Determination of Zinc and Lead in Water Samples by Solvent Sublation Using Ion Pairing of Metal-Naphthoate Complexes and Tetra-*n*-butylammonium Ion

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Solvent sublation has been studied for the separation and determination of trace Zn(II) and Pb(II) in water samples. A synergy producing method was utilized to improve the efficiency of extraction in the sublation using an ion-pair of metal-naphthoate $\{M\text{-}(Nph)_3^-\}$ complexes and tetra-*n*-butylammonium (TBA^+) ion. After the $M\text{-}(Nph)_3^-$ complexes were formed by adding 1-naphthoic acid to the sample solution, tetra-*n*-butylammonium bromide was added in the solution to form the ion-pair. And sodium lauryl sulfate (SLS) was added to make the ion-pair hydrophobic. The ion-pairs of the metal complexes were floated and extracted into methylisobutyl ketone (MIBK) from the aqueous solution by bubbling with nitrogen gas in a flotation cell. Metal ions in MIBK solution were measured by graphite furnace-AAS. Experimental conditions were optimized as follow so. After the pH of a 1.0 L water sample was adjusted to 5.0, 6.0 mL of 0.1 M 1-HNph and 10 mL of 0.03 M TBA-bromide were added to the sample to form ion-pairs, and 2.0 mL of 0.2%(w/v) SLS was added to make the ion-pairs hydrophobic. The solution was bubbled with 30 mL/min N_2 gas for 5 minutes in a flotation cell. Linear calibration curves were obtained for the determination of Zn(II) and Pb(II) in several water samples. Reproducible results of showing a relative standard deviation of < 10% and recoveries of 80-100% could be obtained.

Keywords : Solvent sublation, 1-Naphthoic acid, Ion-pair formation, Solvent extraction, Flotation technique.

Introduction

An application of solvent sublation was studied for the determination of trace Zn(II) and Pb(II) in water samples. Solvent sublation is a combined method of solvent extraction[1-7] and flotation technique[8-14] for the separation and concentration of trace analytes. This technique[15-17] is used to determine trace elements in water samples by concentrating analytes from a large volume of sample solution in this laboratory.[18,30-32] Inorganic and organic precipitates[19,20-23,24-26] or complex ions[27,28] are floated and directly extracted into a small volume of solvent on the solution.

We have studied this technique for the preconcentration and determination of various trace elements in water samples. Dithizone was used as a ligand for Cd(II), Co(II), Cu(II) and Pb(II) in a solution of pH 4.0.[18] The dithizonate complexes were flotated and extracted into the upper MIBK layer by the addition of 0.2% ethanolic sodium lauryl sulfate and with the aid of small nitrogen gas bubbles. Ammonium pyrrolidine dithiocarbamate (APDC) was used as a complexing agent for trace Cd(II), Co(II), Cu(II) and Ni(II) at pH 2.5[30] under the previous conditions. So, 8-hydroxyquinoline (oxine, HQ) complexes were used to separate and preconcentrate a trace of Co(II), Cu(II) and Ni(II) for determination.[31] The pH was adjusted to 9.0 and cetyltrimethylammonium bromide (CTAB) was added as a surfactant. The preconcentration and determination of trace Au(III), Pt(IV) and Pd(II) was studied with their complexes of 2-mercaptobenzothiazole (MBT) in 2.0 M HCl solution.[32] CTAB was used and MIBK was a solvent. These studies were fairly accurate and reproducible with recoveries of about 100% in spiked samples and an RSD of < 10%.

Aliphatic carboxylates have been widely used as a ligand to extract many kinds of metallic ions into organic solvents, but the use of aromatic carboxylates has seldom been studied for solvent extraction because their metallic complexes are not easily extracted into a solvent.[29] In the present study, the use of one kind of aromatic carboxylates, 1-naphthoic acid, was tried as a ligand to make complex ions of Zn(II) and Pb(II) and their ion-pairs were formed with tetrabutylammonium (TBA^+) ion as a counter ion to utilize a synergistic extraction of them to an organic solvent.

