

# Optimization and Determination of Fe-Oxinate Complex by Using High Performance Liquid Chromatography

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**Abstract.** The need for iron will improve the industrial processes that require iron as its raw material. Control of industrial iron waste is very important to do. One method of iron analysis is to conduct indirect analysis of iron (III) ions by complexing with 8-Hydroxyquinoline or oxine. In this research, qualitative and quantitative tests of iron (III) ions in the form of complex with oxine. The analysis was performed using HPLC at a wavelength of 470 nm with an ODS C18 column. Three methods of analysis were performed: 1) Fe-oxinate complexes were prepared in an ethanol solvent so no need for separation anymore, (2) Fe-oxinate complexes were made in chloroform so that a solvent extraction was required before the complex was injected into the column while the third complex was formed in the column, wherein the eluent contains the oxide and the metal ions are then injected. The resulting chromatogram shows that the 3rd way provides a better chromatogram for iron analysis.

## 1. Introduction

Iron metal in ordinary waters is found in the form of Fe (II) and Fe (III) cations. Fe (II) cations are less stable than Fe (III) cations because they will rapidly oxidize into Fe (III) cations (Arpadjan, 2012). Analysis of iron content and iron ion speciation is very important in determining the quality of a water. Octavia et al. (2008) have performed Fe (II) and Fe (III) simultaneous analyzes through conical formation with salicylic acid and fenantrolin using micro column on ion chromatography. The iron content of iron that exceeds the concentration of 0.31 mg / L in the river can cause rust on clothing, porcelain, water pipe and cause unpleasant taste in drinking water coming from the river (Achmad, 2004).

The use of a complex in quantitative metal analysis using HPLC may increase the sensitivity of separation and selectivity of metal ion separation (Pimrote, 2012). The metal can be converted into complex compounds by extraction of neutral chelate formation in an organic solvent containing a complex (Day 2002).

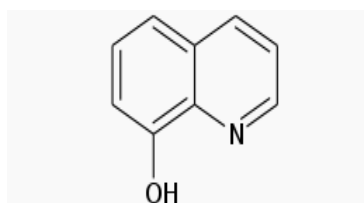
One of the complexing reactions is the formation of chelate complex compounds with organic reagents, ie 8-hydroxyquinoline which is often also called by the name of trivial oxine. Oxine is a widely used substance in the fields of analytical, inorganic and organic chemistry since the 1960s (Morrison, 1965 and Sary, 1963). Further Takeuchi, et al (2001) has also used oxine as a complex in the determination of magnesium and aluminum by using fluorescent HPLC.

Here is a description of iron and oxine. Iron has atomic number 26, density 7,874 g / cm<sup>3</sup> (20°C), electron configuration [Ar] 3d<sup>6</sup> 4s<sup>2</sup>, melting point 1536°C, boiling point 2750 °C, atomic radius 126



pm (coordination number 12), and abundance in earth crust 62000 ppm (Sugiyarto, 2003). Pure iron is quite reactive. Fast iron is oxidized by moist air to form iron (III) oxide hydrate (rust). The metal is easily soluble in mineral acids. With non-oxidizing acids without air, Fe (II) is obtained. In the presence of air or when used HNO<sub>3</sub>, some iron becomes Fe (III). Extremely strong oxidizing media such as concentrated HNO<sub>3</sub> or dichromate-containing acids make passive iron (Cotton, 1989).

Oxine has a molecular weight of 145.15 g / mol with the molecular formula C<sub>9</sub>H<sub>7</sub>ON, is a white crystalline compound with a melting point of 74-76 ° C. It is almost insoluble in water and ether, but is highly soluble in alcohol, chloroform, benzene and mineral acid solutions. Oxy is an amphoteric in solution, because it has a nitrogen group and a phenolic hydroxy group. The chemical reaction between the oxide and the metal forms the inner complex compound, in which the metal ion forms a coordination bond with the Nitrogen (N) atom or oxygen atom (O) of the carboxyl group to form a stable fifth circumference.



