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Development of the Analytical Method of Iron through Optimization Reducing Agent Ability of Iron (III) to Iron(II)

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Abstract

The aim of this study was to develop the analytical methods of iron through optimization reducing agent ability of iron (III) to iron (II) complex with formation of Fe (II) phenanthrolinee by spectrophotometry. Parameter of optimization that was used is acetic buffer pH, time of the complex formation and reducing agent concentrations in the determination of iron level (content). Reducing agents are sodium tiosulfate ($Na_2S_2O_3$), hidroxylamine hydrochloride ($NH_2OH.HCl$) and sodium borohydride ($NaBH_4$). Results showed that the maximum wavelength of Fe (II)-Phenanthroline use all reducing agents is 510 nm, pH optimum of acetic buffer use reducing agent sodium tiosulfate ($Na_2S_2O_3$), hidroksilamin hydrochloride ($NH_2OH.HCl$) and sodium borohydride ($NaBH_4$) is 4.5. Optimum formation of indwelling time of iron (II) complex phenanthrolinee use reducing agent $Na_2\ S_2\ O_3$ and $NH_2OH.HCl$ is 15 minutes, whereas reducing agent $NaBH_4$ is 5 minutes. Optimum concentration of reducing agent $Na_2S_2O_3$ that was used to reduce 5 ppm Fe(III) is 11 ppm, whereas for reducing agent $NH_2OH.HCl$ is 8 ppm and reducing agent $NaBH_4$ is 150 ppm.

Keywords: *hydroxylamine hydrochloride; iron; reducing agent; sodium thiosulfate; sodium borohydride*

1. Introduction

Method of Fe analyzed with ligand 1,10-phenanthroline have directly reduce, selective and without extraction procedure when determination was due on sample [1]. This method was carried out by reduction of Fe^{3+} to Fe^{2+} used by hydroxylamine hydrochloride ($NH_2OH.HCl$) before complex formed with Fe ligand which form specific color (Amonette, 1998). Formed complex by 1.10-phenanthroline with Fe^{2+} more stable with stable Constanta value 21.0 compared with complex between 1,10-phenanthroline with Fe^{3+}, when complex $[Fe(C_{12}H_8N_2)_3]^{2+}$ was formed quantitatively in about pH 2-9 suitable concentration of reagent [2]. Using hydroxylamine hydrochloride reduction have weakness, this reductor could not saved, so it must be made new in every time doing experiment (Xu and Ma, 1996). In this study two reductor would be used as substitute reducing agent, there are sodium borohydride ($NaBH_4$) and sodium thiosulfate ($Na_2S_2O_3$) (Rahayu *et al*., 2007). Sodium thiosulfate is a strong reducing agent for iron and easily obtained; beside that in the earlier research showed that ability of reducing agent sodium thiosulfate to reduce Fe^{3+} to Fe^{2} was obtained at pH 4.5 and 11 ppm sodium thiosulfate could reducing 5 ppm Fe^{3+} with recovery percentage 102.81%. Sodium borohydride also use as reductor to recovery chrome waste and obtained recovery percentage 68.6% with supplementation of sodium borohydride, while recovery percentage 5.42% without redactor (Djunaidi *et al*., 2010).

2. Materials and Method

2.1. Materials

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), 1,10-phenanthroline ($C_{12}H_8N_2$), sodium borohydride ($NaBH_4$), hydroxylamine hydrochloride ($NH_2OH.HCl$), sodium thiosulfate ($Na_2S_2O_3$), sodium acetate (CH_3COONa), acetic acid (CH_3COOH), aceton, aqua DM were used to optimize reducing agent ability of iron (III) to iron (II).

2.2. Determination of maximum wave length of Fe(II)-phenanthroline

Iron (III) standard solution 100 ppm was taken 0.5 mL then was poured in volumetric flask 10 mL. Added 1.1 mL $NH_2OH.HCl$ 100 ppm and 1.5 mL acetic buffer pH 4.5; after that added 5 mL aceton and diluted by aqua DM then homogenized. The solution then let stand for 15 min then measured by spectrophotometer UV-Vis (GENESYS type 10S) at 400-600 nm. This measurement was done twice with a blanksolution as a comparison. The data was used to make a curve to determine the size of the maximum wavelength to wavelength that has been obtained. The same procedure was repeated to reducing $Na_2S_2O_3$ and $NaBH_4$.

