

Development of Spectrophotometric Method for the Determination of Chromium Species With Hypochlorite Agent Based on Complex Formation of Cr(VI)-Diphenylcarbazide

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ABSTRACT

Research of speciation analysis Cr(III) and Cr(VI) using hypochlorite oxidants with visible spectrophotometry has been proposed. This research was carried to obtain optimum conditions of oxidation process Cr(III) into Cr(VI) and the formation of Cr(VI)-Diphenylcarbazide complex to the wavelength, complexing time, oxidizing agent (oxidant) concentration, oxidation temperature, pH, and the influence of foreign ion, so it can be proposed as an alternative method for speciation analysis of Cr(III) and Cr(VI). Optimization results show that the maximum wavelength of Cr(VI)-diphenylcarbazide complex is 542 nm by the stable complex time 16-30 minutes using a hypochlorite (HOCl) oxidant concentration 1×10^{-3} M, temperature 60 °C and pH 1. This method is compared with standard method. The presently developed method is more simple and faster than standard method. Regarding accuracy and precision, the method is quite comparable with the standard methods.

Key word: speciation, Cr(III), Cr(VI), oxidant, hypochlorite, spectrophotometry VIS

INTRODUCTION

Chromium generally exists in nature as two oxidation states. Firstly, chromium(III) which is necessary for human health, and secondly chromium(VI), which is known as a carcinogenic substance. Until now chromium is still widely used in steel and leather tanning industries, which means, the more chromium used in industries the more chromium disposed to the environment. Chromium is a toxin that is harmful to living organism. When chromium enters into the human body, it causes disturbance in the central nervous system, muscle coordination system, birth defects and cancer [1]. Inhalation of chromium in long periods causes asthma, skin allergies, and lung cancer [2]. Therefore, it is very important to control and monitoring the chromium species.

Determination of chromium species can be done in three ways. First, the determination of chromium species on individual basis, based on the determination of Cr(VI) and based on the determination of Cr(III) [3]. Chromium is analyzed using visible spectrophotometer and can be done based on the ability of chromium ions forms a colored complex with chromogenic reagent [4]. This analysis can be applied on the Cr(VI) and Cr(III). The analysis based on the Cr(III) is quite rare. Some existing methods is undertaken by reflux heating process. This is, because a slow reaction process between Cr(III) and chromogenic reagent. Reagent that commonly applied is 3-thiannaphtoyl-3,3,3-

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trifluoroacetone, potassium hexacyanoferrate(II) [5], EDTA, tropolon, derivatives of thiazolylazo such as (2-thiazolylazo)-resorcinol [6], HBIG [7], and α -benzoine oxime [8]. In this study, analysis of chromium was undertaken by spectrophotometry based on Cr(VI). Determination of chromium content by visible spectrophotometry using 1,5-diphenylcarbazide as a reagent. It is common method, due to reaction is fast and high stability. Principle of this method is oxidation of Cr(III) into Cr(VI), which is then reacted to 1,5-diphenylcarbazide (DiPC). The colored solution is obtained, and can be determined spectrophotometrically as total chromium. From the results of total chromium with Cr(VI) without Cr(III) oxidation process, it will be obtained information correlate to the number of Cr(III) as well. So that, this spectrophotometric method is very attractive, low cost, easy to operate and is suitable to be applied.

Oxidation of Cr(III) to Cr(VI) and its complex formation, Cr(VI)-DIPC, normally occurs in acidic condition [9]. The oxidation itself can be performed using oxidizing reagent such as hypochlorite. Speciation of Cr(III) and hypochlorite is strongly influenced by pH solution [10]. At pH 1-2, most of Cr(III) is in the form of Cr^{3+} ion, so the resulting absorbance is maximum at this pH. At the above pH 2, the chromium(III) starts to hydrolyze to hydroxide and form $\text{Cr}(\text{OH})^{2+}$, and at pH 4, Cr(III) starts to form $\text{Cr}(\text{OH})_3$ precipitate [10]. The complex of Cr(VI)-DIPC was formed as a reddish purple and absorbs light at a wavelength of 530-540 (molar absorptivity $40000 \text{ mol.L}^{-1} \text{ cm}^{-1}$) [1]. The detection can done by visible spectrophotometer. The stability of the formed complex is strongly influenced by time. The number of Cr(III) was oxidized to Cr(VI) greatly influenced by the concentration of oxidation agent. Kinetics of the oxidation reaction is very influential in the process of analysis conducted. Oxidizing species and chromium as well as complex formation is strongly influenced by pH. So the effect of complexing time, oxidizing agent concentration, oxidation temperature, and pH will provide optimum condition for speciation. Therefore, it is necessary to study about the optimum condition to perform determination both of chromium species in water samples using this method.

