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An Analysis of Pb(IV) Ion Effects in Determining Fe(II) With 1.10-Phenanthroline at Ph 4.5 using UV-VIS Sprectrophotometer

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Abstract

An analysis of the effect of Pb(IV) ions on Fe(II) -Phenanthroline formation at pH of 4.5 using UV-Vis spectrophotometer have been conducted. 4.5Fe(II) phenatroline complex showed a maximum wavelength of 508 nm. Pb(IV) ion as an ion disturber showed a maxium wavelength of 315 nm. The relation coefficient obtained from the calibrated curve is 0.997 with the linear equation y = 0.118x + 0.020. Determination of Pb(IV) ions showed an increase in iron concentration at 0.2 ppm of Pb(IV) with recovery percentage obtained of 123.160%. A decrease of iron concentration is observed at 6 ppm of Pb(IV) with recovery percentage obtained of 71.108%. 0.

Keywords: *Fe(III); Fe(II); Natrium Thiosulphate; Pb(IV); 1.10-Phenantroline dan UV-VIS spectrophotometer*

I. INTRODUCTION

Iron is a transition metal categorized in the VIIIB group which have an atomic number of 26 and electron configuration of $3d^6$ $4s^2$. Light silver coloured pure metals are tough, strong and melt at 1535°C [1]. There is a surplus of metals inside the Earth's crust by more than 62000 ppm. Iron is the second surplus metal inside the Earth's crust after aluminium and the fourth highest element after oxygen, silicon and aluminium. Iron is more reactive compared to the two metals categorized in the VIIIB group or other triad groups. Irons have a crucial role in industries and biology [2].

The general iron oxidation level in the nature is +2,+3 and +4. However, oxidation level of +4 is very rare [3].The iron(II) salts are derived from iron(II) oxide (FeO). The iron(III) salts are derived from iron(III) oxide, where iron(III) is more stable than iron(II) [1].

Complex compound is a compound comprised of metal ions with one or more ligands donating their lone pairs of electrons to the metal ions to form coordinated covalent bonds . A ligand that are normally complexed with iron is 1.10 phenantroline or ortho-phenantroline and α,α'-Dipyridyl [4]. In acid solution, α,α'-Dipiridyl forms a dark red complex of bivalent cation $[Fe(C5H4N2)]^{2+}$ as a result of reaction with Fe(II) which is not suitable with the spectrophotometer analysis. Therefore, 1.10-phenanthroline is used in this research to form a complex with Fe(II). 1.10-phenantroline could form a strong complex compound with Fe(II). Fe(III) does not have any effects, therefore it has to be reduced first in order for it to be in a bivalent condition [5].

Iron(III) can be reduced to iron(II) by using a reduction agent. The reduction agent normally used is sulphur dioxide mixed with hydrogen sulfide, hydroxylamine hydrochloride and natium thiosulphate. The sulphur dioxide reduction solution and hydrogen sulfide reagent is dissolvable in water and easily disposable by boiling them. However, both of these gases are toxic and emit a bad smell, hence they are both hardly used [6]. In the research conducted by Sri, hydroxylamine hydrochloride reduction agent was used, however special treatments were needed such as it had to be freshly made and preheating was needed. Other than that, a large concentration was needed, therefore the reaction given by natrium thiosulphate reduction agent went quick and did not produce any side effects [6].

1.10-phenantroline (Ph) produced a reasonably strong ligand field that can cause spin to pair up with iron(II), therefore forming reasonably stable ions that could be isolated with large anions. 1.10-phenantroline has a pair of nitrogen atoms that could form covalent bonds with iron(II). The three orthophenantroline molecules could form a complex compound with one iron(II) ion, generally known as ferroin or (Ph) Fe^{2+} . $(Ph)Fe^{2+}$ generally have red colour, however it has significant colour changes [7] and can be analysed with UV-Vis spectrophotometer.

During this research, iron(III) by 5 ppm was used which was reduced into iron(II) with Na2S2O3 by 11 ppm with a ratio of 1:2. There has to be an excess use of natrium thiosulphate in order to ensure that all of iron(III) had been reduced into iron(II) using an optimum pH of 4.5. Iron(II) was complexed with 1.10-phenantroline whereby its iron content analysis could be conducted using UV-Vis spectrophotometry. Fe(II) phenantroline formed a red complex compound that could be detected on UV-VIS spectrophotometer which emitted a wavelength of 508 nm [8].

