Solid Phase Extraction of Trace Cu(II), Mn(II), Pb(II) and Zn(II) in Water Samples with Pulverized Silica-salen(NEt$_2$)$_2$

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The use of chemically modified silica-salen(NEt$_2$)$_2$ was studied for the separation and concentration of the metal ions from an aqueous solution by a solid phase extraction. After the salen(NEt$_2$)$_2$ was synthesized, it was chemically bonded to silica gel by a diazonium coupling reaction. The adsorption capacities and binding constants were obtained with respect to Cu(II), Mn(II), Pb(II) and Zn(II) by a graphical method. Some experimental conditions were optimized for the determination of the trace elements. After the silica-salen(NEt$_2$)$_2$ was pulverized in a sample solution of which the pH was adjusted, the solution was stirred to pre-concentrate the metal ions. The metal ions adsorbed were desorbed with nitric acid solution. And the concentrated analytes were determined by a flame AAS. The method proposed here was so rarely influenced by a sample matrix that the procedure was applied to 3 types of water samples. The reproducible results of less than 10% RSD were obtained at the concentration level of *ca.* 100 ng/mL and the recoveries of 95-109% were obtained in the spiked samples in which given amounts of analytes were added.

Key Words : Solid phase extraction, Silica-salen(NEt$_2$)$_2$, Trace elements, AAS, Trace elements

Introduction

Up to now, organometallic compounds of the salen have been widely and extensively used as a catalyst in various organic reactions since Mn-salen complex called as "Jacobsen catalyst" was used as a catalyst in the formation of epoxy resin having a stereo regularity.[1-7] And it is known that the use of the salen has been actively studied in biochemical fields.[8-10] Several salen compounds have been importantly used for the structural identification of DNA and nucleic acids by being used as a cleaving agent. In addition, the synthesis of a conducting polymer by the use of Co-salen derivative complex as a catalyst was reported by Richard.[11] Even the metal complexes of salen and its derivatives have been widely used in various fields as described, they have nearly not used in an analytical field, especially for the trace analysis of metallic elements. But only the solid phase extraction of Cu(II)[12] and the solvent extraction of Mn(II)[13] by using salen derivative have been reported up to now. A salen derivative physically adsorbed on the silica gel was used as an adsorbent in the determination of Cu(II). In this case, the result was significantly influenced by the pH of solution because the surface of silica gel was sensible to the proton concentration. The direct extraction of Mn(II) with a salen complex was not so sensitive that it could be not applied to the trace analysis.

As described above, salen and its derivatives were nearly not used for the trace analysis. Therefore the analytical use of one kind of salen derivatives, salen(NEt$_2$)$_2$, was tried to be applied and developed for the separative determination of trace Cu(II), Mn(II), Pb(II) and Zn(II) by chemical bonding it on silica in this work. Probably the result of this work together with our previous studies could be contributed to expand the use of salen and its derivatives in an analytical field. In our previous work, the salen, one Sciff's base, was successfully used for the determination of trace metal ions by a solvent extraction and another kind of solid phase extraction.[14,15] In this work, silica-salen(NEt$_2$)$_2$ was synthesized by chemically bonding the salen(NEt$_2$)$_2$ on silica gel to be used as an adsorbent for trace analysis of metal ions. A diazonium coupling reaction was occurred in the synthesis.

Experimental Section

Reagents and water. All reagents used were of analytical grade and they were used without any further purification. Water was the de-ionized water purified with Millipore Milli-Q water system.

Instrument. NMR spectrometer of OXFORD Mercury 300, Varian Co. and FT-IR spectrometer of Exccaliber[TM] Bio-Rad Co. were used to confirm the synthesized salen (NEt$_2$)$_2$ and silica-salen(NEt$_2$)$_2$. Flame atomic absorption spectrophotometer of Perkin-Elmer model 2380 was used to measure the absorbance of analytical elements. The air/acetylene flame was used. The instrumental conditions were given in Table 1. And Metrohm's pH meter of Model-744 was used to measure pH.

