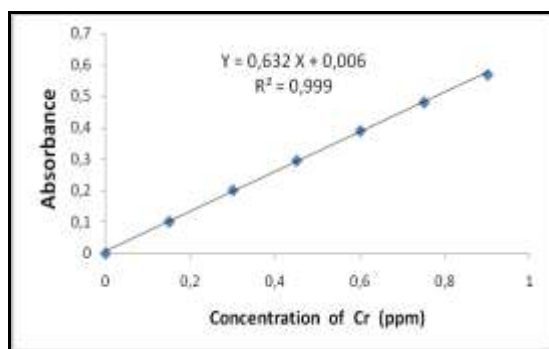


Figure 8. Standard curve of Cr(VI)-DPC for determination of detection limit.

Regression equation for calculate limit of detection (Figure 8):

$$Y = 0.632381 X + 0.006429$$

Equation for calculate limit of detection:

$$Y - Y_b = 3 \times SB$$

$$SB = S_y/x$$

$$SB = \frac{\sqrt{\sum(Y_i - Y^{\wedge})^2}}{n - 2} = \frac{\sqrt{0.00856}}{5} = 0.0413$$

$$Y - Y_b = 3 \times SB$$

$$Y = 0.00632381 + (3 \times 0.04129294957) = 0.1303088488$$

By insert value of  $Y = 0.1303088488$

to the equation of :  $Y = 0.632381 X + 0.006429$

so limit of detection (X) can be calculated as :

$$0.1303088488 = 0.632381 X + 0.006429$$

$$\text{Limit detection (X)} = \frac{0.1303088488 - 0.006429}{0.632381} = 0.1959086$$

Analysis of artificial samples ( $Fe^{3+}$  interference) and overcome the interference (adding 5% NaF solution)

Making the Standar curve of  $Cr^{6+}$

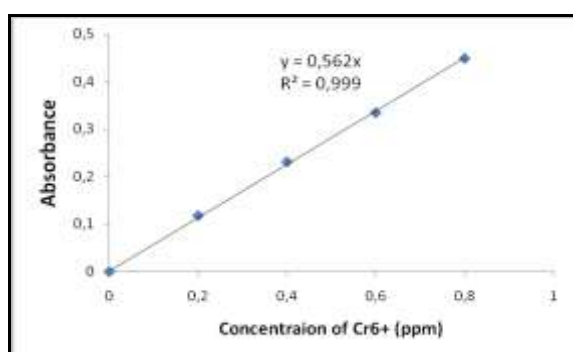


Figure 9. Standard curve of Cr(VI)-DPC

Measuring Cr(VI) in the artificial sampel 0.5 ppm Cr(VI).

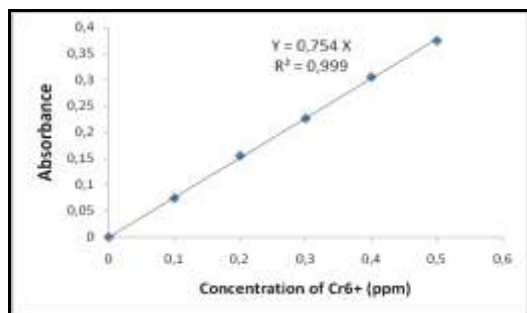
The absorbance of each solution (column 3, Table 3) were extrapolated to the standard curve of Cr(VI), Figure 10 and concentration Cr(VI) can be known (column 4, table 3). From this experiment (table 3) known that 6 mL 5 % NaF solution can overcome the  $Fe(III)$  interference comparing to 4 mL and 2 mL 5% NaF solution.