2.3. Determination of optimum pH of acetic buffer solution

Iron (III) standard solution 100 ppm was taken 0.5 mL then was poured in volumetric flask 10 mL. Added 1.1 mL $NH_2OH.HCl$ and 1.5 mL acetic buffer 100 ppm with various pH 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0. Mixture was added 1.5 mL 1.10-phenanthroline 1000 ppm and 5 mL aceton then diluted by aqua DM and shaken then let stand for 15 min. Absorbance of solution were measured by spectrophotometer UV-Vis twice. The data was used to make a curve between absorbance to acetic buffer pH. The same procedure was repeated to reducing $Na_2S_2O_3$ and $NaBH_4$.

2.4. Determination of optimum reducing time

Iron (III) standard solution 100 ppm was taken 0.5 mL then was poured in volumetric flask 10 mL. Added 1.1 mL $NH_2OH.HCl$ 100 ppm as a reducing with various time for 0, 5, 10, 15, 20, 25, 30, 45, 60, 75 min and 1.5 mL acetic buffer with optimum pH. Mixture was added 1.5 mL 1.10-phenanthroline 1000 ppm and 5 mL aceton then diluted by aqua DM and shaken then let stand for 15 min. Absorbance of solution were measured by spectrophotometer UV-Vis

twice. The data was used to make a curve between absorbance to reducing time. The same procedure was repeated to reducing $Na_2S_2O_3$ and $NaBH_4$.

2.5. *Determination of optimum concentration of Fe(II)-phenanthroline*

Iron (III) standard solution 100 ppm was taken 0.5 mL then was poured in volumetric flask 10 mL. Added $NH_2OH.HCl$ 100 ppm with various concentration 3-14 ppm as reducing and 1.5 mL acetic buffer with optimum pH. Mixture was added 1.5 mL 1.10-phenanthroline 1000 ppm and 5 mL aceton then diluted by aqua DM and shaken then let stand for 15 min. Absorbance of solution were measured by spectrophotometer UV-Vis twice. The data was used to make a curve between absorbance to reducing concentration. The same procedure was repeated to reducing $Na_2S_2O_3$ and $NaBH_4$.

2.6. Determination of calibration curve of Fe(II)-phenanthroline

Determination of calibration curve each reductor were done by added standard solution Fe(III) 100 ppm 0.1, 0.2 , 0.3 , 0.4 ; 0.5 ; 0.6 , 0.7 and 0.8 mL respectively to volumetric flask 10 mL then added 1.1 mL $NH_2OH.HCl$. Added 1.5 mL 1,10-phenanthroline 1000 ppm, 1.5 asetic buffer solution pH 4.5 100 ppm and 5 mL aseton, then diluted by aqua DM until 10 mL. Mixture were shaken and let stand for 15 min. Solution were measured absorbance used by spectrophotometer UV-Vis twice. The data was used to make a curve between absorbance to various concentration of Fe(III). The same procedure was repeated to reducing agent $Na_2S_2O_3$ and $NaBH_4$.

3. Result and Discussion

3.1. Result

Result of determination maximum wavelength of Fe(II)-phenanthroline to reducing agent sodium thiosulfate, $NH_2OH.HCl$ and $NaBH_4$ in between 400-600 nm with 1 nm interval showed at Figure 1. Based on this curve, it was known that maximum wavelength of complex Fe(II)-phenanthroline on reducing agent sodium thiosulfate ($Na_2S_2O_3$), hydroxylamine hydrochloride ($NH_2OH.HCl$) and sodium borohydride ($NaBH_4$) have highest absorbance at wavelength (λ) 510 nm. In Figure 2 showed the curve absorbance of acetic buffer pH of sodium thiosulfate, hydroxylamine hydrochloride and sodium borohydride and based on this curve the highest peak was obtained at pH 4.5.