After the ion-pairs were made hydrophobic by adding sodium lauryl sulfate as a surfactant, they were floated and extracted into a small volume of MIBK on the surface of the sample solution. The absorbances of analytical elements were measured in the solvent by GF-AAS. Various experimental conditions, the pH of the sample solution, the added amount of 1-naphthoic acid and TBA-bromide, stirring time, the type and added amount of surfactant, and bubbling rate and time of nitrogen gas, were optimized for the complete formation and effective flotation of ion-pairs.

This procedure was applied to the analysis of in-land water samples to investigate its practical usefulness and applicability. And a relative standard deviation in the analytical results and recoveries of spiked amounts in the samples were obtained to evaluate the precision and accuracy of this method.

Experimental Section

Reagents and instruments. Purified water by Millipore Milli-Q system was used in all experiments and the reagents used were of analytical grade or better.

Standard solutions of Zn(II) and Pb(II) were prepared from 1,000 μg/mL SRM (standard reference material) solutions of NIST (National Institute of Standard and Testing, U.S.A.) by diluting with deionized water to the proper concentrations. A 0.1 M 1-naphthoic acid (Aldrich Co.) in ethanol was used for the ligand, 0.03 M solution of tetrabutylammonium bromide (Aldrich Co.) for a counter ion, and 0.2%(w/v) of sodium lauryl sulfate (Aldrich Co.) for a surfactant.

A pH meter (Model PHM-2000 from Tokyo Rikakikai Co. and Ingold combined electrode) was used after it was corrected with buffer solutions. Zn(II) and Pb(II) in MIBK were determined with a Perkin-Elmer model 2380 atomic absorption spectrophotometer (AAS) equipped with HGA-400 graphite furnace system (GF). Instrumental conditions are given in Table 1.

Experimental procedure. After the water sample was filtered to remove floating materials, 1.00 L of the sample was accurately taken in an Erlenmeyer flask. An 8.0 mL sample of 0.1 M 1-naphthoic acid (HNPh) solution was added and the pH was adjusted to 5.0 with dilute HNO_3. The solution was stirred for 4 minutes by a magnetic stirrer to form Zn(II)- and Pb(II)-naphthoate (NPh_3^-) complexes completely. Ion pairs were created by adding 10 mL of 0.03 M tetra-*n*-butyl ammonium bromide for a counter ion. A 2.0 mL sample of 0.2%(w/v) sodium laurylsulfate solution was added and the experimental solution was additionally stirred for 4 minutes. It was then transferred to a flotation cell, and nitrogen gas was bubbled at the flow rate of 30 mL/min for 5 minutes to float and extract the ion-pairs of analytes into 20.00 mL MIBK on the solution surface. The absorbances of the elements were directly measured in MIBK solution by GF-AAS.

A series of standard solutions (up to 12 ng/mL for both elements) was prepared from NIST-SRM solutions and the solutions were treated with the same procedure as that for samples. Calibration curves were plotted and metal ions were determined by application of the curves.

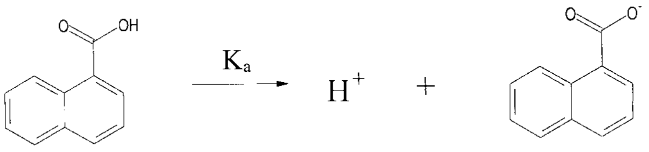
Table 1. Operating conditions of AAS and heating programs for a graphite furnace

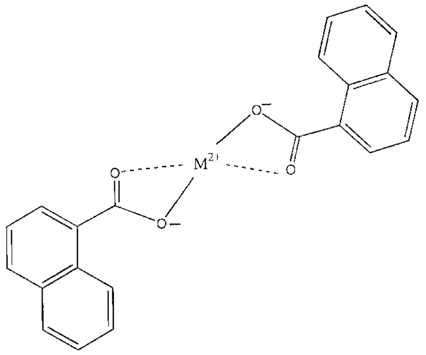
	Zinc	Lead
Wavelength (nm)	213.9	283.3
Current (mA)	30	30
Band width (nm)	0.7	0.2
Temperature programs for a graphite furnace[a]		
Drying	110 °C 5s[b](5s)[c]	150 °C 3s[b](3s)[c]
Charring	300 °C 3s (8s)	800 °C 3s (6s)
Atomization	1800 °C 2s (1s)	2400 °C 2s (2s)
Cleaning	2600 °C 3s (3s)	2600 °C 3s (3s)