**Table 3. Measuring the artificial 0.50 ppm Cr(VI) with Fe(III) interference and adding NaF solution.**

Solution added to Cr(VI)	Repli- cates	Abs.	Cr6+ (ppm)	Cr6+ measured	Mean of measured $\pm$ SD	SD (%)
6 mL NaF 3 mL Fe <sup>3+</sup> 3 mL H <sub>3</sub> PO <sub>4</sub> 3 mL DFC	1	0.279	0.4964		0.4988 $\pm$ 0.0027	0.54
	2	0.280	0.4982			
	3	0.282	0.5018			
4 mL NaF 3 mL Fe <sup>3+</sup> 3 mL H <sub>3</sub> PO <sub>4</sub> 3 mL DFC	1	0.258	0.4591		0.4549 $\pm$ 0.0037	0.81
	2	0.255	0.4537			
	3	0.254	0.519			
2 mL NaF 3 mL Fe <sup>3+</sup> 3 mL H <sub>3</sub> PO <sub>4</sub> 3 mL DFC	1	0.174	0.3096		0.3049 $\pm$ 0.0054	1.78
	2	0.172	0.3061			
	3	0.168	0.2989			

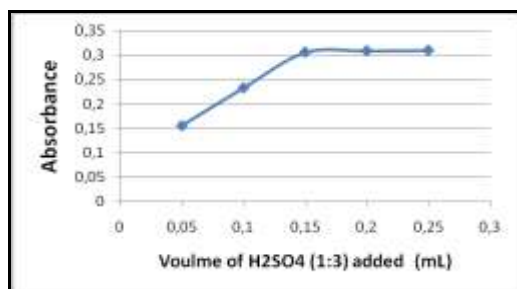
**Determination of Cr(III) via oxidation of Cr(III) to Cr(VI)***Making standard curve of Cr(VI)*

Standard curve of Cr(VI)-DPC is presented in Figure 10

**Figure 10. Standard curve of Cr(VI)-DPC**

Selection of H<sub>2</sub>SO<sub>4</sub> solution as acid media for the oxidation of Cr(III) to Cr(VI).

From the experimental results as presented in Figure 12, have been known that volume of solution of H<sub>2</sub>SO<sub>4</sub> (1: 3) optimum is 0.15 mL.

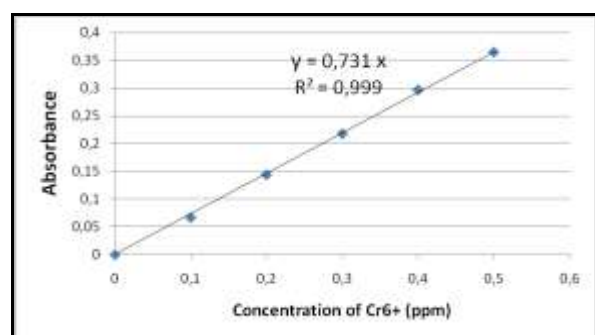
**Figure 11. The effect of H<sub>2</sub>SO<sub>4</sub> solution as acid media to the oxidation of Cr(III) to Cr(VI)**

Measurement of the sample (artificial) Cr(III) which was oxidized to Cr(VI) by KMnO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> as acid media.

The absorbance of each solution (column 3, Table 4) were extrapolated to the standard curve of Cr(VI), Figure 11 and concentration Cr(III), as Cr(VI), can be known (column 4, table 4). From the the table 4, it can be seen that the solution NaF can overcome the Fe(III) interference.

**Table 4. Measuring Cr(III) in the artificial solution of Cr(III) with Fe(III) interference and adding NaF solution.**

ppm Cr <sub>3+</sub>	Repli-cates	Abs.	Cr <sub>3+</sub> measured (ppm)	Mean of Cr <sub>3+</sub> measured ± SD	SD (%)
0.20	1	0.156	0.2069	0.2034 ± 0.0041	1.99
	2	0.154	0.2042		
	3	0.150	0.1989		
0.30	1	0.258	0.3024	0.3059 ± 0.0033	1.09
	2	0.255	0.3064		
	3	0.254	0.3090		
0.40	1	0.174	0.4005	0.4036 ± 0.0028	0.68
	2	0.172	0.4058		
	3	0.168	0.4045		

**Measuring Cr in the artificial samples solution containing of 0.2 ppm Cr(VI) and 0.2 ppm Cr(III)***Making standard curve of Cr(VI)***Figure 12. Standard curve of Cr(VI)-DPC**

