1036 *Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 10

Young-Sang Kim et al.

anions were observed for Zn/Al-LDH. A molecular recognition ability of intercalation into Zn/Al-LDH is in the order AQ26 > TP >> NA26. The shape of the anion plays an important role in the specific intercalation.

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Studies on Solvent Extraction and Flotation Technique Using Metal-Dithizone Complexes(II). Determination of Trace Elements in Water Samples by Solvent Sublation

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The preconcentration and determination of trace elements in water samples were studied by a solvent sublation utilizing dithizonate complexation. After metal dithizonates were formed, trace amounts of cadmium, cobalt, copper and lead were floated and extracted into small volume of a water-immiscible organic solvent on the surface of sample solution and determined in the solvent directly by GF-AAS. Several experimental conditions as formation condition of metal-dithizonate complexes, pH of solution, amount of dithizone, stirring time, the type and amount of surfactants, N_2 bubbling rate and so on were optimized for the complete formation and effective flotation of the complexes. And also four kinds of light solvents were compared each other to extract the floated complexes, effectively. After the pH was adjusted to 4.0 with 5 M HNO_3, 8.0 mL of 0.05% acetone solution of dithizone was added to 1.00 L water sample. The dithizonate complexes were flotated and extracted into the upper methyl isobutylketone (MIBK) layer by the addition of 2.0 mL 0.2% ethanolic sodium lauryl sulfate solution and with the aid of small nitrogen gas bubbles. And this solvent sublation method was applied to the analysis of real water samples and good results of more than 85% recoveries were obtained in spiked samples.

Introduction

At present, an importance and necessity of accurate informations about trace elements in various kinds of samples increases with the industrial development in our society. Spectrochemical, electrochemical and radiochemical methods are widely used for the determination of trace elements to get the information. But although such methods

Studies on Solvent Extraction and Flotation Technique

Bull. Korean Chem. Soc. **1998**, Vol. 19, No. 10   1037

provides excellent sensitivity, selectivity, accuracy and precision in the elemental analysis, the separation and preconcentration is necessary to determine the analytes existed under the detection limits of the methods.

Solvent extraction,[1-3] precipitate,[4] ion-exchange resin[5,6] and flotation[7-27] techniques are widely used as separation and preconcentration methods of the trace elements. Our laboratory has applied flotation techniques[15,18-22] to various water samples because they have great advantages of a good concentration efficiency and an easy treatment in a large volume of sample. Then the flotation technique is classified to precipitate and ion methods depending on the type of material floated. An inorganic or organic precipitation[8-13,18-22] is applied for precipitate flotation and the formation of bulky metal-complex ions[14-17] is used for the ion flotation. Besides, a solvent sublation has also been applied for preconcentration of trace elements recently, which is defined as a combination technique of the flotation technique and a solvent extraction.[23-28]

The solvent sublation has good advantages that analytes of complexed forms can be directly extracted into solvent by the flotation and determined in the solvent as a concentrated state[25,26] by the above analysis methods. But the solvent should have special properties. That is, it can rapidly dissolve metal-complex formed and make water-immiscible stable layer on the sample solution. It should be so nonvolatile that any loss does not occur during the experimental procedure and give a small background in the determination of elements by an analytical method.

Kotsuji and coworkers[23,24] have applied the solvent sublation to the determination of trace iron and copper by the metal-complexes formation of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT). After the iron of μg level in 160-500 mL seawater was reduced to Fe(II), the Fe(II)-PDT complex formed was floated and extracted into the upper layer of 5.0 mL 3-methyl-1-butanol(isoamyl alcohol) by aids of sodium dodecyl sulfate as a surfactant and tiny bubbles of nitrogen gas. The iron was directly determined as the complex in the organic phase by UV/Vis spectrophotometry. The copper was also sublated and determined into the mixed solvent of 3-methyl-1-butanol and butyl acetate as a Cu(I)-PDT comlex with the same procedure as iron. And Cervera and cowokers[27] applied this solvent sublation for the determination of copper by the formation of Cu(II)-dithizonate complex and flotation of the complex into MIBK using sodium dodecyl sulfate as a surfactant. The copper was determined in MIBK by flame-atomic absorption spectrophotometry (AAS).