Synthesis of salen(NEt$_2$)$_2$ and silica-salen(NEt$_2$)$_2$. After two equivalents of 4-diethylaminosalicylaldehyde was dissolved in 150 mL methyl alcohol (HPLC-grade, Baker Co., U.S.A.) under ambient conditions, one equivalent of ethylenediamine (Aldrich Co., U.S.A.) was slowly added to this solution with stirring. The solution was stirred for 4 hour to make pale yellow powder of salen(NEt$_2$)$_2$. The powder

Table 1. Instrumental conditions for atomic absorption spectrometer

Element	Cu(II)	Mn(II)	Pb(II)	Zn(II)
Wavelength (nm)	324.7	279.5	283.8	213.9
Slit width (nm)		0.7		
Fuel/Oxidant (flow rate)	C_2H_2(2.0L/min) / Air (14.0 L/min)			
Replicate		7		

was dissolved in the cold methanol and re-crystallized to be purified. The solid supporter used was silica gel 60^{TM} (MERCK). The synthesized salen(NEt$_2$)$_2$ was chemically bonded to the silica gel by a diazonium coupling reaction. The procedure was shown in Scheme 1.
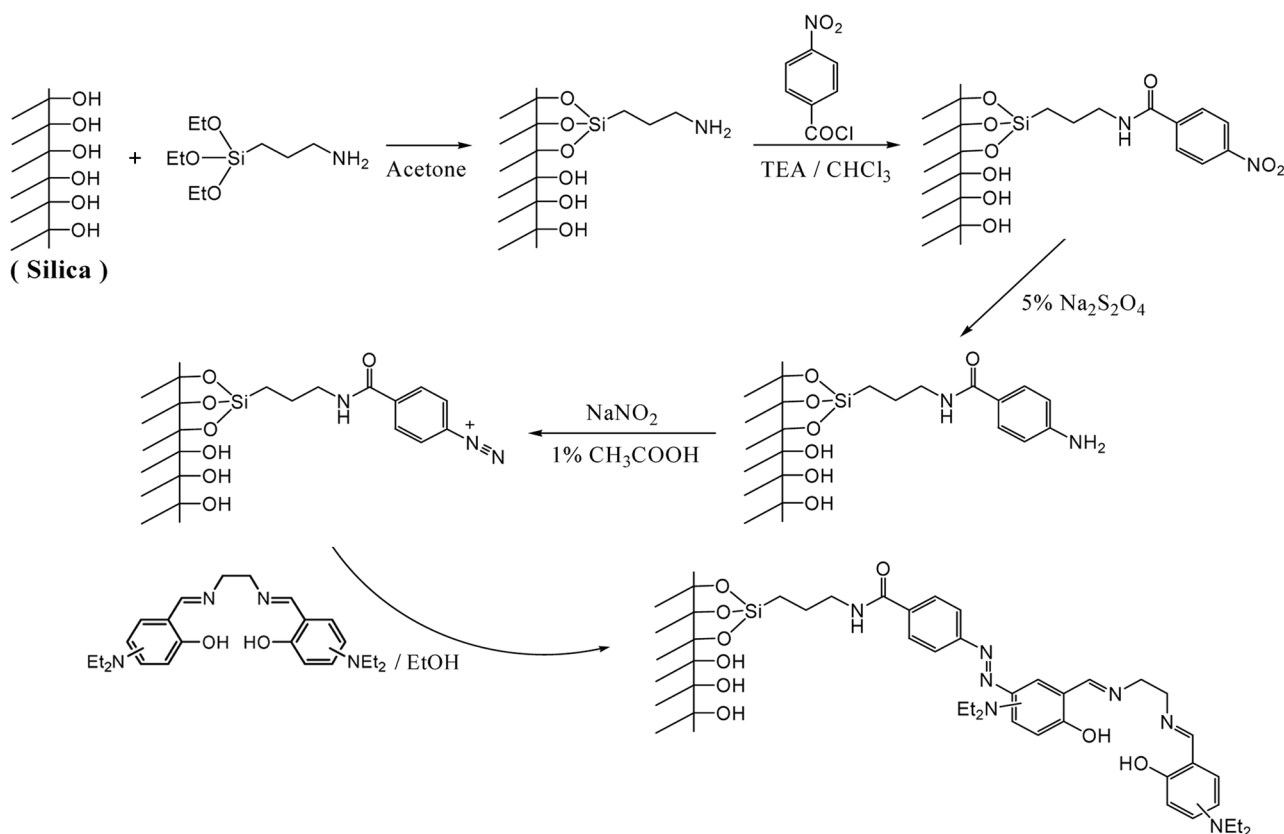
The synthesized salen(NEt$_2$)$_2$ and the silica-salen(NEt$_2$)$_2$ were characterized. The spectra were shown in Figure 1. Each of NMR and IR spectra was summarized in Table 2. The salen(NEt$_2$)$_2$ could be identified with proton NMR peaks of δ 8.362 (s, 1H) as an imine compound. And the silica-salen(NEt$_2$)$_2$ could be characterized with a –C=N stretching band at 1647 cm^{-1}.