[a] Sample injection : 20 μL, Graphite tube : pyrolytically coated. [b] Holding time. [c] ( ) values : Ramping time

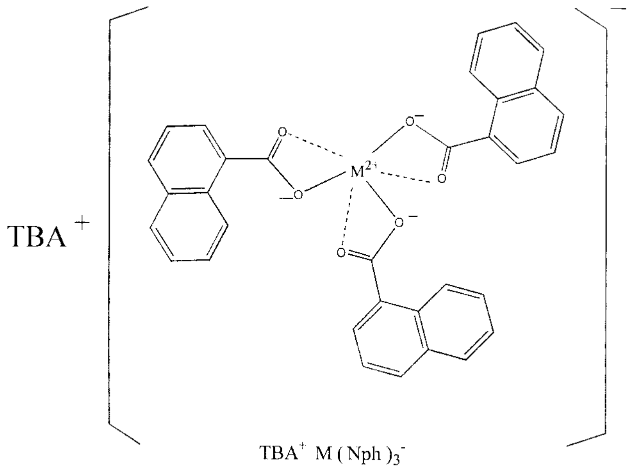
Results and Discussion

Ligand, metal-complexes and ion pairs. 1-Naphthoic acid as a ligand has the following structure, and its carboxylic acid group is ionized in an aqueous solution. The carboxylate anion coordinates with metallic ions to form neutral complexes in the equivalent concentrations of both di-valent ions.





But anionic metal complexes are formed in the presence of excess HNph. And the anionic complexes form ion pairs with TBA$^+$ ion by the addition of tetra-*n*-butylammonium bromide solution as follow:[2,3]



These ion pairs are extracted into a proper solvent such as MIBK.

The excess of ligand should be added to the sample solution to form good complexes with metal ions. If too much in excess, then some problems occur in the process of flotation and extraction because too much materials were created in the solution together with the ligand. Therefore, a proper amount of the ligand is needed. Therefore, the extrac-

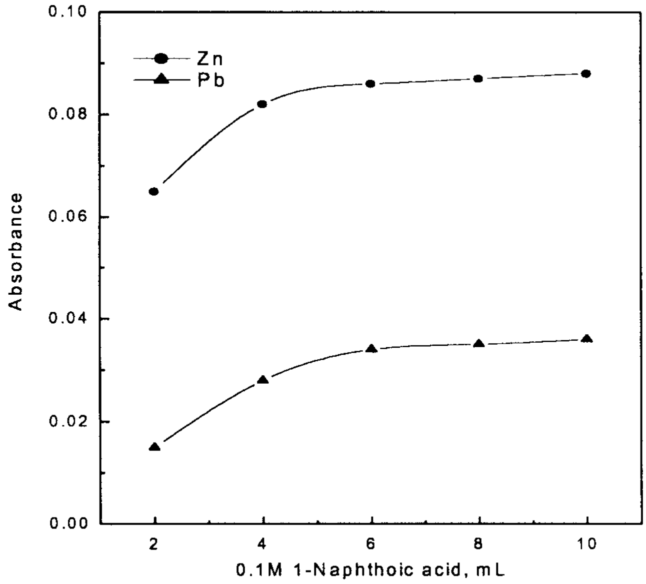


Figure 1. Amount of complexing agent for the effective complexation and solvent sublation of analyte ions. Zn: 4 ng/mL, Pb: 2 ng/mL.

tion extents of ion pairs were measured by changing the volume of 0.1 M 1-HNph in the solution of 1.00 L from 2.00 to 10.00 mL (see Figure 1). The concentrations of Zn(II) and Pb(II) ions in the studied solution, initially were 4.0 and 2 ng/mL at pH 5.00, respectively. All other conditions were the same as in the experimental procedure for the water samples. As shown in Figure 1, constant absorbances could be obtained from the addition of 6.0 to 10 mL of 0.1 M 1-HNph solution. Therefore, 8.0 mL of the solution was added.