In analyzing iron with 1.10-phenantroline complex, ion disturbance test was carried out to see if it had effects on the iron(II) percentage recovery. From the previous studies, Sb(III) phenantroline has a wavelength of 510 nm. Sb(III) ion could disturb the Fe(II) analysis by decreasing the recovery percentage by 75,54% on a small concentration of 0.05 ppm [9]. A study on analysis on the effects of Cu(II) ions towards iron analysis have also been implemented, which showed that Cu(II) phenantroline compound have a wavelength of 405 nm [4]. Cu(II) ions could disturb the iron analysis by decreasing the recovery percentage by 64,42% in a concentration of 0.3 ppm [10].

II. MATERIALS AND METHODS

2.1 Making 100 ppm Iron(III) Stock Solution

100 ppm Fe(III) solution was produced by dissolving 0.0483 gram of $FeCl_3 \cdot 6H_2O$ with 10 mL of demineralized water. Afterwards, the solution was put into a 100 mL volumetric flask and added with demineralized water until it reaches the 100 mL mark.

2.2 Making 100 ppm Natrium Thiosulfate PentahydrateStock Solution

The 100 ppm $Na_2S_2O_3 \cdot 5H_2O$ stock solution was made by dissolving 0.0157 gram of $Na_2S_2O_3 \cdot 5H_2O$ crystals with 100 mL demineralized water in a 100 mL volumetric flask.

2.3 Making 1000 ppm 1.10 – Phenantroline Complex Solution

0.1 gram of $C_{12}H_8N_2$ compound was dissolved in a 100 mL demineralized water inside a beaker and subsequently put into a 100 mL volumetric flask. Demineralized water was added again into the volumetric flask until it reaches the 100 mL mark.

2.4 *Making Acetate 4.5 Buffer Solution*

The acetate buffer solution was made by dissolving 3,97 gram of natrium acetate (CH_3COONa) into 5 mL glacial acid (CH_3COOH) ($K_a = 1{,}75 \times 10^{-5}$) and by subsequently adding demineralized water until it reaches a volume of 50 mL.

2.5 *Making 100 ppm Pb(IV) Solution*

100 ppm Pb(IV) solution was made by dissolving 0.01155 gram of PbO_2 crystal with a small amount of 12 M chloride acid (HCl) . Next, the solution was mixed with demineralized water until it reaches a volume of 100 mL.

2.6 Determining The Maximum Wavelength of Fe(II) Phenantroline on pH 4.5

Determining the Maximum Wavelength of Fe(II) on pH 4.5 was conducted by making a standard 100 ppm Fe(III) solution by 0.5 mL and puring it into a 10 mL volumetric flask. Next, 1,1 mL of 100 ppm Na2S2O3·5H2O solution, 1.5 mL of 1000 ppm phenantroline solution, 1.5 mL of pH 4.5 buffer acetate, and 5 mL of acetone, all were added into the mixture inside the 10 mL volumetric flask. Afterwards, demineralized water was added until the volume reaches 10 mL limit. The mixture was shaken and left idle for 10 minutes, and the adsorbance was measured using a wavelength of 450-590 nm. Each procedure was repeated three times. The maximum wavelength was determined based on the maximum adsorbance [11]

2.7 Determining the Maximum Wavelength of Pb(IV) Phenantroline at pH 4.5

Determining the Maximum Wavelength of Pb(IV) at pH 4.5 was done by making a standard 0.5 mL of 100 ppm Pb(IV) solution and eventually poured into a 10 mL volumetric flask. Afterwards, 1.5 mL of 1000 ppm phenantroline solution, 1,5 mL of pH 4.5 buffer acetate solution and 5 mL of acetone was added to the mixture before adding demineralized water until the maximum volume (10 mL) is reached. The mixture was shaken and left idle for 10 minutes, and the adsorbance was measured at a wavelength of 310-340 nm. Each procedure was repeated three times. The maximum wavelength was obtained based on the noted maximum adsorbance [12]

2.8 Making the Calibration Curve at pH 4.5

Making the calibration curve was done by using a standard 100 ppm Fe(III) solution with a varied volume of 1 ppm; 2 ppm; 3 ppm; 4 ppm; and 0.5 ml, where each subsequently were inserted into a 10 ml volumetric flask. Consequently, 1,1 mL of 100 ppm Na 2S2O 3·5H 2O; 1,5 mL of 1000 ppm phenantroline solution; 1,5 mL of pH 4.5 buffer acetate solution and 5 mL of acetone were added to the mixture, before demineralized water was also added until a maximum volume of 10 mL is reached. The mixture was shaken, left idle for 15 minutes, and its adsorbance was measured using the maximum wavelength of Fe(II) Phenantroline. Each of the varied volumes were repeated three times. The maximum wavelength was calculated based on the maximum adsorbance [12].