Experimental procedure. The distribution of analytes from an aqueous solution to silica-salen(NEt$_2$)$_2$ was investigated by changing a solution pH. After the pH of 50 mL aqueous solution including a given amount of metallic elements was adjusted up to 11 with an acid or base, 500 mg of the lab-synthesized silica-salen(NEt$_2$)$_2$ was added in the solution. And the solution was stirred for 30 minutes with a magnetic stirrer to homogenize silica-salen(NEt$_2$)$_2$ in the solution. Then the silica-salen(NEt$_2$)$_2$ was filtered out and
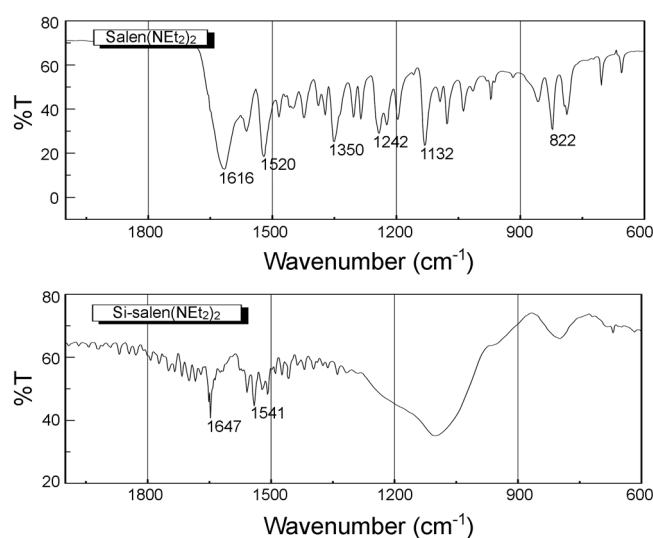
Figure 1. IR spectra of salen(NEt$_2$)$_2$ and silica-salen(NEt$_2$)$_2$.

the contents of metals remained in the solution were determined by a flame atomic absorption spectrophotometry to obtain the distribution ratio of the analytes to the solid phase.

The maximum adsorption capacity of silica-salen(NEt$_2$)$_2$ toward analyte elements was experimentally obtained. Each analytical ion was added into 50 mL of 0.1 mol/L NaNO$_3$ solution of 500 mg silica-salen(NEt$_2$)$_2$ up to 8 mg/L for Cu(II) and Mn(II), 25 mg/L for Pb(II), and 2.0 mg/L for Zn(II). After the pH was adjusted with proper buffer solutions,

Scheme 1. Synthesis procedure of silica supported salen(NEt$_2$)$_2$[silica-salen(NEt$_2$)$_2$].

Table 2. IR and NMR data of intermediate, silica-salen(NEt$_2$)$_2$ and salen(NEt$_2$)$_2$

| Chemical	IR spectrum $\nu_{C=N}$	^{1}H NMR spectrum
Silica-salen(NEt$_2$)$_2$	1647 cm^{-1}	
Salen(NEt$_2$)$_2$	1616 cm^{-1}	δ8.306 (s, 1H), δ3.941 (t, 1H), δ6.091-6.945 (m, 3H), δ3.360 (H), δ1.141 (H).

the solution was stirred for 30 minutes with a magnetic stirrer. The concentrations (C, mg/L) of the remained analyte ions in the solution were determined by a calibration curve method. And the amount (n, mg/g) of the attached ion on silica-salen(NEt$_2$)$_2$ was obtained by subtracting the remained amount from initially given amount.

In order to determine trace elements in real water samples, the ionic strength of the sample solution was controlled by adding 4.24 g NaNO$_3$ into 500 mL sample solution. The pH of the solution was adjusted to about 10 with a buffer solution of NaHCO$_3$/NaOH. Silica-salen(NEt$_2$)$_2$ 500 mg was added into this solution and the solution was stirred for 30 minutes for the complete adsorption of analytes. After the silica-salen(NEt$_2$)$_2$ was filtered out with a membrane filter, the silica-salen(NEt$_2$)$_2$ was put in 10 mL of 1.0 mol/L HNO$_3$ and the adsorbed analytes were desorbed by an ultrasonic vibrator. The desorbed elements were determined by flame-AAS.