**Figure1.** Oxine Structure (Day, 2002)

The Fe (III) ion is extracted quantitatively with the oxine in a pH atmosphere between 1.9 to 12.5 producing Fe-Oxinate, wherein the complex dissolves in chloroform by forming a yellow color and gives absorption at a wavelength of 470 nm by a spectrophotometer (Stary, 1963). The reaction between Fe (III) with the oxin takes place with the reaction equation as follows:



The oxine is very soluble in alcohol and alcohol can also dissolve easily in water. With this fact there can be several methods in the formation of Fe-oxinate complexes, ie if the oxides and metal ions can form complex compounds in alcohol, no solvent extraction step is required to separate the organic phase. Then the complex can also be formed directly in the chromatographic column and the latter complex is formed by using oxine in chloroform and then followed by solvent extraction before entering into the separation column. All Fe-oxinate analyzes were performed using HPLC and ODS C-18 columns.

In this research, we have determined the Fe (III) ion by using oxine as complexing by doing 3 complex forming method and analysis. A comparison of these three methods can be used to determine Fe (III) content indirectly using HPLC.

## 2. Experimental

### 2.1. Apparatus

The experimental apparatus was assembled from a HPLC Agilent 1120 with an injection-loop volume of 20 µl, UV-Vis detector, a ODS C-18 column (150×4.6 mm I.D.). Spektronik Genesys 20 D, pH meter merk Hanna Instrument HI2211, analytical balance, separating funnel, glassware (measuring flask, test tube, beaker, dropper, stirring rod) and reagent bottle.

### 2.2. Chemicals

Analytical reagent grade chemicals were purchased from Merck, unless otherwise noted. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Oxine, Chloroform, Methanol, Ethanol, Asetonitril, HNO<sub>3</sub>, NaOH dan aquades.

### 2.3. Research Procedure

**2.3.1. Determination of Wavelength of Fe-Oxinate Complex.** A total of 1 mL of Fe (III) solution of 10 ppm was added to the reaction tube and 3.5 mL of 0.1 M oxine was dissolved in ethanol. The directly formed complex is measured using Spectronic at a wavelength of 400 - 600 nm.

**2.3.2. Determination of Stability Time of Metal Oxinate Complex.** The 10 ppm Fe (III) ion solution is inserted into the separating funnel. Then 0.1 M oxine is added to solution. Extract for 20 minutes for Fe (III) to water phase and separate organic phase. Taken its organic phase and measured its complex uptake with a variation of measuring time duration of 0-150 minutes with a span measurement of 10 minute absorbance value using Spectronic.

**2.3.3. Determination of Fe-Oxinate complex analysis using HPLC.** There are 3 methods for the analysis of Fe oxidation complex as follows :

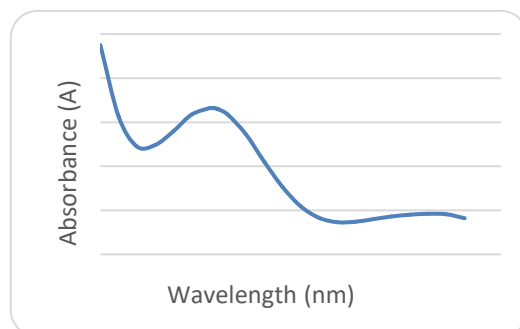
- The Fe-Oxinate complex is formed by using oxine dissolved in ethanol. The complex formed does not need to be separated and then injected into HPLC for further analysis. The Fe-oxinate complex is injected 20  $\mu$ l into the ODS C18 column at maximum wavelength using the mobile phase Ethanol: Water = 50: 50 with an eluent flow rate of 0.8 mL / min.
- Formation of Fe-oxinate complex using oxine dissolved in chloroform. Fe oxinate complex that is formed needs to be separated by solvent extraction. Then as much as 20  $\mu$ L sample is injected into the injector. The analysis was performed using the ODS C 18 column at maximum wavelength. The mobile phase Ethanol: Water = 50: 50 with an eluent flow rate of 0.5 mL / min.

Fe (III) ion analysis is done by forming Fe Oxinate complex in column. Eluen used is 0.1 M oxine in ethanol. The Fe (III) ions injected into the column will then form the Fe oxinate complex when encountered with the oxin in the mobile phase. The analysis was performed using the ODS C 18 column at maximum wavelength. The mobile phase Ethanol: Water = 50: 50 with an eluent flow rate of 0.5 mL / min.

