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Organic Precipitate Flotation of Trace Metallic Elements with Ammonium Pyrrolidinedithiocarbamate (II). Application of Solvent Sublation for Determination of Trace Cd, Co, Cu and Ni in Water Samples

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A solvent sublation was studied for the determination of trace Cd, Co, Cu and Ni in water samples. Ammonium pyrrolidine dithiocarbamate (APDC) was used as a complexing agent. Experimental conditions such as pH of solution, amounts of APDC, the type and amount of surfactant, the type of solvent, etc. were optimized for the effective sublation of analytes. After metal-PDC complexes were formed in sample solutions of pH 2.5, the precipitate-type complexes were floated in a flotation cell with an aid of sodium lauryl sulfate as a surfactant and by bubbling with nitrogen gas. The precipitates were dissolved and separated into the surface layer of methyl iso-butyl ketone (MIBK). The analytes preconcentrated were determined by a graphite furnace atomic absorption spectrophotometry (GF-AAS). Extractability of each element was 88% for Cd(II), 86% for Co(II), 95% for Cu(II) and 76% for Ni(II), respectively. And this procedure was applied to the analysis of real samples. From the recoveries of more than 92%, it was concluded that this method could be simple and applicable for the determination of trace elements in various water samples of a large volume.

Introduction

Recently, the interests for health-related and environmental sciences are widely and rapidly increased and the information about trace heavy elements is also becoming more important. Therefore, developement of accurate determination mehtods for them is necessary to fit such requirements. As a result, various types of powerful and elegant instruments have been developed up to present for a qualitative and quantitative analysis of materials in view of composition as well as structure. Besides, various instrumental techniques have been extensively developed to improve the sensitivity, precision, selectivity and efficiency of the analytical methods, but the combination of an appropriate preconcentration technique with these methods remains unsettled in the field of trace inorganic analysis to achieve successful analyses in many kinds of samples.

The solvent extraction,[1-3] adsorption, ion-exchange,[5,6] and coprecipitation[4] are commonly used as preconcentration techniques for the atomic spectrometric determination of trace heavy elements. However, these methods need relatively long time and troublesome operation for a large volume of sample. On the other hand, a flotation technique[7-27] is rapid and conveniently compared to such preconcentration techniques and can be performed with an unskillful technique. And this mehtod is also able to concentrate many elements from a large sample volume of several liters to less than 10 mL, simultaneously.

The flotation technique is defined as a separation procedure by which various substances in a solution are selectively floated to the surface with the aid of tiny gas bubbles. The flotation technique can be classified as precipitate flotation[8-13,18-22] and ion flotation.[14-17] The precipitate technique is further divided into organic and inorganic precipitate flotations according to the type of precipitate.

In this work, a modified flotation technique so called "solvent sublation"[23,24] was investigated for separative preconcentration of heavy elements in water samples. The solvent sublation is a technique that analytes floated onto the surface layer by gas-bubbling are collected in a water-immiscible organic solvent just like in solvent extraction. Various surfactants are frequently used in the process of flotation to float analytes effectively by making the materials hydrophobic. Generally, the solvent sublation is more rapid

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and convenient than other flotation techniques because analytes are directly and immediately dissolved in a solvent. But the type of organic solvent which can be used is very limited. That is, the organic solvent must be lighter than sample solution and immiscible with aqueous solution in the flotation cell. And also it has to have low volatility to keep the concentration of analyte constant through the treatment of floats and the measurement of analytes. The floated analytes must be quantitatively dissolved in the solvent. From this view point, this sublation is more difficult to obtain optimum conditions than other flotation techniques.

Kotsuji et al.[25,26] had applied the solvent sublation for the preconcentration of trace elements. A microgram quantity of Fe(III) in 160-500 mL of seawater (pH 2.5-3.5) was reduced to Fe(II) and converted into a complex by the reaction with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT), and then the complex was floated with sodium dodecyl sulfate by bubbling nitrogen gas for 10-15 min. The floated Fe(II)-PDT complex was collected in 5.0 mL of 3-methyl-1-butanol(isoamyl alcohol) on the solution surface, and iron in the organic phase was determined by spectrophotometry. Similarly, trace Cu(II) was converted into the Cu(I)-PDT complex after reduction to Cu(I), floated with sodium dodecyl sulfate, and collected in the mixed solvent of 3-methyl-1-butanol and butyl acetate. The analytical application of this sublation technique was investigated in connection with the separation and preconcentration of trace metals as the form of dithizonates by Cervera et al.[27] Methyl isobutyl ketone solution of dithizone was used as a collector with help of sodium lauryl sulfate. Under suitable experimental conditions, this procedure made the quantitative separation of trace Cu(II) possible through the easy handling of sample solutions up to several liters.