Results and Discussion

Dependency of pH on the adsorption of metal ions. An adsorption isotherm was investigated at various pH to obtain the adsorption capacity of analytes on the silica-salen(Net$_2$)$_2$. And also the effect of pH was studied to find the optimum condition for the determination of trace analytes. Each 500 mg of silica-salen(NEt$_2$)$_2$ was added to 50 mL of 0.1 M NaNO$_3$ solution of analytes for the adsorption isotherm and to 500 mL of 0.1 M NaNO$_3$ of analytes to obtain optimum pH for the real sample analysis. Each concentration of Cu(II), Mn(II), Pb(II) and Zn(III) was given in figures. And the pH of solutions was adjusted to 4 to 11 with HNO$_3$ and NaOH solutions in both cases. The mixture was stirred with a magnetic stirrer to be homogeneous. A calibration method was applied to obtain the extraction percentages of analytes for the adsorption capacity of silica-salen(Net$_2$)$_2$ toward analytes. But only absorbance of analytes was measured to obtain an optimum pH for the analysis of real samples. Figure 2 shows the extraction percentage (**2a**) and absorbance (**2b**) of metal ions at various solution pH.

As shown in Figure 2(a), Mn(II) and Zn(II) were adsorbed on silica-salen(NEt$_2$)$_2$ in basic condition, especially Mn(II) was shown narrow pH range. This phenomenon was due to the fact that hydroxyl group of salen(NEt$_2$)$_2$ on silica-salen(NEt$_2$)$_2$ was de-protonated in a basic media. This effect is the same as in our previous studies.[14,15] But Cu(II) and
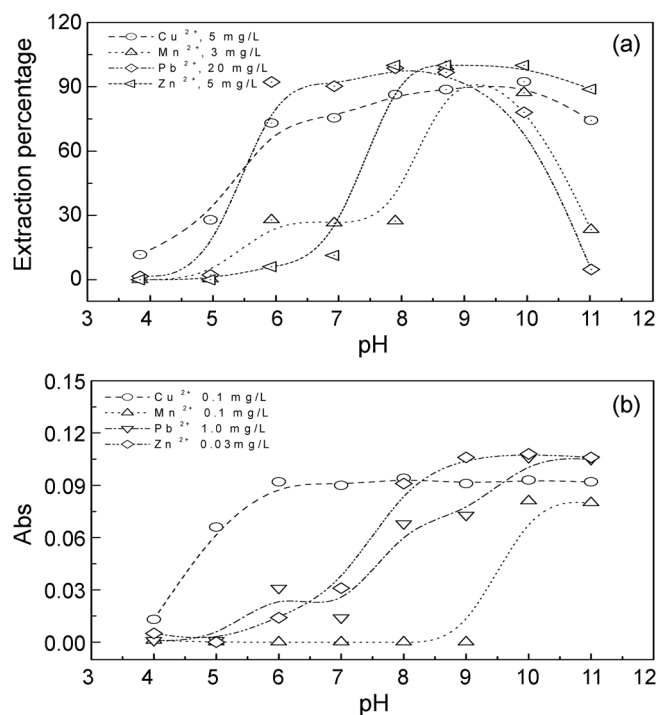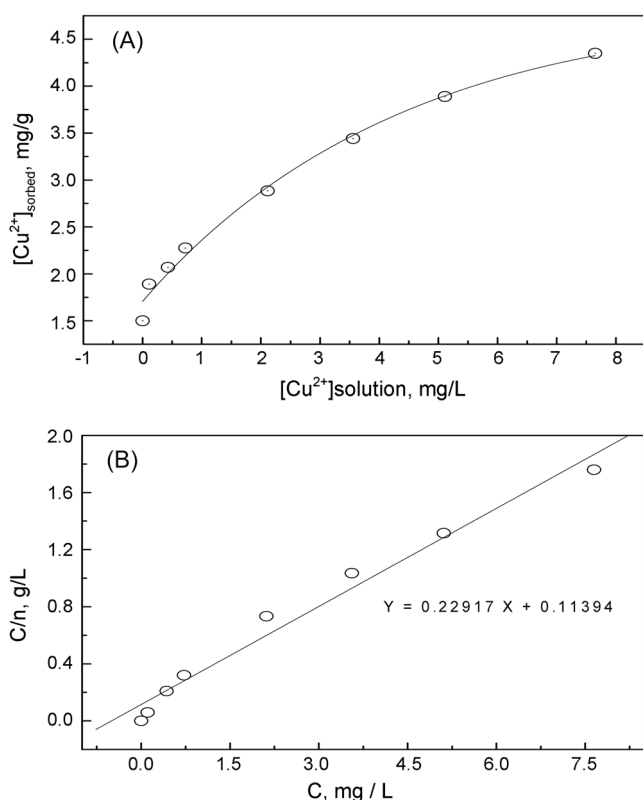

Figure 2. Effect of solution pH on adsorption of analyte ions on silica-salen(NEt$_2$)$_2$. (a) Extraction percentage of analytes at high concentration for the adsorption capacity. (b) Absorbance of metal ions adsorbed for the trace analysis of real samples.

