Study on Solvent Extraction Using Salen(NEt₂)₂ as a Chelating Agent for Determination of Trace Cu(II), Mn(II), and Zn(II) in Water Samples

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Solvent extraction using a Schiff-base, salen(NEt₂)₂, as a chelating agent has been conducted on several water samples to study the determination of trace Cu(II), Mn(II) and Zn(II). Experimental conditions for the formation and extraction of metal complexes were optimized with an aqueous solution similar in composition to the samples. The matrix difference between the sample and standard solutions was approximately matched, and the pH of each sample solution was adjusted to 9.5 with NaHCO₃/NaOH buffer. The concentration of salen(NEt₂)₂ was 7.3×10^{-3} mol/L, and the complexes were extracted into MIBK solvent followed by the measurement of AAS absorbance. The potential interference of concomitant ions was investigated, but no interference from alkaline and alkali earth ions was shown in this procedure. The given procedure is precise, as judged from the relative standard deviation of less than 5% for five measured data. The recovery of 93-103% shows that this method is quantitative for such trace metal analysis.

Key Words : Salen(NEt₂)₂, Trace analysis, Copper, Manganese, Zinc

Introduction

Developments in science and technology have enhanced the performance and reliability of analytical instruments but the complicated matrices of samples and the interference of concomitants still impose limitations. Therefore, separation techniques are needed to remove error sources, such as interference, or to separate and concentrate analytical constituents. Separation and pre-concentration techniques usually require the close attention of the experimenters and are relatively lengthy processes, but they are highly selective in the isolation of analytes and lower the detection limit of the corresponding analytical method.[1]

Advances in analytical techniques and the development and application of new analytical reagents are as important in trace analyses as the development of analytical instru-

Figure 1. Structures of salen and other cyclic compounds.

ments. Salen compound used for the synthesis of stereo selective epoxy resins can be employed as a new and effective analytical reagent.[2] In this regard, a look at its molecular structure is informative. That is, even though salen is an intermediate compound between 14-crown-4 and porphyrin as shown in Figure 1, salen can be more easily synthesized than other compounds, and the formation of some salen derivatives with substitutes is so easy that it can be used as a chelating agent for metal complexes. Furthermore, salen can form metal complexes of various sizes because of its opened structure.

Studies on the application of salen and its derivatives have been conducted in many fields of synthetic chemistry. Jacobsen *et al.*[3] used the Mn(II)-salen complex as a catalyst for the synthesis of chiral epoxy. Fukuda[4] synthesized the Co-salen-Br complex for use as a catalyst in the formation of a stereo selective cyclopropane. Li *et al.*[5] studied the synthesis of Ni-calix salen complex, concentrating on its structure, properties, and availability as a catalyst for polymerization. Jha *et al.*[6] used the Al-salen complex as a catalyst for the Michael addition reaction. Bandini *et al.*[7] synthesized the Cr-salen complex for use as a catalyst and examined its structure. Yamada[8] reviewed the synthesis of Ni- and Co-salen complexes and delved into their structures and spectroscopic properties. Metal-salen complexes are widely used as a stereo selective catalysts for organic reactions such as the Meerwein-Ponndorf-Verley reduction, Friedel-Craft reaction, Oppenaur oxidation, ene reaction, and aldol condensation.[9] Moreover, the application of metal salen complexes has been intensively studied in semiconductor technology and biochemistry.[10,11]

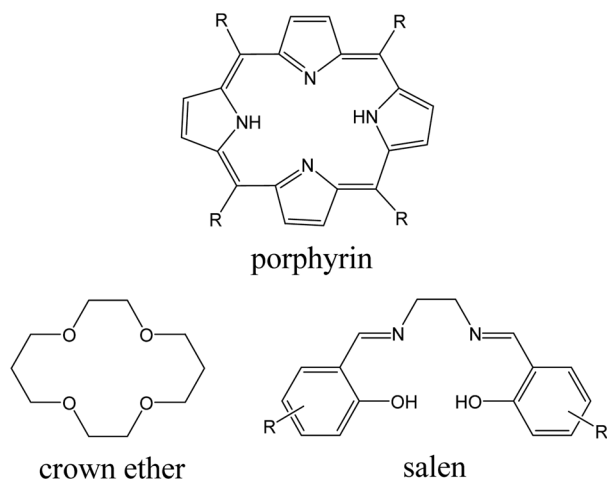In spite of their wide applicability, salen compounds are rarely used in a chemical analyses because of two serious

drawbacks. Salen compounds are insoluble aqueous solutions and they decompose easily in acidic solutions, limiting their use to basic condition.[12]

In the present work, a salen derivative, salen(NEt$_2$)$_2$ {*N,N'-bis*(4-diethylaminosalicylidene)ethylenediamine}, was synthesized to overcome these disadvantages and to be used as a chelating agent for the solvent extraction of trace Cu(II), Mn(II) and Zn(II) in an aqueous samples. An ethanolic solution of salen(NEt$_2$)$_2$ was directly added to the sample solutions to form metal complexes. Experimental conditions were optimized for the quantitative determination of the above elements in water samples by solvent extraction.

