Articles

Extraction Equilibria and Solvent Sublation for Determination of Ultra Trace Bi(III), In(III) and Tl(III) in Water Samples by Ion-Pairs of Metal-2-Naphthoate Complexes and Tetrabutylammonium Ion

Young-Sang Kim,* Yoon-seok Choi, and Won Lee†

Department of Advanced Material Chemistry, Korea University, Jochiwon, Choongnam 339-700, Korea
†Department of Chemistry, Kyunghee University, Seoul 130-701, Korea
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The solvent sublation using ion pairs of metal-2-naphthoate(2-HNph) and tetrabutyl ammonium (TBA^+) ion has been studied for the concentration and determination of ultra trace Bi(III), In(III) and Tl(III) ions in water samples. The partition coefficients (K_D) and the extraction percentages of 2-HNph and the ion pairs to methyl isobutyl ketone (MIBK) were obtained as basic data. After the ion pair $TBA^+ \cdot M(Nph)_4^-$ was formed in water samples, the analytes were concentrated by the solvent sublation and the elements were determined by GF-AAS. The pH of the sample solution, the amount of the ligand and counter ion added and stirring time were optimized for the efficient formation of the ion pair. The type and amount of optimum surfactant, bubbling time with nitrogen and the type of solvent were investigated for the solvent sublation as well. 10.0 mL of 0.1 M 2-HNph and 2.0 mL of 0.1 M TBA^+ were added to a 1.0 L sample solution at pH 5.0. After 2.0 mL of 0.2%(w/v) Triton X-100 was added, the ion pairs were extracted into 20.0 mL MIBK in a flotation cell by bubbling. The analytes were determined by a calibration curve method with measured absorbances in MIBK, and the recovery was 80-120%.

Key Words : Solvent sublation, 2-Naphthoic acid, Ion-pair formation, Solvent extraction, Flotation technique

Introduction

Following studies on the concentration and determination of trace elements by solvent extraction,[1-3] flotation[4,5] and solvent sublation[6-10] in this laboratory, the solvent sublation using ion pairs of metal-2-naphthoate (2-HNph) and tetrabutyl ammonium (TBA^+) ion has been studied for the concentration and determination of ultra trace Bi(III), In(III) and Tl(III) ions in water samples. Solvent sublation[11] is a combined separation technique of solvent extraction[12-15] and flotation.[16-23]

Usually organic ligands, which are well studied for this procedure of a high selectivity to analytical elements, have been used in this solvent sublation method.[6-10] It is not easy to select an optimum ligand, but aliphatic carboxylic acids have been widely used as a ligand.[24] Aromatic carboxylic acids have not been widely used because of their low extraction utility for metal complexes.[19] Yamada and others[25] have studied the solvent extraction of Co(II), Ni(II) and Cu(II), using 1-and 2-naphthoic acid as a ligand. Benzene or 1-octanol was used as a solvent. The partition coefficients and extraction constants of the ligands were obtained, and the analytical results of the ppt level of Mn(II) were reported by a catalytic method using several derivatives of the naphthoic acid synthesized.[24,25]

Also the formation of ion pair was used to enhance the extraction efficiency by the synergistic effect.[26-33] The complex ions became neutral. TBA^+ ion has been widely used for this purpose. Nasu *et al.* synergistically extracted thiocyanate complexes of Cu(I) and Cu(II).[26] Fe(II) and Fe(III)[27] into chloroform, and Cu(II) into MIBK[28] by the formation of ion pair with TBA^+. Haiping *et al.*[34] studied the equilibrium on the extraction of Li(I) complex of water-soluble porphyrin by the formation of ion pair in the presence of TBA^+.

In the present work, the basic research was on the solvent sublation of Bi(III), In(III) and Tl(III), using 2-naphthoic acid(2-HNph)[35] and TBA^+. The distribution ratio and extraction rate of the ion pair, $TBA^+ \cdot M(Nph)_4^-$ were obtained as well as the distribution ratio of 2-HNph between aqueous solution and MIBK. These basic data were utilized to optimize experimental conditions (pH, the amount of ligand and counter ion, and so on) for the application of solvent sublation to the analysis of real samples (tap water, river water, etc.). The efficient flotation was also studied by investigating the effects of surfactants, such as Triton-X 100. The applicability was evaluated with recoveries obtained from real samples.

Experimental Section

Reagents and instruments. All reagents were analytical grade and the deionized water used was purified by Millipore Milli-Q water system. The standard solutions of 100 μg/mL analytes were prepared with NIST reference material

for In(III) and KRISS references for Bi(III) and Tl(III) for the working standard solutions. The 0.1 M solution of 2-naphthoic acid was prepared in an ethanol with a guaranteed-grade reagent (Aldrich Co.) without further purification. A 0.2%(w/v) ethanolic solution of Triton X-100 was used as a surfactant.

A pH meter of Japan Tokyo Rikakikai Co. (Model PHM-2000) was used with an Ingold composite glass electrode, and it was adjusted with a buffer solution before use. The absorbances were measured with an atomic absorption spectrophotometer of Perkin-Elmer, Model 2380, equipped with HGA-400 programmer. The UV/Visible spectrophotometer was Shimadzu, Model UV 2100.