Pb(II) were shown with the highest plateau of extraction percentage at higher than pH 5.5. These were different from XAD-4-salen in our previous study.[15] That is, more wide plateau was shown with the silica-salen(NEt$_2$)$_2$ than XAD-4-salen. This phenomenon could be explained by following fact. That is, the electron donating capacity of chelating resin was influenced by functional group of salen and the character was improved by diethyl amino substrate on salen(Net$_2$)$_2$.

In addition, the solution pH was investigated for the determination of trace analytes in real water samples of a large volume again. As shown in Figure 2(b), similar tendencies of pH effect were shown in the solution of low concentration of analytes even there is a little difference. Therefore the pH of the sample solution was adjusted to about 10 with NaHCO$_3$/NaOH buffer solution.

Adsorption isotherm. The knowledge of an adsorption capacity was known to be helpful for the separation and concentration of trace elements by the adsorption on a solid adsorbent. The maximum adsorption capacity of each element on silica-salen(NEt$_2$)$_2$ was obtained according to the modified Langmuir equation.[16,17] Experimental procedure given above was applied for this. The ratio, (C/n), was plotted against the concentration C (Fig. 3). The adsorption capacity could be calculated from the slope obtained by fitting the plot to a following Langmuir equation:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) C \qquad (1)$$

Figure 4. Absorbance of the desorbed elements according to the type of acid used.

Figure 3. (A) Adsorption isotherm of silica-salen(NEt$_2$)$_2$ for copper. (B) Langmuir plot for copper adsorption on silica-salen(NEt$_2$)$_2$.
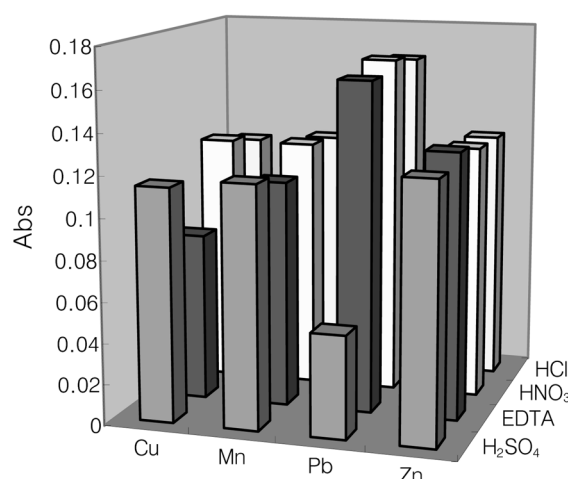
where, C (mg/L) is the concentration of the remained metal ion in the aqueous solution, n (mg/g) is the concentration of the attached ion on silica-salen(NEt$_2$)$_2$, n_m is the adsorption capacity of silica-salen(NEt$_2$)$_2$ to a metal element, and K is a binding constant.

The adsorption capacity on silica-salen(NEt$_2$)$_2$ was different each other between elements as followings: 4.36 mg/g for Cu(II), 2.34 for Mn(II), 10.06 mg/g for Pb(II), and 11.30 mg/g for Zn(II). The capacities were so much large compared to the content of analytes in our water samples that the taken amount of silica-salen(NEt$_2$)$_2$ was enough for the extraction of analytes. Figure 3 shows typical adsorption isotherm and Langmuir plot of Cu(II) as a typical example. And all data for the adsorption capacity are summarized in Table 3.

Type of acid for desorption. The desorption of the adsorbed analytes from the silica-salen(NEt$_2$)$_2$ is also important in the separative determination of trace elements by the adsorption of the analytes on the solid phase. After the analyte ions were adsorbed on the surface of solid sorbent under given conditions, the desorbing efficiency was investigated with 1.0 mol/L solutions of H$_2$SO$_4$, HCl, HNO$_3$ and EDTA, respectively. The absorbance of the desorbed elements was measured. The results were shown in Figure 4. All of four elements were efficiently desorbed with most of used acids, but Pb(II) was nearly not desorbed in sulfuric acid. Nitric acid could show not only the highest desorbing efficiency for these elements, but also a stable atomization in a flame for AAS measurement. Therefore, HNO$_3$ was used as a desorbing acid.