In our study, trace amounts of Cd(II), Co(II), Cu(II) and Ni(II) were converted into the metal-PDC complexes by adding ammonium pyrrolidine dithiocarbamate (APDC), and then the complexes in aqueous sample solution were rendered hydrophobic by the addition of 0.1% ethanolic sodium lauryl sulfate as a surfactant and floated on the solution surface by bubbling N₂ gas. The floated substances were collected in MIBK on the sample solution. This organic phase containing the analytes was transfered to a vial with a pipet. The analytes in organic phases were determinated with a graphite furnace atomic absorption spectrophotometer (GF-AAS).

The various experimental parameters such as pH of the aqueous solution, amounts of APDC, stirring time, the type and amount of surfactant, and so on were optimized in the flotation procedure. And the extraction abilities of several organic solvents such as cyclohexane, diisopropyl ketone, methyl isobutyl ketone and o-xylene were compared for the quantitative dissolution of complexes. Finally, this procedure was applied for water samples.

Experimental

Apparatus and reagents. All reagents and solvents of analytical-reagent grade were used without further purification. A 0.2% (w/v) surfactant solution was prepared by dissolving sodium lauryl sulfate in an absolute ethanol. A 1.0% APDC solution was made by dissolving 1.0 g APDC

in 100.0 mL deionized water. Because APDC solution is unstable in an acidic solution, it was prepared just before use. Each 1,000 mg/L stock solution of cadmium, cobalt, copper and nickel was prepared by dissolving a corresponing fine metal powder in an acid solution. A series of standard solutions for calibration curves were prepared by dissolving a given amount of each Cd(PDC)₂, Co(PDC)₂, Cu(PDC)₂ and Ni(PDC)₂ in methyl isobutyl ketone (MIBK) and diluting the solution. These metal-PDC complexes were synthesized by the reaction of metal ion and APDC and purified by recrystalization in our laboratory.

The solvent sublation vessel was a 1.0 L pyrex cylinder fitted with a sintered-glass filter of porosity-4 (5-10 μm) (Figure 1). A nitrogen was used as the bubbling gas and the flow was regulated with a needle valve. The gas flow rate was measured by a bubble rotameter of Dwyer Co.

Perkin-Elmer model 2380 atomic absorption spectrophotometer equipped with HGA-400 as the heating programming device for the graphite furnace was used for the absorbance measurement of analytical elements. The instrumental parameters and heating program were given in Table 1. MIBK having analytes were directly injected in a graphite furnace so that the temperatures of drying and ashing step should be higher than the ordinary condition to reduce the background.

Experimental procedure. In an erlenmeyer flask, 2.0 mL of 1.0% APDC solution was added to 1.0 L of an aqueous sample and the pH was adjusted to 2.5 with nitric acid. The solution was stirred with a commercial magnetic stirrer for 10 minutes to form metal-PDC complexes, completely. After 0.5 mL of 0.2% ethanolic sodium lauryl sulfate was added, the solution was stirred for more than five minutes. All the content was transferred to a flotation cell (Figure 1) and 20 mL of MIBK was added on the cell. Then, nitrogen gas was bubbled at the flow rate of 60 mL/min from the
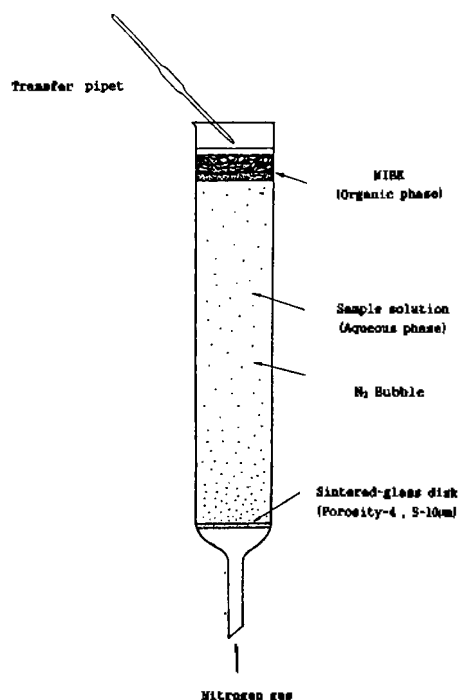

Figure 1. Flotation cell for a solvent sublation.