Partition coefficient of 2-naphthoic acid. A 1.0 mL of 1.435×10^{-3} M 2-HNph was added to 100 mL of purified water, and the solution's pH was adjusted from 2.0 to 12.0 with 0.1 M HNO_3 and 0.1 M NaOH solutions. The ligand was floated from the aqueous solution to 100 mL MIBK in a flotation cell by bubbling with nitrogen gas for 5 minutes. The phase was separated by 5 minutes standing, the remaining 2-HNph was measured with a UV/Visible spectrophotometer and the content was calculated by a standard calibration curve method to get the distribution ratio.

Distribution ratios of metal complexes and ion pairs. After the pH was adjusted to 5.0 in 100 mL aqueous solution of given concentrations of analytical ions, 2-HNph 1,000 times the total metallic concentration was added, and this solution was stirred 5 minutes to form stable complexes. To form ion pairs, TBA^+ 1,000 times each ion concentration was added, and the solution was stirred 5 minutes. This solution was transferred into a flotation cell to float the complexes and ion pairs by bubbling nitrogen gas 5 minutes. After 5 minutes standing, the absorbances of the metal ions were measured in the aqueous solution to calculate distribution ratios with the concentrations of the remaining metal ions.

Solvent sublation. A 10.0 mL ethanolic solution of 0.1 M 2-HNph was added to 1.0 L of the filtered sample solution in an Erlenmeyer flask, and the pH was adjusted to 5.0 with HNO_3 and stirred 5 minutes. 2.0 mL of the 0.1 M TBA^+ ion and 2.0 mL of a 0.2%(w/v) Triton X-100 solution were combined by stirring 5 minutes. The solution was floated in a flotation cell by bubbling nitrogen gas at the rate of 30 mL/min for 5 minutes to extract the ion pairs into 20.0 mL MIBK. The concentration of analytical ions were determined in the solvent directly by measuring absorbances with GF-AAS. The instrumental conditions of GF-AAS are shown as in Table 1.

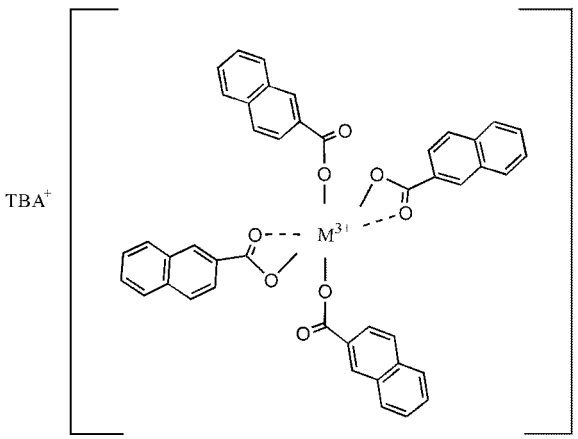
Table 1. Instrumental conditions for Perkin-Elmer 2380 GF-AAS and heating programs for HGA-400 graphite furnace

	Bi	In	Tl
Wavelength (nm)	223.1	303.9	276.8
Current (mA)	30	30	30
Bandwidth (nm)	0.7	0.7	0.7
Signal mode		Absorbance	
Inert gas		Argon	
Tube Type		uncoated tube	
Drying (°C)	110 °C, [3s], (5s)	110 °C, [3s], (5s)	110 °C, [3s], (5s)
Charring (°C)	400 °C, [3s], (2s)	800 °C, [2s], (10s)	600 °C, [3s], (10s)
Atomization (°C)	2300 °C, [3s], (2s)	2400 °C, [3s], (3s)	2300 °C, [3s], (2s)
Cleaning (°C)	2600 °C, [3s], (3s)	2600 °C, [3s], (3s)	2600 °C, [3s], (3s)

Sample injection: 20 μl. (solvent: MIBK). [ ]: Holding Time. ( ): Ramping Time

Results and Discussion

Metal complexes and ion pairs. The 2-HNph[36] reacts with three valent metal ions to form complex ions. And they form ion pairs with TBA^+ as follows[37]:



$TBA^+ \cdot M(Nph)_4^-$

As shown in Figure 1, the absorption pattern of 2-naphthoic acid is so different from the spectra of its metal complexes that the studies on the chemical behavior of the ligand and complexes were possible with UV/Visible spectra.

Partition coefficient of 2-naphthoic acid. The partition coefficient of 2-naphthoic acid between aqueous solution and MIBK solvent is indicated as follows:

$$K_p = \frac{[HNph]_{org}}{[HNph]_{aq}} \quad (1)$$

But the acid dissociation constant (K_a) in an aqueous solution is

$$K_a = \frac{[H^+]_{aq}[Nph^-]_{aq}}{[HNph]_{aq}} \quad (2)$$

and the value is 1.45×10^{-4} (298 K). Therefore, a distribution ratio (D_r) can be defined as follows[38]:

$$D_r = \frac{C_{org}}{C_{aq}} = \frac{[HNph]_{org}}{[HNph]_{aq} + [Nph^-]_{aq}} \quad (3)$$