EXPERIMENT

Chemicals and instrumentation

The water sample was taken from a river water tannery waste disposal plant from PT. Kasin Malang, Indonesia. Meanwhile, all the chemicals used have analytical reagent grade or the highest purity available. The chemicals used including chromium nitrate (Merck, Germany), potassium dichromate (Merck, Germany), sodium hypochlorite (Sigma), 1,5-diphenylcarbazide (Merck, Germany), sulfuric acid, nitric acid, acetone (Merck, Germany), sodium hydroxide (SAP chemical), potassium permanganate (Merck), sodium azide (Merck), and demineralized water.

The instruments used in this study include analytical balance (adventer Model AR. 2130), UV-VIS spectrophotometer (Shimadzu UV-1601), hot plate, glassware, and pH meter.

Procedure reaction

Procedure for Cr(III) determination using the proposed method

A 2.0 mL of sample solution containing Cr(III) 10 mg/L and sulfuric acid 1.0 mL (0.01 M) were mixed in a 10 mL-volumetric flasks. It was added 1.0 mL of the optimum concentration of oxidation reagent 0.01 M and 0.2 mL of 1,5-diphenylcarbazide solution (0.25 M). This solution mixture, then, were quantitatively diluted until the mark with demineralized water. This solution was further analysis their absorbance at the maximum wavelength (542 nm). A calibration graph was also resulted using similar conditions.

Standard method

Sample solution containing Cr(III) 10 mg/L (2 mL) and sulfuric acid 0.01 M (1 mL) were mixed in a 10 mL-volumetric flasks. The sample solution was further oxidized to convert Cr(III) into Cr(VI) using potassium permanganate. This mixture was heated and then spectrophotometrically analyzed using 1,5-diphenylcarbazide (DiPC) at 540 nm.

RESULT AND DISCUSSION

Maximum wavelength

The complex of Cr(VI)-diphenylcarbazide showed maximum absorption at 542 nm (Figure 1) with absorbance of 1.195. This absorbance gives a value for molar absorptivity 3.1×10^4 mol/L.cm. The resulted absorptivity very much similar to the values for theoretical molar absorptivity of chromium, 4.0×10^4 mol/L.cm. It can be concluded, that, at the maximum wavelength Cr(VI)-DiPC complex has good sensitivity. Therefore, all subsequent measurements were performed using these maximum wavelengths.

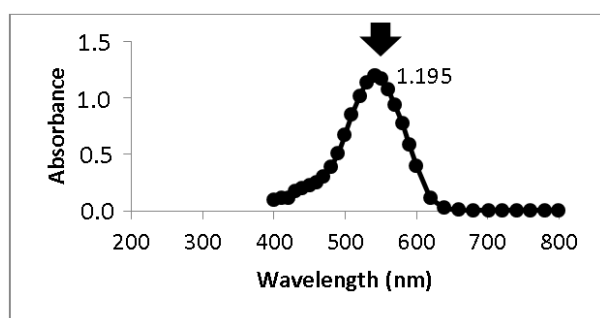


Figure 1. Graph determination of the maximum wavelength

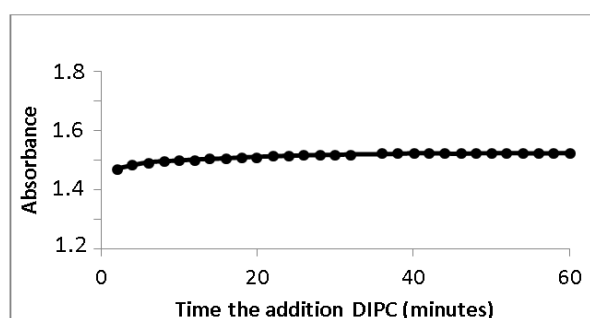


Figure 2. Graph stability of complex formation

Stability of complex formation

Determination of the stability of complex formation was aimed to determine the stability of chromium reacts with DiPC in the range of 0 to 60 minute. Based on the result (Figure 2), it was found, that resulted complex between Cr(VI) and 1,5-diphenylcarbazide (DiPC) during the reaction is relatively stable. The graph indicates a constant line during a given period time (0-60 minute). The absorbance was recorded in between 1.45 and 1.57 unit. Based on a statistical test with 95% confidence, it has interval range of stability of the complex formation occurs between 16 and 30 minute. In this study, complex formation time of Cr(VI) and 1,5-diphenylcarbazide used is 20 minute.

