Study of linearity and stability of Pb(II)-1,10-phenanthroline complex with the presence of Fe (II) dan Mg (II) matrix ions using UV-Vis spectrophotometry

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Abstract. The effect of Fe (II) and Mg (II) as matrix ions in the determination of Pb (II) based on 1,10-phenanthroline complexing agent at pH 7 had been investigated. The objective of this study is to determine the effect of Fe (II) and Mg (II) on the determination of Pb (II) using the complexing agent 1,10-phenanthroline. The absorbance determination using a spectrophotometer was conducted at a wavelength of 302.5 nm for Pb (II)-1,10-Phenanthroline. Linear correlation between the investigated absorbance on Pb concentration was represented by a linear equation of $y = 0.0131 x + 0.8693$ ($R^2 = 0.9613$). From the linear equation, it was obtained the increase in sensitivity and linearity for Mg (II), as well as the decrease in sensitivity and linearity for Fe (II). It revealed that Fe (II) and Mg (II) affects the analysis of Pb (II) using 1,10-phenanthroline complexing agent. In order to achieve stability of Pb (II)-1,10-Phenanthroline, it was compared with Mg (II)-1,10-Phenanthroline and Fe (II)-1,10-Phenanthroline. It suggested that Pb (II), Mg (II) and Fe (II) had an equivalent binding strength against 1,10-Phenanthroline.

1. Introduction

The contamination of heavy metal in the environment still become a major problem. Besides it present naturally by geological or geochemical activities [1–5], the intense uses by the construction [6]and industry [7,8]make the metal pollution has caused exposure in many cases[9–11] This can be more dangerous because the heavy metal can transport from an ecosystem to others [12] and poisoning the organism[13].

Lead (Pb) is one of the hazardous heavy metals which threatens the life of humans and animals. Pb is also a component that is commonly used as an additive in water pipe [14], paint [15], and octane number reducing agent in premium gasoline [16]. The use of Pb in those materials is due to its specific function and low price [17].

Pb can be accumulated in bone tissue [18,19], which further damages the nervous system and enzymatic function stem from its neurotoxicity [17]. This case often occurs on children [20], including...
brain damage. The toxicity of Pb is a big problem due to its broad use. Therefore, the presence of Pb essentially needs to be analyzed in a periodical manner to observe the level of pollution. It further helps the decision-making on the countermeasures. Based on the stated problems, Pb analysis has to be carried out.

Several methods had been applied to analyze Pb, either conventional or instrumental methods. Determination of Pb for both methods requires specific criteria in terms of quantity and types of samples. The instrumental determination usually is more sensitive due to its ability to measure Pb up to the smallest concentration unit. Some methods used for Pb determination includes Atomic Absorbance Spectroscopy (AAS), Graphite Furnace AAS, chemiluminescence, potentiometry, Anodic Stripping Voltammetry and UV-Vis spectrophotometry [21]. Concentration determination of Pb through UV-Vis spectrophotometry had been used widely due to its quick, easy, and cheap operation. Pb (either in the form of Pb (II) or Pb (IV)) is firstly required to be priorly complexed using Pb ions complexing agents. Some Pb complexing agents include dithizone[22], 5-Bromo-2-hydroxy-3-methoxy benzaldehyde-hydroxybenzoic hydrazine[23], diphenylcarbazone and 1,10-phenanthroline [24].

Spectrophotometry methods with Pb complexing agent, dithizone, has been studied by dithizone [22]. On the stated method, acidic medium (concentrated HNO₃) was used within the presence of 50 matrix cations during the determination of Pb (II). Meanwhile, B. Saritha, A. Giri, and T. Sreenivasulu Reddy studied a similar method; however, they used different complexing agents (-Bromo-2-hydroxy-3-methoxy benzaldehyde-hydroxybenzoic hydrazine). At optimum pH (between 7-9) [23,24], it was reported that the quantity of metal ions and anions did not affect the determination of Pb (II). Mikula et al., 2009 conducted research using phenanthroline complexing agents and Pb adsorbent. Complexing agent 1,10-phenanthroline is a simple reagent that can be used to complex aqueous Pb (II).