## 3. Results and Discussion

### 3.1. Determination of Wavelength of Fe-Oxinate Complex

The determination of the maximum wavelength of Fe-oxinate complex has been determined by the following conditions; as much as 1 ml of Fe (III) solution of 10 ppm inserted into the reaction tube added 3.5 mL of 0.1 M oxine which has been dissolved in ethanol. The complex is formed yellow. The formed complexes are not separated by solvent extraction because there is no phase difference between the water solvent and the ethanol solvent. With such method it is possible to save the analysis time without treating solvent extraction such as separation method with other complex formation. So that the formed complex can be directly measured using Spectronic UV-Vis at wavelength 400 - 600 nm.

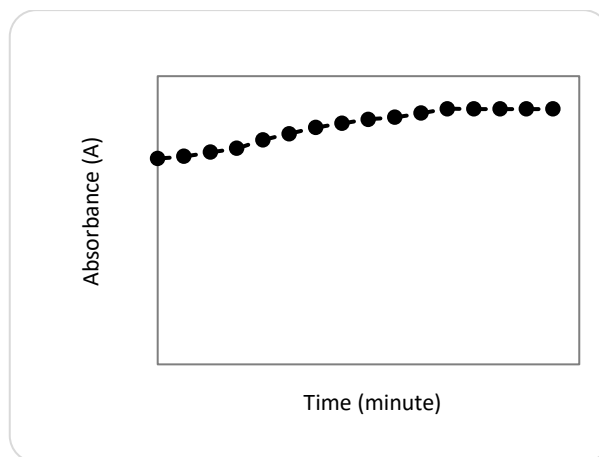


**Figure 2.** Wavelength curve of Fe-oxinate complex.

Based on the data of the maximum wavelength determination in figure 2 above, it was found that the Fe-oxinate complex formed in ethanol gave maximum wavelength in the 465-470 nm range. The wavelength 470 nm was chosen as wavelength in measurement by HPLC.

### 3.2. Determination of Wavelength of Fe-Oxinate Complex

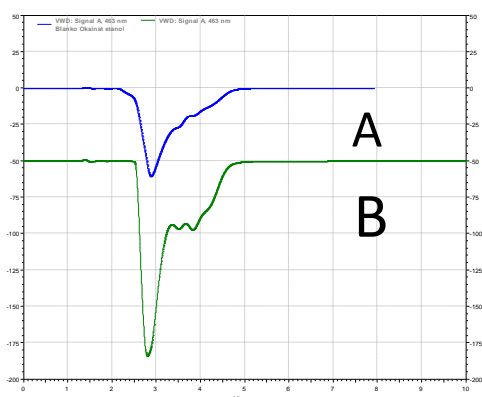
At intervals of 110 to 150 minutes there is a stable uptake of the Fe (III) -Oxinate complexes formed. So that at 110 min is the optimum time of the stability of Fe (III) -Oxinate complex which is good for analysis.