Measurement Cr in the sample solution (artificial) containing Cr(VI) and Cr(III), which was oxidized to Cr(VI)

The absorbance of each solution (column 4, Table 5) were extrapolated to the standard curve of Cr(VI), Figure 12 and concentration Cr(III) can be known (column 5, Table 5). From the table 5, show that : in solution no. 1, 2, 3 : only Cr(VI) were measured, because it does not use KMnO<sub>4</sub> oxidation. Solution no.2 less the 0.20 ppm because it was not added NaF solution. In solution no. 4, 5, 6 : Cr(III) and Cr(VI) were measured, because they were oxidized by KMnO<sub>4</sub> solution. Solution no.5 less the 0.40 ppm because it was not added NaF solution.

**Table 5. Measuring the artificial mixing solution of 0.20 ppm Cr(III) and 0.20 ppm Cr(VI) with Fe(III) interference and adding NaF solution.**

Solution Added to Cr solution	Repli-cates	Abs.	Cr <sub>6+</sub> measured (ppm)	Mean of Cr <sub>6+</sub> measured ± SD	SD (%)
None	1	0.146	0.1997	0.2020 ± 0.0012	0.59
	2	0.149	0.2038		
	3	0.148	0.2025		
3 mL Fe(III)	1	0.117	0.1601	0.1596 ± 0.0021	1.31
	2	0.115	0.1573		
	3	0.118	0.1614		
3 mL Fe(III) + 6 mL NaF	1	0.143	0.1956	0.1965 ± 0.0028	0.45
	2	0.146	0.1997		
	3	0.142	0.1943		

KMnO <sub>4</sub>	1	0.294	0.4022	0.4004 ± 0.0025	0.63
	2	0.289	0.3953		
	3	0.295	0.4036		
3 mL Fe(III) + KMnO <sub>4</sub>	1	0.233	0.3187	0.3128 ± 0.0032	1.02
	2	0.229	0.3119		
	3	0.225	0.3078		
3 mL Fe(III) + KMnO <sub>4</sub> + 6 mL NaF	1	0.291	0.3981	0.3949 ± 0.0028	0.72
	2	0.288	0.3940		
	3	0.287	0.3926		

### The influence of the Cu (II) and Zn (II)

Absorbance was measured at the maximum wavelength is 540 nm with a UV-vis spectrophotometer. From the results of this experiment can be seen, Zn (II) and Cu (II) does not affect the solution of Cr (VI)-DFC (Figures 13 and 14).

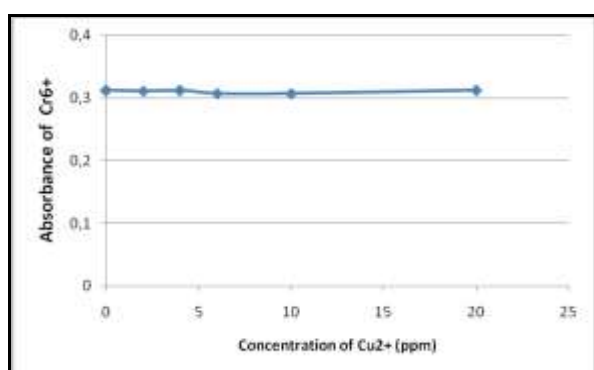


Figure 13. The effect of adding of Cu(II) to absorbance of Cr(VI)