In the present work, trace amounts of Co(II), Cu(II), Cd (II) and Pb(II) were sublated into MIBK as M(II)-dithizonate complexes by the flotation with aids of 0.1% ethanolic sodium lauryl sulfate as a surfactant and tiny N_2 bubbles. The analytes were determined in MIBK taken from the upper layer of sample solution with a pipet by a graphite furnace atomic absorption spectrophotometry (GF-AAS). Finally, recoveries were obtained in sample solutions in which given amounts of analytes were spiked.

Experimental

Apparatus and Reagents. Dithizone and all other chemicals were used as guaranteed reagent grade. A

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

Atomic absorption spectrophotometer: Perkin-Elmer model			
	Cobalt	Copper	Cadmium	Lead
	240.9	324.8	228.8	283.3
Current	30	30	4	10
Band	0.7	0.7	0.7	0.7
Temperature programs for a graphite furnace			
Drying	Cobalt	Copper	Cadmium	Lead
	100°C 5s*(5s)	150°C 5s(5s)	110°C 5s(5s)	110°C 3s(3s)
Charring 1	900°C 2s(4s)	800°C 6s(6s)	300°C 5s(5s)	1000°C 2s(4s)
2	1200°C 5s(5s)			
Atomization	2400°C 4s(4s)	2600°C 3s(8s)	1800°C 2s(2s)	2000°C 2s(2s)
Cleaning	2700°C 3s(3s)	2700°C 3s(3s)	2700°C 3s(3s)	2700°C 3s(3s)

Sample injection: 20 μL
Graphite tube: pyrolytically coated
*: Holding time
( ): Ramping time

deionized water eluted through Milli-Q system was used in this experiment.

Stocks solutions of 1,000 μg/mL Co(II), Cu(II), Cd(II) and Pb(II) were prepared by dissolving given amounts of cobalt powder (Fluka Chem. Co.), copper powder (Aldrich Chem. Co.), cadmium metal (99.99%, Fluka Chem. Co.) and lead nitrate (Junsei Chem. Co.) in 1 : 1 nitric acid and then diluting to 1,000 mL with a deionized water. The working solution were prepared by diluting the stock solution with a dionized water. Dithizone (Aldrich Chem. co.) was dissolved in an acetone at the concentration of 0.05% (w/v). Ethanolic sodium lauryl sulfate (Hayashi Chem. Co.) solution [0.2% (w/v)] was used as a surfactant.

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.

Experimental Procedure. After a water sample was filtered with glass filter and then transferred into an erlenmeyer flask. A 0.05% (w/v) acetonic dithizone solution 8.0 mL was added to 1.0 L sample solution and pH was adjusted to 4.0 with 5.0 M HNO_3. The solution was stirred with Eyela magnetic stirrer for 40 min. After 0.2% ethanolic sodium lauryl sulfate 2.0 mL was added, the solution was stirred for 5 min again. The solution was transferred into a flotation cell as shown in reference 21 and 20.0 mL MIBK was added on the solution. Nitrogen gas was bubbled at the flow rate of 50 mL/min through the sintered glass disk from the bottom of the cell for 20 min. And 10.0 mL MIBK solution into which M(II)-dithizonates extracted was taken with a 10.0 mL pipette to determine analytic elements by GF-AAS, directly.

Results and Discussion
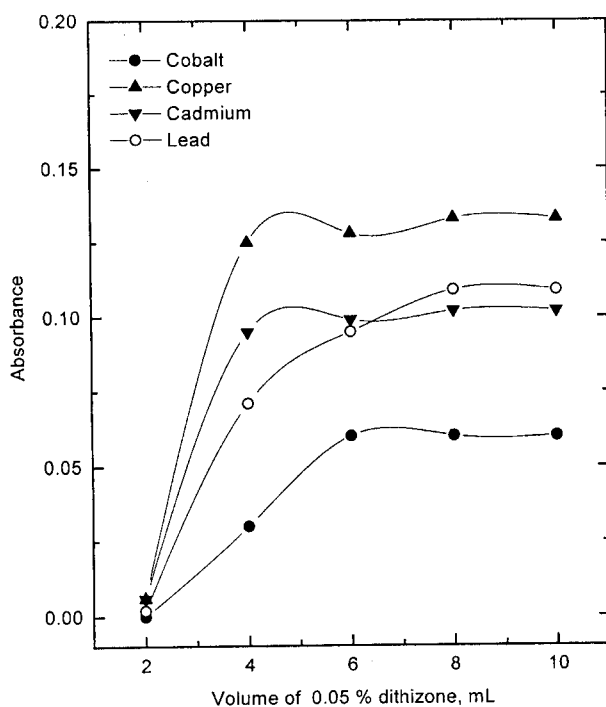
Dithizone as a Complexing Agent. According to the