pH effect. The formation of metal-1-naphthoate complexes was influenced by solution pH and Zn(II), and Pb(II) ions can form hydroxide precipitates in a strongly basic solution. The completeness of complex formation was investigated by changing the pH from 2 to 7 (see Figure 2). The absorbances of the metals were nearly absent in the acidic range of pH 2-3 because the analytes could not be extracted into MIBK. This is due to the difficult formation of complexes because 1-HNph is nearly un ionized in such an acidic solution. The maximum absorbances were observed in the weak acidic solution of around pH 5.0. Hydroxide precipitates also were not formed in this range.

The solution, in which 0.1 M 1-HNph solution was added at pH 5, was stirred. The change of absorbances for analytes was measured was according to stirring time. The maximum absorbance was obtained at 4 minutes in the case of Zn(II), but the absorbance of Pb(II) was constant at > 4 minutes. Such phenomena are explained by the fact that the stability of the 1-Nph$^-$ complex of Zn(II) is not so good compared with Pb(II). The complex is considered to be dissociated by repeated stirring of a long duration.[2]

The effect of TBA$^+$ ion. As described above, Zn(II) and Pb(II) ions form anionic complexes with an excess of 1-HNph, and the ions form ion pairs with the TBA$^+$ ion. The amount of the TBA$^+$ ion affects the stability of the ion pair, TBA$^+$ · M-(Nph)$_3^-$.

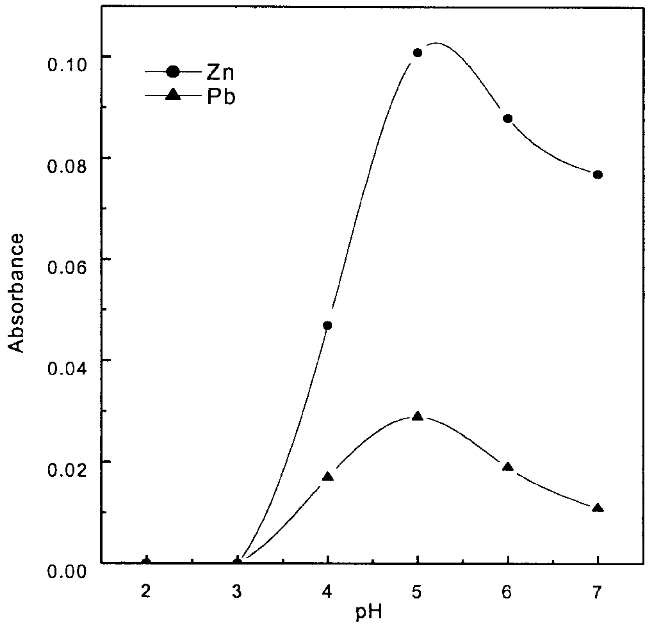


Figure 2. Effect of pH on the complexation of analyte ions with 1-naphthoic acid for a solvent sublation.

Under other optimum conditions, the efficiencies of solvent sublation were investigated by changing the volume of 0.03 M TBA$^+$ ion from 5.0 to 25.0 mL. The absorbances of analytes in MIBK were plotted against the amount of TBA$^+$ ion (see Figure 3). The constant absorbances appeared with the addition of >10.0 mL. From this result we found that 10.0 mL of 0.03 M TBA$^+$ ion was sufficient to form ion pairs for the sublation with additional stirring for 4 minutes.