52 *Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 1

Young Sang Kim et al.

Table 1. Operating conditions of atomic absorption spectrometer and heating programs for graphite furnace

Atomic absorption spectrophotometer: Perkin-Elmer model 2380

	Cadmium	Cobalt	Copper	Nickel
Wavelength (nm)	228.8	240.7	324.8	232.0
Current (mA)	4	30	30	30
Band width (nm)	0.7	0.2	0.2	0.7

Temperature program of graphite furnace

	Cadmium	Cobalt	Copper	Nickel
Drying	100 °C 2s*(5s)*	150 °C 5s (5s)	150 °C 5s (5s)	150 °C 5s (5s)
Charring tomization	600 °C 3s (9s)	900 °C 6s (6s)	800 °C 5s (5s)	1000 °C 3s (8s)
Cleaning	1800 °C 2s (1s)	2600 °C 2s (5s)	2600 °C 3s (8s)	2400 °C 2s (4s)

Sample injection: 20 μL (Cd: 10 μL), Graphite tube: pyrolytically coated, *: Holding time, ( )*: Ramping time.

bottom for 45 minutes. The floated metal-PDC complexes were collected in upper MIBK layer, and MIBK phase in which analytes were concentrated was taken in a small vial with a transfer pipet to determine analytes by GF-AAS.

Results and Discussion

Metal-PDC complexes. The pyrrolidine dithiocarbamate ion is bidentate ligand having ability to form stable 1 : 2 metal-ligand complexes with divalent metal ions and has been widely used as a complexing agent for the extraction to concentrate and separate many kinds of metal ions from an aqueous solution.[31,32] The extraction of metal-PDC complexes into ketonic solvents such as MIBK is a particularly well known method. The structure of this complex is shown as following:
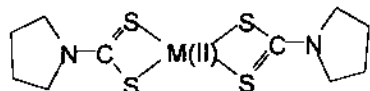
At low pH (pH < 2), APDC is decomposed into a pyrrolidine and carbodithioate group by the protonation of pyrrolidine.[33] That is, the protonation determines the rate of this decomposition, and the rate increases rapidly with pH lowering. But if the solution becomes alkaline by addition of a base such as ammonium hydroxide, APDC would be so stable that it is not necessary to prepare the solution, daily.[34] If metal-PDC complexes are formed by the addition of APDC to a metal ion solution, these complexes become more stable and are affected only at a very low pH. On the other hand, the formation of metal-PDC complexes are not complete at a high pH because of competition with a metal hydroxide formation. Therefore, the pH of solution should be adjusted to the range from weak acidic to weak basic. In general, an excess of complexing agent is used to allow the complete formation of metal complex and eliminate the interferences of other concomitant metal ions.

pH of sample solution. As described in previous section, pH of the solution is very important factor for the effective solvent sublation because the hydrogen ion concentration affects the stability of APDC and the formation of metal complexes. Therefore, the pH range should be optimized for the simultaneous sublation of the complexes of trace analytes such as Cd(II), Co(II), Cu(II) and Ni(II) ions.

An experiment was performed by changing the pH from 1.5 to 6.0 with nitric acid in 1.0 L of an aqueous solution in which 0.4 μg Cd(II), 5.0 μg Co(II), 4.0 μg Cu(II), and 20 μg Ni(II) were contained as analyte ions (Figure 2). From the Figure 2, the highest efficiencies for the preconcentration were found around pH 2.5. The efficiency was reduced with the increase of pH because metal hydroxide precipitation occurred competitively as mentioned above.

On the other hand, if hydrochloric acid is used to adjust pH, halide precipitation can occur to interfere with the complexation.[35] Therefore, nitric acid was used for it.