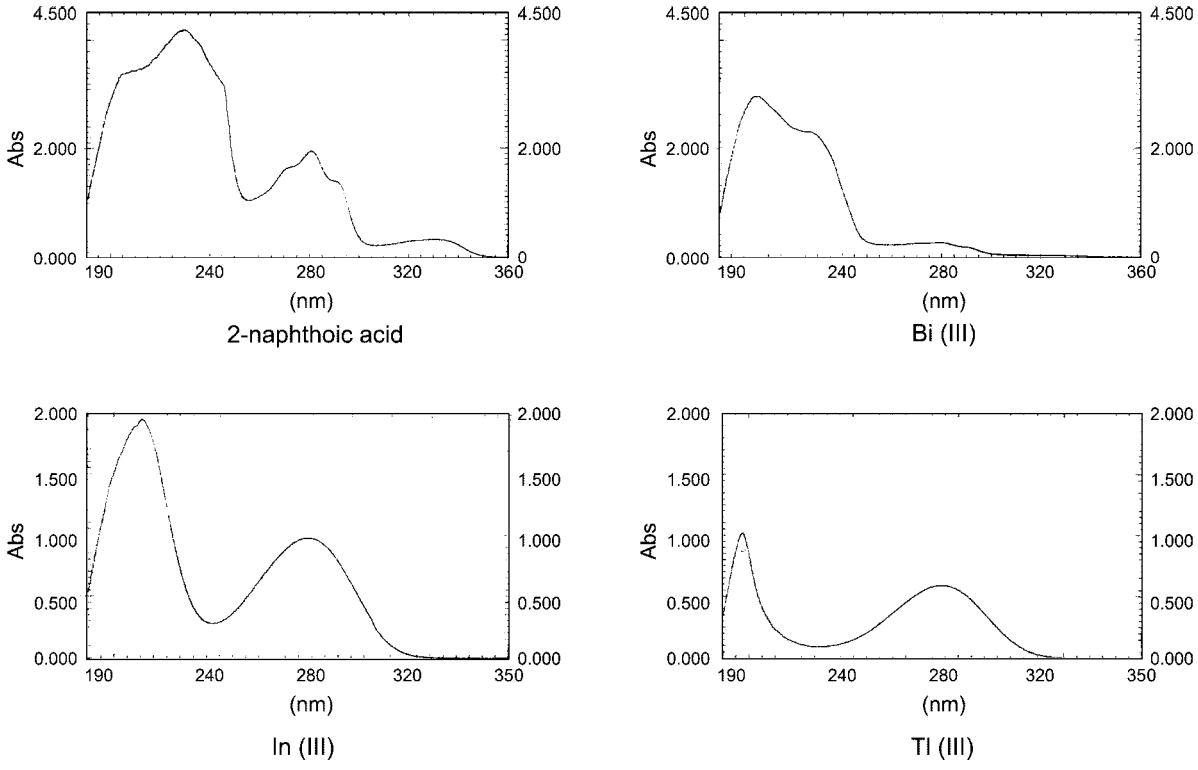


Figure 1. The UV/Vis spectra of 2-naphthoic acid and M-(Nph)$_3$.

The distribution ratio of 2-HNph between an aqueous solution and organic MIBK was calculated using UV/Vis absorbance of 2-HNph remaining in the original aqueous solution and the equilibrated aqueous solution after an extraction. The values of distribution ratio were plotted from pH 2.0 to 12.0 as shown Figure 2.

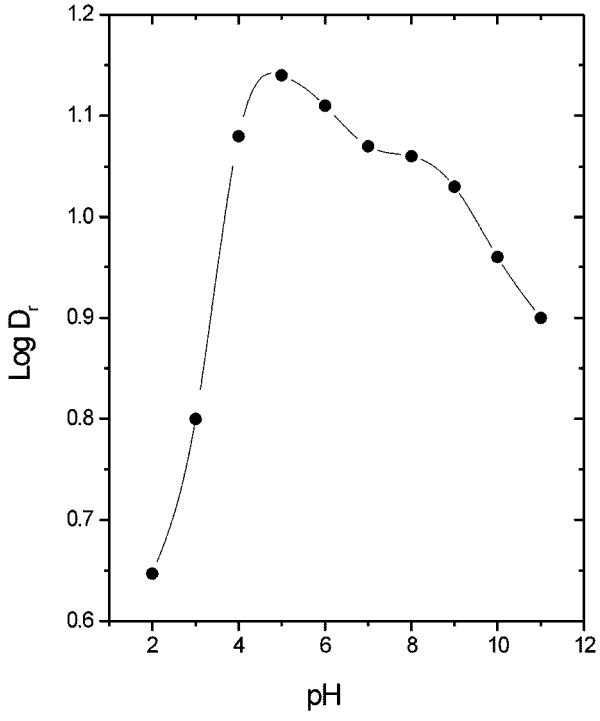


Figure 2. The effect of pH on the log D_r of 2-naphthoic acid between aqueous solution and MIBK. [2-HNph] = 1.435×10^{-5} M

Equation (3) was changed by the substitution of equations (1) and (2):

$$\frac{1}{D_r} = \frac{1}{K_p} + \frac{K_a}{K_p[H^+]} \quad (4)$$

There are two ways to obtain the K_p value. The reciprocal of the distribution ratio, $1/D_r$ was plotted versus the reciprocal of hydrogen concentration, $1/[H^+]$. The K_p value can be calculated from the intercept and slope of the curve with a known value of the dissociation constant at 298 K. The same K_p value of 5.55×10^5 was obtained in this work.