Type and amount of surfactant. In general, a surfactant is added to float some materials in an aqueous solution by making them hydrophobic.[18,21,30] Hydrophobic materials can

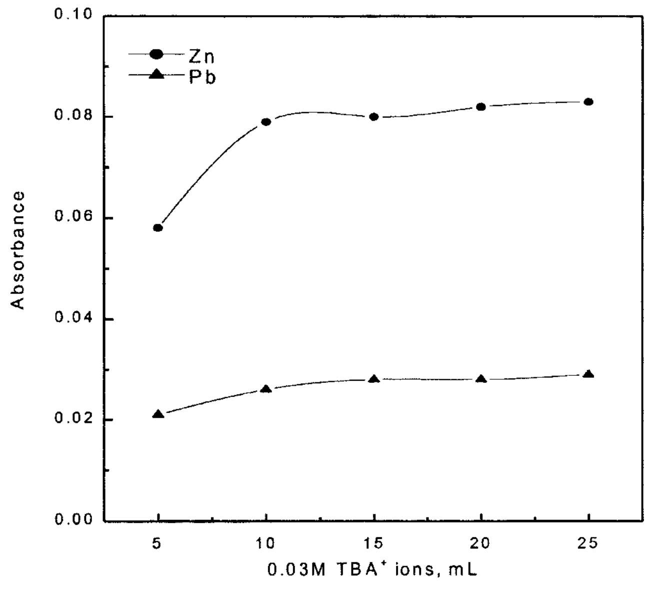


Figure 3. Amount of TBA+ ion for the formation of ion pair with metal-naphthoate.

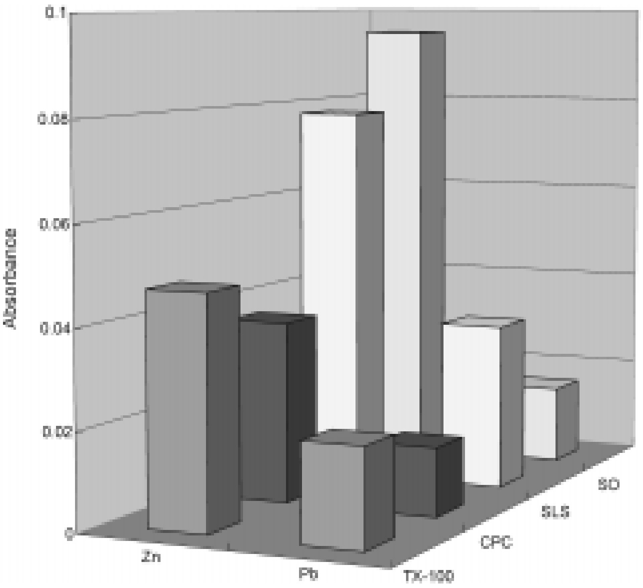


Figure 4. Comparison of flotation efficiencies according to various surfactants. TX-100: triton X-100, CPC: cetylpyridinium chloride, SLS: sodium lauryl sulfate, SO: sodium oleate.

more effectively secede from an aqueous solution than hydrophilic materials. The material can be a precipitate, complex ion or ion-pair. $TBA^+ \cdot M\text{-}(Nph)_3^-$ was the ion-pair in this flotation technique.

In the present study, the efficiencies of flotation by the type of surfactant were evaluated using aionic surfactants of sodium oleate (SO) and sodium laurylsulfate (SLS), neutral TX-100, and cationic cetylpyridinium chloride (see Figure 4). Two kinds of anionic surfactants and neutral TX-100 showed better efficiencies than cathionic surfactants.

Such phenomena can be interpreted to mean excess TBA^+ around $M\text{-}(Nph)_3^-$ complexes create the ion pairs of positive charge.[2] Therefore, the addition of anionic surfactant improves the efficiencies of flotation, but the efficiencies are lowered by cationic surfactant. SO showed the best flotation for Zn(II), but SLS provided better efficiencies for both analytes. Therefore, SLS was chosen.

The flotation efficiency was so significantly affected by the amount of surfactant that the change of absorbances was obtained in the floated solution by changing the volume of 0.2% SLS solution from 0.1 to 3.0 mL (see Figure 5). The efficiencies gradually increased with the volume of ligand up to 2.0 mL, and constant absorbances were observed on the addition of > 2.0 mL surfactant solution. But if a large volume were added, then some problems occurred due to the amount of foam. The minimum volume of 2.0 mL was fixed.