The references in introduction to prove the finding by author which used as the basis in this research, several references for the Pb existence both naturally and manmade. It also describe the case of Pb exposure on human life and the disease appeared. This description is the reason why Pb identification is important. Other references described about the recent various methods used for Pb. These are well methods in accuracy and reliability but less ones in simplicity and cost. These descriptions provided the basis why the UV-Vis offered as a quick, easy and cheap methods.

Analysis of Pb spectrophotometrically using complexing agent 1,10-phenanthroline was affected by several metal ions such as nickel and cadmium [25]. Nickel and cadmium ions affect the determination of Pb ions by decreasing the absorbance. A study by B. Yusuf, A. and S. Nurliana, at pH 8.5, the linear equation was found to be Y = 0.1596 X + 0.1932 , with R² = 0.9991[26]. Furthermore, M. Yayinie, M. Anza, and T. Shifaraw in 2015 conducted the same study at pH 10-11.5, where the determination yielded a sensitivity as high as 0.014 with R² = 0.99781, standard deviation = 0.01793 and recovery = 93.8% [27].

As discussed above, it appears that the studies of matrix ions were merely conducted against metal ions from the transition group due to its similar properties. Nonetheless, in this work, we present an investigation results on Mg (II) and Fe (II) ions. Both metals are commonly found in an aqueous sample, which motivates our work in finding how those metal ions affect the stability of 1,10-Phenanthroline Pb (II) complex.

2. Instruments and materials
UV-Vis Shimadzu 1800 Spectrophotometer, glassware (Pyrex), pH-meter Bran Orion Star.

2.1. Materials
Pb (NO₃)₂ , FeCl₂.6H₂O, Mg (NO₃)₂, 1,10-Phenanthroline, Buffer Solution pH 7 NaOH and acetone were purchased from Merck.
2.2. Methods
Preparation of Pb stock solution. Pb (II) stock solution (100 ppm) was taken using pipette as much as 0.1 - 0.5 mL and added into a volumetric flask 10 mL to give Pb (II) solutions with 1-5 ppm.

Into each volumetric flask, 1.5 mL 1,10-Phenanthrolin 1000 ppm was added, followed by 1.5 mL buffer solution NaOH pH 7, 5 mL acetone, and distilled water until the total volume reached 10 mL. The mixture was shaken, then left for 5 min. The mixture was measured for its absorbance at maximum wavelength using UV-Vis spectrophotometer. This procedure was repeated three times. Then, the calibration curve was constructed between the absorbance and the Pb (II) concentration. The linear equation and R^2 were obtained from the plot.

Absorbance Measurement In Determination of Fe (II) and Mg (II) on Pb (II) analysis at pH 7 Pb Pb(II) stock solution (1-5 ppm) was then respectively added with 0.01 mL and 0.05 mL Fe (II) solution 100 ppm, where it was followed by the addition of 1.5 mL 1,10-Phenantroline 1000 ppm, 5 mL buffer solution NaOH pH 7 and 5 mL acetone. Next, the distilled water was poured until the volume reached 10 mL. The mixture was shaken and left for 5 min. It was then measured for the absorbance at maximum wavelength using UV-Vis spectrophotometer. This procedure was conducted with three times repetitions. The same procedure was also applied for Mg (II) solution.

Investigation of complex stability (K_c) of Pb (II), Fe (II) and Mg (II) on 1,10 phenanthroline complexing agent.

The investigation of complex stability(K_c) of Pb (II), Fe (II) and Mg (II) with 1,10 phenanthroline ligand which had been affected by the used ions.

3. Results and discussion
In this research, we studied the comparative matrix effect of Fe (II) and Mg (II) against Pb (II) analysis using 1,10-Phenanthroline complexing agent at pH 7 with UV-Vis spectrophotometer. This work was initiated by complexing Pb (II) with 1,10-Phenanthroline forming Pb (II)-1,10-Phenanthroline complex, which appeared colourless. Pb (II)-1,10-Phenanthroline complex at pH 7 [23-24] was measured for its absorbance to determine the maximum wavelength using spectrophotometer UV-Vis. The effect of Fe (II) and Mg (II) against the maximum wavelength of Pb (II) would be discussed in this work.