Distribution ratio of metal complexes and ion pairs. 2-Naphthoate (Nph$^-$) ion reacts with a metal ion to form a complex in an aqueous solution and the complex is extracted into an organic solvent, such as MIBK. The reaction can be written as follows:

$$M^{3+}_{(aq)} + 3Nph^-_{(aq)} = M(Nph)_{3(org)} \quad \text{(reaction 1)}$$

The distribution ratio of the metal ion is indicated as:

$$D_r = \frac{C_{org}}{C_{aq}} = \frac{[M(Nph)_3]_{org}}{[M^{3+}]_{aq} + [M(Nph)_3]_{aq}} \quad (5)$$

But $[M(Nph)_4^-]$ anion is formed by the Nph^- ion dissociated from some excess 2-HNph in the aqueous solution. And it forms a ion pair of $TBA^+ \cdot M(Nph)_4^-$ with TBA^+ ion to be extracted into the organic solvent.

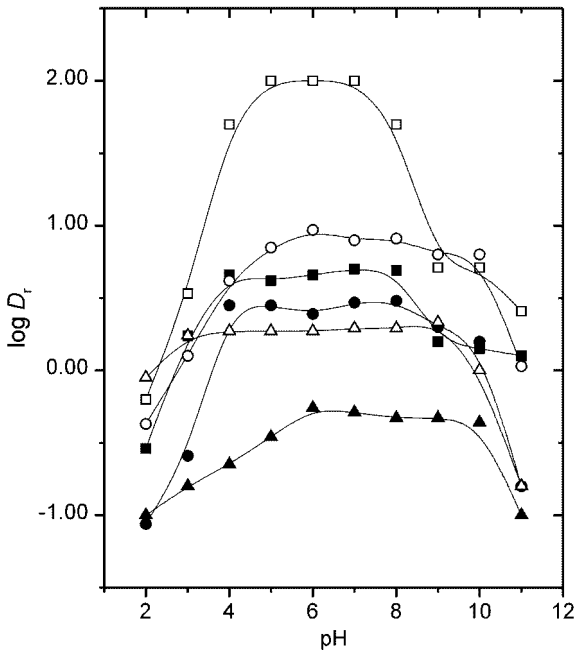


Figure 3. The effect of pH on the distribution of metal-2-naphthoate complexes and the ion pairs between aqueous solution and MIBK. ■ : [Bi(Nph)$_3$], □ : [TBA$^+$·Bi(Nph)$_4^-$], ● : [In(Nph)$_3$], ○ : [TBA$^+$·In(Nph)$_4^-$], ▲ : [Tl(Nph)$_3$], △ : [TBA$^+$·Tl(Nph)$_4^-$].

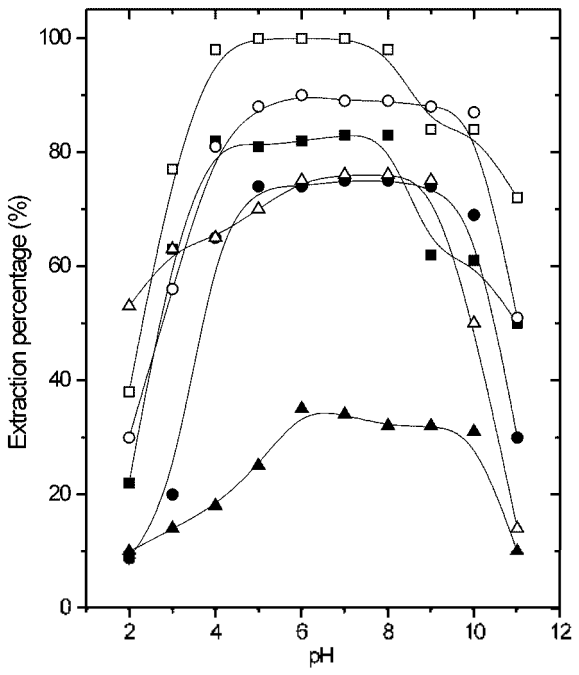


Figure 4. The pH dependencies on extraction percentage of metal-2-naphthoate and ion pairs from aqueous solution into MIBK. ■ : [Bi(Nph)$_3$], □ : [TBA$^+$·Bi(Nph)$_4^-$], ● : [In(Nph)$_3$], ○ : [TBA$^+$·In(Nph)$_4^-$], ▲ : [Tl(Nph)$_3$], △ : [TBA$^+$·Tl(Nph)$_4^-$].

$$M^{3-}_{(aq)} + 4Nph^-_{(aq)} + TBA^+_{(aq)} = [TBA^+ \cdot M(Nph)^-_4]_{(org)}$$

(reaction 2)

Therefore, the distribution ratio of the ion pair can be calculated as follow:

$$D_t = \frac{C_{org}}{C_{aq}} = \frac{[M(Nph)_3]_{org} + [TBA^+ \cdot M(Nph)^-_4]_{org}}{[M^{3+}]_{aq} + [M(Nph)_3]_{aq} + [TBA^+ \cdot M(Nph)^-_4]_{aq}} \quad (6)$$

In Figure 3, the variation of the distribution ratio for the complexes and ion pairs at each pH of an aqueous solution is shown for the addition of TBA$^+$ ion.