Stirring time also was investigated. That is, the change of absorbance was observed by changing stirring time up to 7 minutes (see Figure 6). Maximum absorbances were observed at 4 minutes for both analytes and the flotation efficiencies decreased with time extended beyond maxima. Such a decrease is considered to be due to instability in the formation of ion-pairs as well as the relatively weak binding between ion-pair and surfactant. The absorbance of zinc decreased more abruptly with the increase in stirring time than the absorbance of lead. This also could be explained by the fact that the complex and ion pair of zinc was weaker than that of lead. In addition, Pb(II) can partially form a neutral complex of $Pb\text{-}(Nph)_2$ so that this neutral complex is present in the solution together with the ion pair of $TBA^+Pb\text{-}(Nph)_3^-$. As a result, the absorbance was lower than Zn(II) and this decrease was smoothly compared with Zn(II).

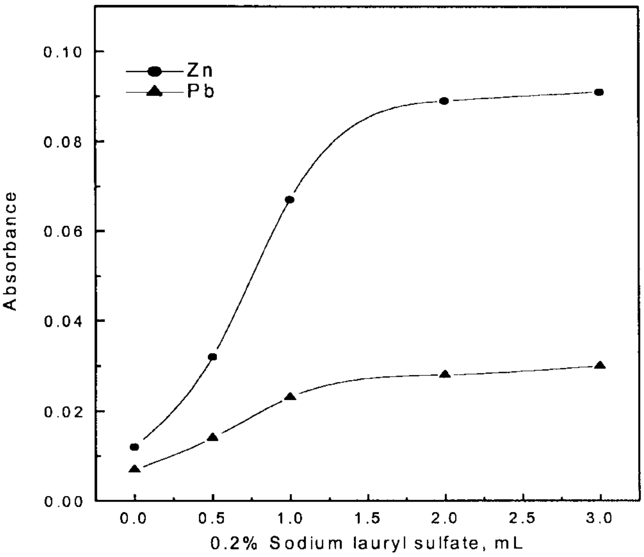


Figure 5. Amount of a surfactant for the effective sublation of ion pairs.

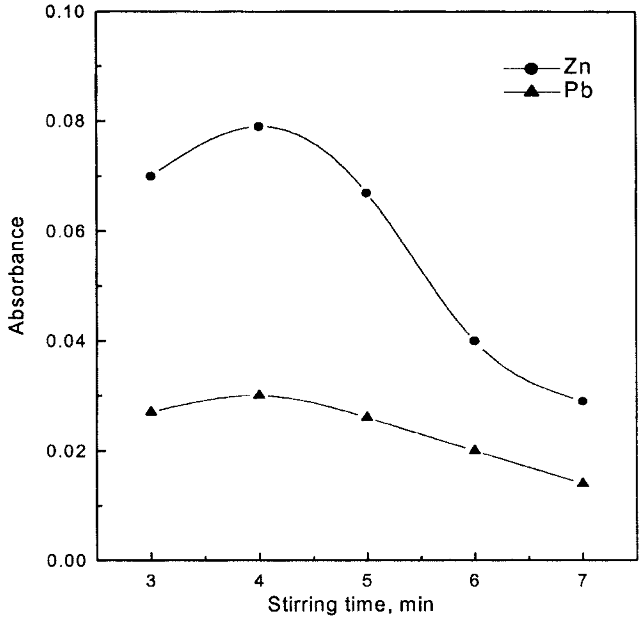


Figure 6. Stirring time after the addition of sodium lauryl sulfate as a surfactant for the hydrophobic precipitation of the ion-pairs.

Bubbling by nitrogen gas. Nitrogen gas plays an important role to float the ion pairs of analytes by bubbling.[12] The efficiency of flotation and the shapes of floated materials depend on the bubble size of nitrogen gas which is determined by the flow rate of the gas through a porous plate of