The plot obtained revealed that the maximum absorbance was observed at 302.5 nm, which suggested that the maximum wavelength for Pb (II)-1,10-Phenanthroline was 302.5 nm [15]. 1,10-Phenantroline is a complexing agent that is capable of reacting with various types of metal to form complex compounds. 1,10-Phenantroline could form a strong complex with Pb (II) and appeared colourless as shown by Figure 1.

![Figure 1. Reaction of Pb (II) with 1,10 phenanthroline complexing agent](image)

Table 1 presents the effect of Fe (II) and Mg (II) against the linearity of Pb (II)-phenanthroline complex. In line with the sensitivity, the R^2 and experimental t [25-26], it can be observed that the presence of Fe (II) and Mg (II) in the Pb (II) measurement system using 1,10 phenanthroline complexing agent, affected the determination[24]. The value of sensitivity on Pb (II) determination (1-5 ppm) changed significantly by the presence of both ions. The difference was significantly based on the t-experimental which is far above the t-theoretical on the Pb (II) sensitivity before and after the presence
of the matrix ions (Fe (II) and Mg (II)). The t-test was carried on the sensitivity for n = 3 at confidence level of 95% (t-theoretical = 2.353). Matrix effect is given by Fe (II) 0.1 ppm and Fe (II) 0.5 ppm decreased the measurement sensitivity as much as 8 x 10^{-4} and 1.6 x 10^{-3}, respectively. Next, the effect of Mg (II) against the linearity of Pb (II) (1-5 ppm) had caused a significant increase in the sensitivity, which reached 9.1 x 10^{-2} and 9.52 x 10^{-2} for Mg (II) 0.1 ppm and Mg (II) 0.5 ppm, respectively.

Table 1. Sensitivity and linearity of Pb (II)-1,10-phenanthroline complex with the presence of matrix ions Mg (II) and Fe (II).

|                | b (Sensitivity) | R² | t experimental |
|----------------|-----------------|----|---------------|
| [Pb] (1-5 ppm) | 0.0131 ± 0.00012 | 0.9613 |               |
| [Pb] (1-5 ppm) + Fe 0.1 ppm | 0.0123 ± 0.00021 | 0.9544 | 8.32          |
| [Pb] (1-5 ppm) + Fe 0.5 ppm | 0.0115 ± 0.00015 | 0.9274 | 13.6          |
| [Pb] (1-5 ppm) + Mg 0.1 ppm | 0.1038 ± 0.00035 | 0.9867 | 30.9224       |
| [Pb] (1-5 ppm) + Mg 0.5 ppm | 0.1083 ± 0.00179 | 0.9908 | 7.24          |

Pb ion analysis using 1,10-Phenanthroline complexing agents could be affected by several matrix ions such as nickel and cadmium [25]. 1,10-Phenanthroline could form a complex with all bivalent metals [16]. In this work, it can be observed that the presence of Mg (II) and Fe (II) within Pb (II)-1,10-Phenanthroline complex system affected the absorbance at each investigated Pb concentration. It suggested that Mg (II) and Fe (II) contributed in the uncertainty of Pb (II) analysis using 1,10-Phenanthroline complexing agent. It is owing to the reactivity of Mg (II), and Fe (II) is higher than Pb (II) in binding 1,10-Phenanthroline [15]. The proposed reactions occurred when Mg (II) and Fe (II) was complexed with 1,10-Phenanthroline are depicted by Figure 2.

Figure 2. The effect of Mg (II) and Fe (II) against the stability of Pb (II)-1,10-Phenanthroline complex.

In this work, the linearity of Pb (II)-1,10-Phenanthroline complex for Pb (II) with a concentration ranged from 1-5 ppm was investigated for its complex equilibrium constant (Kc) profile for both Mg (II) and Fe (II). Tables 2 and 3. present the values of equilibrium constant (Kc) of Pb (II)-1,10-Phenanthroline with and without the presence of matrix ions (Mg (II) and Fe (II)) [18]. Kc values of Pb (II)-1,10-Phenanthroline without the presence of matrix ions were relatively the same, compared with the presence of Mg (II) and Fe (II) matrix ions, either for 0.1 ppm or 0.5 ppm.
Table 2. Kc Profile of Pb (II)-1,10-Phenanthroline with the addition of Mg (II) 0.1 and 0.5 ppm.

