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Optimization and analysis of some oxinate metal complex system as introduction test for HPLC analysis

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Abstract. Heavy metals are metals that have a mass of more than 5 g / cm3 in the lower right corner of the periodic system. Heavy metals rarely form atoms themselves in water, but are usually bound by other compounds to form molecules. Heavy metal is a chemical compound that has the potential to cause environmental pollution problems. Methods of heavy metal content analysis in the aquatic environment developed simultaneously are still being developed. The simultaneous analysis provides an advantage in terms of time and cost efficiency. In this study is being developed heavy metal analysis based on the formation of complexes with oxin compounds. It is known that the oxide can form a yellow complex with several metal ions. The use of oxine as a complex is selected based on the color and pH of the complexes formed. By performing optimization and analysis of the complex system formed it is expected to produce an excellent method for the analysis of several heavy metals simultaneously using High Performance Liquid Chromatography (HPLC).

1. Introduction

The presence of heavy metals in the environment comes from mining, household, agricultural, industrial waste and others. Of the four types of waste, the most commonly heavy metal waste is industrial waste [1]. Uncontrolled heavy metals give an opportunity for accumulation of heavy metals in the environment. Heavy metals can enter into the plant tissue through the roots and stomata leaves, then will enter into the food chain cycle [2].

Heavy metals, although in small amounts, can have a considerable effect on the food chain. This is caused by the buildup of heavy metals in each biota. Some heavy metals can contaminate the environment and are toxic, including Cr, Ag, Cd, Pb, Zn, Hg, Cu, Fe Mo, Ni, Sn, Co and elements included in light metals such as As, Al and Se [3]. Although some heavy metals in small concentrations are essential for living things as necessary for the body's metabolism. However, the presence of heavy metals in rivers that exceed the threshold value can cause harmful effects to living things [4]. This is due to the nature of heavy metals that can not decompose through biodegradation such as organic pollutants. Heavy metals can also accumulate mainly in river sediments as they can be bound to organic and inorganic compounds through the process of adsorption and the formation of complex compounds [5].

Methods of heavy metal analysis can be done qualitatively and quantitatively. Qualitative analysis is usually based on metal precipitation reactions using certain reagents such as hydrochloric acid, hydrogen

sulfide, ammonium sulfide and ammonium carbonate. Quantitative analysis can be done using several methods, namely Flame Atomic Absorption Spectrometry (FAAS), Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) method is costly and less practical [6, 7, 8]. So in this study used a more practical chromatographic technique for the analysis of heavy metal content.

The science of separation and analysis plays a very important role in the application of analytical chemistry, the latest techniques and substances associated with such analysis techniques continue to grow [9]. Since its introduction in 1975, ion chromatography has been the dominant method of analysis in the determination of organic and inorganic ions [10]. The determination of inorganic ions has been carried out not using ion exchange columns [11, 12] but also by using other stationary phases [13, 14, 15, 16]. Chromatography technique is an analytical technique that has many advantages such as can determine the content of organic compounds, inorganic, metal, amino acids either in solid, liquid or gas samples in a single measurement.

In addition to the determination of ions directly, it can also be determined the ions are indirectly by reacting the ion first with a ligand so as to form a complex. Quantitative metal ion analysis can be done by changing the metal ion into a complex compound. High Performance Liquid Chromatography (HPLC) can be used as a tool for determining complex compounds and will increase the sensitivity and selectivity of metal ion separation [17]. Metal ions can be transformed into compounds of neutral complexes using organic compounds such as oxine to form compounds of metal-oxinate complexes [18]. Most such complexing reagents are weak acids that react with most metals to form uncharged complexes dissolved in organic solvents such as ether, hydrocarbons, ketones, chloroform and carbon [19]. Among them are oxides (8-hydroxyquinoline) which form a stable chelate complex with several types of metal ions [20, 21, 22].

