

Studies on Equilibria and Analytical Applications of Synergistic Solvent Extraction(I). Determination of Trace Ni(II), Cd(II) and Pb(II) in Sea Water using Dithizone and Thiocyanate Ion

Young-Sang Kim,* Yoon-seok Choi, and Kyo In

Department of Chemistry, Korea University, Jochiwon 339-700, Korea

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Many elements in a sea water even though trace levels have been affecting human and living things in the various fields such as biochemistry, geology and so on. Therefore, much interest and effort have been devoted on the studies for the determination of these elements. Most of such elements are presented at lower level than the detection limits of common analytical methods and their determination is spectroscopically and chemically interfered with other major constituents such as NaCl. Much effort has been tried to solve difficulties of such interferences by the development of various techniques.^{1,2}

In order to eliminate the interferences, a solvent extraction has been commonly applied for the separative concentration of trace elements from the sample matrix.³⁻⁸ For the effective extraction of them, the ions are formed as complexes with proper ligands such as dithiocarbamates,^{3,5,6} dithizone and its derivatives^{4,9} and oxine.¹⁰ This technique has advantages of relatively easy experimental procedure and good selectivity as well as a disadvantage of low concentration efficiency. Thus, a synergistic system has been sometimes utilized to enhance the concentration efficiency and to increase the extraction velocity. That is, some auxiliary ligands have been used together with a main ligand.^{11,12} Hideo and coworkers had increased the extraction velocity of Co(II) and Ni(II) by using pyridine base as an auxiliary ligand in the solvent extraction with TBPO (tributyl phosphine oxide) and specially much enhanced the concentration of Co(II).

Such synergistic extractions have been also studied in our laboratory. The extraction efficiency of Mo(VI) ion in sea and natural water samples as an alizarin red S complex was enhanced by the aid of aliquat-336. The ion-pair of the Mo(VI) complex with the aliquat-336 was formed and extracted into chloroform for a spectrophotometric determination.^{13,14} And also the velocity as well as the efficiency in dithizone-chloroform extraction system of Co(II) and Cu(II) could be increased by the addition of thiocyanate ion as an auxiliary ligand.¹⁵

In this study, the application of above synergistic procedure was studied to separately preconcentrate trace Ni(II), Cd(II) and Pb(II) ions in sea water of complex matrix for the GF-AAS determination. The pH of solution, shaking conditions, the amount of dithizone and thiocyanate ion added, and back-extraction conditions were investigated to be optimized. This procedure was applied to real samples and recovery tests were also performed to evaluate a practical

usefulness of this method.

Experimental Section

Apparatus and Reagents. A deionized water purified with Mill-Q system and reagents of special or reagent-grade were used in this experiment. Each stock solution of 1,000 $\mu\text{g/mL}$ Ni(II), Cd(II) and Pb(II) ion was prepared by dissolving a given amount of nickel powder (99.99%, Fluka Chem. Co., Japan), cadmium metal (99.99%, Fluka Chem. Co.) and lead metal (special-grade, Wako. Chem. Co., Japan) in 1 : 1 nitric acid solution and then diluting to 1,000 mL with a deionized water. Dithizone (Aldrich Chem. Co., USA) was dissolved in a chloroform to the concentration of 0.02% (w/v). Ethanolic sodium thiocyanate (special-grade, Wako Chem. Co.) solution of 0.05 M was used as an auxiliary ligand. Tokyo Rikakikai Model PHM-2000 pH analyzer with Ingold glass electrode was used for pH measurement. A Perkin-Elmer model 2380 GF-AAS equipped with HGA-400 programmer was used for the measurement of atomic absorbances with operating conditions and temperature programming given in Table 1.

Procedure. After filtered with glass filter, then 100 mL sea water was taken as a working solution in a 250 mL separatory funnel. A 0.05 M ethanolic thiocyanate solution 1.0 mL was added to the funnel and the pH was adjusted to 8 with a buffer solution. Chloroform solution 10.0 mL of

Table 1. Operating conditions of AAS and heating programs for a graphite furnace

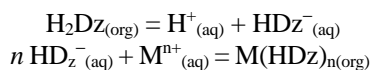
Atomic absorption spectrophotometer : Hitach model			
	Nickel	Cadmium	Lead
Wavelength (nm)	232.0	228.8	283.3
Current (mA)	10.0	7.5	7.5
Band width (nm)	0.2	1.3	1.3
Temperature programs for a graphite furnace			
	Nickel	Cadmium	Lead
Drying	100 °C (5s)	150 °C (5s)	110 °C (5s)
Charring	700 °C (30s)	300 °C (30s)	400 °C (30s)
Atomization	2700 °C (3s)	1400 °C (3s)	2000 °C (10s)
Cleaning	2800 °C (3s)	1800 °C (3s)	2400 °C (3s)
Sample injection : 20 μL			
Graphite tube : pyrolytically coated			
() : Holding time			

0.02% (w/v) dithizone was added into the sample solution. The funnel was shaken with a mechanical shaker for 30 min. After the organic phase were separated from the aqueous solution, the chloroform layer was drained into an another separatory funnel. A 0.05 M nitric acid 10.0 mL was pipetted into the funnel and the funnel was shaken for 40 min to back-extract metal ions into an aqueous solution. The aqueous phase of 20 μ L was injected into a graphite tube for GF-AAS determination.