Figure 1. Amount of a complexing agent(dithizone) for the effective complexation and solvent sublation of analyte ions. Co (II): 20.0 ng/mL; Cu(II): 2.5 ng/mL; Cd(II): 2.0 ng/mL; Pb(II): 2.5 ng/mL.
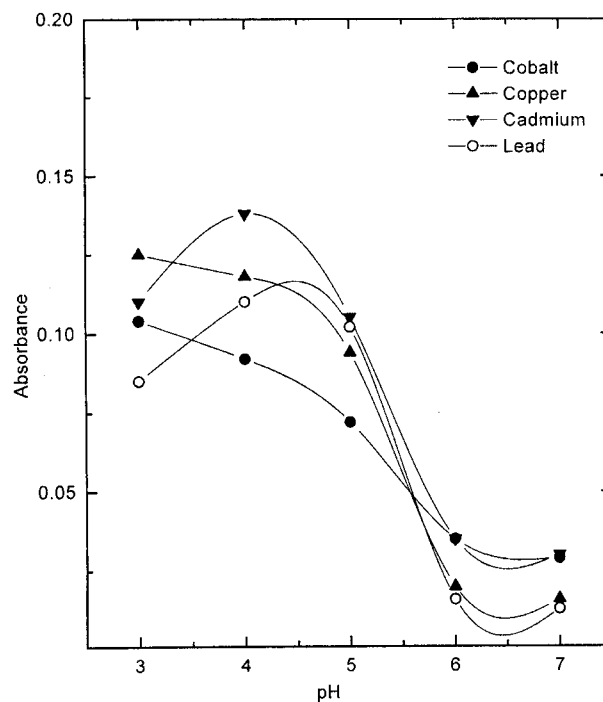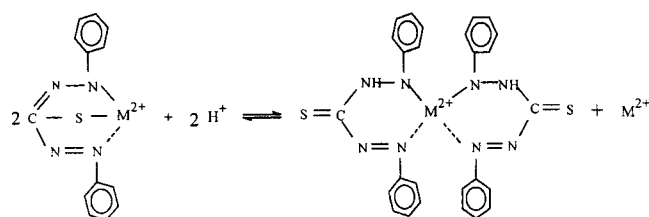

Figure 2. Effects of pH on the complexation of analyte ions with dithizone for a solvent sublation. With the same concentrations of analytes as in Figure 1.

results of our laboratory on the extraction of metal ions using several ligands, dithizone forms stable complexes with many kinds of metal ions and its complexes are effectively partitioned into various organic solvents.[28] Of course, although the partition coefficient depends upon the kind of metal ion and solvent, dithizone have been frequently used to extract elements into a solvent from an aqueous solution. And dithizone is usually insoluble in a water so that it should be dissolved in an acetone prior to be mixed in a water. An amount of dithizone added into a sample solution is very important to make trace elements complexes, quantitatively.

After pH of 1.0 L aqueous solution containing 20.0 μg/L Co(II), 2.5 μg/L Cu(II), 2.0 μg/L Cd(II) and 2.5 μg/L Pb(II) was adjusted to 4.0 with 5.0 M HNO$_3$, 0.05% (w/v) acetonic dithizone was variably added from 2 to 10 mL (Figure 1). And each solution were sublated with optimized conditions for the complexation and flotation. Atomic absorbance of each element measured in MIBK was plotted versus the volume of dithizone solution added (Figure 1).

The Figure 1 showed that the complexes was effectively formed on the addition of more than 6.0 mL of 0.05% dithizone for the Co(II), 4.0 mL for Cu(II) and Cd(II), and 8.0 for Pb(II). Therefore, 8.0 mL of 0.05% dithizone solution was added to the 1.0 L of sample solution as a complexing agent. This amount of ligand was excess of about 1,000 times of trace analytes in mole ratio.

pH of Sample Solution. The pH of sample solution must be adjusted for the simultaneous sublation of the analyte ions by the effective formation of complexes. As reported, dithizone complexes are stable in acidic solution[29] because of the formation of enol-form complexes in basic

solution.