Complexing agent. As known well, APDC can make stable complexes with many kinds of metal ions and the metal complexes are easily extracted into various organic solvents.[31,32] Therefore, it is widely used as a complexing agent to concentrate and separate metal ions by extraction.

In this work, APDC was chosen as a complexing agent to separate and determine trace Cd(II) Co(II) Cu(II) and Ni (II) in water samples. The amount of APDC was important to form complexes quantitatively with trace metal ions in an
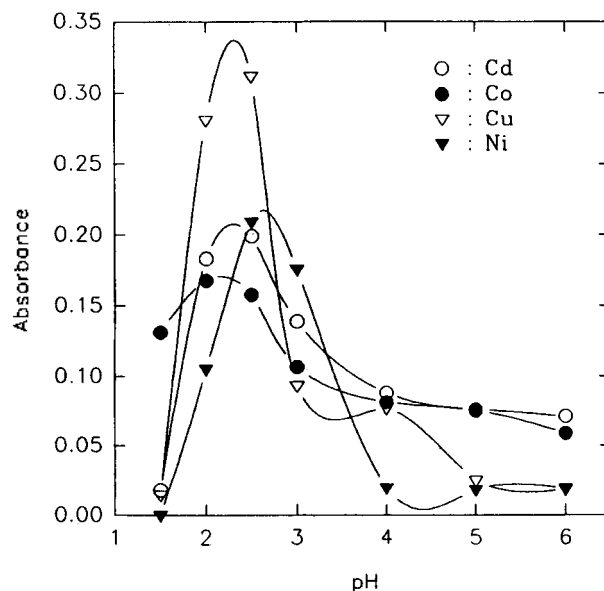

Figure 2. Effects of pH on the solvent sublation at the optimum conditions of other parameters. Analyte concentrations were Cd (II): 0.4 ng/mL, Co(II): 5.0 ng/mL, Cu(II): 4.0 ng/mL and Ni(II): 20 ng/mL.

aqueous solution. In order to fix the suitable amount of APDC, the sublation experiment was performed by changing the volume of 1.0% APDC solution added into 1.0 L of the standard solution including analyte ions of 0.4 µg Cd(II), 5.0 µg Co(II), 4.0 µg Cu(II), and 20 µg Ni(II) (Figure 3).

As shown in the Figure 3, the complexes of analyte ions were effectively formed on the addition of more than 2.0 mL of the APDC solution. This means that the quantitative formation of metal-PDC complex could be achieved by addition of about 250 times APDC of trace elements in mole ratio to the sample solution. The excess of complexing agent compensates for the loss due to the decomposition under an acidic condition as well as the presence of other competing ions.

On the other hand, the solution should be thoroughfully stirred to enhance the complexation of analyte ions with APDC. In order to examine the stirring effect, the stirring time was varied from 1 to 30 minutes at 180 rpm by using EYELA magnetic stirrer with 2 cm bar (Figure 4).

Figure 4 showed that the absorbances of all analytes except cadmium were almost constant on stirring for more than five minutes and the absorbance was constant on stirring for more than ten minutes in the case of cadmium. The Cd-PDC complex seemed to be more slowly formed than other analytes. In this work, the sublation was carried out after ten minute stirring.

Extracting solvent. As in solvent extraction, the affinity between organic solvent and metal complex also affects the extraction efficiency in solvent sublation. Therefore, the solvent has such an important role on the sublation that the type and volume of the solvent should be investigated to secure extracting quantitatively.