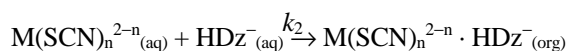
Besides, 100 mL of synthetic sea water containing analytes of 10 ng/mL Ni(II), 1.0 ng/mL Cd(II) and 1.0 ng/mL Pb(II) was used to optimize experimental conditions used for the effective extraction of analyte ions in a real sea water.

Results and Discussion

Extraction Mechanism. It is well known that dithizone can form stable complexes with many kinds of metal ions. After the dithizone is one-step ionized to dithizonate ion, it forms a complex with metal ion and the complex can be extracted into an organic solvent as following:



But if thiocyanate ion is present in an aqueous solution as an auxiliary ligand, metal ion reacts with thiocyanate ion to make its complex at first. After that, the complex of SCN^- reacts with HDz^- ion, which is come from chloroform, to form ternary complexes as following reaction in the extraction process:



Such a partition of the ternary complex into chloroform proceeds rapidly by vigorous shaking of the solution so that the reverse reaction, $-k_2$, can be ignored.¹⁵

Dithizone. The extraction efficiency of metal ion as the ternary complex into a chloroform is greatly influenced by the complete formation of metal dithizonate complex. And the stable complex can be formed with an excess of the dithizone under given other conditions. Therefore, the efficiency was investigated by changing the concentration of dithizone in a chloroform.

In order to determine the optimum concentration of dithizone, the ions in the synthetic sea water were extracted with chloroform contained 0.001 to 0.06% (w/v) dithizone according to the procedure previously described. The atomic absorbance of each element was measured in 10 mL aqueous solution in which the ions were back-extracted from the chloroform solution. The absorbances were plotted against the concentration of dithizone used (Fig. 1).

It could be known that the complexes for all metal ions was effectively formed by adding 10 mL chloroform solution of more than 0.02% (w/v) dithizone. This concentration indicated that much excess of the ligand was added compared to the amounts of analytes. That is, the amount of dithizone added was more than 10,000 times of total metallic

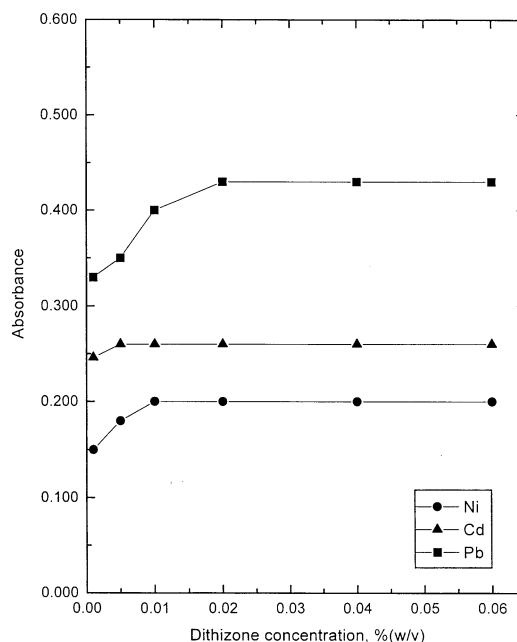


Figure 1. Effects of dithizone concentration on extraction efficiency of analytes in synthetic sea water under optimum other conditions. Ni: 10 ng/mL, Cd.: 1 ng/mL, Pb: 1 ng/mL

ions as a mole.

In fact, the dithizone is well known as a ligand to form complexes with many kinds of metal ions under proper conditions, but usually it cannot react with alkaline and alkali earth metal ions. Except such metal ions, most of other metal ions are commonly presented in a sea water at the trace levels so that they do not seriously interfered with each other in the extraction of other ions. But the concomitant ions compete with analyte ions in their complex formation if enough ligand is not added to a sample solution. Even if parts of the concomitant complexes are extracted together with analytes, their interferences can be eliminated at the step of absorbance measurement. Such a competition can be solved by the addition of excess dithizone.

Auxiliary Ligand. It had been reported that an extraction efficiency was increased by using an auxiliary ligand together with a main ligand.¹¹ Several ligands have been used as an auxiliary one to improve the extraction of metal ions into a chloroform having dthizone. Creatine, hydroquinone, thioacetamide, sodium thiocyanate and dimethylglyoxime were added to the sample solution prior to the extraction, respectively. The extraction efficiencies under the same other conditions were compared each other in this work as in Figure 2.