Extraction percentage of ion pairs. In general, an extraction percentage is indicated in the following equation (7)[33]:

$$E(\%) = 100 \times \left[D_t / \left(D_t + \frac{V_{aq}}{V_{org}} \right) \right] \quad (7)$$

The extraction percentages of ion pairs at each solution pH according to this equation are given in Figure 4 for the addition of TBA$^+$ ion and no addition. The maximum extraction percentage was 100% for Bi(III) at pH 5-7, 90% for In(III) at pH 6-7 and 73% for Tl(III) at pH 6.0, respectively. All of these values are much higher than values for the corresponding complexes.

Solution pH for the solvent sublation. Based on the above consideration of the extraction equilibria, the solvent sublation, which was the combined technique of flotation and solvent extraction, was applied to separate and concentrate Bi(III), In(III) and Tl(III) in water samples for the determination. Various experimental conditions were investigated to fix an optimum procedure.

First, the pH was studied in an aqueous solution because 2-HNph should be ionized to 2-naphtoate(2-Nph$^-$) ion to form stable metal complexes.[37] The sublation efficiencies of three elements were investigated, changing the pH from 2.0 to 11.0 with the absorbances of the analytes in MIBK. The maximum absorbances appeared at a pH range of 4.0-6.0 (Figure 5). The acid dissociation constant of 2-HNph at pH 2.0-3.0 was very low with an K_a of about 10^{-4}, so the efficiencies decreased with increasing acidity. On the other hand, the efficiencies also decreased with increasing basicity, because the analyte ions usually formed insoluble hydroxide precipitate. Therefore, the pH was adjusted to 5.0 for further sublation.

Amount of ligand, 2-HNph. Usually, an excess of ligand is needed for the formation of metal complexes. The amount of 2-HNph required to form stable metal complexes was investigated. The absorbances of analytes in MIBK were measured changing the adding volume of 0.1 M 2-HNph from 2.0 to 16.0 mL in the aqueous solution of 2.0 ng/mL of each metal ion. As shown in Figure 6, the absorbances plateaued on the addition of more than 10.0 mL, which means more than 10,000 times in the mole ratio of analytes.

Type and amount of surfactant. A neutral TBA$^+$ ion pair of complexes can be floated and extracted in MIBK, but a surfactant has been used to improve the flotation. This is due to the fact that a surfactant not only can support an ion pair by forming foams, but can also make the surface of the ion

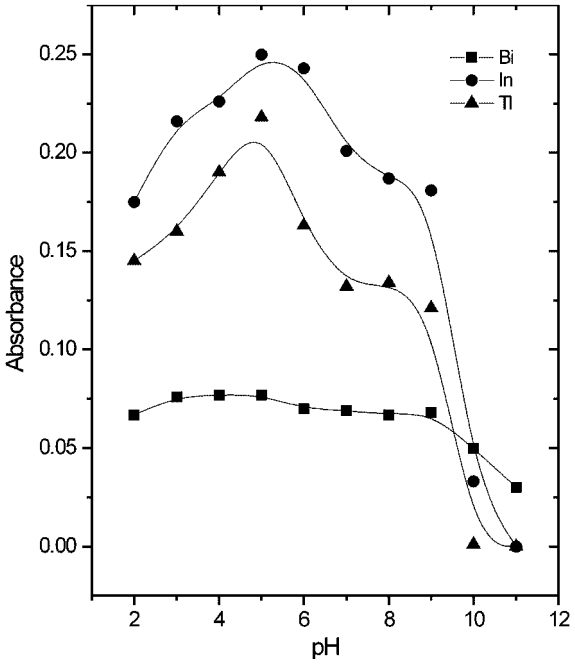


Figure 5. Effect of pH on the complexation of 2.0 ng/mL analyte ions with 2-naphthoic acid for an efficient solvent sublation.

pairs hydrophobic.[17-20]

The flotation efficiencies of the ion pairs were investigated by the addition of the surfactants sodium oleate (SO)[17,18] and sodium lauryl sulfate (SLS)[19,20] as anionic surfactants, TX-100 as a neutral one, and cetylpyridinium chloride (CPC) as a positive surfactant. TX-100 indicated the best efficiency among the surfactants, as shown in Figure 7. Such a fact could be explained by the neutral structure of TBA^+-$M(Nph)_4^-$ by the addition of TBA^+ ion to $M(Nph)_4^-$ solution. Bi(III) was not greatly influenced by TX-100 compared with In(III) and Tl(III).

