METHOD OF ANALYSIS FOR DETERMINATION OF THE CHROMIUM (Cr) SPECIES IN WATER SAMPLES BY SPECTROPHOTOMETRY WITH DIPHENYL CARBAZIDE

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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-nutrients for the human body, while the Cr(VI) is highly toxic and carcinogenic. Chromium(VI) in the water can be analyzed by spectrophotometry with diphenylcarbazide as the reagent on pH=1 at the maximum wavelength of 540 nm. The experimental result showed that Cr(VI) could be analyzed using diphenylcarbazide in the concentration of 0.0015% and H₃PO₄ solution as acidic in 0.03 mol/L. The absorbance was measured at minutes 5 after preparation. There was interference from ion Fe(III) at least 6.0 ppm and this interference could be overcome by 0.3 % NaF solution. The limit of detection of this method was the samples, the mix of Cr(III) and Cr(VI), could be analyzed by this method without oxidated by KMnO₄ solution. While Cr(III) in the artificial samples, the mix of Cr(III) and Cr(VI), could be analyzed by this method via oxidation by KMnO₄ solution in the acidic media (H₂SO₄), the result of this analysis was the total concentration of Chromium. The concentration of Cr(III) could be calculated via subtracting the total of Cr concentration by the concentration of Cr(VI).

Keywords: speciation, Cr(III), Cr(VI), spectrophotometry, diphenylcarbazide, Fe(III), interference.

1. 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 (Lan, et al., 2005).

Toxic chromium enter 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 (Capeans, et al., 2005). In the marine environment, species Cr(VI) are in the form of CrO₄²⁻ or HCrO₄⁻. While Cr(III) is in the form of hydroxide compounds as Cr(OH)₃(₅⁰₄). The average concentration of total chromium in the sea water and rain water row by 0.2 to 1 gL⁻¹ and 0.04 to 0.5 mgL⁻¹. Total chromium concentrations in surface water of 0.5 to 2 gL⁻¹, where the dissolved chromium in the form of 0.02 to 0.3 mgL⁻¹ (Motomizu, et al., 2015; Gomez & Callao, 2006).

Chromium is an element that is abundant on the order of 21 in the earth’s crust at an average concentration of 100 ppm (Emsley, 2001). Chromium compounds found in the environment, because of the erosion of rocks containing chromium and may come from volcanic eruptions. The range of concentrations in the soil is between 1 - 3000 mg kg⁻¹, and in rivers and lakes 26 μg L⁻¹ to 5.2 mg L⁻¹ (Kotaš and Stasicka, 2000).

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-nutrients 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 (Cornelis, et al., 2005).
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 (Rakhunde, et al., 2012).

The Government of Indonesia through governance 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$^{-1}$ (Pemerintah Republik Indonesia, 1990). 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 [Papassiopi, et al., 2009]. Iron(III) can interfere to the analysis of Cr(VI) due to Fe(III) can form complexes with diphenylcarbazide [Harrington, et al., 2009; Nam and Kim, 2012]. By using magnesium sulfate/phosphate buffer, interference of the metal can be deposited primarily of Fe(III) (Ku and Eidi, 2006).

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 diphenyl carbazide (DPC) with Cr(VI) at a pH of 1.0 (Andruch, et al., 2003; Pressman and Aladstadt, 2003; Scindia, et al., 2002 and 2004).

Spectrophotometric analysis of the magenta chromagen ($\lambda$ max $\approx$ 540 nm) which is formed by the reaction of Cr(VI) with 1,5-diphenylcarbazide (DPC) in strongly acidic solution (Ashley, et al., 2003).

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.

### 2. MATERIAL AND METHODS

#### 2.1. Reagent and Standard Solution.

Stock solution of Cr(III) 1000 mg L$^{-1}$ was prepared by dissolving Chromium nitrate nonahydrat, Cr(NO$_3$)$_3$.9H$_2$O in a nitric acid solution of 0.01 mol L$^{-1}$. Stock solution of Cr(VI) 1000 mg L$^{-1}$ was prepared by dissolving Sodium chromate tetrahydrate (Na$_2$CrO$_4$.4H$_2$O) in a solution of nitric acid of 0.01 mol L$^{-1}$. A solution of 1,5-diphenylcarbazide (DPC) 0.05% dissolved in acetone. Phosphoric acid solution (H$_3$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.