Optimum concentration of agents

This step was focused to understanding the effect of oxidant quantity, hypochlorite, optimizing formation of Cr(VI) from Cr(III). Theoretically, the higher oxidant concentration easily convert Cr(III) much faster and it give higher complex formation Cr(VI) with DiPC. Variation of hypochlorite applied from 1.0×10^{-4} until 40×10^{-4} M, and the result is displayed in Figure 3. In general, it can be seen that the higher concentrations of hypochlorite give the higher oxidized Cr(III) to Cr(VI). Using Cr(III) 2 mg/L, the optimum concentration of hypochlorite was reached at 1.0×10^{-3} M. The hypochlorite concentration was 9 times higher than that of the stoichiometry concentration 1.15×10^{-4} M. When the concentration increased, from 1.0×10^{-3} to 4.0×10^{-3} M, the absorbance value was relatively constants. The optimum condition, by comparing the absorbance resulting from the oxidation of Cr(III) to Cr(VI) with absorbance Cr(VI) at the same concentration (2.0 mg/L) can be determined by percentage

value of the Cr(III) oxidized. Based on this result, it can be calculated the percentage Cr(III) become Cr(VI) reached to 66.05%. The hypochlorite concentration applied to oxidize Cr(III) into Cr(VI), in fact, is very much higher than that as stoichiometric amount. This fact, probably due to the oxidation reaction is an equilibrium reaction, and its equilibrium constant is relatively small. As a result, in order to direct the oxidation reaction to the products-side, it requires a large concentration of the oxidant, hypochlorite. However, after the equilibrium is achieved, the addition of hypochlorite concentration does not provide significant oxidation product, Cr(VI). Applying the oxidant concentration more than 10×10^{-4} M gives declining absorbance values. Concentration oxidant between 20×10^{-4} and 40×10^{-4} M, in fact, provides a similar result (Figure 3).

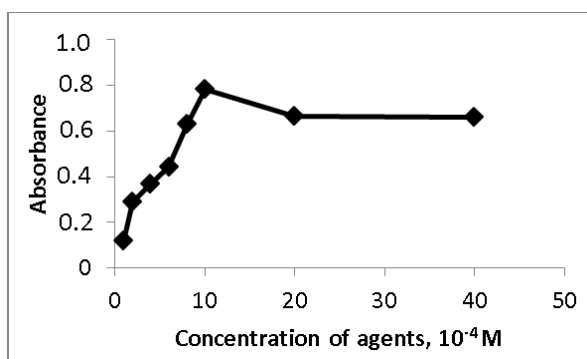


Figure 3. Effect of oxidant (hypochlorite) concentration toward oxidation of Cr(III)

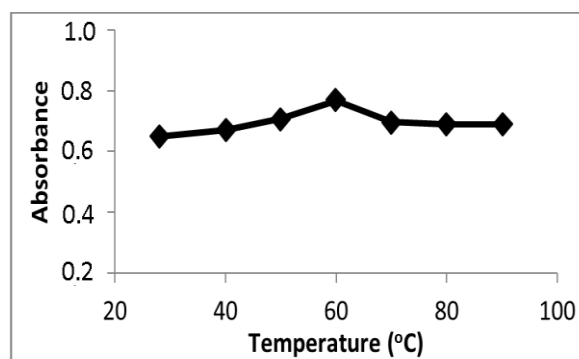


Figure 4. Effect of reaction temperature toward oxidation reaction of Cr(III)

The optimum temperature

The oxidation of Cr(III) become Cr(VI) was studied by increasing of the reaction temperature. Range temperature applied in between 28 and 90 °C. The method applied is following general procedure for analysis and using a constant concentration of hypochlorite. The result is showed in Figure 4. It was found that increasing reaction temperature improve the absorbance value, means, increasing of Cr(VI) quantity. Formation of Cr(VI) was detected optimum at temperature 60 °C. The reaction recorded giving the absorbance value about 0.75 unit. Subsequently, the absorbance value steadily declined and reached to about 0.64 unit of absorbance at temperature 90 °C. More precisely, constant values of absorbance were detected in a range reaction temperature between 70 and 90 °C. However, in overall, it can be summarized that oxidation of Cr(III) become Cr(VI) using hypochlorite as oxidator is relatively afford constant product during studied temperatures.