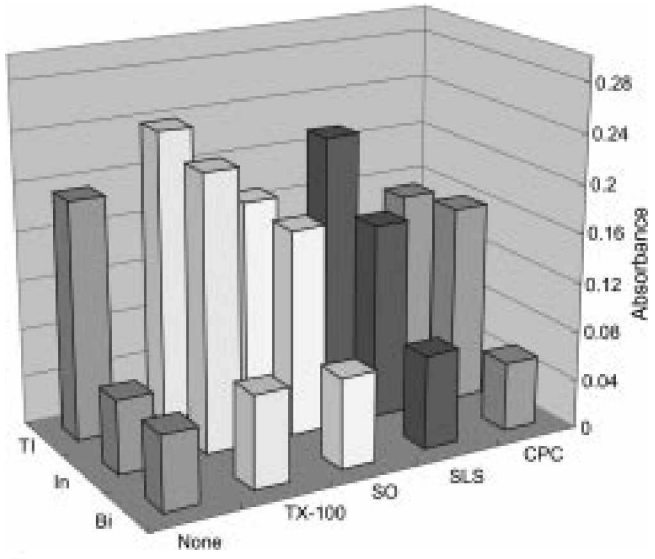


Figure 7. Comparison of flotation efficiencies of 2.0 ng/mL, according to various surfactants. TX-100: Triton X-100, CPC: cetylpyridinium chloride, SLS: sodium lauryl sulfate, SO: sodium oleate.

In general, the flotation is also influenced by the amount of surfactant. Therefore, a variation of absorbances was observed (in Figure 8) by changing the volume of 0.2% TX-100 solution from 0.5 to 5.0 mL. Bi(III) and In(III) showed a plateau on the addition of more than 2.0 mL of 0.2% TX-100 solution, but the absorbance of Tl(III) did plateau with more than 3.0 mL of 0.2% TX-100 solution. Therefore, 3.0 mL of

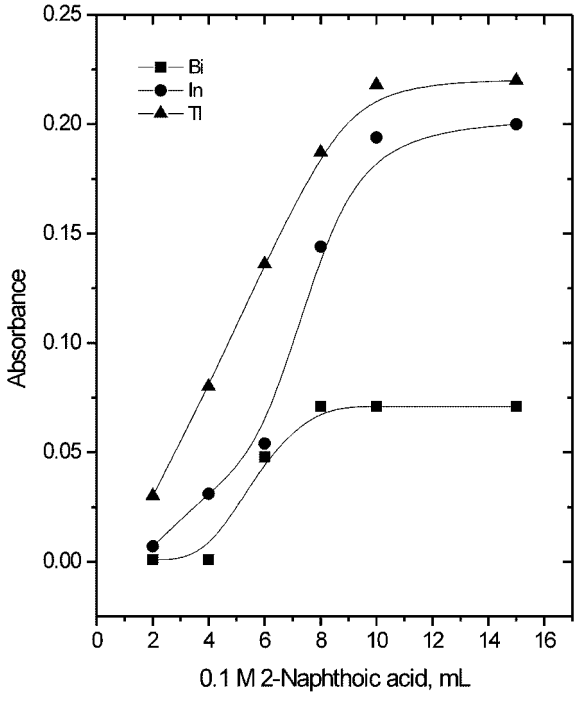


Figure 6. Amount of ligand to form the stable complexes for the effective solvent sublation of 2.0 ng/mL analyte ions.

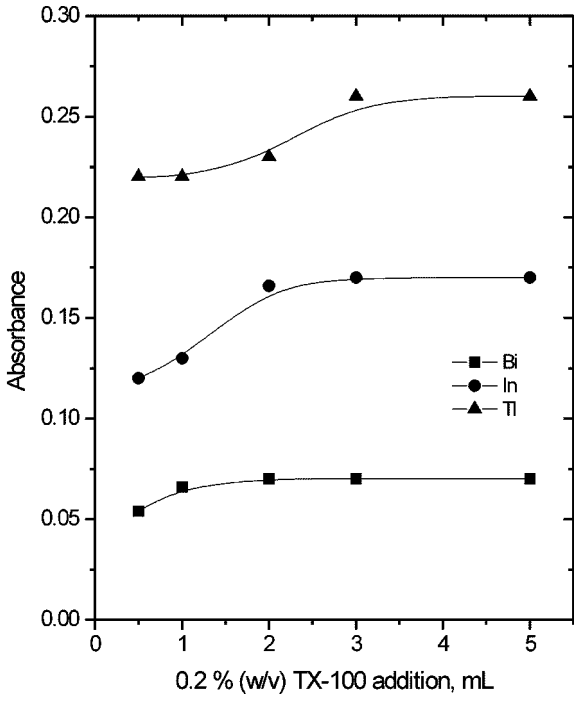


Figure 8. Amount of a surfactant for the effective sublation of ion pairs of 2.0 ng/mL analytes.

0.2% TX-100 was added in this experiment.

The solution should be stirred to promote the stable formation and efficient sublation of complexes after the addition of TX-100. The optimum stirring time was investigated by the observation of absorbances, changing stirring time from 3 to 21 minutes. From the results, 5 minutes was fixed, but the absorbances of In(III) and Tl(III) were gradually decreased with the time. Such phenomena happened because $TBA^+ \cdot M(Nph)_4^-$ ion pairs had partially weak positive charge. This made the hydrophilic properties stronger than the interfacial tension, which were overcame by the delayed stirring. The complex of Bi(III) was less influenced by stirring because this complex has a larger hydrophilic property owe to the more intense neutral structure of $Bi(Nph)_3$ compared with other ions.