Oxygen is given a HOx notation, a bidentate ligand which has two donor atoms on oxygen atoms in phenolic hydroxy group and nitrogen on its cyclic chain so as to form a neutral chelate complex with metal. This complex is formed by replacing the hydrogen atoms in the hydroxyl group by the metal and the coordination bond of the nitrogen atom with the metal forming an uncharged chelate ring compound. The metal complex is insoluble in water but soluble in organic solvents such as chloroform [18]. The metal-oxinic complex is a color complex so that the metal concentration can be detected using UV-Vis detector on HPLC instrument.

In this research, we have investigated the condition of the formation of metal oxinate complexes of some heavy metal ions such as Fe (III), Pb (II), Ni (II), Co (II), Cu (II) and Zn (II) maximum waves, pH, complex stability, stirring time, ligand concentration. The results of this study will be used for the separation of the metal ions in complex form with oxine using HPLC.

2. Experimental

2.1. Apparatus
Determination of wavelength using Spectronic Genesys 20 D, pH of the solution was determined using a pH meter Hanna Instrument HI2211, weighing chemicals to make reagents using analytical balance, separating funnel used for organic phase separation, glassware and reagent bottle.

2.2. Chemicals
All of chemicals are obtained from Merck, unless otherwise noted. $ZnSO_4$, $CuSO_4.5H_2O$, $Ni(NO_3)_2.6H_2O$, $CoCl_2.6H_2O$, $Pb(NO_3)_2$, $Fe(NO_3)_3.9H_2O$, C_9H_6NOH (Oxine), Chloroform, Methanol, Ethanol, Asetonitril, HNO_3, NaOH dan aquades.

2.3. Research Procedure

2.3.1. Determine Complex Wavelength. A solution of metal ions with a concentration of 10 ppm taken as much as 1 mL was reacted with 3.5 mL of oxine 0.1 M (dissolved in ethanol) in a test tube. The complex wavelength formed is measured using Spectronic at a wavelength of 400-600 nm.

2.3.2. Determine Optimum Oxine Concentration in Complex Formation. The absorbance for the metal-oxinate complex of each metal ion solution was measured after oxine added with a concentration of 0.01; 0.05; 0.1; 0.15 and 0.2 M of 3.5 mL into each of the metal ion solutions, the optimum oxine concentration will be obtained when the absorbance of the metal-oxinate complex is flat.

2.3.3. Determine effect of pH in Complex Formation. 1 mL of 10 ppm metal ion solution was introduced into each of 6 separating funnel pieces with a pH varied ie pH 3, 4, 5, 6, 7, 8 The pH variation was made by adding 0.5 M NaOH or HNO_3 0.5 M drops to the desired pH. Then add them into each 3.5 mL 0.1 M separating mouthpiece in chloroform. Extract for 5 minutes until the water phase and organic phase are separated

2.3.4. Determine Shaking Time in Complex Formation. 1 mL of 10 ppm metal ion solution was introduced into the separating funnel and 3.5 mL of 0.1 M oxine was added and the pH of the solution was adjusted according to the optimum pH of the complex. Extract for 5 minutes until the water phase and organic phase are separated. The organic phase (metal-oxinate complex) is measured at the optimum wavelength within 5 minutes. Continue the uptake measurements after extraction for 10, 15, 20, 25 and 30 min by making a new metal-oxinate complex solution for each measurement

2.3.5. Determine Complex Stability Time. Determination of complex stability time is done by reacting 10 ppm metal ions with 0.1 M oxine in a separating funnel. The metal-oxinate complex formed on the organic phase is separated and measured using spectronic at maximum wavelengths. Measurements are made at 0 to 150 minutes every 10 minutes.