Concentration of nitric acid. In order to fix the optimum concentration of nitric acid as a desorbing acid, the adsorbed elements were desorbed by an ultra sonic vibration for 5 minutes changing the concentration of the nitric acid from 0.01 to 3.0 mole/L. As shown in the Figure 5, three elements

Table 3. Maximum capacity and binding constant of metal ions on solid sorbent

	Cu(II)	Mn(II)	Pb(II)	Zn(II)
Slope	0.2292	0.4469	0.0994	0.0885
Intercept	0.1139	2.904	0.1493	0.0263
Binding constant K (L/mol)	2.013	0.146	0.670	3.362
Capacity n_m (mg/g)	4.36	2.34	10.06	11.30
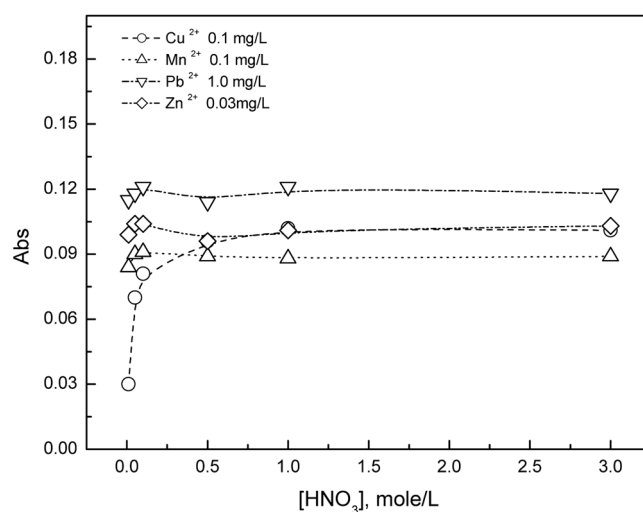
Figure 5. Concentration dependency of nitric acid on the desorbing efficiency of analytical ions from silica-salen(NEt$_2$)$_2$.

Table 3. Analytical results of real samples by the proposed method

Sample		Tap-water		River-water		Sea-water	
Cu(II)	Added (mg/L)	0.00	100.0	0.00	100.0	0.00	100.0
	Found (mg/L)	11.42	121.24	4.9	100.4	1.29	101.5
	RSD (%)		3.17		3.64		0.90
	Recovery (%)		109.76		95.5		101.2
Mn(II)	Added (mg/L)	0.00	100.0	0.00	100.0	–	–
	Found (mg/L)	0.00	118.8	42.1	151.7	–	–
	RSD (%)		5.99		6.08	–	–
	Recovery (%)		118.8		109.5	–	–
Zn(II)	Added (mg/L)	0.00	80.0	0.00	80.0	0.00	30.0
	Found (mg/L)	0.94	79.3	20.8	100.3	0.48	32.6
	RSD (%)		8.16		2.01		4.39
	Recovery (%)		97.92		99.18		105.2
Ni(II)	Added (mg/L)	0.00	1.00	0.00	1.00	0.00	1.00
	Found (mg/L)	0.00	1.004	0.00	0.958	0.00	0.986
	RSD (%)		6.03		3.34		1.69
	Recovery (%)		100.4		95.8		98.6

Number of determination, n = 5.

gave the maximum absorbance at 0.1 mol/L HNO_3 and the absorbance showed a plateau at the higher concentration than it. But Cu(II) was completely desorbed at higher than 1.0 mol/L HNO_3. Thus 1.0 mol/L nitric acid was used to strip the adsorbed trace ions in this experiment.

Analysis of real samples. An optimized procedure was applied to the analysis of real samples.

Three kinds of water samples were analyzed for trace amounts of Cu(II), Mn(II), Pb(II) and Zn(II) (Table 3) and the recoveries were also obtained to evaluate the reliability about the obtained data. For the recoveries, the concentrations of 0.1, 0.1, 0.08 and 1.0 mg/L were spiked to real samples for Cu(II), Mn(II), Pb(II) and Zn(II) respectively and the respective total concentrations of them were determined by a given procedure. The obtained recoveries of 95 to 120% could make this procedure reliable for such trace analysis.

By the way, high concentrations of various salts were presented in sea-water. Therefore the applicability of a given procedure was examined with synthetic sea-water. But alkali earth metals, such as Ca(II) and Mg(II), of higher than 40 mg/L concentration interfered with the extraction of Mn(II) seriously. Therefore Mn(II) was not determined in the sea water.

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