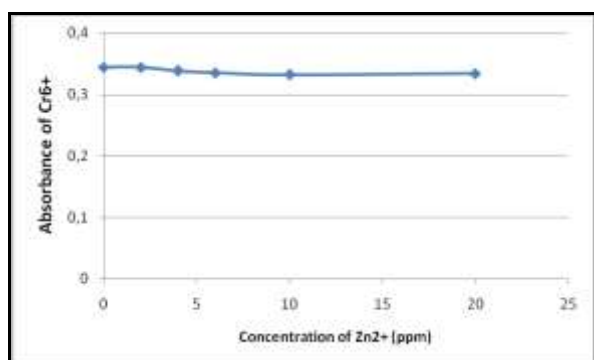
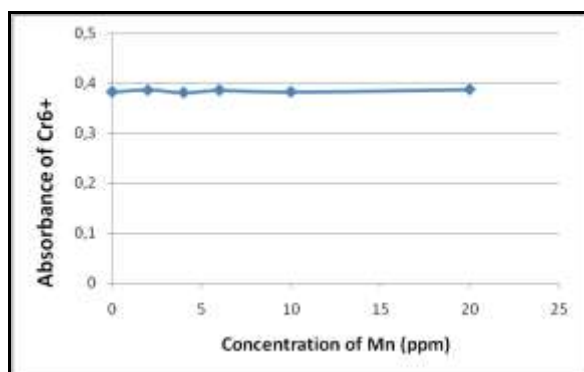


Figure 14. The effect of adding of Zn(II) to absorbance of Cr(VI)

### The influence of the Mn (II)

Absorbance was measured at the maximum wavelength is 540 nm with a UV-vis spectrophotometer. From the experimental results in Figure 15, can be seen Mn (II) does not affect the absorbance of solution of Cr (VI)-DPC.



**Figure 15.** The effect of adding of Mn(II) to absorbance of Cr(VI)

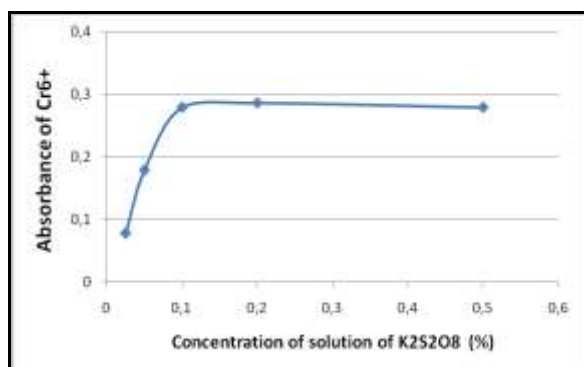
#### Determination of Cr<sup>3+</sup> through oxidation with NaClO and HClO<sub>4</sub>

Results oxidation with HClO and HClO<sub>4</sub> do not produce discoloration after oxidation resulting solution added with H<sub>3</sub>PO<sub>4</sub> reagent and diphenylcarbazide solution.

#### Determination of Cr<sup>3+</sup> through oxidation with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Experiments variation K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution concentration.

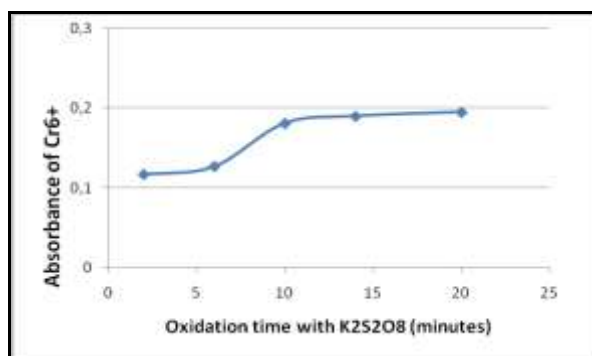
The results of the experiments are presented in Figure 16. The next experiments, selected for optimum concentration of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution of 0.1



**Figure 16.** The effect of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution to absorbance of Cr<sup>6+</sup>

Experiment of variations of oxidation time of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Results of the experiments are presented in Figure 18. The next experiments selected for optimum oxidation time of 10 minutes (Figure 17).



**Figure 17.** The effect of oxidation time to absorbance of Cr<sup>6+</sup>

### Variations H<sub>2</sub>SO<sub>4</sub> as an acid on oxidation with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Results of the experiments are presented in Figure 19 below. The next experiments selected for optimum H<sub>2</sub>SO<sub>4</sub> volume is 0.2 mL (Figure 18).

