

Studies on Solvent Extraction Using Salphen for Separative Determination of Trace Fe(II) and Fe(III) in Water Samples

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Solvent extraction using salphen as a ligand has been investigated for the selective separation and determination of trace Fe(II) and Fe(III). A salphen ligand was synthesized, and solvent extraction variables, such as solution pH, the concentration of salphen, the type of organic solvent, auxiliary agents, oxidants and the effect of interference were optimized. Salphen is stable at pH 3-4, and Fe(III)-salphen complexes can be selectively extracted into an MIBK(4-methyl-2-pentanone) phase from an aqueous solution within this pH range. For the determination of the total amount of iron in 100 mL of aqueous solution, Fe(II) ions were completely oxidized using 0.05 mL of 3.5% H₂O₂ without side reactions. To evaluate its applicability, the proposed method was applied to determine trace Fe(II) and Fe(III) in several kinds of water samples. Reproducible results were obtained with RSD of less than 3.0%, and the recoveries for this reliability were obtained with 91-112%.

Key Words : Solvent extraction, Selective separation, Fe(II), Fe(III), Salphen

Introduction

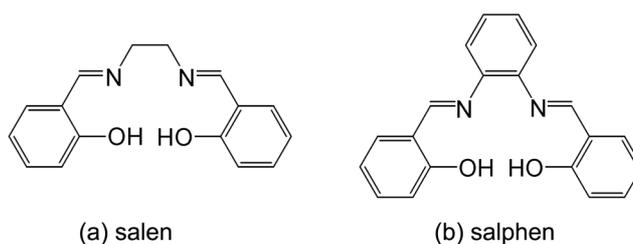
Since Schiff bases were first used as homogeneous catalysts for epoxy resins, they have been also widely employed as catalysts in various organic syntheses in the form of metal-Schiff base complexes.¹⁻³ Recently the application of metallosalen complexes has determined protein structures and DNA base sequences using the complexes' site selective binding with a nucleic acid and DNA.^{4,5} In addition, conducting polymer thin films containing metallosalen derivatives have been studied for semiconductor applications.^{6,7} These various surveys are based on the fact that a wide variety of chiral Schiff base complexes are easily synthesized by introducing substituents.

Although Schiff bases are important to researchers in various scientific fields, they are not widely used in analysis, because most Schiff bases are not only water insoluble but also unstable in the acidic region.⁸ As a result, salphen has very few analytical applications.

Qyaizusms⁹ reported the crystal structure of a salphen-Cr(III) complex and its reactivity. Fitzsimmons¹⁰ reported the study on spin-state equilibrium in an Fe-salphen complex. Recently Schiff base salphen was applied to determine nickel, cobalt and copper by solvent sublation and foam fractionation in our laboratory.¹¹

The structure and reactivity of the Schiff base salphen prepared by the condensation reaction of salicylaldehyde with phenylenediamine are similar to those of salen.¹² The main difference between them is size a result of the introducing of a phenyl group containing reactant. This size difference can decrease water solubility but also reduce the effects of protons by lowering the electronic density of the lone pair electrons of nitrogen atoms.

Because the analytical applicability of salphen has been



Scheme 1. The structures of salen(a) and salphen(b).

shown in previous studies, extended investigations into the analytical applications of Schiff base salphen are needed. As mentioned above, Schiff bases are easily decomposed in the acidic range, therefore their use in the separation and concentration of metal ions in acidic range is limited.¹² Particularly iron can form iron hydroxide above pH 4, so spectrophotometric determination of Fe(II) and Fe(III) in the basic range is far too difficult.

In the present study, we synthesized salphen (*N,N'*-bis-salicylidene phenylenediamine) and used it as an organic chelating agent to extract and determine trace Fe(II) and Fe(III) in aqueous solutions. For the application to analysis, solvent extraction conditions such as solution pH, the types of organic solvents, the concentration of salphen chelate, the influence of auxiliary reagents and interference ions were examined. Based on optimized conditions, we performed determination of trace Fe(II) and Fe(III) in water samples for an estimation of availability.