Bubbling of N_2 gas. In the flotation technique, an inert gas is bubbled through a fritted porous glass disc from the bottom of the solution to float some precipitate, complex, ion pair, etc. Such floated materials are extracted into a light organic solvent in the solvent sublation technique. Therefore, the bubbling velocity and time as well as the size of gas bubbles are very important to float and support materials on the surface of the solution.[8,9]

After the bubbling velocity was fixed in this experiment, the bubbling time was investigated at the given velocity for efficient sublation to find the volume of the bubbling gas. Nitrogen gas was used because it is inert and inexpensive. The bubbling time was changed from 3 to 21 minutes to fix an optimum value (Figure 9). The absorbances of In(III) and Tl(III) were decreased by bubbling of more than 5 minutes. Such phenomena were due to the redistribution of ion pairs

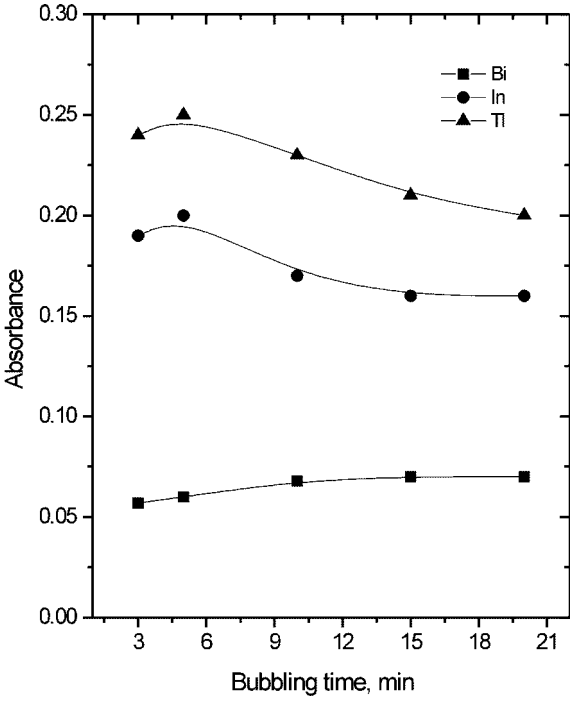


Figure 9. Bubbling time of a nitrogen gas for the effective sublation of the ion pairs at the concentration of 2.0 ng/mL.

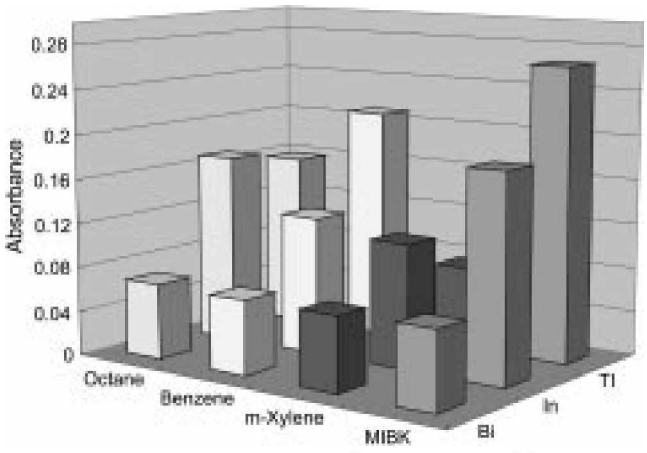


Figure 10. Sublation efficiencies for ion pairs of 2.0 ng/mL analytes, according to the type of solvent.

coated with the surfactant. That is, the interface of gas-liquid on the $ML_4^- \cdot TBA^+$ ion pair was broken by liquid-liquid face. Bi(III) was only partially influenced by longer bubbling because the surface was already more hydrophobic than other ions.

Organic solvent. The partition of the floated material into a solvent is different according to type.[9] It depends on the affinity of the material to the solvent. Therefore, an optimum solvent should be found for the perfect partition of ion pairs. First of all, the solvent must be lighter than water because analyte material is floated and extracted into a solvent on an aqueous solution by a gas bubbling. And it must not interfere with the measurement of absorbance by AAS.

Benzene, *m*-xylene, MIBK and octane were used in this experiment. This was done under other optimum conditions. MIBK indicated the best absorbances for three kinds of analytes and is known to have the lowest background in the measurement of absorbance by a graphite furnace AAS. Therefore, MIBK was used as a solvent (Figure 10).

Analytical results. The optimized experimental conditions obtained above were applied to the analysis of real samples to investigate the usefulness of this procedure. A series of 1.0 L standard solutions for Bi(III), In(III) and Tl(III) were prepared, and given volumes of 0.1 M 2-HNph, 0.1 M TBA^+ ion and 0.2%(w/v) Triton X-100 were added to this pH-adjusted solution with stirring. The ion pairs were sublated in a flotation cell to measure the absorbances in 20.0 mL MIBK. Calibration curves were prepared with these absorbances and concentrations (Figure 11).

Using these calibration curves, Bi(III), In(III) and Tl(III) were determined in real samples: tap water, Mihocheon water, Kobok reservoir water and edible mineral water. The given procedure in the experimental section was used for this and the results are given in Table 2.