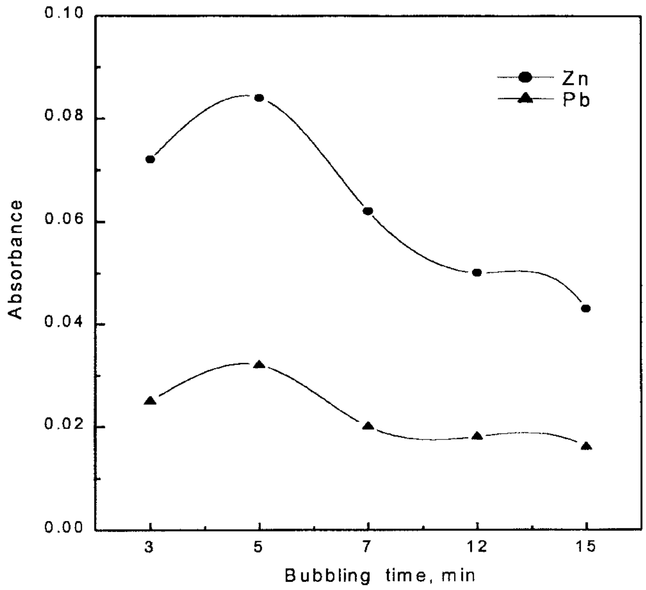


Figure 7. Bubbling time of a nitrogen gas for the effective sublation of the ion pairs.

fritted glass as well as the hole sizes in the plate. Such bubbles float ion pairs to the surface of solution by making an interface between surface-activated complexes and bulk aqueous solution.

In our papers,[18,30-32] such porosity of glass plate and flow rate of gas were optimized for the general flotation and the same flotation cells as used were used in this work. The absorbances were observed by changing the bubbling time form 3 to 15 minutes (see Figure 7). The maximum absorbances were shown for both elements at 5 minute bubbling. But the absorbances showed to be decreased after 5 minutes. The decrease was due to the dissociation and redistribution of ion pairs or even complexes into bulk solution. Such phenomena happened by the weak bonds in complexes and ion pairs as well as weakening of the hydrophobic activity of the surfactant on the surface of ion pairs by the strong agitation of a long time.

Organic solvent. The proper choice of the solvent is very important to dissolve and extract the floated ion pairs into the solvent. The solvent is lighter than an aqueous solution having the density of < 1.0 g/mL, it should float on the solution. And it has to give a low background in the measurement of absorbance because the absorbance is measured as a state of ion pair in a solvent.[30-32]

In the present study, the extraction efficiencies were investigated with the light solvents, such as benzene, xylene, MIBK and hexane (see Figure 8). As shown in the figure, MIBK was chosen as a solvent because of the maximum absorbances and the lowest backgrounds for both elements.

Analytical results. To examine the above optimized conditions, the usefulness of this procedure was investigated by applying it to real water samples. Calibration curves were prepared with standard solutions according to the given procedure. The curves were linear with correlation factors of > 0.99 as shown in Figure 9. The samples were one tap water, one river water and one irrigation reservoir water in and around Jochiwon, South Korea. The contents were 0.03 to 1.42 ng/mL for Zn(II) and 0.07 to 2.22 ng/mL for Pb(II)

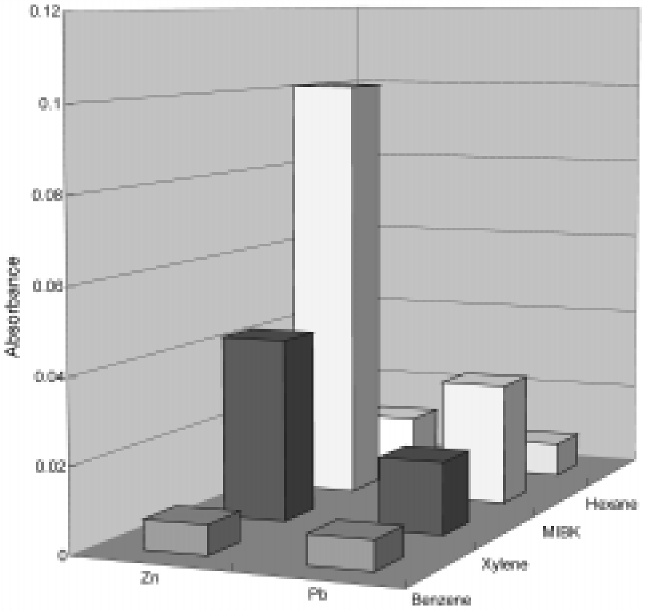


Figure 8. Sublation efficiencies according to the type of solvent. MIBK: methylisobutylketone.