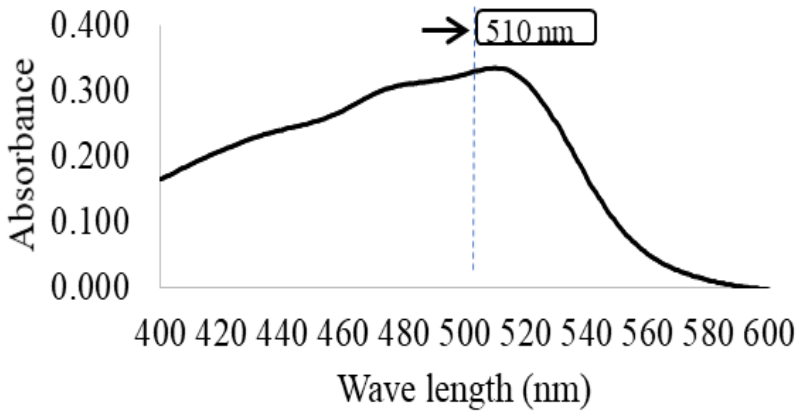


Figure 1: Curve of maximum wavelength Fe(II)-phenanthroline vs absorbance reducing agent sodium thiosulfate, $NH_2OH.HCl$ and $NaBH_4$

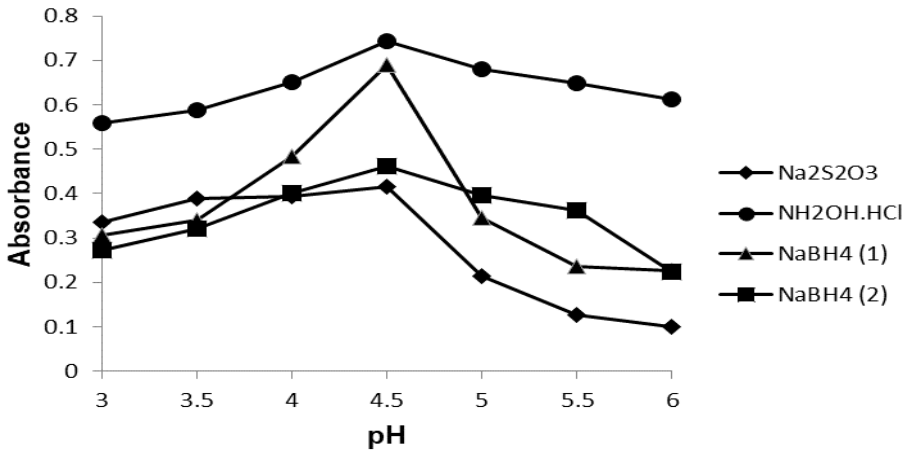


Figure 2: Optimum pH of acetic buffer of Fe(II)-phenanthroline used by reducing agent $Na_2S_2O_3$, $NH_2OH.HCl$ and $NaBH_4$