The optimum pH solution

Study the effect of acidity for analysis Cr(III) by creating variation of pH conditions toward the detection of complex Cr(VI)-DiPC was undertaken. The pH condition was defined from pH 1, 2, 3, 4, 5, and 6. The result is displayed in Figure 5. It can be seen that applying condition at pH 1 is optimum for oxidation of Cr(III) into Cr(VI) and formation of complex compound between Cr(VI) and 1,5-diphenylcarbazide (DiPC). The absorbance value was recorded about 0.8 unit absorbance. It was assumed this is due to the oxidation of Cr(III) become Cr(VI) and its complex formation Cr(VI)-DPC occurs requiring acidic condition. In previous literature, it was reported that speciation of Cr(III) and hypochlorite strongly influenced by lower pH [9]. At pH around 1-2, Cr(III) commonly stable as Cr^{3+} ion, and it will be resulting stable absorbance as well. In addition, the result gives a small declining

absorbance value subsequently. A sharp declining was resulted at pH 3 until 6. The absorbance value was detected about 0.76 until lower below 0.4 unit absorbance. Above pH 2, the Cr(III) generally stable as $\text{Cr}(\text{OH})_2^+$ form. This form probably hampers it to form complex with DiPC, and result in lowering absorbance value. Condition at pH above 4, Cr(III) normally exist as $\text{Cr}(\text{OH})_3$ precipitate, and oxidation of Cr(III) into Cr(VI) will not be effective. Besides that, this form substantially could inhibit complex formation Cr(VI) with DiPC.

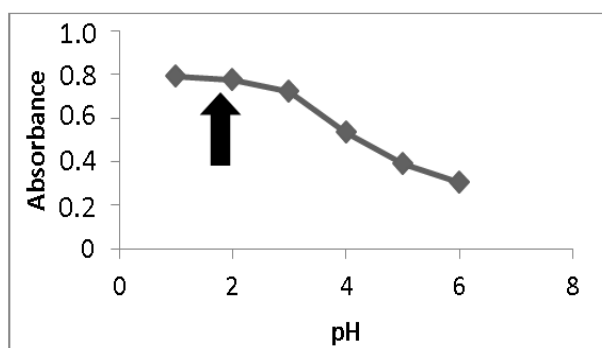


Figure 5. Effect pH condition on chromium determination

Oxidation of Cr(III) into Cr(VI) is more effective with hypochlorite in the HOCl form, because HOCl species has the greatest reduction potential rather than the other oxidator. However, the existence of HOCl species is commonly stable maximum at range pH 4-6. According to the result, it was found that pH optimum was recorded at pH 1. This fact is easily to be understood that during the oxidation reaction, oxidation of Cr(III) become Cr(VI) occurs more favor at that pH. And directly, the Cr(VI) resulted was transformed into its complex compound with DiPC, formed Cr(VI)-DiPC complex.

Table 1. The effect of foreign ions against %-recovery of oxidation Cr(III) to Cr(VI).

Ratio of Foreign ions and Cr(III)	Foreign ion Cl^-		Foreign ion HCO_3^-		Foreign ion OH^-	
	Average absorbance	% recovery	Average absorbance	% recovery	Average absorbance	% recovery
0	0.694	100.00	0.694	100.00	0.694	100.00
1	0.622	89.63	0.674	97.12	0.643	92.65
10	0.612	88.20	0.718	103.46	0.614	88.47
50	0.592	85.30	0.754	108.65	0.612	88.18
100	0.462	66.57	0.795	114.55	0.566	81.56

Effect of foreign ion

During the analysis, all the the species from reagent involved affects the transformation Cr(III) into Cr(VI), including affects complex formation, Cr(VI)-DiPC. So that the presence of foreign ions can participates and affected the reaction. Table 1 is presented the study results. Three type foreign ions were investigated, such as chloride (Cl^-), hydrogen carbonate (HCO_3^-), and hydroxide (OH^-) ions. Their presence is correlated toward recovery percentage from oxidation Cr(III) become Cr(VI). In general, it was found that the recovery percentage with the presence of HCO_3^- and OH^- ion, formation of complex Cr(VI)-

DiPC was not affected. However, for addition of chloride ion affects the analysis of complex formation. This effect basically can be displaced by addition more concentration of hypochlorite, HOCl.