Experimental Section

Reagents and instruments. Analytical grade reagents were used without further purification and deionized water was obtained by the purification of distilled water with the

Table 1. Operating conditions of flame atomic absorption spectrophotometer

	Fe
Wavelength (nm)	248.0
Curren (mA)	30
Slit width (nm)	0.7
Signal mode	Absorbance
Fuel (L/min)	C ₂ H ₂ (2.0)
Replicate	7

MILLIQTM water system of Millipore Company. An analytical grade ammonium ferrous sulfate hexahydrate and ammonium ferric sulfate dodecahydrate (Fluka Co., U.S.A.) were dissolved with a small volume of HNO₃ and diluted to 10,000 mg/L with a deionized water, which were diluted to the proper concentration for use. Salphen was synthesized by the method reported previously by this laboratory,¹¹ and it was characterized by FT-IR (Fourier transform infrared spectroscopy) and NMR (Nuclear magnetic resonance) spectroscopy. All solvents used were of HPLC grade. We conformed the synthesized salphen with an Oxford Mercury 300 NMR spectrometer and an Excalibur FT-IR spectrometer. A Perkin-Elmer model 2380 flame atomic absorption spectrophotometer was used to measure the absorbance of analytes. The instrumental conditions are given in Table 1.

Experimental procedure. A 100 mL of sample solution was taken in a 250 mL separatory funnel, and a given amount of NaCl was added to control solution matrix at 0.3 mol/L of NaCl. The pH was adjusted at 3 by adding potassium hydrogen phthalate/HCl buffer solution. The oxidation of Fe (II) was performed by adding 0.05 mL of 3.5% H₂O₂ to quantify total iron in solution. 3 mL of 0.3% salphen in DMF(dimethylformamide) was added to the prepared solution, followed by extraction with 10 mL of MIBK. The absorbance of the extracted complexes in the organic phase was measured by Atomic absorption spectroscopy. A series of Fe(III) standards was prepared, and their absorbance was measured by AAS to construct a calibration curve. This calibration curve was used for the determination of Fe(III).

Results and Discussion

The effect of pH on the extraction of Fe(II)- and Fe(III)-salphen complex. A stable complex of metal-salphen should be formed for it to be effectively extracted with solvent.¹³ And the formation of the complex is strongly influenced by solution pH because the salphen is a weak dibasic acid. Therefore, we investigated the extraction efficiency of salphen complexes of Fe(II) and Fe(III) by changing the pH of the aqueous solution. The absorbance of analytes was measured and compared over the pH 1-8 range to examine changes in the extraction efficiency as a function of pH. But the solution of water-insoluble salphen in DMF was added to sample solutions.

As shown in Figure 1, the extraction efficiency of both

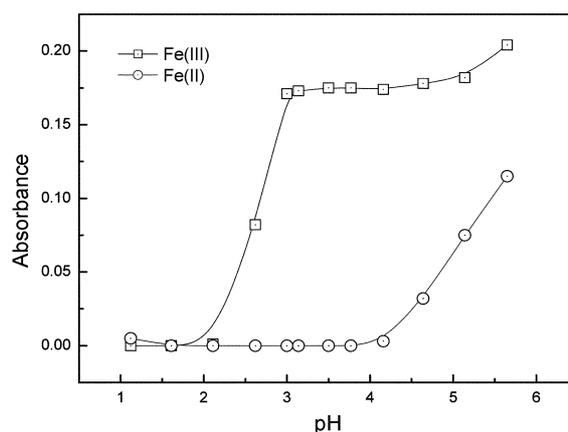


Figure 1. Extraction efficiency of salphen complexes of Fe(II) and Fe(III) depending on the pH of sample solutions under other optimum conditions. Concentrations of Fe(II) and Fe(III): each 0.3 mg/L, added salphen: 3 mL of 0.3% DMF solution.

Fe(II) and Fe(III) was low at pH values less than 2. Fe(II) was rarely extracted at pH 2-4, whereas the extraction efficiency of Fe(III) started to increase rapidly at pH 2. The acidic form of salphen did not form complexes with Fe(II) and Fe(III) below pH 3, but the salphen as organic chelating agent did form a stable complex with Fe(III) above pH 3. In addition, Fe(II) did not form a stable complex and, thus, could not be extracted below pH 4. Therefore, if the pH of an aqueous solution is adjusted to pH 3-4, Fe(II) and Fe(III) can be separated and determined selectively. Also, we determined salphen to be stable under weak acidic conditions because it formed a complex with Fe(III) in a weak acidic solution.

Meanwhile, the extraction efficiency of Fe(II) increased at pH values higher than 4 because of increased salphen anions with the decrease in acidity in aqueous solution. But we do not see this phenomenon as distorting the result, *i.e.* if the pH of an aqueous solution is adjusted to pH 3-4, Fe(III) can be extracted selectively.

In the present study, both Fe(II) and Fe(III) were extracted simultaneously and selectively by controlled pH. So, the pH of the aqueous solution was adjusted to pH 3 using potassium hydrogen phthalate/HCl buffer solution.