2.9 Effects of Pb(IV) on pH 4.5 Conditions

Tests on Pb(IV) effects was conducted by using a standard Iron(III) by 0.5 ml and inserted into a 10 mL volumetric flask. Afterwards, 1,1 mL of 100 ppm Na2S2O3·5H2O solution, Pb(IV) solution of 0.2; 0.4; 0.6; 0.8; 1; 2; 3; 4; 5; 6; and 7 ppm, 1.5 ml of 1000 ppm 1.10-Phenantroline solution 1.5 ml of pH 4.5 buffer acetate and 5 ml of acetone were also inserted into the mixture. The mixture was shaken, left idle for 15 minutes and its adsorbance was measured on the maximum wavelength of Fe(II) Phenantroline. The measurement was repeated three times and the results were plotted on a percentage recovery vs Pb(IV) concentration chart. From the curve, the amount of Pb(IV) concentration that started to cause disturbance on iron analysis could be found [12].

III. RESULT AND ANALYSIS

3.1 Determining the Fe(II) Phenantroline Wavelength

First stage in determining the Fe(II) Phenantroline wavelength is by reducing Fe(III) to Fe(II) using natriumthiosulphate, as follows:

$$2Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2Fe^{2+}(aq) + S_4O_6^{2-}(aq)$$

$E^o = +0.691$

The second stage is to complex Fe(II) with 1.10-phenantroline. Adding 1.10-phenantroline as a bidentate ligand will result in a complex with Fe(II) that have coordinated covalent bonds, therefore forming a red Fe(II) Phenantroline complex compound. The following reaction was obtained

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

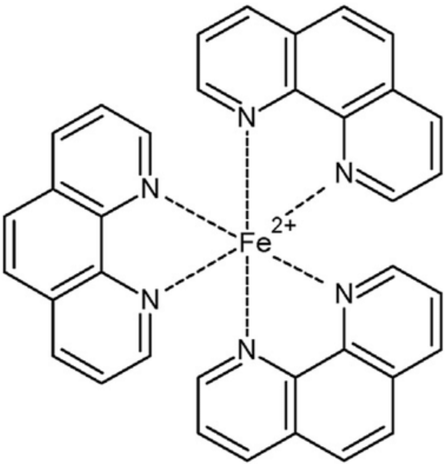


Figure 1. The shape of a Pb(II) Phenantroline complex compound.

The next stage was adding pH 4.5 buffer acetate since Fe(II) works optimally during the specified pH. Acetone is added to increase the solubility of Fe(II)-Phenanthroline complex, considering that Fe(II) is an organometallic compound. . This process was repeated three times with regard to obtaining an accurate result. Measuring the Fe(II) Phenantroline maximum wavelength was conducted using UV -VIS spectrophotometer.

An estimation of the wavelength used was 450 -590 nm with an interval of 1 nm with respect to obtaining better precision. The absorbance vs wavelength curve is shown on Figure 1.

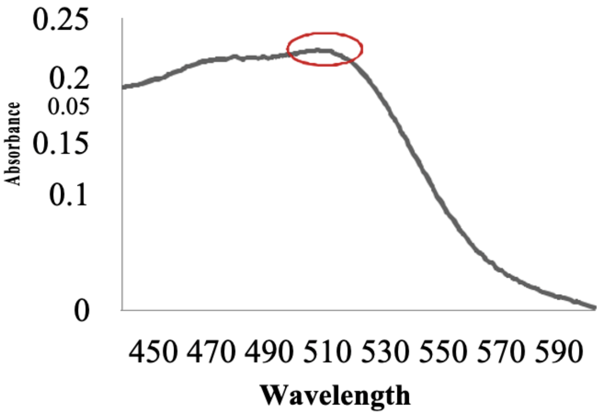


Figure 2. Wavelength vs Fe(II) Phenantroline Curve

Determining the Fe(II) phenantroline maximum wavelength could be seen from the largest resulted adsorbance. Based on the results, it can be said that the maximum Fe(II) phenantroline wavelength is 508 nm with adsorbance of 0.223. Due to this, for the next measurement, a wavelength of 508 nm will be used.

3.2 Determining Pb(IV) Phenantroline Wavelength

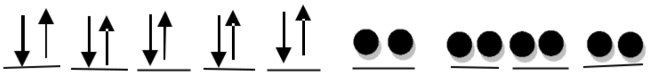
Determining Pb(IV) phenantroline wavelength was conducted by using a similar method as the one used for the Fe(II) Phenantroline, which was complexing Pb(IV) with 1.10-phenantroline, therefore obtaining a Pb(IV) Phenantroline compound. The reaction that occurred during the process is shown below.

$$Pb^{4+}_{(aq)} + 2C_{12}H_8N_{2(aq)} \longrightarrow [Pb(C_{12}H_8N_2)_3]^{4+}_{(aq)}$$

The following is the electron configuration of Pb(IV)

${}_{82}Pb$ $= 4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{2}$
${}_{82}Pb^{4+}$ $= 4f^{14}\ 5d^{10}\ 6s^{0}\ 6p^{0}$

The hybridization of Pb(IV) Phenantroline complex compound is as follows.