In summary, the optimum conditions of the developed methodology for determination chromium by formation Cr(VI) with 1,5-diphenylcarbazide can be summarized (Table 2). It was concluded the wavelength optimum at 542 nm, and formation of complex Cr(VI)-DiPC about 16-30 minute reaction, optimum oxidator concentration 1.0×10^{-4} M, and the optimum pH applied for analysis in pH 1. This optimum condition is already reported in this paper and its calculation will be reported elsewhere by author soon including linear range detection, limit detection, and its reproducibility.

Table 2. Selected analytical parameter obtained on the optimized experiments

Parameters	Studied range	Selected value
Wavelength/ λ_{\max} (nm)	400-800	542
Time of formation of the complex (minutes)	0-60	16-30
Concentration of agents (M)	$1.0 \times 10^{-4} - 40 \times 10^{-4}$	1.10^{-3}
Optimum temperature($^{\circ}$ C)	28-90	60
pH	1-6	1
Linier range (mg/L)	0.001-5	0.1-1
Limit of detection (mg/L) (Cr(III))	-	0.0179
Reproducibility (% RSD) (Cr(III))	-	2-5
Regression coefficient (Cr(III))	-	0.997

Table 3. Data chromium concentration and percent recovery in synthetic samples

Species	Actual concentration (ppm)	Absorbance		Chromium concentration (ppm)		Chromium recovery (%)	
		Proposed method	Standard method	Proposed method	Standard method	Proposed method	Standard method
Cr(VI)	0.5	0.279	0.279	0.532	0.532	104.5	104.5
Cr(III)	0.5	0.203	0.207	0.419	0.434	94.2	96.4

Validation method

In order to get a valid method, a validation step was also been undertaken. A prepared synthetic sample concentration was determined using developed method (Table 3). Including, comparison study between the developed or proposed method and standard or general methods for chromium determination both for analysis a synthetic and real samples (Table 4).

In overall, the developed method significantly giving similar out puts to that reported using standard method (Table 3). The detected chromium(VI) using both developed procedure and standard method give Cr(VI) concentration in 0.532 ppm, in fact, the real concentration prepared is 0.5 ppm. Similar result was also obtained for %recovery of Cr(VI) after analysis (104.5%).

The accuracy and precision of measurement is reported in Table 4. Both of the developed/proposed method and standard method was applied using real sample taken from river. In all measurement, it was found that both method give similar result. The accuracy range from 91.44-99.53% for proposed method, meanwhile the standard method provided range 97.72-103.33% in all given concentration. However, the precision resulted give a slight

different. But, in overall, the recovery and accuracy reveals that developed method successfully can be applied for determination of Cr(III) and Cr(VI) in natural water sample in regards to standard method.

Table 4. Data concentration and percent recovery of chromium added to the real sample.

Repetition	Concentration (proposed method) (ppm)			Concentration (standard method) (ppm)		
	0.3	0.5	0.7	0.3	0.5	0.7
1	0.273	0.475	0.651	0.311	0.510	0.668
2	0.273	0.523	0.659	0.295	0.527	0.689
3	0.277	0.495	0.677	0.324	0.539	0.695
Repetition			Accuracy (%)			
1	91.00	95.00	93.00	103.67	102.00	95.43
2	91.00	104.6	94.14	98.33	105.40	98.43
3	92.33	99.00	96.71	108.00	107.80	99.29
Accuracy	91.44	99.53	94.62	103.33	105.07	97.72
Precision (%CV)	0.86	4.20	2.00	4.69	2.78	2.01

CONCLUSION

To summarized, it can be concluded that hypochloride (HOCl) agent is potential oxidation reagent for the spectrophotometric determination of Cr(III) and Cr(VI). The advantages of presently developed method are simple and selective without removal of color from oxidizing process. Regarding to accuracy and precision, this method is quite comparable to that of the standard methods. The method can be waived interference from foreign ions and hence can be used for routine analysis of chromium(III) and chromium(VI) in water sample.

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