In this figure, dimethylglyoxime showed the best efficiency for all ions. This is because dimethylglyoxime by itself could effectively form complexes with these kinds of ions. Such good results were supported by the selectivity of dimethylglyoxime for these ions, especially Ni(II).¹⁶ On the other hand, sodium thiocyanate has been known to enhance not only the extraction efficiency, but also the rate of extraction at same time. So it was selected as an auxiliary ligand in this work. The analyte ions were extracted into the chloro-

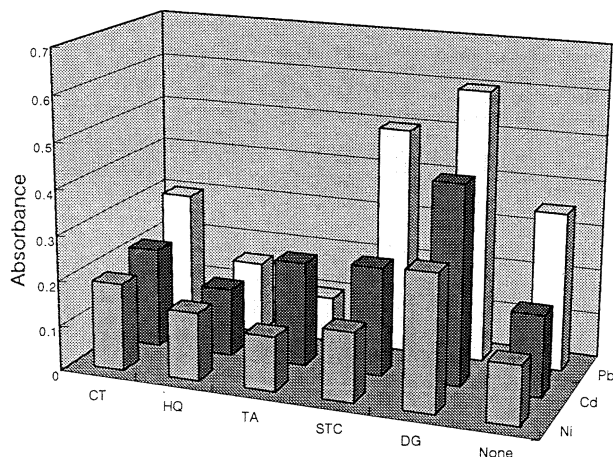


Figure 2. Comparison of extraction efficiencies according to the type of ligand under the same conditions as in Figure 1. CT: Creatine. HQ: Hydroquinone. TA: Thioacetamide, STC: Sodium thiocyanate. DG: Dimethylglyoxime.

form solution of dithizone after metal thiocyanate complexes were formed in an aqueous solution.

As described in introduction section, thiocyanate ion is substituted with water molecule in the aqueous complex of metal ion and dithizone reacts with the complex to make it the ternary complex by the acidic dissociation of dithizone. And this ternary complexes were finally extracted into chloroform. The optimum concentration of thiocyanate ion as an auxiliary ligand should be determined to increase the extraction efficiency of metal ions in an aqueous solution.¹⁵ Therefore, the absorbance of each element extracted into chloroform was measured in the back-extracted solution at 0.002 to 0.1% concentrations of thiocyanate ion. The best efficiency was obtained on the addition of more than 0.01% SCN^- ion. And the extraction time was also shortened by the addition of thiocyanate ion as well.

pH of Sample Solution. In general, the complex formation of metal ion and weak acidic or basic ligand for the solvent extraction is much influenced by H^+ ion concentration because the donation ability of electron-pair to metal ion is responsible to the solution pH. Besides, the solvent extraction together with the complex formation are also influenced by the variation of pH, directly.² Because the hydroxide precipitation of some metallic ions interfere with the complex formation of metallic ions, the extraction efficiency can be decreased in a basic solution of high pH. Therefore, the pH should be carefully optimized for the simultaneous extraction of ions in the extraction system of multi-elements. But dithizone is known to be an excellent ligand to form complexes with metal ions even in basic solution.

The effect of pH on the extraction efficiency was investigated by adjusting the pH from 3 to 12. The complexes were extracted under other optimum conditions at each given pH and the atomic absorbances were measured in back-extracted solution (Fig. 3).

As shown in the figure, the complexes of three analyte ions were extracted in the relatively wide range of pH from 6 to 11. The similar experiments were performed in the solu-

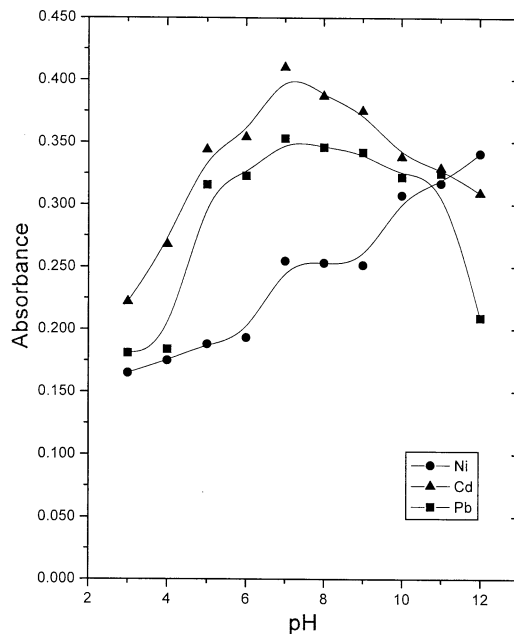


Figure 3. Effects of pH for the extraction of analytes in synthetic sea water with thiocyanate ion as an auxiliary ligand under other optimum conditions.

tion without thiocyanate ion. But the extraction of Ni(II) and Pb(II) was much decreased compared to the solution with thiocyanate ion.