3. Results and Discussion

3.1. Determine Complex Wavelength

The maximum wavelength of each metal oxinate complex is determined to obtain the optimum wavelength of the entire complex for simultaneous determination. 1 ml of 10 ppm metal ion was added with 3.5 ml oxine 0.1 M. In this study all the complexes formed were yellow. In this procedure, oxine is dissolved in ethanol, so the advantage is that the complex compounds formed do not need to be separated. This causes faster analysis time. Furthermore, the complex was analyzed using spectronic at a wavelength of 400 to 600 nm. The wavelength for each metal oxinate complex can be seen in Figure 1 below.
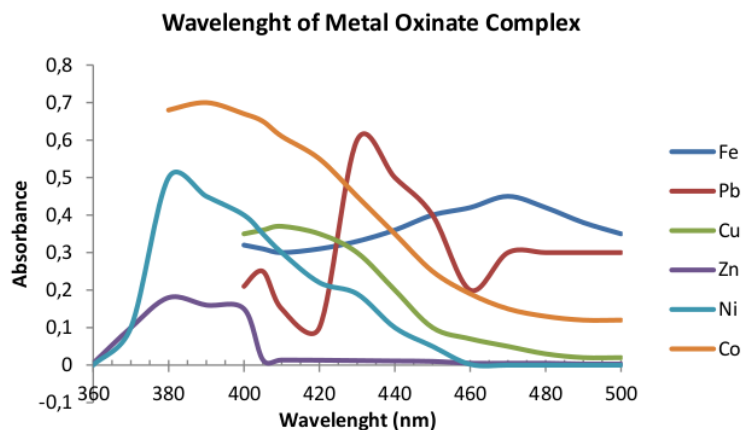
Figure 1. Wavelenght for metal oxinate complex

3.2. Determine Optimum Oxine Concentration in Complex Formation

Determination of optimum oxine concentration aims to obtain the correct oxine concentration reacts with metal ions so that the oxine is used optimally and not excessively in the reaction. In general, an increase in the oxide concentration will increase the amount of metal ions which are transacted to the organic phase until they reach a point called the optimum point. Having reached the optimum point of increase the oxine concentration only slightly affects the extraction of metal ions. The following curve relation influence the variation of oxine concentration to absorbance value of metal oxinate complex compound can be seen in Figure 2.
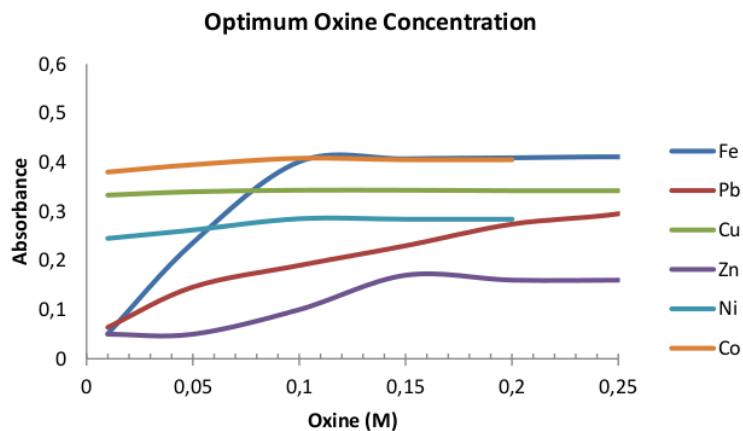

Figure 2. Concentration of Oxine to form metal oxinate complex

3.3. Determine effect of pH in Complex Formation

Determination of the effect of pH on the formation of oxinate metal complex compounds aims to obtain a suitable pH range of the metal ion extraction process. The stability of complex formation is strongly influenced by the pH of metal ion solution. At low pH, the abundance of H^+ ions causes the reaction equilibrium to tends toward the formation of metal ions and oxides rather than the formation of oxinate