Annotation:

●● = Lone pairs of 1,10-phenanthroline electrons

From the above annotation, it can be confirmed that Pb(IV) Phenantroline complex compound have the geomteri of a tetrahedral with sp^3 hybridization.

In determining the Pb(IV) phenantroline wavelength, an approximate wavelength of 310-340 nm with interval of 1 mm was used.

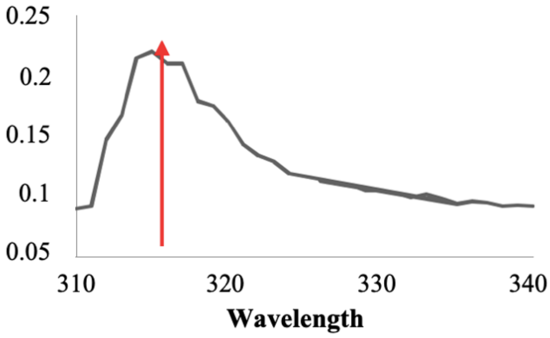


Figure 3. Wavelength vs Pb(IV) Phenantroline Absorbance Curve.

The Pb(IV) phenantroline maximum wavelength can be determined from the absorbance vs wavelength curve. From the results obtained, it can be seen that the Pb(IV) phenantroline maximum wavelength is 315 with the highest absorbance of 0.22 (Figure 3). Also from the experiment, by comparing the length of the Fe(II) Phenantroline wavelength with the furthest length of the Pb(IV) wavelength, it can be decided whether if Pb(IV) caused a disturbance towards Fe(II) Phenantroline at a high concentration concentration or it did not cause any disturbance at all.

3.3 Plotting the Calibration Curve

Plotting the calibration curve was constructed by making an Fe(II) solution with a varied concentrations of 1, 2, 3, 4, and 5 ppm and subsequently complexing each one of them with 1.10-phenantroline in order to obtain a red mixture which can be examined using UV-VIS spectrophotometer.

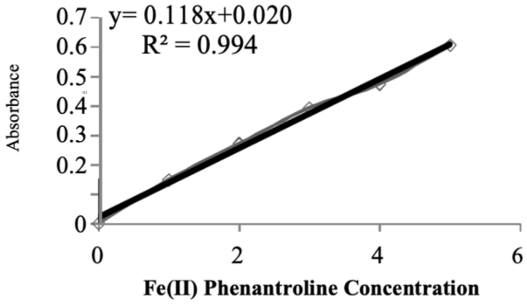


Figure 4. Fe(II) Phenantroline Calibration Curve

The absorbance values of the Fe(II) solution with varied concentrations of 1, 2, 3, 4 and 5 ppm all can be seen in Figure 4. By doing calculation based on the linear calibration curve, straight line linear equation can be obtained, which is y= 0.118x+0.020. The correlation coefficient value obtained (r) was 0.997 and regression value (r^2) obtained was 0.994. The correlation coefficient from the calibration curve nearing to 1 suggests that there is a correlation between concentration and absorbance. This corresponds to the Lambert-Beer Law, which is A=abc, where absorbance (A) is proportional to the concentration value (c).

The optimum regression value lies on the range of $0.9< r^2<1$. A regression value of 0.994 means that the value lies on the same straight line with the best gradient line and have the optimum precision. The validity of the calibration curve can also be determined from t-test. By doing so, the correlation between concencetration and absorbance can be identified using the criteria tcalculated>ttable, whereby if the results fit the criteria, it can be judged that the data obtained are correlated to one another. From the experiment, the value of tcalculated obtained was 29.404, whilst the value of ttable obtained from the critical value of t distribution was 2.78 with a reliability range of 95% and degree of freedom of (n-2). With this being said, the value of tcalculated acquired was bigger than ttable, therefore the rejected Ho can be found, which meant that there was a correlation between the absorbance and the concentration [13].