Keto-form complexes are known to be stable better than enol-form complexes. So the efficiency of solvent sublation was investigated by changing the pH from 3.0 to 7.0 for the 1.0 L of aqueous solution containing analytic ions as in previous section. As shown in Figure 2, the best efficiency was obtained at around pH 4.0.

Stirring Time. The solution should be stirred for the effective formation of complexes because each metal has a different complexation rate.

The solution containing metal ions and dithizone was stirred by Eyela Magnetic Stirrer RC-2 (Tokyo Rikakikai Co., Expt.) at the stirring speed of about 180 r.p.m. (Figure 3).

The Figure 4 showed that the absorbances of Co(II) and Cd(II) were increased with the increase of stirring time, but Cu(II) and Pb(II) were decreased after 40 min stirring. Such facts were considered because of the slow rate of complexation for Co(II) and Cd(II)[30] and the decomplexation of their complexes in case of Cu(II) and Pb(II). In this work, the sublation was carried out after 40 min stirring.

Surfactant. The metal-dithizonate complexes themselves are so significantly hydrophobic that they can be floated without any surfactant only by bubbling nitrogen gas. However, the use of a surfactant is expected to make
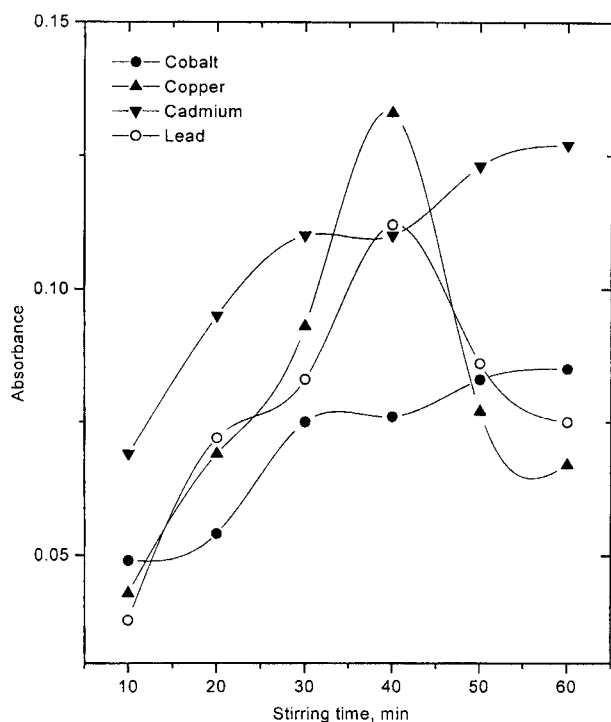
Figure 3. Stirring time for the complexation of analyte ions after the addition of dithizone and pH adjustment. With the same concentration of analytes as in Figure 1.

the flotation more efficient. Several kinds of surfactants were investigated to test their abilities for the more effective flotation of metal-dithizonate complexes into MIBK layer on the solution: cetyltrimethyl ammonium bromide and cetylpyridinium chloride for cationic surfactants; sodium lauryl sulfate and sodium oleate for anionic surfactants; Triton X-100 for nonionic surfactant (Figure 4).

As a results of the comparison for the flotation efficiencies, the efficiency was a little increased by adding the anionic surfactants only in case of Co(II) and other
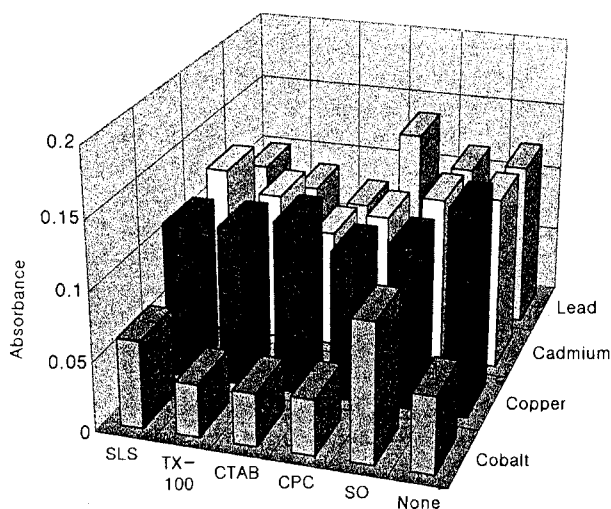