metal complex compounds, so that the compound of the metal oxinate complex is formed very little. At high pH, decreasing H^+ ions and increasing OH^- ions in solution metallic ions tend to react with OH^- ions forming $Fe(OH)_3$ or $Pb(OH)_2$ [23]. Reduced metal ions reacting with the oxine cause the compound of the oxinate complexes formed slightly. The determination of pH optimum is based on the high absorbance value in the uptake of oxinate metal complex compounds.
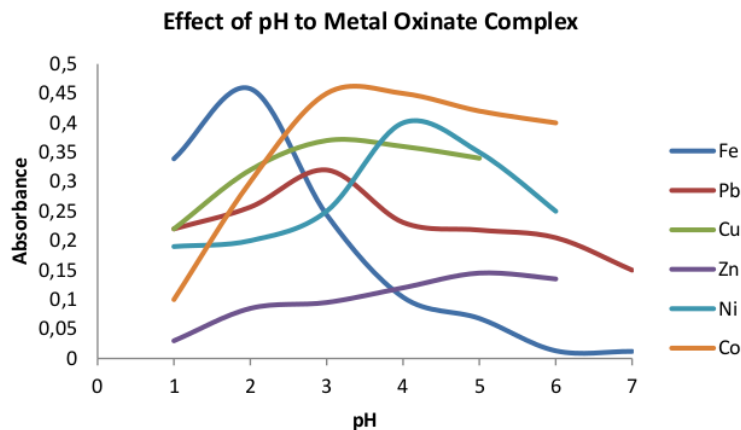

Figure 3. Effect of pH to form metal oxinate complex

3.4. Determine Shaking Time in Complex Formation

Determination of the effect of shaking time on the formation of metal oxinate complex compounds aimed to obtain optimum time so that all metal ions extracted into the organic phase form oxinate complex compounds. If the time for shaking is less, it will be a little complex that is formed. Optimum conditions will be obtained when the addition of time does not provide additional value of absorbance.
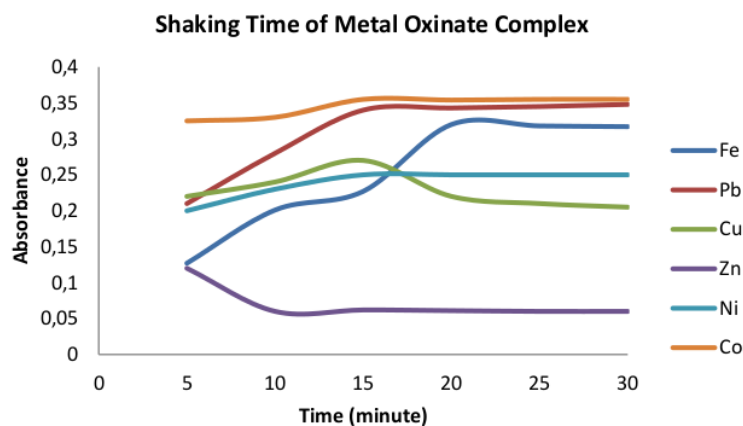

Figure 4. Shaking time to form metal oxinate complex

From Figure 4 it can be seen that the absorbance value of Fe (III) -Oxinate and Pb (II) -Oxinate complexes against shaking time signifies the amount of Fe (III) ions or Pb (II) ions extracted into the organic phase. The optimum shaking time for the Fe (III) -Oxinate complex comprises at shaking time of 20 min and for the Pb (II) - Oxinate complex ie at shaking time of 15 min. The small influence of the variation of the shuffling time on the obtained extraction results indicates that the oxine reaction with Fe (III) and Pb (II) ions occurs rapidly. Despite the variation of shuffle time, the absorbance value obtained is not much different. For the duration of subsequent shaking in the extraction of Fe (III) ions with the oxine was carried out for 20 min and the extraction of Pb (II) ions for 15 min.