#### 2.2. 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 HNO$_3$ for 24 hours.

#### 2.3. Procedure for chromium(VI):

1. 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 H$_3$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 $\lambda$ of 540 nm with a UV-vis spectrophotometer.

2. Optimum volume solution of phosphoric acid (H$_3$PO$_4$).

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$_3$PO$_4$ 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 $\lambda$ of 540 nm with a UV-vis spectrophotometer.
3. 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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer with variation of time: 5, 15, 45, 75, 105, 135 minutes after preparation.

4. 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 FeCl₃ 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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

5. 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 FeCl₃ 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 of 1 M H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.


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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

7. 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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

8. 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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

9. 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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

11. Samples analysis of artificial (interference of Fe³⁺) and overcome this interference with NaF solution.

A. Standard curve Cr (VI).

Prepared a series of solvent solution of Cr(VI) 100 ppm in a 100 mL volumetric flask, namely: 0.0; 0.1; 0.2; 0.3; 0.4; 0.5 mL of Cr(VI) of 100 ppm. Each plus 3 mL of 1 M H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

B. 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.).

<table>
<thead>
<tr>
<th>No.</th>
<th>The solution is added to Cr(VI) before dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>6 mL NaF + 3 mL Fe(III) + 3 mL H₃PO₄ + 3 mL DPC</td>
</tr>
<tr>
<td>2.</td>
<td>4 mL NaF + 3 mL Fe(III) + 3 mL H₃PO₄ + 3 mL DPC</td>
</tr>
<tr>
<td>3.</td>
<td>2 mL NaF + 3 mL Fe(III) + 3 mL H₃PO₄ + 3 mL DPC</td>
</tr>
</tbody>
</table>

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

C. Procedure for chromium(III):
1) Determination of Cr (III) via oxidation of Cr(III) to Cr(VI).

A) 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 H₃PO₄ 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 λ of 540 nm with a UV-vis spectrophotometer.

B) 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 H₂SO₄ (1:3) is different, namely: 0.05; 0.10; 0.15; 0.20; 0.25 mL. Each one is oxidized with KMnO₄ solution drop wise in a test tube that is inserted in the beaker glass containing water that is heated on a hot plate, as in Figure 1. The addition of KMnO₄ solution is stopped when there is little excess KMnO₄ solution which marked the formation of a permanent red color.

When it is cold, each solution was added with 3 mL of 1 M H₃PO₄ 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 λ 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.

C) 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 H₂SO₄ (1:3). Each one is oxidized with KMnO₄ 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 KMnO₄ solution is stopped when there is little excess KMnO₄ solution which marked the formation of a permanent pink color.

When it is cold, each plussolution was added with 3 mL of 1 M H₃PO₄ and 3.0 mL of 0.05% DPC.

Each solution was diluted with distilled water to 100 mL. Absorbance was measured at the maximum λ 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.

2) 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.

A) 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 H₃PO₄ and 3.0 mL of 0.05% solution DPC.

Each solution was diluted with distilled water to 100 mL. Absorbance was measured at the maximum λ of 540 nm with a UV-vis spectrophotometer.

B) 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>
<thead>
<tr>
<th>No.</th>
<th>Addition of Fe(III) and NaF solution</th>
<th>Oxidation with KMnO₄</th>
<th>Cr measured as</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0 mL Fe(III) and 0 mL NaF</td>
<td>Without oxidation</td>
<td>Cr(VI) only</td>
</tr>
<tr>
<td>2.</td>
<td>3 mL Fe(III) and 0 mL NaF</td>
<td>Without oxidation</td>
<td>Cr(VI) only</td>
</tr>
<tr>
<td>3.</td>
<td>3 mL Fe(III) and 6 mL NaF</td>
<td>Without oxidation</td>
<td>Cr(VI) only</td>
</tr>
<tr>
<td>4.</td>
<td>0 mL Fe(III) and 0 mL NaF</td>
<td>Oxidation by KMnO₄</td>
<td>Cr(III)</td>
</tr>
<tr>
<td>5.</td>
<td>3 mL Fe(III) and 0 mL NaF</td>
<td>Oxidation by KMnO₄</td>
<td>Cr(VI) and Cr(III)</td>
</tr>
<tr>
<td>6.</td>
<td>3 mL Fe(III) and 6 mL NaF</td>
<td>Oxidation by KMnO₄</td>
<td>Cr(VI) and Cr(III)</td>
</tr>
</tbody>
</table>

No. 1, 2, 3 : each in a 100 mL volumetric flask, added 3 mL of 1 M H₃PO₄ 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 H₂SO₄ (1:3). Each one is oxidized with KMnO₄ 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 KMnO₄ solution is stopped when there is little excess KMnO₄ 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 H₃PO₄ and 3.0 mL of 0.05% DPC.