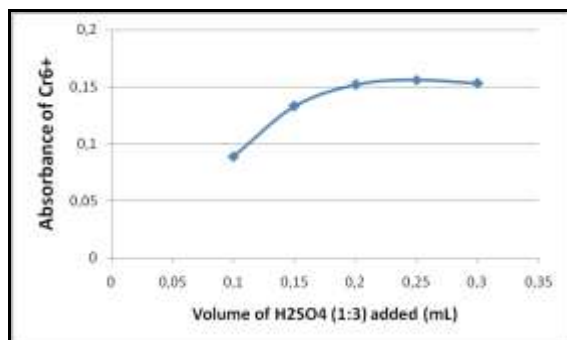


Figure 18. The effect of volume H<sub>2</sub>SO<sub>4</sub> to absorbance of Cr<sup>6+</sup>

A mixture of Cr(VI) to Cr(III) in artificial water sample Standard curve Cr<sup>6+</sup>

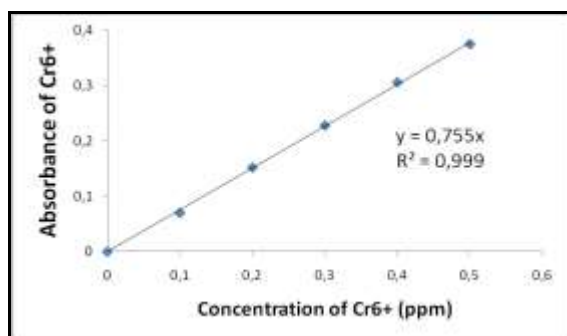


Figure 19. The standard curve of Cr<sup>6+</sup>

### Determination of a mixture of Cr<sup>6+</sup> and Cr<sup>3+</sup> after oxidized with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

From without oxidation, there is only Cr<sup>6+</sup>, while oxidation with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> there are total of Cr<sup>6+</sup> and Cr<sup>3+</sup>. Deviation measurement results Cr<sup>6+</sup> is large enough as indicated by the price of SD is > 4% (Table 6).

Table 6. Absorbance and Cr<sup>6+</sup> measurable after a mixture of Cr<sup>6+</sup> 0.2 ppm and 0.2 ppm Cr<sup>3+</sup> is oxidized with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Oxidation with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Replication	Abs.	Cr <sup>6+</sup> (ppm)	Cr <sup>6+</sup> measured	Mean of Cr <sup>6+</sup> measured ± SD	SD (%)
Without oxidation	1	0.146	0.199377		0.201324 ± 0.000726	0.36
	2	0.153	0.202649			
	3	0.156	0.201947			
Oxidation with K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1	0.295	0.390728		0.401325 ± 0.016984	4.23
	2	0.305	0.403974			
	3	0.309	0.409271			

The influence of time on color stability of the complex Cr-DPC, after Cr<sup>3+</sup> oxidized to Cr<sup>6+</sup> with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and reacted with DFC.

Oxidation result of Cr<sup>3+</sup> with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> provide Cr<sup>6+</sup> unstable as indicated by a decrease in the intensity of the color complex Cr-DFC that is 30 minutes after preparation.



**Figure 20. The colour of complex, 5 minutes after preparation**



**Figure 21. The colour of complex, 30 minutes after preparation**

## Conclusion

The experimental result show that Cr(VI) can be analyzed using 0.0015% diphenylcarbazide as reagent and  $\text{H}_3\text{PO}_4$  solution as acidic media in 0.03 mol/L. The absorbance was measured at 5 minutes after preparation. There is interference from ion Fe(III) at least 6.0 ppm and this interference can be overcome by using 0.3 % NaF solution. The limit of detection of this method is 0.1959 ppm. Chromium(VI) in the artificial samples, mix of Cr(III) and Cr(VI), can be analyzed by using this method without oxidation by  $\text{KMnO}_4$  solution. While Cr(III) in the artificial samples, mix of Cr(III) and Cr(VI), can be analyzed by using this method via oxidation with  $\text{KMnO}_4$  solution in the acidic media ( $\text{H}_2\text{SO}_4$ ), the result of this analysis is the total concentration of chromium. The concentration of Cr(III) can be calculated via subtracting the total of Cr concentration by concentration of Cr(VI).

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