3.5. Determine Complex Stability Time
The timing of the formation stability of the complex is determined to determine how long the formed complex remains stable and is good for analyzing. This is because the possibility of re-decomposition of complex compounds that have been formed or the formation of colloids that will interfere with measurements [23].
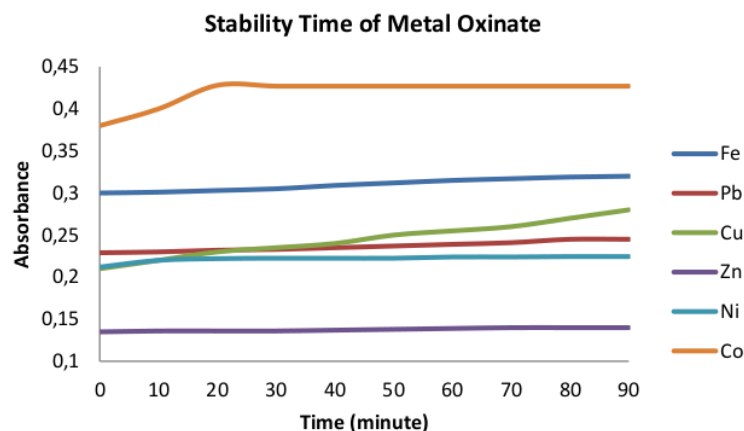

Figure 5. Stability time of metal oxinate complex

From the curve above can be seen that the longer time complexing the higher the absorbance value. This suggests that more and more complex nickel metals as time goes by. The optimum period of time is 20 minutes for all metal oxinates complex, which means that at this time the formation of nickel metal complex with the most stable oxine.

4. Conclusion
Conclusions that can be taken based on research data are as follows:
- The optimum condition of Fe(III)-Oxinate is obtained at 470 nm, optimum oxine concentration 0.1 M, optimum agitation time for 20 min, optimum pH is pH 2 and stability time of Fe(III)-Oxinate formed is at the time to-20 minutes.
- The optimum condition of the compound complex of Pb(II)-Oxinate was obtained at the wavelength of 405 nm, the optimum concentration of 0.35 M oxine, the optimum time of shaking for 15 min, the optimum pH is pH 3 and the stability time of Pb(II)-Oxinate formed is at the time to-20 minutes.
- The optimum condition of the compound of Cu(II)-Oxinate was obtained at 411 nm, optimum concentration of 0.1 M oxine, optimum time of shaking for 15 min, optimum pH is pH 3 and time of stability of Cu (II)-Oxinate formed is at the time to-10 minutes.

- The optimum condition of Zn(II)-Oxinate is obtained at wavelength 381 nm, optimum concentration of 0.15 M of oxine, optimum time of shaking for 10 min, optimum pH is pH 5 and stability time of Zn(II)-Oxinate formed is at the time to-10 minutes.
- The optimum condition of Ni(II)-Oxinate was obtained at 381 nm, optimum oxine concentration 0.1 M, optimum time of shaking for 15 min, optimum pH is pH 4 and time of stability of Ni(II) - Oxinate formed is at the time to-20 minutes.