Each solution was diluted with distilled water to 100 mL. Absorbance was measured at the maximum λ 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.

3. RESULT AND DISCUSSION

3.1. Diphenylcarbazide(DPC) optimum concentration.

Absorbance was measured at the maximum λ of 540 nm with a UV-vis spectrophotometer. From Figure 2 taken 0.0015% DPC as the optimum concentration.
3.2. Selection the optimum concentration of H₃PO₄ solution

Absorbance was measured at the maximum wavelength of 540 nm with a UV-vis spectrophotometer. From the Figure 3 taken 0.03 M H₃PO₄ as optimum concentration.

3.3. The influence of the absorbance measurement time after preparation.

Absorbance was measured at the maximum λ of 540 nm with a UV-vis spectrophotometer with variation of time: 5, 15, 45, 75, 105, 135 minutes after preparation. From the Figure 4, the optimum time is 5 minutes after preparation.

3.4. Effect of Fe(III) interference.

Absorbance was measured at the maximum λ of 540 nm with a UV-vis spectrophotometer. From Figure 5 chosen concentration of 6.0 ppm Fe(III).

3.5. Overcome Fe(III) interference using NaF solution

From this experiment as presented in Figure 6, NaF optimum concentration is 0.3%.
3.6. Selection of the range of concentrations of Cr (VI) which meets the Beer Lambert law.

Absorbance was measured at the maximum $\lambda$ 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 7).

3.7. Determination limit ditection (Miller and Miller, 2010).

A. Making the standard curve Cr6+

B. Making the curve for Determination Limit of detection.

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

\[ Y - Yb = 3 \times SB \]

\[ SB = \frac{\sum (Yi - Y)^2}{n-2} = \sqrt{\frac{0.0085255384230025}{5}} = 0.04129294957 \]

\[ Y - Yb = 3 \times SB \]
Y = 0.00632381 + (3 x 0.04129294957) = 0.1303088488

By inserting the 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

Limit of detection (X) = 0.1303088488 - 0.006429 = 0.1959086

So the limit of detection is 0.1959 ppm

C. Analysis of artificial samples (Fe3+ interference) and overcome the interference (adding 5% NaF solution)

1. Making the Standard curve of Cr6+

2. Measuring Cr(VI) in the artificial sample 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).

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

<table>
<thead>
<tr>
<th>Solution added to Cr(VI)</th>
<th>Repli-cates</th>
<th>Abs. Cr6+ measured (ppm)</th>
<th>Mean of Cr6+ measured ± SD</th>
<th>SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mL NaF</td>
<td>1</td>
<td>0.279</td>
<td>0.4964</td>
<td>0.4988</td>
</tr>
<tr>
<td>3 mL Fe3+</td>
<td>2</td>
<td>0.280</td>
<td>0.4982</td>
<td>± 0.0027</td>
</tr>
<tr>
<td>3 mL H3PO4</td>
<td>3</td>
<td>0.282</td>
<td>0.5018</td>
<td>0.4549</td>
</tr>
<tr>
<td>3 mL DFC</td>
<td>1</td>
<td>0.255</td>
<td>0.519</td>
<td>0.0037</td>
</tr>
<tr>
<td>4 mL NaF</td>
<td>2</td>
<td>0.255</td>
<td>0.519</td>
<td>0.0037</td>
</tr>
<tr>
<td>3 mL H3PO4</td>
<td>3</td>
<td>0.255</td>
<td>0.519</td>
<td>0.0037</td>
</tr>
</tbody>
</table>

From this experiment (table 3) known that 6 mL 5% NaF solution can overcome the Fe(III) interference comparing to 4 mL and 2 mL5% NaF solution.

D. Determination of Cr(III) via oxidation of Cr(III) to Cr(VI).

1. Making standard curve of Cr(VI)

Standard curve of Cr(VI)-DPC is presented in Figure 11.

2. Selection of H2SO4 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 H2SO4 (1: 3) optimum is 0.15 mL.
3. Measurement of the sample (artificial) Cr(III) which was oxidized to Cr(VI) by KMnO₄ in H₂SO₄ 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).