The amount of salphen needed for the efficient extraction. In general, the concentration of chelating agent greatly affects extraction efficiencies in solvent extraction because excess chelate can form a stable and stoichiometric metal chelate. In other words, if the amount of chelate is not enough to form complexes with metal ions, errors should occur.¹³ In addition, the direct addition of salphen to an aqueous solution also can be an effective way of stoichiometric complexation with metal ions. Therefore, we dissolved salphen in DMF. To fix the optimum concentration of salphen as a chelating agent, the changes in the separation and extraction efficiency of Fe(II) and Fe(III) were examined adding 3 mL of salphen solution in the concentration range from 0.1% to 0.7%.

As shown in Figure 2, Fe(III) was well separated from

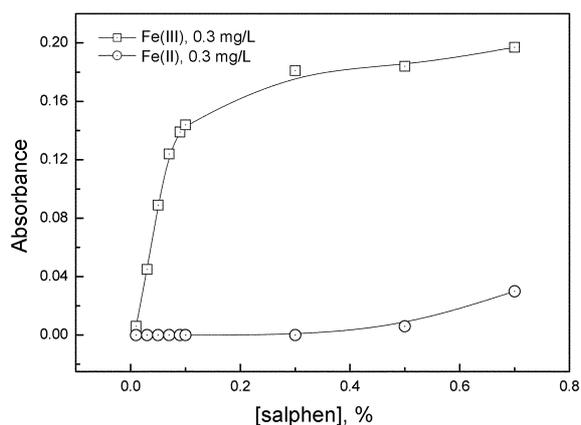


Figure 2. Separation and extraction efficiencies of Fe(II) and Fe(III) according to the concentration of salphen used. Concentrations of Fe(II) and Fe(III): each 0.3 mg/L, solution pH: 3.

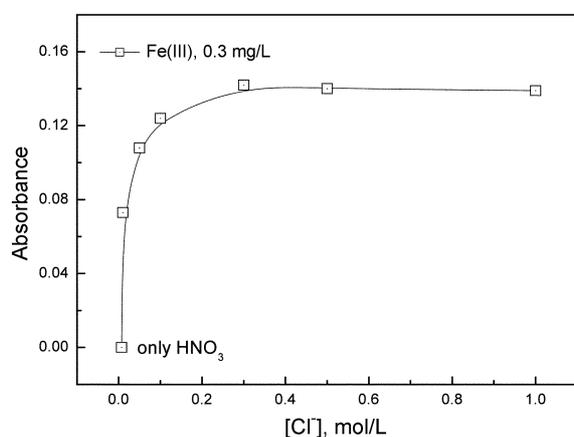


Figure 3. Variation of extraction efficiency of Fe(III)-salphen depending on the concentration of chloride ion under other optimum conditions.

Fe(II) and extracted quantitatively at 0.3% salphen. Thus 3 mL of 0.3% salphen solution (2.84×10^{-4} mol/L) was used in this experiment.

Effects of auxiliary reagent on extraction. An analyst cannot determine the sample matrix at his or her convenience, and so the suggested analytical method can be applied to samples with various matrices.¹³ Solvent extraction is achieved by exploiting the differences in the distribution of complexes between solvents with different properties, and therefore, fast phase separation and overcoming matrix differences are necessary.

In the present study, Fe(III)-salphen complexes in an aqueous solution have charge because of the unbalanced charge between salphen and Fe(III). The charge must be neutralized to be distributed in the less polar organic phase. To satisfy all requirements, NaCl was added to the aqueous solution, and the extraction characteristics of Fe(III) were examined at different Cl⁻ ion concentrations (Figure 3).

There was no Fe(III) extraction without Cl⁻ ions. That means Fe(III)-salphen complexes are positively charged and cannot be distributed within the organic layer without charge

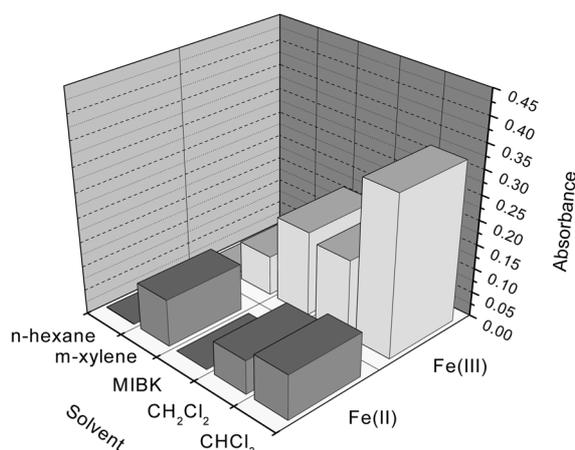


Figure 4. Separation and extraction efficiencies of Fe(II) and Fe(III) depending on the type of solvent under optimum condition of each solvent used.

neutralization. The extraction efficiency of Fe(III) increased with increasing chloride concentration. All Fe(III)-salphen complexes were neutralized by 0.3 mol/L of chloride ions because the absorbance of Fe(III) is constant at concentration above 0.3 mol/L of chloride ion. Thus, 0.3 mol/L of NaCl was selected as an auxiliary reagent.