| Concentration Pb²⁺ (ppm) | Concentration Mg²⁺ (ppm) | y (Absorbance of Mg²⁺) | x (Concentration of determined Pb²⁺ (ppm)) | Kc (10⁻⁵) |
|--------------------------|---------------------------|------------------------|-------------------------------------------|-----------|
| 1                        | 0                         | 0.881                  | 0.893                                     | 3.970     |
| 2                        | 0                         | 0.898                  | 2.191                                     | 19.474    |
| 3                        | 0                         | 0.911                  | 3.489                                     | 62.019    |
| 4                        | 0                         | 0.915                  | 3.489                                     | 62.019    |
| 5                        | 0                         | 0.938                  | 5.244                                     | 116.539   |
| 1                        | 0.1                       | 0.881                  | 0.857                                     | 3.810     |
| 2                        | 0.1                       | 0.91                  | 2.337                                     | 20.771    |
| 3                        | 0.1                       | 0.923                  | 3                                          | 40.0      |
| 4                        | 0.1                       | 0.934                  | 3.561                                     | 63.311    |
| 5                        | 0.1                       | 0.967                  | 5.245                                     | 116.553   |
| 1                        | 0.5                       | 0.89                  | 0.644                                     | 2.8630    |
| 2                        | 0.5                       | 0.92                  | 2.485                                     | 22.086    |
| 3                        | 0.5                       | 0.93                  | 3.098                                     | 41.309    |
| 4                        | 0.5                       | 0.941                  | 3.773                                     | 67.076    |
| 5                        | 0.5                       | 0.977                  | 5.9816                                    | 132.924   |

Table 3. The effect of Fe (II) ions addition.

| Concentration Pb²⁺ (ppm) | Concentration Fe²⁺ (ppm) | y (Absorbance of Fe²⁺) | x (Concentration of determined Pb²⁺ (ppm)) | Kc (10⁻⁵) |
|--------------------------|---------------------------|------------------------|-------------------------------------------|-----------|
| 1                        | 0                         | 0.881                  | 0.893                                     | 3.970     |
| 2                        | 0                         | 0.898                  | 2.191                                     | 19.474    |
| 3                        | 0                         | 0.911                  | 3.489                                     | 62.019    |
| 4                        | 0                         | 0.915                  | 3.489                                     | 62.019    |
| 5                        | 0                         | 0.938                  | 5.244                                     | 116.539   |
| 1                        | 0.1                       | 0.881                  | 0.857                                     | 3.810     |
| 2                        | 0.1                       | 0.91                  | 2.337                                     | 20.771    |
| 3                        | 0.1                       | 0.923                  | 3                                          | 40.0      |
| 4                        | 0.1                       | 0.934                  | 3.561                                     | 63.311    |
| 5                        | 0.1                       | 0.967                  | 5.245                                     | 116.553   |
| 1                        | 0.5                       | 0.89                  | 0.644                                     | 2.8630    |
| 2                        | 0.5                       | 0.92                  | 2.485                                     | 22.086    |
| 3                        | 0.5                       | 0.93                  | 3.098                                     | 41.309    |
| 4                        | 0.5                       | 0.941                  | 3.773                                     | 67.076    |
| 5                        | 0.5                       | 0.977                  | 5.9816                                    | 132.924   |

Therefore, it could be stated that the stability of Pb (II)-1,10-Phenanthroline was relatively the same with Mg (II) -1,10-Phenanthroline and Fe (II) -1,10-Phenanthroline complexes. It was ascribed to the surrounding reaction condition at pH 7, where at the stated pH, Pb could perform optimally [24]. It could
also be associated with the atomic radius of Fe (II) cations, which is smaller than that of Pb (II) cation [17].

4. Conclusion
Mg (II) and Fe (II) could affect the analysis of Pb (II)-1,10-Phenantroline, due to the change of sensitivity and linearity of the formed complex. Therefore, a more sensitive method is required in analyzing the metal complex. The Kc values of Pb (II)-1,10-Phenantroline were relatively similar to that of Mg (II)-1,10-Phenantroline and Fe (II)-1,10-Phenantroline. It implied that Pb (II)-1,10-Phenantroline has a similar strength in binding 1,10-Phenantroline, in comparison with Mg (II)-1,10-Phenantroline and Fe (II)-1,10-Phenantroline.

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