**Figure 3.** The curve of the relationship between complex stability time and absorbance.

### 3.3. Determination of Fe-Oxinate complex analysis using HPLC

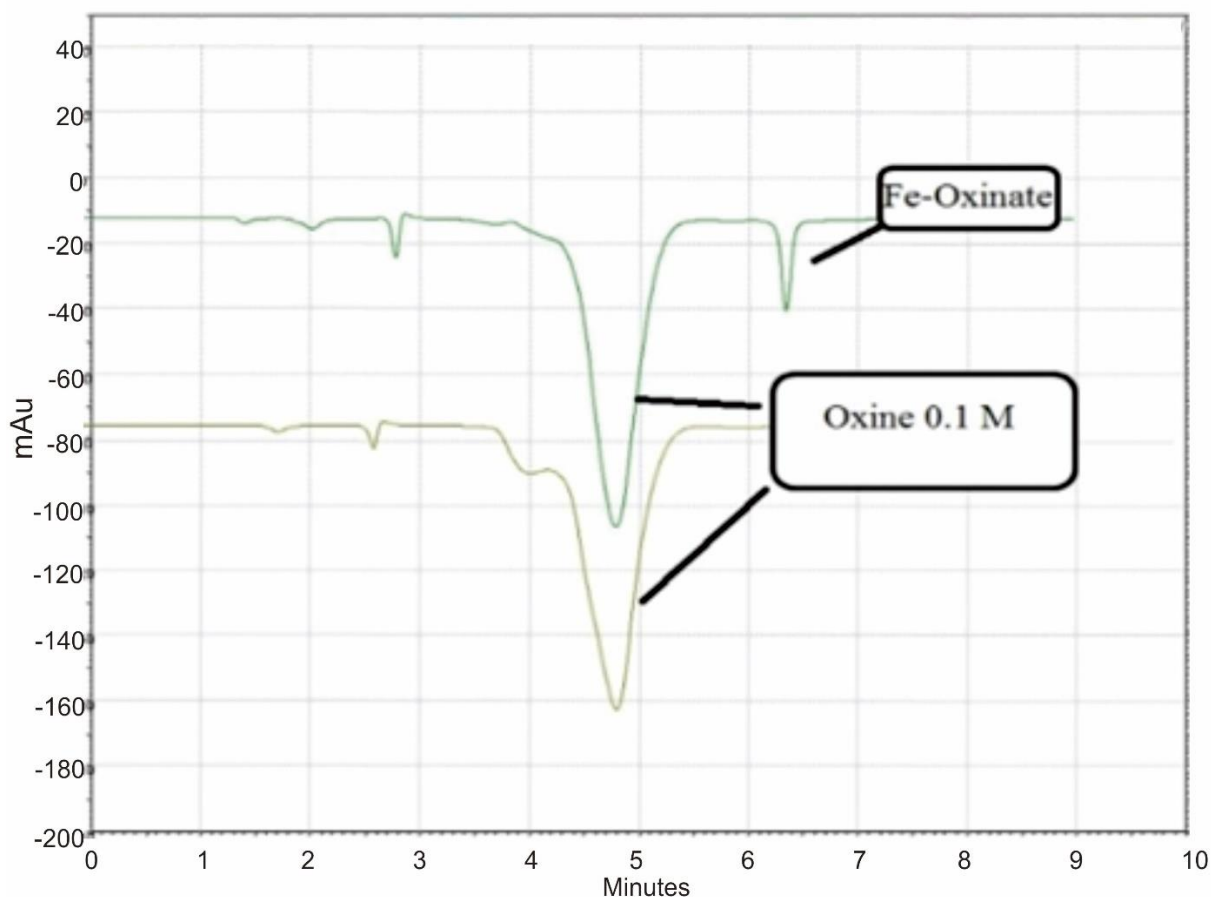
**3.3.1. The first method.** The Fe-Oxinate complex is formed by using oxine dissolved in ethanol. The complex is formed in ethanol, so there is no need for extraction. The formed complex is then injected 20  $\mu$ L into the ODS C18 column at 470 nm wavelength using the mobile phase Ethanol: Water = 50: 50 with an eluent flow rate of 0.8 mL / min. The retention time of the Fe-Oxinate complex arises at minute 2.8



**Figure 4.** Chromatogram of Fe (III) metal ion analysis in the form of oxinate complex; A) Oxine blends in ethanol and B) Fe-oxinate Complex.