The types of organic solvent for the extraction of the Fe(III)-salphen complex. The solvent's affinity for the complexes greatly influences the extraction efficiency and detection limit of the analyte in solvent extraction. Therefore, organic solvents must effectively solvate metal-salphen complexes in aqueous phase. For the best choice, in general, the polarity of complexes and organic solvents must be considered. But we could not precisely determine the structure of the Fe(III)-salphen complexes. Therefore, the extraction and separation efficiencies of Fe(II) and Fe(III), using solvents of different polarity, such as CHCl₃, CH₂Cl₂, MIBK, *m*-xylene and *n*-hexane, were examined for the best organic solvent choice.

As shown in Figure 4, CHCl₃ and CH₂Cl₂ showed higher extraction efficiencies but low separation efficiencies, and *m*-xylene and *n*-hexane showed lower absorbances and separation efficiencies. MIBK showed a lower extraction efficiency compared with more polar solvents, but it could selectively separate Fe(III). Differences in solvent polarity should influence the extraction efficiencies of solvents. On the other hand, MIBK has been widely used as a solvent for solvent extraction because of high extraction efficiency and low background in the atomic absorbance measurement.¹² Most of all, MIBK exhibits ideal combustion properties in trace analysis. On considering such phenomena, MIBK was selected as a proper solvent.

The types and concentration of oxidants. The purpose of our study is to separate and concentrate Fe(III) from the sample solution, which includes Fe(II) and Fe(III). But, if only Fe(II) has to be determined, the oxidation of unextracted Fe(II) to Fe(III) is necessary for determining the total amount of iron by given procedure.¹⁴

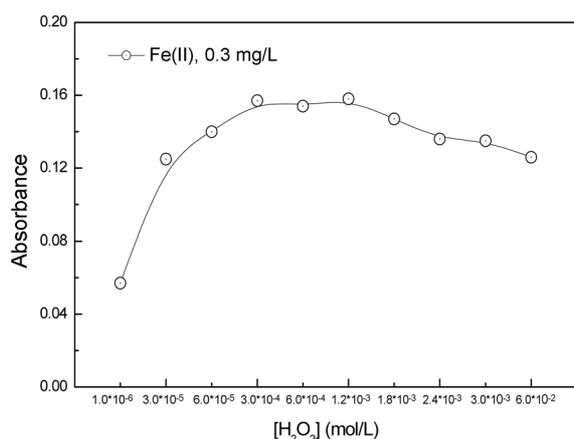


Figure 5. Optimum concentration of hydrogen peroxide for oxidation of Fe(II).

Various oxidizing agents are available, but increasing the ion amount by adding oxidizing agents to an aqueous solution is not favorable. Therefore, the oxidation of Fe(II) to Fe(III) was performed with H₂O₂. To determine the optimum concentration of H₂O₂ as an oxidant, the oxidation of Fe(II) in 100 mL of 0.3 mg/L Fe(II) solution was performed over the range of 1.00×10^{-6} mol/L ~ 6.00×10^{-2} mol/L H₂O₂.

As shown in Figure 5, Fe(II) could be quantitatively oxidized at higher than 3.00×10^{-4} mol/L H₂O₂; however, complex extraction decreased at higher than 1.80×10^{-3} mol/L H₂O₂. This problem occurs because of the decomposition of salphen by excess H₂O₂. Therefore, 50 μ L (0.05 mL) of 3.5% H₂O₂ (1.80×10^{-3} mol/L) was used for quantitative oxidation of Fe(II) in 3 mg/L of Fe(II) solution. The oxidation was also performed at different a concentration of Fe(II) and Fe(III) to evaluate whether oxidation is quantitative.