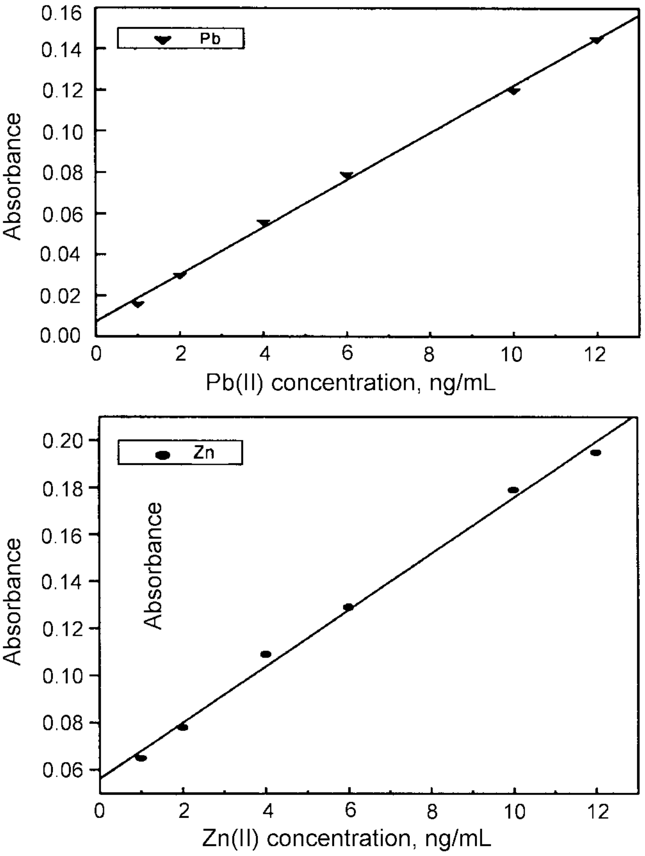


Figure 9. Calibration curves for the determination of analytes by solvent sublation.

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

Sample	Elements	Spiked[c]	Measured[c]	Recovered[c]	Recovery (%)
Tap water	Zinc	0.00	0.03		
		12.00	10.22 (2.2)[d]	10.02	85
	Lead	0.00	0.07		
		2.00	1.71 (2.5)[d]	1.66	83
Miho-chun[a]	Zinc	0.00	0.04		
		12.00	10.98 (3.9)[d]	10.92	91
	Lead	0.00	2.22		
		2.00	4.02 (3.2)[d]	1.80	90
Kobok[b]	Zinc	0.00	1.42		
		12.00	11.78 (4.0)[d]	10.44	86
	Lead	0.00	1.97		
		2.00	3.76 (3.5)[d]	1.78	89

[a] a riverside around Jochiwon, [b] an irrigation reservoir around Jochiwon, [c] Unit : ng/mL, [d] RSD (%) for 4 determinations.

(see Table 2). After the given amounts of analytical elements were added to the real samples with standard solutions, the spiked contents were determined by the experimental procedure to obtain recoveries for the evaluation of the accuracy of this method. The recoveries were 80 to 100%. These values could be considered to be fairly accurate. The RSD of < 10% for measured values of recoveries show that this method is relatively reproducible for such water samples with trace contents.

Conclusion. Trace Zn(II) and Pb(II) in several water samples of adjusted pH 5.0 were determined by a solvent sublation using an ion pair of metal-1-naphthoate anion and tetrabutylammonium ion for the utilization of a synergistic effect. The hydrophobic ion pairs created by the addition of sodium lauryl sulfate were floated and extracted into MIBK by bubbling nitrogen gas. This procedure was applied to the analysis of several real water samples and recoveries of 80 to 100% were obtained in spiked samples of given amounts of analytes. The RSD of < 10% was obtained for standard spiked samples. Such results show that this is a fairly accurate and reproducible method and can be applied to similar samples.

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