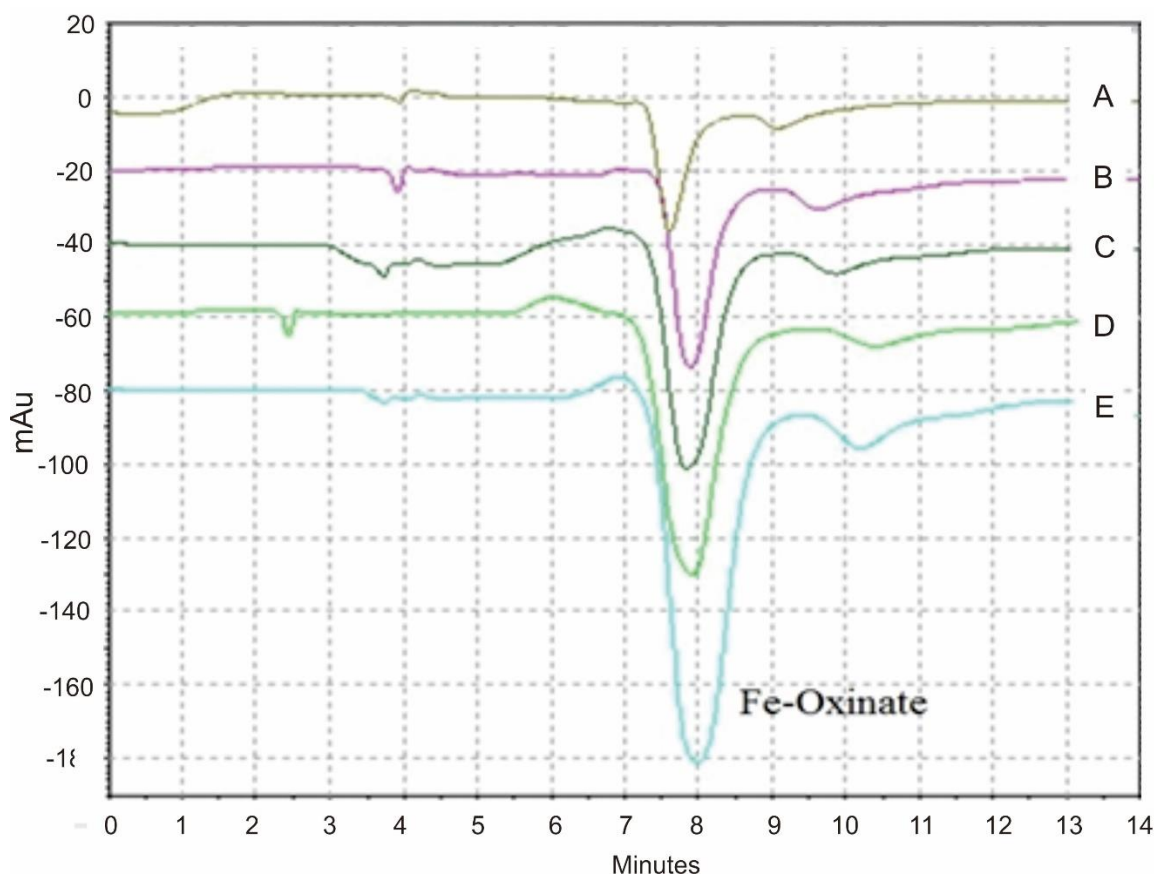
**3.3.2. The second method.** Formation of Fe-oxinate complex using oxine dissolved in chloroform. The complex is formed in chloroform, so there is need for extraction. The formed complex is then injected 20  $\mu$ L into the ODS C18 column at 470 nm wavelength using the mobile phase Ethanol: Water = 55:

45 with an eluent flow rate of 0.5 mL / min. The retention time of the Fe-Oxinate complex arises at minute 7.1.



**Figure 5.** Chromatogram of Fe (III) metal ion analysis in the form of oxinate complex, by using chloroforms as solvent.

*3.3.3. The last method. Fe (III) ion analysis is done by forming Fe Oxinate complex in column. The complex is formed in column HPLC, so there is no need for extraction. The ion  $\text{Fe}^{3+}$  is then injected 20  $\mu\text{l}$  into the ODS C18 column at 470 nm wavelength using the mobile phase Ethanol: Water = 55: 45 with an eluent 0.1 M oxine in ethanol, flow rate of 0.5 mL / min. The retention time of the Fe-Oxinate complex arises at minute 2.8.*



**Figure 6.** Chromatogram of Fe (III) metal ion analysis in the form of oxinate complex, by using oxine as mobile phase.

#### 4. Conclusion

Based on the results obtained can be concluded that: The Fe-oxinate complex may form in an organic phase at a maximum wavelength of 470 nm. The optimum time of the stability of Fe (III) -Oxinate complex is 110 minutes. There are 3 methods of determining the concentration of Fe-oxinate complex. The complex formation in the chromatographic column provides the best chromatogram in the analysis.

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