Cyclohexane, diisopropyl ketone, methyl isobutyl ketone and o-xylene were chosen as solvents for the selection of optimum solvent (Figure 5). These solvents were positioned on the upper zone of a flotation cell because their densities were 0.77-0.88 g/mL. And the solvent loss could be ig-
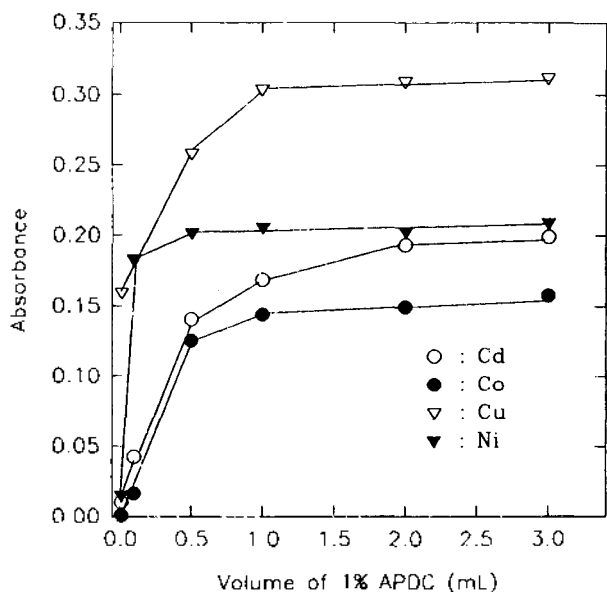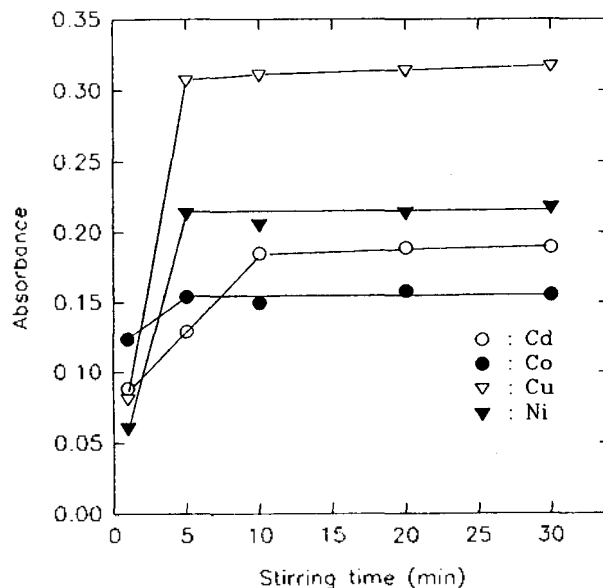

Figure 4. Optimization of stirring time with a magnetic stirrer for the effective complexation of anlyte ions.

nored during the experiment owing to the relatively low volatility except cyclohexane. As shown in the figure, all analytes were most efficiently extracted into methyl isobutyl ketone (MIBK) among above solvents and only copper showed almost constant extraction with all solvents.

Surfactant. Usually, metal-PDC complexes are so hydrophobic in an aqueous solution that their solvent sublation can be successfully achieved with the aid of numerous tiny gas bubbles. However, if a surfactant is used, then more complete extraction of analytes into the upper solvent layer can be expected owing to the effective flotation. That is, the hydrophobic functional group of the surfactant makes the complex more hydrophobic by formation of an electrostatic linkage with the complex so that the hydrophobic property enhances the partition of the complex into the organic layer, more efficiently.

Several kinds of surfactants were investigated in this work: cetyltrimethyl ammonium bromide and cetylpyridinium chloride as a cationic surfactant, sodium oleate and sodium
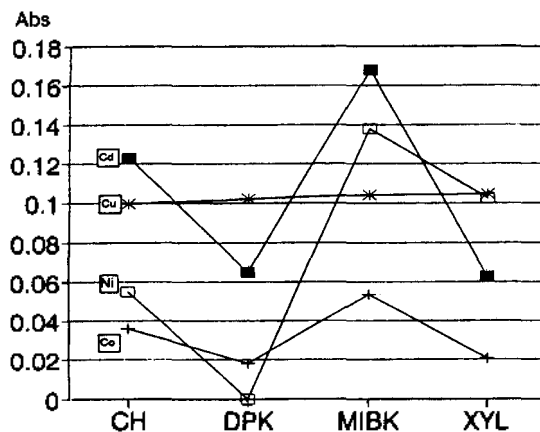

Figure 3. Volume dependencies of 1.0% APDC (complexing agent) solution on the sublation efficiencies at the same condtions as in Figure 2.

Figure 5. Comparison of several solvents for the extraction of analytes by the solvent sublation at the same conditions as in Figure 2.

lauryl sulfate as an anionic surfactant, and triton X-100 as a nonionic surfactant (Figure 6). Sodium lauryl sulfate and triton X-100 were more effective than other surfactants in our study. Non-ionic surfactant was expected to be the most excellent because metal-PDC was formed as a neutral precipitate in an aqueous solution. The experimental results for triton X-100 were consistent with such an expectation. But sodium lauryl sulfate was considered to have a good sublation ability because it has a function to support the floated materials. Besides, sodium lauryl sulfate gave more reproducible data and lower background than triton X-100 when absorbances of analyte ions were measured in the MIBK solution by Graphite Furnace AAS. Thus, sodium lauryl sulfate was chosen as a proper surfactant.