Figure 4. Comparison of flotation efficiencies according to various surfactants. SLS: sodium lauryl sulfate, SO: sodium oleate, CTAB: cetyl trimethyl ammonium bromide, CPC: cetylpyridinium chloride, TX-100: triton X-100.
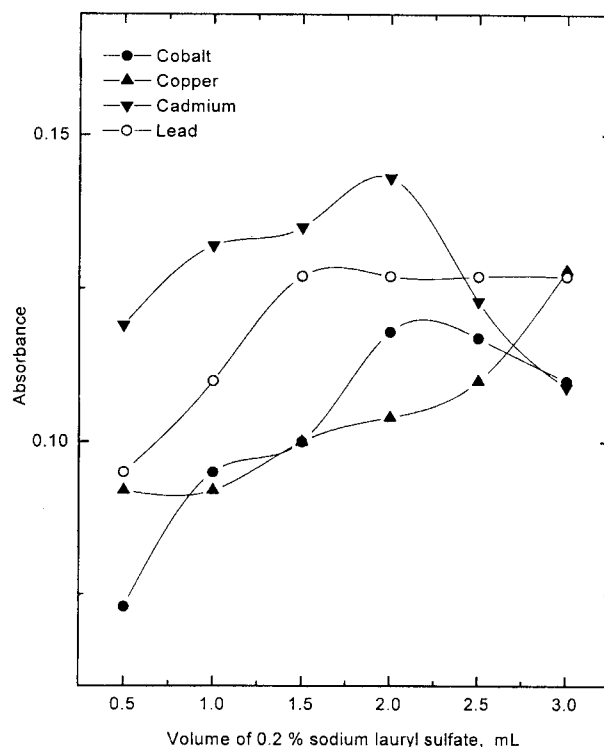

Figure 5. Amount of a surfactant for the effective sublation of metal-dithizonate complexes. With the same concentration of analytes as in Figure 1.

metal ions did show little differences regardless the use of any surfactants. So the sodium lauryl sulfate was selected as a surfactant because it provided more reproducible flotation than sodium oleate by the capability to support the foams formed on the solution[31] and also it was known to give a low background in the measurement of atomic absorbance by GF-AAS.[32]

Besides, the minimum amount of sodium lauryl sulfate was found for the quantitative sublation of complexes by changing the volume of 0.2% solution from 0.5 to 3.0 mL (Figure 5). The best efficiency was obtained on the addition of 2.0 mL as shown in the Figure 5.

On the other hand, stirring time after the addition of the surfactant was known to affect the flotation efficiecy signficantly so that it was also investigated from 2 to 12 min. Cu(II) and Cd(II) complexes were almost constantly floated by stirring for more than 5 min, but Co(II) and Pb(II) were decreased with the time after 5 min stirring (Figure 6). Usually, Co(II)-dithizonate complexation rate was slow and in the rate determining step complex charge was positive. Therefore, the absorbance was increased by stirring time after the addition of the surfactant, but decreased with time. Such fact was considered because of the keto-form of Co(II) complex was so hydrophobic.