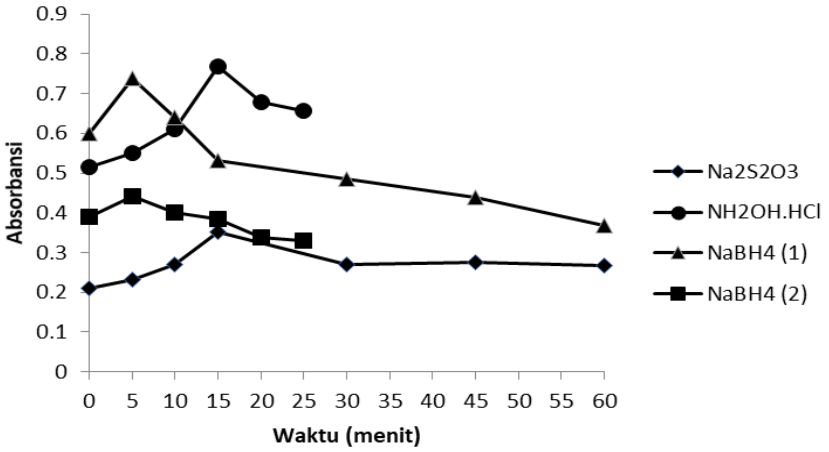
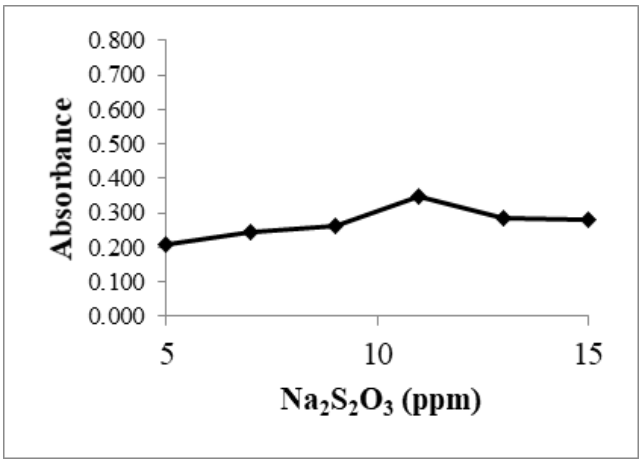
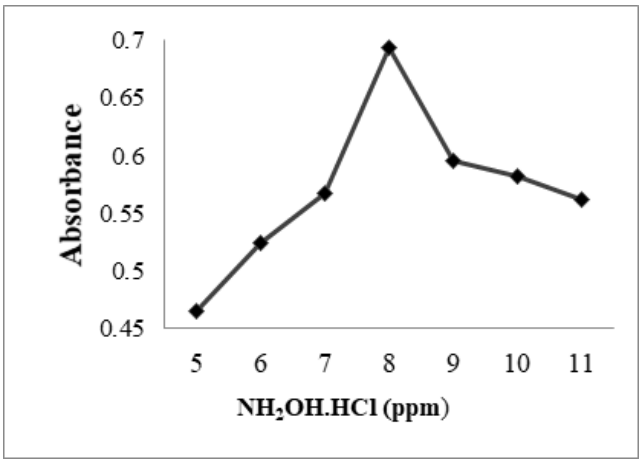
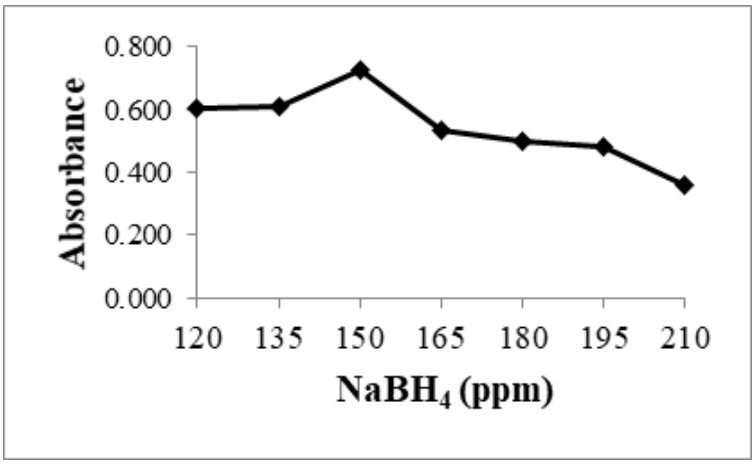


Figure 3: Reducing time of Fe(II)-phenanthroline used by reducing agent $Na_2S_2O_3$, $NH_2OH.HCl$ and $NaBH_4$





(a) (b)



(c)

Figure 4: Optimum concentration of Fe(II)-phenanthroline used by reducing agent (A) $Na_2S_2O_3$, (B) $NH_2OH.HCl$ and (c) $NaBH_4$

In Figure 3 showed that optimum reducing time of $Na_2S_2O_3$ and $NH_2OH.HCl$ was 15 min respectively, but optimum reducing time of $NaBH_4$ was 5 min. In Figure 4 showed optimum concentration of Fe(II)-phenanthroline used by reducing agent $Na_2S_2O_3$, $NH_2OH.HCl$ and $NaBH_4$. Based on this curve was obtained optimum concentration to reduce Fe(III) to Fe(II) used by reducing agent $NH_2OH.HCl$ was 5 ppm, reducing agent $Na_2S_2O_3$ was 8 ppm and reducing agent $NaBH_4$ was 150 ppm.