The amount of the surfactant used for the solvent sublation was optimized by changing the volume of the 0.2% ethanolic sodium lauryl sulfate solution. The absorbances of the analytes extracted were almost constant if more than 0.5 mL of the solution was added (Figure 7). The minimum volume, 0.5 mL surfactant solution, was added in this experiment because the separation of aqueous and organic layers was hampered by addition of a large volume.

The other important parameter is the gas bubbling rate which depends on the type of flotation technique and the quantity of sample. It is controlled by the gas pressure at the outlet of gas bomb and the porosity of the sintered-glass plate fitted in the flotation cell. The optimum bubbling rate was established through a preliminary experiments to obtain the maximum efficiency of the solvent sublation within a minimum operating time, and 60 mL/min was finally adopted as an optimum rate. At above 60 mL/min, large bubbles were produced so that the extraction of all metal-PDC complexes was delayed owing to reduction of the gas-liquid interface and too violent agitation. The bubbling time under 60 mL/min gas flow was also varied in the range of 5 to 50 minutes to see how long time was needed for the complete sublation (Figure 8). Figure 8 shows that absorbances of all analyte ions were almost constant when the bubbling time
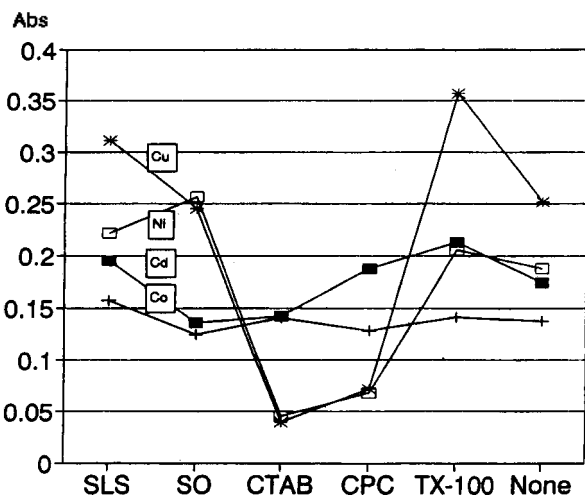

Figure 7. Optimum volume of 0.2% sodium lauryl sulfate solution for the effective solvent sublation of anlytes.

exceeded 40 minutes. In this work, the sublation was carried out for 45 minutes under about 60 mL/min nitrogen flow.

Extraction ability. In this section, the extractability (E) of each analyte was calculated under the optimized conditions of the solvent sublation. The extractability was given by following equation:[35]

$$E(\%) = 100 \times C_{org}/C_{tot} = 100 \times C_{org}/(C_{aq} + C_{org})$$

where, C_{tot}=total amount of analyte in the initial sample, C_{org}=amount of analyte in an organic phase after extraction, and C_{aq}=amount of analyte remained in aqueous solution after extraction.

The experiment was carried out using 1,000 mL standard aqueous solution containing 0.4 μg Cd(II), 5.0 μg Co(II), 4.0