The solution was shaken by a mechanical shaker (Kukjae Instrument Co.) for the formation of complexes to be extracted effectively. The absorbances were measured in the back-extracted solution by changing shaking time from 10 min to 120 min. The constant extractions could be obtained by shaking the solution more than 30 min.

Acid Concentration for Back-Extraction. When analyte ions are directly measured in chloroform by GF-AAS, the chloroform is not completely burnt in the graphite tube so that the absorbance measurements are interfered with the unburned matrix. Such phenomena can increase or change the blank absorbance and the detection limit and precision are significantly damaged. Because the chloroform is volatile, it is not easy to store the extracts and the concentration of the metal ion is gradually increased with time. In order to solve such problems, metal complexes should be back-extracted into an aqueous solution.

In general, nitric acid is known to be a suitable medium for the preservation of extracted metal ions during a storage and transportation in the laboratory and it is also compatible with GF-AAS. Therefore, dilute nitric acid was selected to back-extract the complexes from chloroform phase. The back-extraction was studied by changing the concentration of nitric acid in an aqueous solution from 0.005 to 0.7 M. The constant efficiencies were shown at the concentration of more than 0.05 M.

And also additional shaking was necessary to back-extract the complexes so that optimum time was determined by the variation of shaking time from 10 to 120 min with the mechanical shaker. The back-extraction with 0.05 M HNO_3

Table 2. Analytical results of metal ions in sea water samples

Sample	Elements	Spiked ^d	Measured ^d	Recovered ^d	RSD (%) ^e	Recovery(%)
Sample A ^a	Nickel	0.00	101.6		6.20	
		100.0	202.9	101.3	7.70	101
	Cadmium	0.00	8.50		1.40	
		10.0	18.2	9.70	0.60	97
	Lead	0.00	15.9		0.20	
		10.0	31.2	15.3	0.50	153
Sample B ^b	Nickel	0.00	80.2		5.20	
		100.0	180.3	100.1	5.30	100
	Cadmium	0.00	12.5		2.35	
		10.0	22.4	9.90	2.18	99
	Lead	0.00	21.4		2.32	
		10.0	32.3	10.9	1.20	109
Sample C ^c	Nickel	0.00	65.0		2.20	
		100.0	153.2	88.2	2.16	88
	Cadmium	0.00	8.25		0.98	
		10.0	21.5	13.3	1.28	133
	Lead	0.00	30.2		1.20	
		10.0	40.2	10.0	1.30	100

^athe west seaside around Daechun. ^bthe west sea around Byunsan peninsular. ^cthe southern sea around of Dadaepo. ^dUnit: ng/mL ^erelatively standard deviation.

solution was executed over 40 min shaking.

Analytical Results and Recoveries. In order to evaluate the usefulness of this method, the procedure was applied to the determination of these three elements in real sea waters. A series of standard solutions were prepared with a synthetic sea water in volumetric flasks to prepare calibration curves. These standard solutions as well as a blank solution were treated with the same procedure as for real samples. Measured absorbances of analytes were plotted against their concentrations after the back grounds were corrected with the absorbances of blank solution. The curves were linear with linearities of 0.99937 in the concentration range of 25-200 ng/mL for nickel, 0.9943 in 4-16 ng/mL for cadmium and 0.99868 in 6-20 ng/mL for lead, respectively. The analytical results were given in Table 2.

Detection limits corresponding to the three times absorbance of standard deviation for a blank were calculated from the calibration curves. The values were 0.05 ng/mL for Ni(II), 0.02 ng/mL for Cd(II), and 0.87 ng/mL for Pb. In order to evaluate the reliability of this procedure, recovery data were obtained in real samples in which given amounts of analytes were added. Recoveries of 88-153% meant that this synergistic extraction was relatively quantitative in the determination of trace levels of Ni(II), Cd(II) and Pb(II) in

sea water samples.

Conclusion

The preconcentration of trace amounts of Ni(II), Cd(II) and Pb(II) for GF-AAS determination were studied by a synergistic solvent extraction using dithizone as a main ligand and thiocyanate ion as an auxiliary ligand. The ternary complexes were formed at pH 8. Extraction time could be shortened and extraction efficiency was increased by the addition of the auxiliary ligand. Detection limits obtained were Ni(II): 0.05 ng/mL, Cd(II): 0.02 ng/mL and Pb: 0.87 ng/mL and recoveries of 88-153% were obtained from real samples spiked with given amounts of analytes. From such results, this procedure could be concluded to be a promising preconcentration technique of trace elements in seawater samples.

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