References

[1]   Rochyatun, 2006. Distribusi Logam Berat dalam Air dan Sedimen di Perairan Muara Sungai Cisadane. MAKARA, SAINS, Vol. 10
[2]   Alloway, B.J. 1990. "Heavy Metal in Soils". New York: John Willey and Sons inc
[3]   Purwaningsih, Diah. 2009. "Adsorpsi Multi Logam Ag(I), Pb(Ii), Cr(Iii), Cu(Ii) dan Ni(II) Pada Hibrida Etilendiamino-Silika Dari Abu Sekam Padi". Jurnal Penelitian Saintek, Vol. 14, No. 1.
[4]   Firdaus, 2011. Studi Perbandingan Berbagai Adsorben Sintetis dan Alami Untuk Mengikat Logam. Universitas Bengkulu
[5]   Ika. 2012. Analisis Logam Timbal (Pb) dan Besi (Fe) Dalam Air Laut Di Wilayah Pesisir Pelabuhan Ferry Taipa Kecamatan Palu Utara. Jurnal Akademik Kimia. Vol 4. Hal 181-186
[6]   Wang, P. 1997. Recent Aplications of High-Performance Liquid Chromatography The Analysis Of Metal Complexes. Journal Of Chromatography A. Vol. 789. Halaman 437-451.
[7]   Arpadjan, S. 2012. Field Sampling, speciation, and determination of dissolved iron (II) and iron (III) in waters. Bulgarian chemical Communications, Vol 44, 299-306.
[8]   Deswati, 2013. Optimasi Penentuan Besi, Kobalt dan Nikel dalam Air Laut secara Votammetri Stripping Adsorptif (AdSV). Jurnal Prosiding Semirata FMIPA di Universitas Lampung. Padang: UNAND.
[9]   Sarzanini, Corrado. 1997. Determination and speciation of metals by liquid chromatography. Journal of Chromatography. Vol 798. Page 301 – 312.
[10]   Yan, Z., Haddad, P. R., Fritz, J. S., 2003, Ion chromatography on reversed-phase materials coated with mixed cationic and nonionic surfactants, J. Chromatogr. A, 985, 359-365
[11]   Amin, M., Lim, L. W., Takeuchi, T., 2007, Tunable separation of anions and cations by column switching in ion chromatography,Talanta, 71, 1470.
[12]   Kaiser, E. J., Rohrer, S., Jensen, D., J. (2001), Determination of trace anions in high-nitrate matrices by ion chromatography, J. Chromatogr. A, 920, 127-133.
[13]   Oktavia, B., Lim, L.W., Takeuchi, T., 2008, Simultaneous determination of Fe(III) and Fe(II) via Complexation with Salicylic Acid and 1,10 Phenanthroline in Microcolumn Ion Chromatography, Analytical Sciences, Vol 24, 1487-1492.
[14]   Ito, K., Takayama, Y., Makabe, N., Mitsui, R., Hirokawa, T., 2005, Ion chromatography for determination of nitrite and nitrate in seawater using monolithic ODS columns, J. Chromatogr. A, 1083, 63-67.
[15]   Rong, L., Takeuchi, T. (2004), Determination of iodide in seawater and edible salt by microcolumn liquid chromatography with poly (ethylene glycol) stationary phase, J. Chromatogr. A. 1042: 131-135.
[16]   Connolly, D., Paull, B., 2002, Fast ion chromatography of common inorganic anions on a short ODS column permanently coated with didodecyldimethylammonium bromide, J. Chromatogr. A, 953, 299-303.
[17]   Pimrote, W. 2012. Simultaneous Determination of Heavy Metals In Drinking Waters And Wines By Methods : Ion Pair Reversed Phase High Performance Liquid Chromatography And Capillary Zone Electrophoresis. International Food Research Journal, Vol.19, No.3, Halaman : 1079-1088.
[18]   Day dan Underwood. 2002. Analisa Kimia Kuantitatif. Jakarta : Erlangga.
[19]   Skoog, Douglas. 2004. Fundamental of Analytical Chemistry. Eight Edition.Canada.

[20] Stary, J., 1963, Systematic study of the solvent extraction of metal oxinates, Anal. Chim Acta, Vol 28, 132-149.

[21] Nagaosa, Y. 1995. Reversed-Phase High-Performance Liquid Chromatographic Determination Of Molibdenum And Manganese In Sea Water As Chelates With 8-Hidroxyquinoline. International Journal Enviromental Analytical Chemistry. Vol. 61, pp 231-237.

[22] Takeuchi, T., Inoue, S., Yamamoto, M., Tsuji, M., Miwa, T., 2001, Fluometric determination of magnesium and aluminium via complexation with oxine in high performance liquid chromatography, Journal of Chrom., A., Vol 910, 373-376.

[23] Devita, Liza. 2012."Penggunaan Beberapa Pelarut Organik Dalam Ekstraksi Besi(III) Dengan Oksin Secara Ekstraksi Pelarut". Jurnal Saintek. Vol IV No. 2:175-184

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