Recoveries were obtained with such real samples in which given amounts of analytes were spiked. The values are shown as 81-122%. This procedure is considered to be applicable for the determination of such trace elements in various kinds of water.

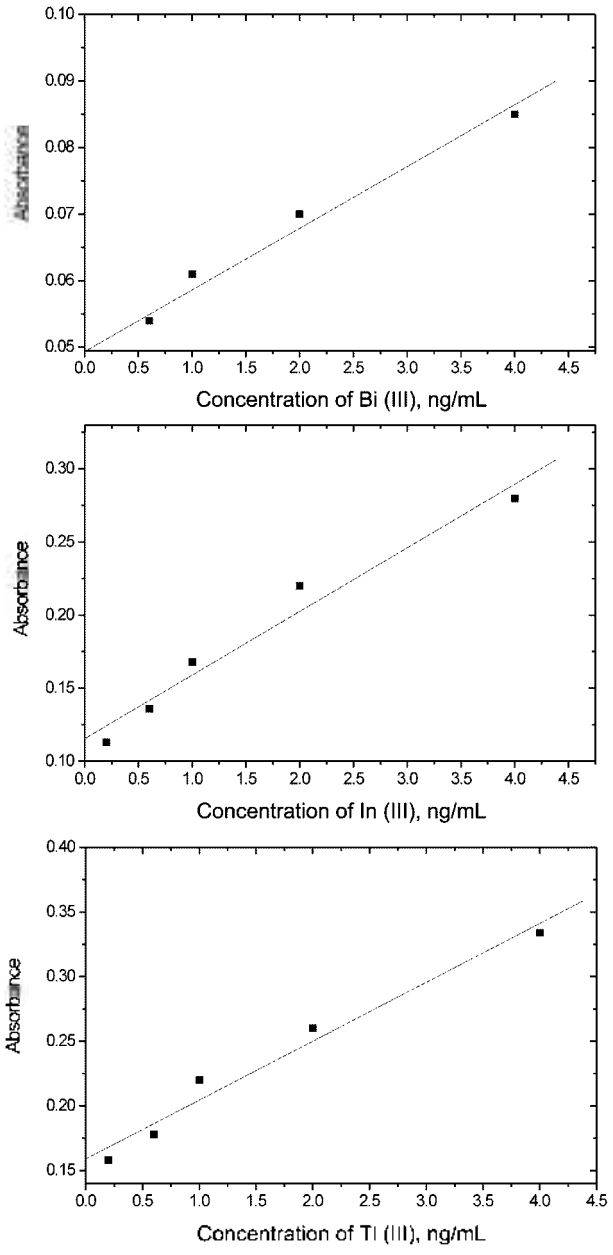


Figure 11. Calibration curves for the determination of analytes.

Conclusion

Basic data of extraction equilibria, distribution ratio and extraction percentage, were obtained for the solvent sublation of trace Bi(III), In(III) and Tl(III) as $TBA^+ \cdot M(Nph)_4^-$ ion pairs. These elements were determined in several kinds of water samples by a given procedure of optimized conditions.

1. The distribution ratio, K_D of 2-HNph between aqueous solution and MIBK was 5.55×10^5 at room temperature.

2. The extraction percentages of elements as an ion pair were 100% for Bi(III) at pH 5.0, 90% for In(III) at pH 6.0 and 73% for Tl(III) at pH 6.0.

3. These three elements could be simultaneously concentrated by a solvent sublation at pH 5.0, and a synergistic effect was obtained by the formation of the ion pairs.

Table 2. Analytical results of analytes in real samples by a solvent sublation (Unit : ng/mL)

Sample	Elements	Spiked	Measured	Recovered	RSD (%)	Recovery (%)
Tap water	Bi(III)	0.00	0.97		3.09	
		2.00	3.25	2.28	0.87	109
	In(III)	0.00	0.68	2.94		
		2.00	3.07	2.39	0.04	115
	Tl(III)	0.00	0.00			
		2.00	2.32	2.32	2.15	116
[b]Miho-cheon	Bi(III)	0.00	0.00			
		2.00	1.98	1.98	1.52	99
	In(III)	0.00	0.00			
		2.00	2.35	2.35	0.85	117
	Tl(III)	0.00	1.56		2.56	
		2.00	3.20	1.64	1.22	90
[a]Kobok reservoir	Bi(III)	0.00	0.97		5.15	
		2.00	2.76	1.79	5.02	93
	In(III)	0.00	0.75		2.67	
		2.00	3.20	2.45	0.41	116
	Tl(III)	0.00	0.57		3.51	
		2.00	2.19	1.62	3.09	85
Mineral water	Bi(III)	0.00	0.00			
		2.00	2.23	2.23	1.34	111.5
	In(III)	0.00	0.15		6.67	
		2.00	2.34	2.19	2.28	109
	Tl(III)	0.00	0.00			
		2.00	2.27	2.27	2.15	114

[a]an irrigation reservoir around seochang campus of Korea Univ. [b]a riverside around seochang campus of Korea Univ.

4. A given procedure was applied to real water samples and recovery was 81-122%.

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