Experimental Section

Reagents and Instruments. Analytical grade and solvents of HPLC grade were used without any further purification. All solutions were made with deionized water obtained by filtering distilled water through a Millipore MILLI-Q^{TM} water system. The salen(NEt$_2$)$_2$ was synthesized by the method reported previously by this laboratory,[12,13] and it was characterized by FT-IR and NMR spectroscopy.

Artificial seawater was prepared to optimize experimental conditions for the trace analysis of elements. Only 10 major chemical species are present at concentrations of more than 1 mg/L in seawater. Therefore, the seawater was prepared with those elements at known concentrations.[14]

The absorbance of metal ions extracted was measured by a Perkin-Elmer model 2380 atomic absorption spectrometer. Table 1 lists the instrument's operating conditions. We measured the pH with a pH meter (Model 744, Metrohm. Ltd., Herisau, Switzerland, correcting it with buffer solutions before measurements.

Procedures. The ionic strength of 100.0 mL of sample solution was adjusted to 0.1 mol/L by adding 2.9 g of NaCl, and the solution's pH was adjusted to 9.5 by the addition of 10 mL buffer solution of NaHCO$_3$/NaOH buffer solution. 10 mL of the ethanolic solution of salen(NEt$_2$)$_2$ (1.22 × 10^{-4} mol/L) was added to the sample solutions to form its metal complexes. The solution was transferred into a 250 mL separation funnel. 10 mL of MIBK were added into the funnel and it was shaken in a mechanical shaker for 10 minutes. The solution was left to stand 30 min to separate the organic phase from the aqueous solution, after which the absorbance of the extracted metal ions was directly measured by flame-AAS in the MIBK solution. This procedure was applied to real samples of tap water, river water and seawater.

Table 1. Instrumental operating parameters of flame-AAS

Element	Cu(II)	Mn(II)	Zn(II)
Wavelength (nm)	324.7	279.5	213.9
Bandwidth (nm)		0.2	
Fuel/Oxidant (L/min.)		C$_2$H$_2$/air (2.0/14.0)	
Replicate		7	

Results and Discussion

Optimum Organic Solvents. For solvent extraction, metal-complexes should be quantitatively distributed into organic phase from an aqueous phase. The metal complexes are extracted from an aqueous phase into an organic solvent, where the complexes can be stabilized. The solvent polarity can have a significant influence on extraction efficiency because a solvent can usually dissolve solute of a similar polarity. The efficiency of several organic solvents should be compared for the best extraction of metal complexes.

In the present work, the extraction efficiency of salen-(NEt$_2$)$_2$ complexes of Cu(II), Mn(II) and Zn(II) was investigated using CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$, *n*-hexane, *m*-xylene, and MIBK. This investigation should be performed under other optimized experimental conditions to compare efficiency by type of solvent. Also, the metal complexes were back extracted from the organic solvent into 10 mL of 1.0 mol/L HNO$_3$ solution to avoid the matrix effect of different solvents, that is, the kind of matrix effect that arises from the different combustion of each solvent during absorbance measurement by flame-AAS, Results are shown in Figure 2.

The Cu(II) and Zn(II) complexes showed similar extraction efficiencies with CH$_2$Cl$_2$, CHCl$_3$, xylene and MIBK, but not with non-polar *n*-hexane. In comparison, Mn(II) complex was comparatively efficiently extracted with CH$_2$Cl$_2$, CHCl$_3$ and MIBK. Polar solvents proved more efficient than non-polar solvents. The most efficient extraction occurred when the complexes were an ion pair in a solution of high NaCl concentration. This result was nearly identical to our previous studies.[12]

MIBK was selected as a solvent because it could be used as an aqueous solution in the absorbance measurement by flame-AAS. In addition, MIBK showed a low background as well as optimum combustion. As shown in Table 1, a low fuel/oxidant ratio was used for MIBK because it is also a fuel.