3.2. Discussions

The maximum wavelength of Fe (II) phenanthroline is not affected by the type of reducing agent, as are the results obtained by Dhita and Sugiarso (2018) (Dhita and Sugiarso, 2018); where a maximum wavelength of 510 nm was chosen because the maximum wavelength is the area with the highest sensitivity; meaning that if there is a change in the concentration of the substance to be determined it will be detected and Lambert - Beer law is still valid (Malik, 2000; Skoog et al., 2002). Iron (II) -phenanthroline is stable under acidic and alkaline conditions in the pH range 2-9 [2]. In this study the reaction of iron (II) was complexed with 1,10-phenanthroline to form orange (red orange) from a solution of $[Fe\ (C_{12}H_8\ N_2)_3]^{2+}$ which was stable under conditions of pH range 2-9, however, in this study, acetic buffer solution was used in an acidic state because if there was an alkaline ion, it was one of the ligands that could compete with 1,10-phenanthroline ligands. Complex formation reactions as shown below:

$Fe^{2+}_{(aq)} + 3(C_{12}H_8N_2)H^+_{(aq)} \rightarrow [Fe(C_{12}H_8N_2)_3]^{2+}_{(aq)} + 3H^+_{(aq)}$

In Figure 3, it can be seen that the $NaBH_4$ reducing agent requires faster time to reduce Fe (III) to Fe (II) compared to other reducing agents ($Na_2S_2O_3$, and $NH_2OH.HCl$), so that $NaBH_4$ can be used as an alternative to substitute the two reducing agents. In Figure 4, the optimum concentration of reducing agent $Na_2S_2O_3$ to reduce iron (III) 5 ppm is 11 ppm, for reducing agent $NH_2OH.HCl$ is 8 ppm, while $NaBH_4$ is 150 ppm. The same results were obtained by Pranata *et al*., 2018 which stated that reducing agent $Na_2S_2O_3$ needed 11 ppm, while Dhita and Sugiarso (2018) obtained results for 5 ppm Fe (III) can be reduced by 10 ppm $Na_2S_2O_3$ and 11 ppm $NH_2OH.HCl$

4. Conclusion

The results of this study was concluded that wavelength of Fe(II) phenanthroline is 510 nm, optimum pH of acetic buffer for all reducing agents is 4.5, optimum reducing time for Fe(II) phenanthroline complex for reducing agent $Na_2S_2O_3$ and $NH_2OH.HCl$ is 15 min, while for $NaBH_4$ is 5 min, and optimum concentration of reducing agent $Na_2S_2O_3$ to reduce iron (III) 5 ppm is 11 ppm, for reducing agent $NH_2OH.HCl$ is 8 ppm, while $NaBH_4$ is 150 ppm.

References

[1] A.K. Malik, J. Agric. Food Chem. 48 (2000) 5808–5811.

[2] D. Lazić, B. Škundrić, J. Penavin-Škundrić, S. Sladojević, L. Vasiljević, D. Blagojević, Z. Obrenović, Chem. Ind. Chem. Eng. Quarterly/CICEQ. 16 (2010) 193–198.

[3] J. Xu, Y. Ma, J. Microcolumn Sep. 8 (1996) 137–143.

[4] M.C. Djunaidi, K. Khabibi, D. Trisna, J. Kim. Sains Dan Apl. 13 (2010) 12–17.

[5] A. Dhita, D. Sugiarso, Akta Kim. Indones. 3 (2018) 190–202.

[6] D. Skoog, D. West, S. Crouch, Analytical Chemistry : An Introduction, 7th ed., Mc. Graw Hill Company., USA, 2002.