3.4 Effects of Pb(IV) Disturbance Ions Towards Fe(II) Phenantroline Contents

The effects of Pb(IV) disturbance ions towards Fe(II) Phenantroline contents was found by dissolving a 5 ppm Fe(II) solution with Pb(IV) solution with a varied concentrations of 0; 0.2; 0.4; 0.6; 0.8; 1; 2; 3; 4; dan 5 ppm. Next, the mixture was complexed with 1.10-phenantroline, and as a result, a red-orange solution was resulted which can be measured its absorbance using UV-VIS spectrophotometer. The concentrated solution data and the Fe(II) Phenantroline percentage recovery can be seen in Table 1.

From the results presented in Table 1, it is shown that the higher the Pb(IV) concentration, the smaller the Fe(II) Phenantroline percentage recovery. The ideal percentage recovery was approximately 80-120% [14]. By adding 0.2 ppm of Pb(IV), the Fe(II) Phenantroline percentage recovery increased, which was 123.160%. This was due to the increase of the colour intensity during the addition of 0.2 ppm Pb(IV), which at the same time was also due to the presence of a competition between Fe(II) with Pb(IV) to form a complex compound with Phenantroline, hence increasing its absorbance. During the addition of 6 ppm Pb(IV), it was observed that the percentage recovery of Fe(II) Phenantroline decreased, which was 71.108%. This was resulted due to the large wavelength distance between Fe(II) Phenantroline with Pb(IV) Phenantroline, therefore Pb(IV) disturbed the high concentration. Thus it can be interpreted that the disturbing ions of Pb(IV) could disturb the contents of Fe(II) Phenantroline at concentrations of 0.2 and 6 ppm (Figure 5).

Table 1. Concentrated Solution Data and % Recovery of Fe(II) Phenantroline

[Pb(IV)]	[Fe(II) Phenantroline]	% Recovery
0	5	100
0.2	6.158	123.160
0.4	5.989	119.775
0.6	5.897	117.948
0.8	5.669	113.380
1	5.642	112.847
2	4.916	98.325
3	4.732	94.461
4	4.505	90.103
5	4.352	87.038
6	3.555	71.108
7	3.007	60.145

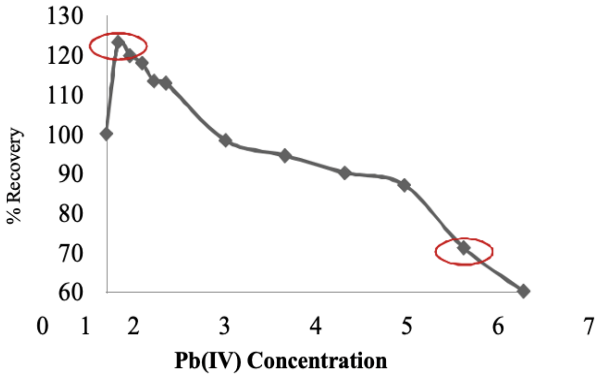


Figure 5. Effects of Disturbing Ions Towards Fe(II) Phenantroline Contents

It was known that there were some data irregularities at the maxiumum and minium limits when the Q test was being carried out. It was obtained that the Q value on the maximum limit (0.2 ppm concentration) was 0.440 and the Q value on the minimum limit (6 ppm concentration) was 0.093. By appling the Q test, we can find out whether if the results are usable. If Qcalculated<Qtable, then it can be approved that the results are usable. From the experiment, the Qtable value on the critical distribution of Q is 0.466 with reliability range of 95% [13]. Based on the Q test results calculations, it was discovered that Qcalculated was smaller than Qtable, meaning that the experiment results on Pb(IV) disturbance ions on 0.2 and 6 ppm concentrations are usable.

The data used to strengthen the experiment results on analyzing Pb(IV) disturbance towards Fe(II) Phenantroline contents were obtained with relative standard deviation (RSD) and coefficient variation (CV). At a Pb(IV) concentration of 0.2 ppm, the RSD and CV acquired was 5.41 ppt and 0.343% respectively. The RSD value could be classified as selective if it has a value below 20 ppt with a CV value below 2% [13], implying that the data collected are usable for the next research.

VI. CONCLUSION

Based on the research conducted, analysis on Fe(II) with 1.10-phenantroline complex using UV-VIS spectrophotometry produced Fe(II)-phenanthroline that could absorb light at a wavelength of 508 nm. From the calibration curve measurement of Fe(II) Phenantroline, a regression of 0.994 was accomplished. Pb(IV) ions increased the absorbance at a concentration of 0.2 ppm and obtained a percentage recovery of 123.160%. On the other hand, at 6 ppm, Pb(IV) ions disturbed the iron concentration by decreasing the absorbance and obtained percentage recovery of 71.108%. From the experiment, the CV and the RSD values collected were 0.541% and 5,41 ppt respectively at 0.2 ppm, and 0.343% and 3.43 ppt respectively at 6 ppm.

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