

Articles

Solvent Sublation of Trace Noble Metals by Formation of Metal Complexes with 2-Mercaptobenzothiazole

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A solvent sublation has been studied for the determination of trace Au(III), Pt(IV) and Pd(II) in waste water with their complexes of 2-mercaptobenzothiazole (MBT). Experimental conditions such as the concentration of HCl, the amount of MBT as a ligand, the type and amount of surfactants, bubbling rate and time, and the type of organic solvent were optimized for the solvent sublation, *i.e.*, 25.0 mL of 2.0 M HCl solution and 30 mL of 0.4% (w/v) MBT ethanolic solution were added to a 1.0 L sample to form stable complexes. The addition of 4.0 mL of 1×10^{-3} M CTAB (cetyltrimethylammonium bromide) solution was needed for the effective flotation accomplished by bubbling nitrogen gas at the rate of 40.0 mL/min for 35 minutes. As a solvent, 20.0 mL of MIBK (methylisobutylketone) was used to extract the floated complexes. The procedure was applied to three kinds of waste waters. Au(III) was determined as 0.68 ng/mL and 0.98 ng/mL respectively for final washed water of two plating industries in Banwol. Pd(II) and Pt(IV) were not detected in any of the three samples. The recovery, which was obtained with analyte-spiked samples, were 95-120%.

Keywords: Solvent sublation, Noble metals, Waste water, 2-Mercaptobenzothiazole (MBT), Graphite furnace atomic absorption spectrophotometry.

Introduction

Platinum group elements such as platinum, palladium and gold are not only important in the use of themselves, but they also have been widely used for industrial catalysts, scientific instruments, medical technology and so on. The separation of such noble metals for recycling became valuable with their increasing use.¹⁻⁴ This called for the accurate analytical methods up to the trace level. Various analytical methods have been reported for practical applications. But if these metals are present at levels lower than the detection limit of analytical instruments or the measurements are interfered with by coexisting major elements, preliminary separation and concentration are required. A solvent sublation technique is applied in the present study.

Solvent sublation⁵⁻⁷ is a very useful technique in which the precipitates, complexes, or ion-pair of analytical elements are floated and extracted into a light and immiscible solvent on the analytical solution by a gas bubbling in a flotation cell. This is a combined technique^{8,9} of solvent extraction¹⁰⁻¹³ and flotation.¹⁴⁻²⁰ The extracted analytes in the solvent can be measured without further treatment. A desired element(s) can be selectively concentrated and determined in a sample solution(s) by adjusting the pH and using a proper ligand.^{9,21}

The present study is based on the fact² that platinum group elements easily form their complexes with thio-organic compounds or long-chained alkyl amines. GF-AAS determination of Au(III), Pt(IV) and Pd(II) was conducted by a solvent

sublation using MBT as a ligand.

Previous works on solvent extraction and sublation of platinum elements have been reported. Ubaltini²² extracted MBT complexes of Pt, Pd, and Ru into a solvent. Kabil *et al.* studied the solvent sublation of Pt(IV) and Pd(II), using 4-phenylthiosemicarbazide²³ and 2-hydroxyimino-3-(2-hydrazonopyridyl)-butane²⁴ as respective ligands and adding oleic acid as a surfactant. More than 99% of Pt(IV) in its alloy and Pd(II) in Nile River water were extracted into kerosene for the determination.

Additional studies on the sublation of other elements are as follow: Kotsuji *et al.*^{6,7} floated Fe(II) and Cu(I) as complexes of 3-(2-pyridyl)-5,6-diphenyl-1,2,3-triazine (PDT), using sodium dodecyl sulfate as a surfactant and extracted into 3-methyl-1-butanol to measure the absorbances with organic phase by UV/Vis spectrophotometry. Takahashi *et al.*²⁵ floated U(VI) ion as a di(2-ethylhexyl) phosphate (D2EHPA) complex adding sodium dodecyl benzene sulfonate (BDS) to extract into a heptane or kerosene having TOPO. Smith *et al.*²¹ continuously floated pyrene and pentachlorophenol (PCP) in a large volume of waste water to concentrate in a light-white mineral oil. This process can be pilot-scaled up to the industrialization level, with much higher efficiency compared with solvent extraction.

In the present study, three kinds of waste water were acidified with concentrated HCl, MBT was added as a ligand in a heated state to form their complexes, followed by cooling to room temperature. After this solution was transferred to a

flotation cell, the complexes were floated by bubbling nitrogen gas to concentrate them separately in methylisobutyl ketone (MIBK) on the solution. A small volume of MIBK solution was injected into a graphite tube to measure their absorbances by atomic absorption spectrophotometry (AAS). Several experimental conditions such as the volume of HCl added, heating time, the amount of MBT, the type and amount of surfactant, and flotation time were optimized and the concentration efficiencies were compared with several organic solvents. Finally, the practical application of this procedure is evaluated by analyzing three kinds of waste water under the optimized conditions.

Experimental Section

Reagents and Instruments. All reagents used were exceeded analytical grade; deionized water purified by distilled water with a Millipore Milli-Q water system was used.