Solution pH. The formation of a stable chelating complex requires that the chelating agent of a Lewis base has a
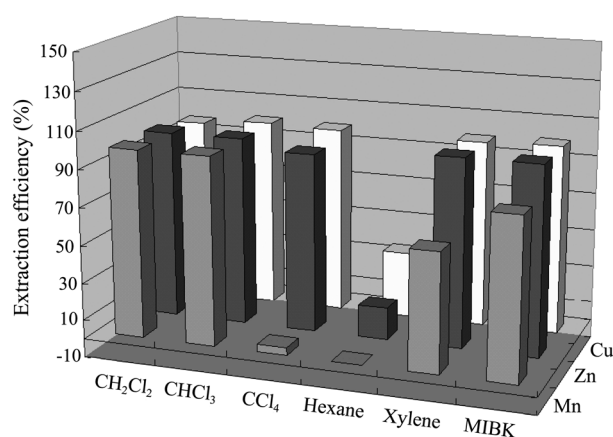

Figure 2. Comparison of extraction percentage for salen(NEt$_2$)$_2$ complexes of Cu(II), Mn(II) and Zn(II) according to the type of several solvents.
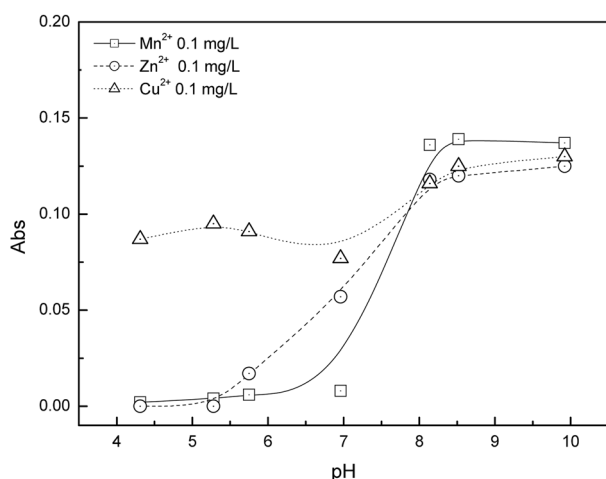
Figure 3. Effect of pH on the formation and extraction of metal salen(NEt₂)₂ complexes. under other optimum conditions.

Figure 4. Optimum concentration of salen(NEt₂)₂ for the extraction of Cu(II), Mn(II) and Zn(II) of each 0.1 mg/L. This experiment was done under other optimum conditions.

functional group. The group could donate its electron pair to metal ions. And it is anadvantage for the agent if it has a negative charge. As shown in Figure 1, salen(NEt₂)₂ used as a chelating agent has two hydroxyl groups and four donating electron pairs, so it can form stable chelates with metal ions. Here two of hydroxyl groups can be ionized in a basic solution.[12]

To confirm this fact, we studied the formation and extraction of metal salen(NEt₂)₂ chelates in the range of pH 4-10. The measured AAS absorbance of extracted metal complexes was plotted versus the solution pH (Fig. 3). The absorbance of three kinds of metals was gradually increased to pH 8, reaching the absorbance plateau at above pH 8. This means that the two of hydroxyl groups ionize and donate their electron pairs to metal ions to form stable chelates. In present work, the pH was adjusted to pH 9.5 with a buffer solution of NaHCO₃/NaOH.

In the case of seawater analysis, alkali earth metal ions such as Ca²⁺ and Mg²⁺ can form hydroxide precipitates, but the precipitation does not interfere with the extraction, as shown in the following section.

Concentration of Salen(NEt₂)₂. As described previously, salen and its derivatives are not commonly used for chemical analysis because they have low solubility in aqueous solution. The insolubility of a chelating agent can cause a serious problem for solvent extraction of metals because the insoluble chelating agent does not form complexes with the metal ion. Therefore, salen(NEt₂)₂ was dissolved in ethyl alcohol before being added to the sample solution.

The ethanolic salen(NEt₂)₂ solution of 0.3%(w/v) was added to the aqueous solutions to raise the salen(NEt₂)₂ concentration from 7.3×10^{-5} to 7.3×10^{-3} mol/L. The concentration of each analyte was 0.1 mg/L in the aqueous solution. The absorbance of each element extracted was plotted versus the concentration of chelating agent, as shown in Figure 4.