Bubbling of Nitrogen Gas. Gas bubbling has a important role in the flotation technique. Usually, nitrogen is widely used for this purpose because it is inert and cheap. The bubbles of nitrogen gas were formed by passing through the porous sintered-glass plate fitted in the bottom of the flotation cell. And also, a little larger flow rate of the nitrogen gas may be possible in a solvent sublation than in other flotation techniques because the complexes of analytes
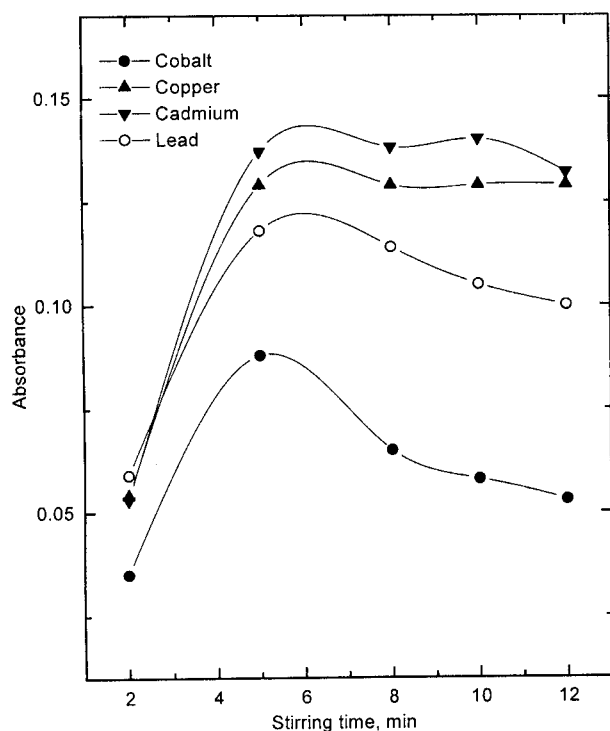
Figure 6. Stirring time to form hydrophobic precipitates of metal- dithizonate complexes after the addition of a surfactant. With the same concentrations of analytes as in Figure 1.
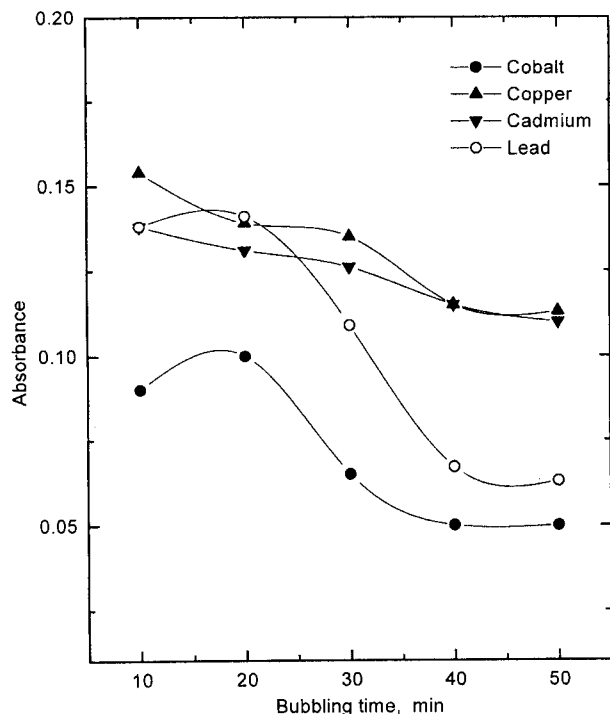

Figure 8. Sublation efficiencies according to the type of solvent. MIBK: methylisobutylketone, DIPK: diisopropylketone σ-X: ortho-xylene, C_6H_{12}: cyclohexane.

In this work, the flow rate of nitrogen gas was adjusted at 50 mL/min, and a bubbling time was investigated at the rate by change it from 10 to 50 min (Figure 7). The sublation of Cu(II) and Cd(II) was hardly affected by the time and Co(II) and Pb(II) was decreased at more than 20 min.

Organic Solvent. Sublation efficiencies of complexes are also influenced by the type of organic solvent as in a solvent extraction in which its efficiency depends upon the solubility of a complexes in the solvent.

Therefore, the sublation efficiencies were investigated according to the type of solvent used with 4 kinds of light solvents having specific gravities of 0.77-0.89 g/mL (Figure 8). That is, methylisobutylketone (MIBK), diisopropylketone, cyclohexane and σ-xylene were used. MIBK showed the best extraction efficiency for all ions and σ-xylene had the second ability to sublate complexes among 4 solvents.

Interferences of Concomitant Ions. It is known that a dithizone is a widely used ligand to form a complex with about 20 kinds of metal ions.[33] Therefore, if any metal ions coexist in sample solutions at the level of major or minor constituents, they can interfere with the complexation and sublation of analyte ions.

But because objective samples were several kinds of water in which most of other ions existed at a trace level and GF-AAS was known to be an excellent element-selective method for the elemental determination, any special treatments for the elimination of interfering ions were not carried out in this investigation. Only a little excess dithizone was added as a ligand to achieve the complete complexation of all metel ions regardless of the type of element.