Figure 6. Comparison of the flotation of metal-PDC complexes onto MIBK layer according to the type of surfactants used. SLS: sodium lauryl sulfate, SO: sodium oleate, CTAB: Cetyltrimethylammonium bromide, CPC: cetylpyridinium chloride, TX-100: Triton X-100.
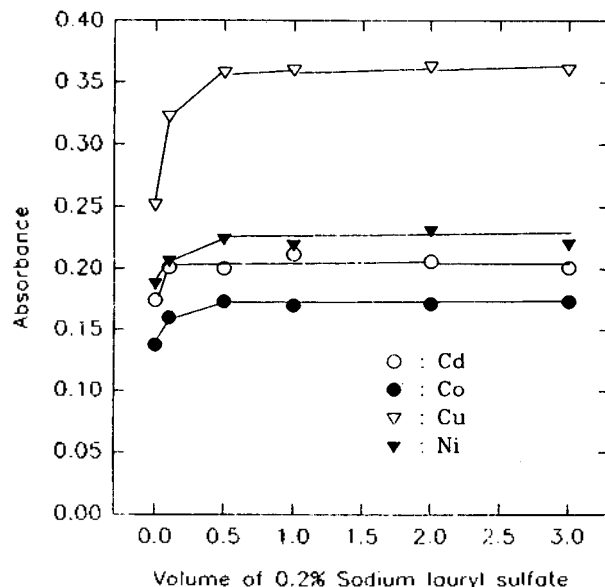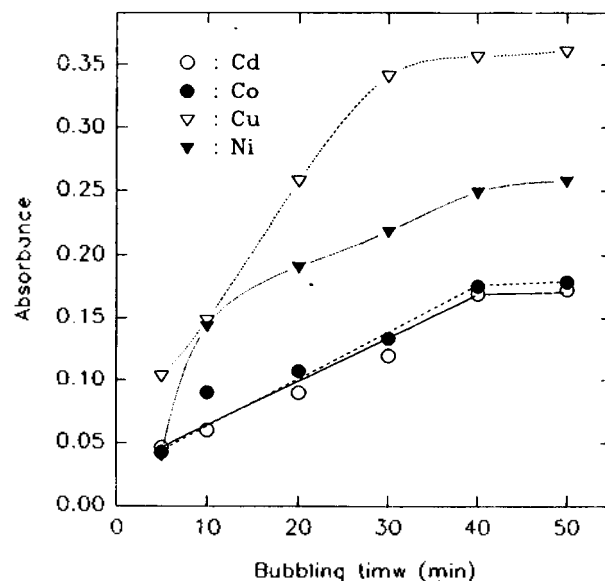

Figure 8. Effect of bubbling time for the effective flotation of the complexes with sodium lauryl sulfate solution.

Solvent Sublation of Trace Elements in Water

Bull. Korean Chem. Soc. **1998**, Vol. 19, No. 1   55

µg Cu(II) and 10 µg Ni(II). The amount in the organic phase was determined by using the calibration curve plotted with the standard solutions. The standard solutions were prepared by dissolving proper amounts of synthesized $Cd(PDC)_2$, $Co(PDC)_2$, $Cu(PDC)_2$ and $Ni(PDC)_2$ in MIBK. The amount of each analyte in the organic phase was 0.35 µg Cd(II), 4.3 µg Co(II), 3.8 µg Cu(II) and 7.6 µg Ni(II), respectively. Therefore, the extractabilities obtained were as follows: 88% for Cd(II), 86% for Co(II), 95% for Cu(II) and 76% for Ni(II).

Influences of interfering ions. It was known that APDC had an ability to combine with more than 35 metal ions including the analytes of this work.[31,32] Therefore, the interferences of other concomitant metal ions were expected by their competition reaction with the analytes in the formation of metal-PDC complexes. But such competitions could be overcame by addition of excess APDC to the analytic solution. On the other hand, a graphite furnace atomic absorption spectrophotometry for the determination of anlytes in the organic phase was so element-selective that the spectral interferences of other metal ions could not be considered in absorbance measurements. And others such as physical and chemical interferences could be ignored because there was one solvent, MIBK, in measuring solution and only trace amounts of other concomitant elements were extracted from water samples into MIBK by the solvent sublation. Thus, any treatment for the correction of interferences was not needed.

Analytical results and recoveries. The method developed in this research was applied to several kinds of water samples such as tap, waste, river and sea waters under the optimized conditions to examine the applicability. The standard solutions for plotting calibration curves were prepared by adding a proper amount of each analyte in 1.0 L deionized water. After the analytes were extracted into
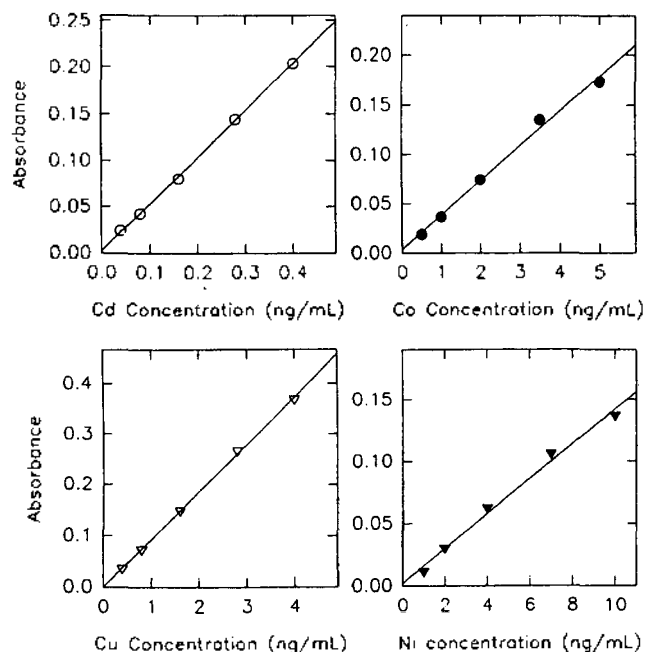