As shown in Table 2, various concentrations of Fe(II) and Fe(III) were evaluated, and reproducible results were obtained

Table 2. Recoveries of total iron from various concentrations of each Fe(II) and Fe(III) in 0.3 mol/L NaCl

Sample	Added (mg/L)			Recovered (mg/L)		
	Fe(II)	Fe(III)	Total	Fe(II)	Fe(III)	Total
1	0.00	0.30	0.30	0.00	0.30	0.31
2	0.05	0.25	0.30	0.05	0.25	0.31
3	0.10	0.20	0.30	0.10	0.20	0.32
4	0.15	0.15	0.30	0.15	0.15	0.31
5	0.20	0.10	0.30	0.20	0.10	0.32
6	0.25	0.05	0.30	0.25	0.05	0.32
7	0.30	0.00	0.30	0.30	0.00	0.31

*RSD(%) 0.7

*Relative standard deviation for the mean value of 7 measurements

Table 3. Interference of concomitant elements in determination of Fe(III) in water samples

Elements	Maximum concentration studied	Interference	Elements	Maximum concentration studied	Interference
Na ⁺		–	Ni ²⁺	1.0 mg/L	–
K ⁺		–	Co ²⁺	1.0 mg/L	–
Ca ²⁺		–	HCO ₃ [–]		–
Mg ²⁺		–	Cl [–]		–
Cu ²⁺	1.0 mg/L	–	NO ₃ [–]		–
Zn ²⁺	1.0 mg/L	–	SO ₄ ^{2–}		–
Mn ²⁺	1.0 mg/L	–			

ed with RSD of less than 0.7%. As a result, all Fe(II) could be oxidize to Fe(III) by using the indicated concentration of H₂O₂.

Interference of concomitant ions. Chelating agents cannot selectively bond to the metal ions of interest, and then analytes compete with concomitant ions bound to

Table 4. Analytical results of real samples

Sample	Total Fe			Fe(III)			Fe(II)		
	Added (mg/L)	Found (mg/L)	Recovered (%)	Added (mg/L)	Found (mg/L)	Recovered (%)	Added (mg/L)	Found (mg/L)	Recovered (%)
Tap Water	0	0.06		0	0.03		0	0.03	
		*0.9			*0.9			*0.7	
	0.30	0.36	100	0.15	0.18	100	0.15	0.17	93
	*2.3			*0.5			*2.1		
River Water	0	0.20		0	0.17		0	0.03	
		*2.2			*1.0			*1.4	
	0.30	0.51	103	0.15	0.34	113	0.15	0.17	93
	*1.0			*1.4			*1.0		
Sea Water	0	0.11		0	0.09		0	0.02	
		*0.7			*0.7			*0.0	
	0.30	0.40	97	0.15	0.24	100	0.15	0.16	93
	*1.0			*0.1			*0.7		

*Relative standard deviation for the mean value of 7 measurements.

chelating agents. Therefore, we experienced a reliability problem with a sample complex matrix. The extent can be estimated by comparing complexation constants, but the estimation for a new chelating agent is not simple, owing to the lack of basic parameters. We considered what should be expected of ions and the interference of concomitant ions within their concentration range (Table 3).

In the present work, interference from concomitant ions was investigated in seawater, which has a complex matrix and concomitant ions competing with iron. There was no interference during the determination of trace ions, using salphen for seawater.

Analysis of real samples. An optimized procedure was applied to the determination of trace Fe(II), Fe(III) or total Fe for several kinds of water samples (tap water, river water, seawater). For the analysis of river water and seawater, 10 mL of concentrated nitric acid was added to 10 L samples to prevent adsorption of analytes to floating materials or container walls. First, according to given procedure, we prepared a series of standard solutions with different concentrations of Fe(III). Fe(III) was extracted with salphen, and the absorbance of iron was measured to build a calibration curve. This calibration curve was used for the quantification of iron. Unknown samples were analyzed using the same methods (Table 4).

As shown in Table 4, trace Fe(II), Fe(III) and total Fe in water samples could be effectively separated and determined.

And finally, a recovery test was performed to evaluate the reliability of the proposed method. 0.3 mg/L of Fe(III) was added to each samples, and the spiked samples were analyzed by the given procedure. Reproducible results of less than 2.5% RSD and the recoveries of 91-112% were obtained. Such results show that the method proposed here is reliable for the analysis of trace Fe.

Conclusion

In the present study, salphen was used as an organic

chelating agent for the determination of trace Fe in water samples through solvent extraction. The results are summarized as follows.

1) Fe(III)-salphen complexes were stable and selectively extracted with MIBK. They complemented decomposition problems of the existing Schiff base in the acidic region.

2) For the quantification of the total amount of iron in an aqueous solution, Fe(II) was completely oxidized to Fe(III), using H₂O₂.

3) There is no interference during extraction and determination of Fe(III), using salphen.

4) The proposed method is reliable for the analysis of trace Fe (II), Fe(III) and total Fe, and the recovery of 91-112% obtained from the three kinds of samples pointed to the proposed method as reliable for the analysis of samples of this type.

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