Analytical Results and Recoveries. This solvent sublation method was applied to real samples such as one kind of tap water and 3 kinds of river water. A series of 1.0 L standard solutions were prepared to plot calibration curves by diluting stock solution with a deionized water. Each standard solution was treated and sublated with the same conditions as for water samples. Of course, background corrections in the measurement of absorbances were

Figure 7. Bubbling time of a nitrogen gas for the effective sublation of complexes.

can be immediately extracted and dissolved in the upper layer of a solvent. As a result, the redistribution of the complexes into a bulky solution is hardly occurred by a convection compared to other flotation techniques in which floated materials should be supported by using a surfactant.
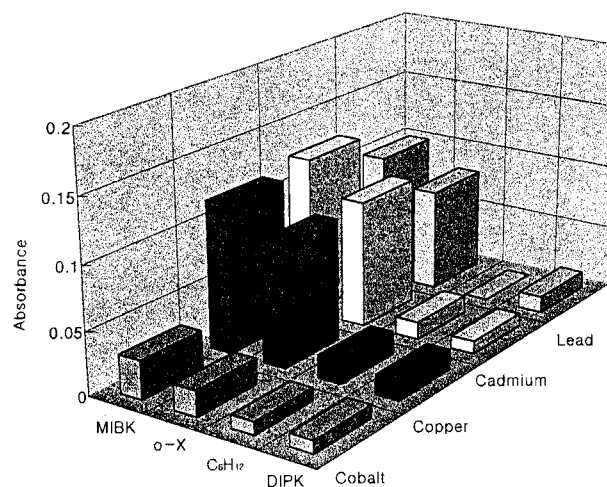
Studies on Solvent Extraction and Flotation Technique

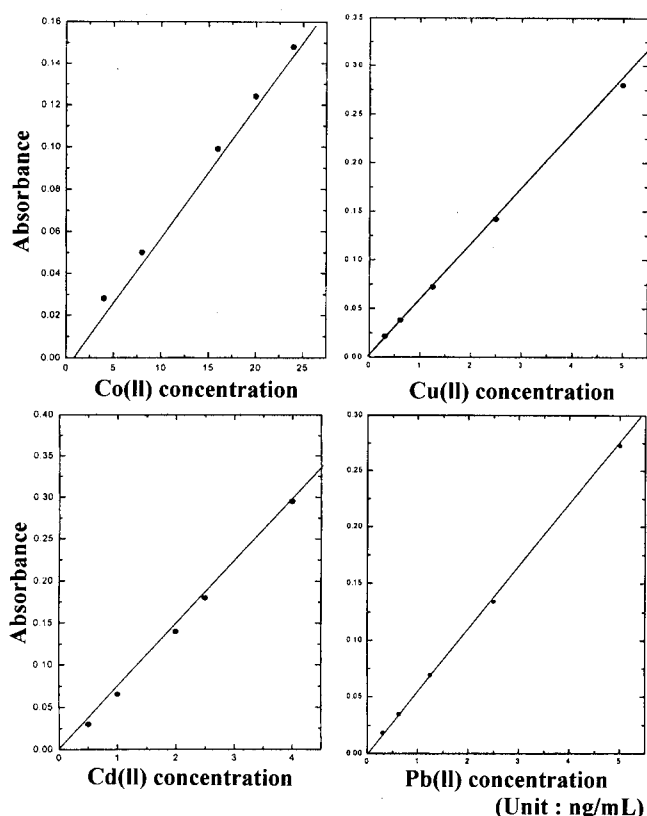*Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 10   1041

Figure 9. Calibration curves for the determination of analytes by a solvent sublation.

done by the same treatment of a deionized water as sample. The linearities were excellent as shown in Figure 9.

Analytical results are given in Table 2. Water samples were filtered through membrane filter prior to sampling. And also recovery data were obtained in the spiked samples in which given amounts of analyte ions were added. Recoveries of 85-120% range indicated that this solvent sublation was a quantitative method for the preconcentration and determination of trace Co(II), Cu(II), Cd(II) and Pb(II) in water samples.

Conclusion

Trace amounts of Co(II), Cu(II), Cd(II) and Pb(II) were preconcentrated by the solvent sublation with their dithizone complexes for the determination of them by a graphite furnace atomic absorption spectrophotometry. The complexes were formed in sample solutions of pH 4.0 adjusted with 5.0 M HNO_3 and MIBK was used as a suitable organic solvent. The flotation efficiency of complexes were increased by the addition of sodium lauryl sulfate as a surfactant and bubbling of nitrogen gas. This procedure could be applied to the analysis of four kinds of water samples and recoveries of analytes in spiked samples were more than 85%. It could be expected that the application of this method were expanded to many kinds of materials for the preconcentration and determination of trace elements.