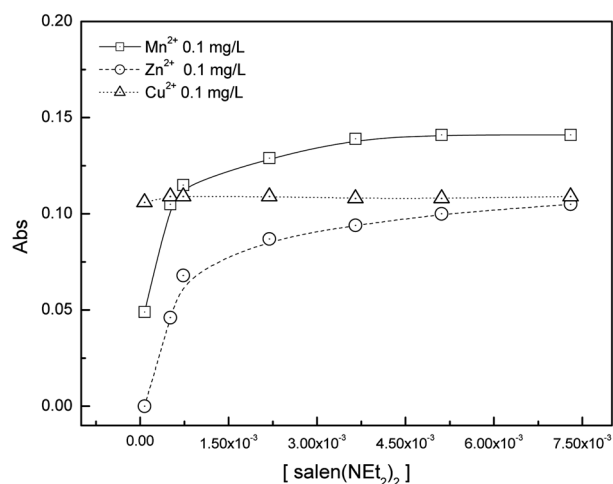Unlike the other ions, Cu(II)-salen(NEt₂)₂ complex was consistently extracted even in the low concentrations of the chelating agent. This can be explained by the fact that salen(NEt₂)₂ forms a more stable complex with Cu(II) than with Mn(II) and Zn(II). This is supported by the result of the pH study, which shows that Cu(II) complex was extracted, however how slightly, even in a weak acidic solution.

Three kinds of elements, including Cu(II), were nearly consistently extracted at higher than 2.0×10^{-3} mol/L salen-(NEt₂)₂ solution. But it is better that an excess of chelating agent is used to form the metal complexes quantitatively. Therefore, the extraction was performed with a final concentration of 7.3×10^{-3} mol/L salen(NEt₂)₂. The amount of salen(NEt₂) was equivalent to more than 2,000 times the total moles of the analyte ions. The limited solubility of salen used in the previous experiment was overcome by its derivative formation to salen(NEt₂)₂. Excess salen(NEt₂)₂ was added to the sample solution to form metal complexes completely.

Other Experimental Conditions. To obtain an accurate result, the matrices of a real sample and the artificial solution used as a standard should be match. A proper amount of an ionic compound was added to the sample solution to compromise such matrix differences, even if very small. Because matrices in our water samples could not be estimated accurately, NaCl was added to the sample solution at the concentration of 0.1 mol/L. The ionic strength in the standard and sample solutions was approximately matched by the addition of NaCl. Also, the NaCl facilitated the phase separation between the weak polar solvent and the aqueous sample solution.

Usually the mixed solution of sample and other reagents should be shaken to distribute the metal complex into organic phase. The shaking time of the separation funnel was increased from 1 minute to 60 minutes at 245 rpm. 10 minutes of was long enough to extract the metal complexes quantitatively. And also this relatively long shaking time helped the formation of metal salen(NEt₂)₂ complexes even though the solubility of the chelating agent is not so high.
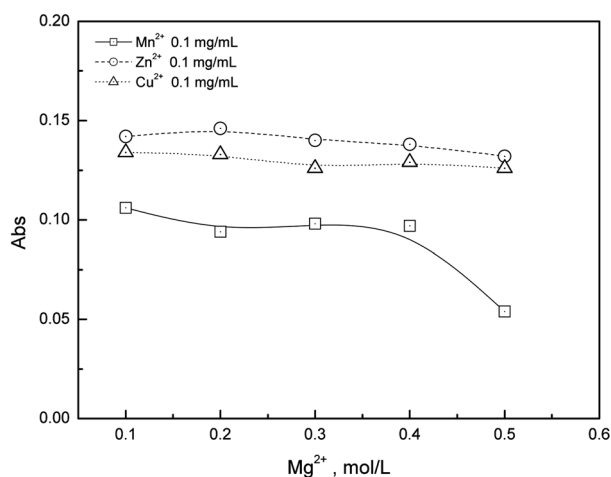
Figure 5. Interference effect of Mg(II) on the extraction of Cu(II), Mn(II) and Zn(II) using salen(NEt$_2$)$_2$.

Interference of Concomitant Ions. Concomitant ions in the sample solution can interfere with the solvent extraction of metal complexes in a trace analysis because the ions may compete with analyte ions in the process of complex formation. Or the spectral lines of the analytes can be overlapped by the spectra of the concomitant ions during the absorbance measurement.

Thus, we investigated the interfering effects of the concomitant ions in the analysis of real samples under optimized conditions. Because a not so negligible amount of alkali and alkaline earth metals was presented in the water samples, the interference of four kinds of elements was investigated (Fig. 5).