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

<table>
<thead>
<tr>
<th>ppm Cr(III)</th>
<th>Repli-</th>
<th>Abs.</th>
<th>Cr₆⁺ measured (ppm)</th>
<th>Mean of Cr₆⁺ measured ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1</td>
<td>0.156</td>
<td>0.2069</td>
<td>0.2034 ± 1.99</td>
</tr>
<tr>
<td>2</td>
<td>0.154</td>
<td>0.2042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.150</td>
<td>0.1989</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>1</td>
<td>0.258</td>
<td>0.3024</td>
<td>0.3059 ± 1.09</td>
</tr>
<tr>
<td>2</td>
<td>0.255</td>
<td>0.3064</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.254</td>
<td>0.3090</td>
<td>0.0033</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>1</td>
<td>0.174</td>
<td>0.4005</td>
<td>0.4036 ± 0.68</td>
</tr>
<tr>
<td>2</td>
<td>0.172</td>
<td>0.4058</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.168</td>
<td>0.4045</td>
<td>0.0028</td>
<td></td>
</tr>
</tbody>
</table>

From the table 4, it can be seen that the solution NaF can overcome the Fe(III) interference.

4. Measuring Cr in the artificial samples solution containing 0.2 ppm Cr(VI) and 0.2 ppm Cr(III).

A. Making standard curve of Cr(VI).

Figure 12. Standard curve of Cr(VI)-DPC

5. 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).

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.

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution Added to Cr solution</th>
<th>Repli-cates</th>
<th>Abs.</th>
<th>Cr₆⁺ measured (ppm)</th>
<th>Mean of Cr₆⁺ measured ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>None</td>
<td>1</td>
<td>0.146</td>
<td>0.1997</td>
<td>0.2020 ± 0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.149</td>
<td>0.2038</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.148</td>
<td>0.2025</td>
<td>0.0012 ± 1.31</td>
</tr>
<tr>
<td>2.</td>
<td>3 mL Fe(III)</td>
<td>1</td>
<td>0.117</td>
<td>0.1601</td>
<td>0.1596 ± 1.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.115</td>
<td>0.1573</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.118</td>
<td>0.1614</td>
<td>0.0021 ± 1.45</td>
</tr>
<tr>
<td>3.</td>
<td>3 mL Fe(III) + 6 mL NaF</td>
<td>1</td>
<td>0.143</td>
<td>0.1956</td>
<td>0.1965 ± 1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.146</td>
<td>0.1997</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.142</td>
<td>0.1943</td>
<td>0.0028 ± 0.63</td>
</tr>
<tr>
<td>4.</td>
<td>KMnO₄</td>
<td>1</td>
<td>0.294</td>
<td>0.4022</td>
<td>0.4004 ± 0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.289</td>
<td>0.3953</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.295</td>
<td>0.4036</td>
<td>0.0025 ± 1.02</td>
</tr>
<tr>
<td>5.</td>
<td>3 mL Fe(III) + KMnO₄</td>
<td>1</td>
<td>0.233</td>
<td>0.3187</td>
<td>0.3128 ± 0.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.229</td>
<td>0.3119</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.225</td>
<td>0.3078</td>
<td>0.0032 ± 1.45</td>
</tr>
<tr>
<td>6.</td>
<td>3 mL Fe(III) + KMnO₄ + 6 mL NaF</td>
<td>1</td>
<td>0.291</td>
<td>0.3981</td>
<td>0.3949 ± 0.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.288</td>
<td>0.3940</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.287</td>
<td>0.3926</td>
<td>0.0028 ± 0.63</td>
</tr>
</tbody>
</table>

From the table 5, show that : in solution no. 1, 2, 3 : only Cr(VI) were measured, because it does not use KMnO₄ 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 KMnO₄ solution. Solution no.5 less the 0.40 ppm because it was not added NaF solution.

6. The influence of the Cu (II) and Zn (II).

Absorbance was measured at the maximum λ 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 14. The effect of adding of Zn(II) to absorbance of Cr(VI)

7. The influence of the Mn (II).

Absorbance was measured at the maximum λ 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)

4. CONCLUSION

The experimental result show that Cr(VI) can be analyzed using 0.0015% diphenylcarbazide as reagent and H₃PO₄ 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 KMnO₄ 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 KMnO₄ solution in the acidic media (H₂SO₄), 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).

5. REFERENCES


Kotaś, J. and Stasicka, Z. 2000. Chromium occurrence in the environment and