Figure 9. Calibration curves of four elements. The absorbances were the values measured in MIBK solution after the solvent sublation of complexes.

Table 2. Analytical results and recoveries obtained in real samples by solvent sublation

Sample	Elements	Spiked	Measured	Recovered	RSD (%)	Recovery (%)
Waste water	Cd(II)	0.000	0.059	0.05	9.3	125
		0.040	0.11		1.1	
	Co(II)	0.00	0.16	0.53	11	106
		0.50	0.69		5.9	
	Cu(II)	0.00	2.1	0.5	3.2	125
		0.40	2.6		0.4	
	Ni(II)	0.0	–	2.4		120
		2.0	2.4		1.1	
Tap water	Cd(II)	0.000	0.048	0.046	9.8	115
		0.040	0.094		4.8	
	Co(II)	0.00	–	0.46		92
		0.50	0.46		3.6	
	Cu(II)	0.00	3.5	0.4	1.1	100
		0.40	3.9		0.2	
	Ni(II)	0.0	–	2.0		100
		2.0	2.0		1.8	
Miho-chun	Cd(II)	0.000	0.039	0.050	11	125
		0.040	0.089		1.4	
	Co(II)	0.00	–	0.53		106
		0.50	0.53		1.7	
	Cu(II)	0.00	1.7	0.4	7.2	100
		0.40	2.1		3.7	
	Ni(II)	0.0	–	2.3		115
		2.0	2.3		4.0	
Sea water	Cd(II)	0.000	0.86	0.05	4.7	125
		0.040	0.14		3.0	
	Co(II)	0.00	–	0.54		108
		0.50	0.54		8.2	
	Cu(II)	0.00	2.3	0.5	4.9	125
		0.40	2.8		1.7	
	Ni(II)	0.0	–	2.1		105
		2.0	2.1		4.9	

MIBK by the solvent sublation with the same procedure as for the samples, the calibration curves were plotted using the measured absorbances of analytes in MIBK (Figure 9). The background was corrected by subtracting the blank absorbance from the measured absorbances. The blank in this case means the MIBK solution which was sublated using a pure deionized water. All calibration curves were linear in the ranges of 0.05 to 0.4 ng/mL for Cd, 0.5 to 5.0 ng/mL for Co, 0.5 to 4.0 ng/mL for Cu and 0.5 to 10 ng/mL for Ni in aqueous solution. The analytical results in real samples were listed in Table 2.

The recoveries were also examined by the above procedure with samples to which each analyte of a given amount was spiked. The recoveries of more than 92% were also obtained for all the analytes as in Table 2. These results indicate that this analytical method could be successfully applied to preconcentration and determination of trace Cd(II), Co(II), Cu(II) and Ni(II) in water samples.

Conclusions

The preconcentration and determination methods of trace

Cd(II), Co(II), Cu(II) and Ni(II) in water samples were developed by the application of solvent sublation using APDC as a complexing agent. The pH of sample solution was adjusted to 2.5 with nitric acid to form metal-PDC complexes, effectively. MIBK was selected as the most suitable organic solvent to extract the complexes. The extraction was aided by adding the surfactant solution of 0.2% ethanolic sodium lauryl sulfate and bubbling nitrogen gas. The extractability by this procedure was 88% for Cd(II), 86% for Co(II), 95% for Cu(II) and 76% for Ni(II), respectively, which are rather good for the solvent sublation of trace metal ions. Finally, the recoveries of more than 92% for each elements in real samples showed that this procedure could be applied for quantitative determination of trace elements in water samples.

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