Table 2. Analytical results of metal ions in real samples by a solvent sublation

Sample	Elements	Spiked[d]	Mea-sured[d]	Reco-vered[d]	RSD (%)[e]	Recovery (%)
Tap water	Cobalt	0.00	0.00		2.00	
		8.00	7.11	7.11	1.50	88
	Copper	0.00	1050		1.00	
	Cadmium	0.00	0.00		1.25	
		2.00	1.94	1.94	1.33	97
	Lead	0.00	0.00		1.15	
		2.50	2.41	2.41	1.34	96
Miho-chun[a]	Cobalt	0.00	0.00		1.83	
		8.00	7.26	7.26	1.09	91
	Copper	0.00	3.21		1.27	
		2.50	5.94	2.73	1.31	110
	Cadmium	0.00	0.29		1.05	
		2.00	2.18	1.89	2.18	95
	Lead	0.00	0.74		1.08	
		2.50	3.66	2.92	1.65	117
Kobok[b]	Cobalt	0.00	0.00		1.30	
		8.00	7.02	7.02	2.16	87
	Copper	0.00	3.00		1.55	
		2.50	4.41	1.87	1.58	106
	Cadmium	0.00	0.54		1.58	
		2.00	4.41	1.87	1.58	93
	Lead	0.00	2.62		1.00	
		2.50	5.27	2.65	1.02	106
Choongjoo-ho[c]	Cobalt	0.00	0.00		1.20	
		8.00	6.93	6.93	1.10	87
	Copper	0.00	2.40			
		2.50	4.97	2.57	0.98	103
	Cadmium	0.00	0.45			
		2.00	2.26	1.81	1.42	91
	Lead	0.00	0.41		1.16	
		2.50	3.07	2.66	1.22	106

[a] a riverside around seochang campus of korea univ. [b] an irrigation reservoir around seochang campus of korea univ. [c] a lake of Choongjoo. [d] Unit: ng/mL [e]relatively standard deviation.

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Laser-Induced Fluorescence Spectroscopy of the S_1-S_0 ($^1B_2$-$^1A_1$) Transition of Dimethyldiazirine

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The fluorescence excitation (FE) spectrum of the S_1-S_0 ($^1B_2$-$^1A_1$) transition of dimethyldiazirine cooled in supersonic jet expansions has been obtained. Dispersed fluorescence (DF) spectra have also been taken for some prominent features of the FE spectrum. Vibrational analyses of the FE and DF spectra with the help of an *ab initio* molecular orbital calculation lead to some new vibrational assignments and refined fundamental frequencies.

Introduction

Diazirines are unique in that they contain a highly strained, three-membered, heterocyclic CN_2 ring. Since these molecules have a strong absorption band in the near ultraviolet (UV) region, they have been the topics of many photochemical and spectroscopic studies since the three-membered ring structure was first established.[1] Diazirines decompose into a carbene radical and an N_2 molecule when photolyzed in the ultraviolet (UV) wavelength.[2,3] While the infrared spectrum of diazirine was first analyzed by Ettinger,[4] most of the early spectroscopic studies on diazirine and substituted diazirines have been performed by Merritt and coworkers.[5-13] They determined the structures of methyl- and dimethyldiazirines with microwave spectroscopy[10,11] and analyzed the infrared spectra of diazirine and methyl-diazirines, confirming the cyclic strucuture.[12,13] Robertson

and Merritt have reported the electronic spectra for the n-π^* transition of various diazirines.[6-9] For diazirine, the simplest member of the group, the strongest band system in UV was assigned to the $\tilde{A}^1B_1$-X^1A_1 transition and the band origin was determined to be located at 31,187 cm^{-1}.[6] A long progression of the C-N symmetric stretching vibration (ν_3) has been observed. Substituted diazirines such as methyl-, dimethyl, bromomethyl-, and chloromethyldiazirines show similar spectra to the unsubstituted counterpart except that the transition frequencies exhibit a significant red shift upon substitution.[7-9] The electronic spectroscopy of difluoro-diazirine was first investigated by Lombardi *et al.*[14] and later by Hepburn and Hollas.[15] Vandersall and Rice have provided the fluorescence spectra from single vibronic levels and investigated the collisional relaxation in the $^1B_1$(n-π^*) electronic manifold.[16] More recently Neusser and coworkers have obtained and analyzed the high-resolution Doppler-free two-photon spectrum providing a more refined excited state geometry and more fundamental frequencies.[17]

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