Even a significant amount, Na, K, and Ca did not interfere with our extraction, but Mg showed some interference. As shown in Figure 5, Mg interfered with the extraction of Mn(II) somewhat, but for Cu(II) and Zn(II) it was of little consequence. An increase in the concentration of Mg brought increased in the extaction of Mn(II). This phenomenon can be explained by the competing reaction of Mg with Mn(II) in the complex formation. If Mg coexists in the solution at a concentration of higher than 150 thousand times the Mn(II)

Table 2. Concentration and tolerance limits of the major cations in sea water

Foreign ions	Average concentration in sea water[*] (mg/L)	Tolerance limit (mg/L)		
		Cu(II)	Mn(II)	Zn(II)
Na$^+$	1.078×10^4	–	–	–
K$^+$	3.80×10^2	–	–	–
Ca^{2+}	4.12×10^2	–	–	–
Mg^{2+}	1.29×10^3	–	1.6×10^4	–
Sr^{2+}	8.0	~	~	~

[*]"*Introduction to ocean science*" D. A. Segar, USA, ITP, 1998, p 118.
−: Not interfered, ~: Not studied element

concentration, the interference is so heavy that the Mn(II) can not be determined by this extraction procedure quantitatively.

But such interferences was not observed in real sample analysis because Mg and other elements did exist at such a high concentration in the types of water samples we used. The concentration and interference of alkali and alkaline earth metals in seawater are summarized in Table 2.

Analysis of Real Samples. The optimized extraction procedure given in the experimental section was applied to the determination of trace Cu(II), Mn(II) and Zn(II) in three kinds of water samples: tap water, river water and seawater. A calibration curve method was used for this determination. The standard solutions for tap and river water were prepared by adding given amounts of analyte ions to distilled water of 0.1 mol/L NaCl. The standard solutions for seawater were prepared with the artificial seawater in which alkaline and alkali earth elements of the given concentrations in Table 2 were included. Analytical data are listed in Table 3. All data are the average values of five measurements and the relative standard deviation of them was less than 5%. This means that the given method is relatively reproducible for the trace analysis.

After the sample water was taken in a polyethylene bottle from the corresponding field, 10 mL of concentrated nitric acid was added a 10 L sample to prevent the formation of insoluble floats and the adsorption of analytes on the inside

Table 3. Analytical results of real samples by proposed method

Sample		Tap-water		River-water		Sea-water	
Cu(II)	Added (ng/mL)	0.00	70.0	0.00	70.0	0.00	70.0
	Found (ng/mL)	25.8	97.7	0.00	69.6	0.00	69.8
	RSD (%)	2.0	1.8		3.07		6.99
	Recovery (%)		102.7		99.4		99.7
Mn(II)	Added (ng/mL)	0.00	70.0	0.00	70.0	0.00	70.0
	Found (ng/mL)	0.00	68.9	68.5	134.9	0.00	69.1
	RSD (%)		3.3	4.5	2.8		4.9
	Recovery (%)		98.4		94.9		98.7
Zn(II)	Added (ng/mL)	0.00	70.0	0.00	70.0	0.00	70.0
	Found (ng/mL)	22.2	89.7	0.00	70.9	0.00	65.2
	RSD (%)	3.3	2.7		2.04		11.2
	Recovery (%)		96.4		101.3		93.1

Number of analysis, n = 5.

wall of the bottle.

To evaluate the reliability of a given method, Cu(II), Mn(II) and Zn(II) were spiked in each sample to the respective concentrations of 0.07 mg/L. These spiked samples were analyzed according to the given procedure. The analytical data were subtracted from those of the spiked samples to obtain the recoveries. The recoveries for all samples were of 93-105%, which shows the good reliability of this method.

Conclusion

Three kinds of trace elements, Cu(II), Mn(II) and Zn(II), were determined by solvent extraction after their salen-$(NEt_2)_2$ complexes were formed in a sample solution of pH 9.5. The chelating agent was added to the solution as an ethanolic solution. The matrices of the sample and standard solutions were approximately matched using 0.1 mol/L NaCl, The complexes were extracted into MIBK, and the AAS absorbance of each element extracted was measured in the solvent. Some interference of concomitant alkaline and alkali earth ions was ignored because their concentrations in the samples were of little consequence. A present procedure can be judged as precise from the relative standard deviation of less than 5% for five measured data. The recovery of 93-103% shows that this method is quantitative in such trace metal analysis.

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