NIST (National Institute of Standard and Technique) standard solutions of 1,000 $\mu\text{g/mL}$ Au(III) and Pd(II) and 300 $\mu\text{g/mL}$ Pt(IV) were used as stock solutions. These solutions were diluted to proper concentrations for use. A ligand solution was prepared by dissolving 2.0 g MBT (Aldrich Co.) in 500.0 mL of ethanol (99.9%, J. T. Baker Co.). A GR grade HCl of Merck Co. was diluted to 2.0 M solution. A 1×10^{-3} M surfactant solution was prepared by dissolving 0.049 g CTAB (Junsei Co.) in ethanol. MIBK from Junsei Co. was used as a solvent.

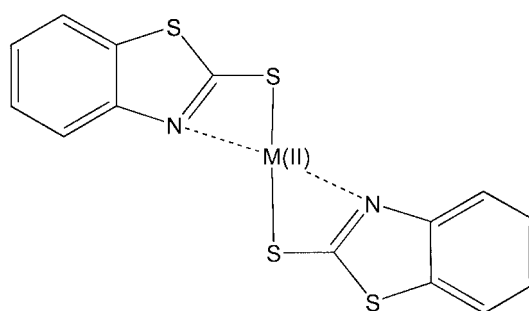
A graphite furnace atomic absorption spectrophotometer (GF-AAS) from Perkin-Elmer (model 2380) was used to measure the absorbance in combination with a HGA-400 heating programmer. Operating conditions are shown in Table 1.

Experimental. After floated materials were removed by filtering, 1.0 L of the water sample was taken in an Erlenmeyer flask. 25.0 mL of 2.0 M HCl solution were added and heated to 80 °C on a hot plate. 30 mL of 0.4%(w/v) MBT

solution were added to this solution and the heating was continued for 10 minutes together with stirring by a magnetic stirrer. 4.0 mL of 1×10^{-3} M CTAB solution were added and stirring continued for 5 minutes. The cooled solution was transferred to a flotation cell. Then, M-MBT complexes were floated by bubbling nitrogen gas at the rate of 40.0 mL/min for 35 minutes to extract them into an organic layer of 20.0 mL MIBK. 20 μL of the organic phase were injected into the graphite tube to measure the absorbances of the analytes by GF-AAS. Calibration curves for the analysis of real samples were prepared with a series of standard solutions.

Results and Discussion

Structure of Metal-MBT Complexes. MBT, having an unpleasant odor, is insoluble in water but soluble in organic solvents such as alcohol, ether, acetic acid, carbon tetrachloride, and benzene. It is a white or pale yellow crystal of needle form.²⁶ Spacu and Kuras²⁷ have observed that an alcoholic solution of MBT can precipitate with ions of gold, silver, copper, lead, bismuth and so on in an acidic or neutral solution. And MBT is known to form chelates by coordinating with other cations,²⁸⁻³² but Pt(IV) does not form a complex with MBT in basic solution, so that the complex formation should be done under HCl condition.^{1,22-24,33} In the present work, an alcoholic solution of 0.4 (w/v)% MBT was added to an aqueous sample solution after MBT was dissolved in ethanol (99.9%). MBT is dissociated to MBT^- and H^+ and the unshared electron pairs of S^- and $=\text{N}-$ in MBT take part in a coordination bond with metal ions. In general, MBT is known to form 1 : 2 complexes with divalent metal ions as in the following illustration, but it can form 1 : 3 complexes with trivalent metal ions such as Au(III), Bi(III), and so on.²⁶



MBT complex of divalent metal ion

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

Operating conditions			
	Au	Pt	Pd
Wavelength(nm)	242.8	265.9	244.8
Current(mA)	10	30	30
Bandwidth(nm)	0.7	0.7	0.7
Signal mode	Absorbance		
Inert gas	Argon		
Tube Type	uncoated tube		
Heating programs for graphite tube			
Drying, °C	150, [5], (5)	150, [5], (5)	150, [5], (5)
Charring, °C	300, [3], (8)	1400, [3], (3)	1500, [3], (3)
Atomization, °C	2100, [3], (3)	2600, [3], (3)	2400, [3], (3)
Cleaning, °C	2500, [3], (3)	2700, [3], (3)	2600, [3], (3)

Sample injection: 20 μL (solvent : MIBK). []: Holding time, in seconds; (): Ramping time, in seconds

HCl Acidic Solution. One sample of waste water from the Cheongju treatment pool and two samples from final washed water of plating companies in the Banwol Industrial Complex were used in this experiment. The pH was 3-6. According to Diamantatos,³³ Pt(IV) forms a complex well in HCl acidic solution, but not in the basic and neutral range. The complex formation in HCl solution has been described in many papers.^{1,22-24} As described by Kabil *et al.*²³ in their study of the structure for the 4-phenylthiosemicarbazide (HPTS) complex of Pt(IV) as $\text{Pt}(\text{HPTS})_2\text{Cl}_2$, Cl^- ion is

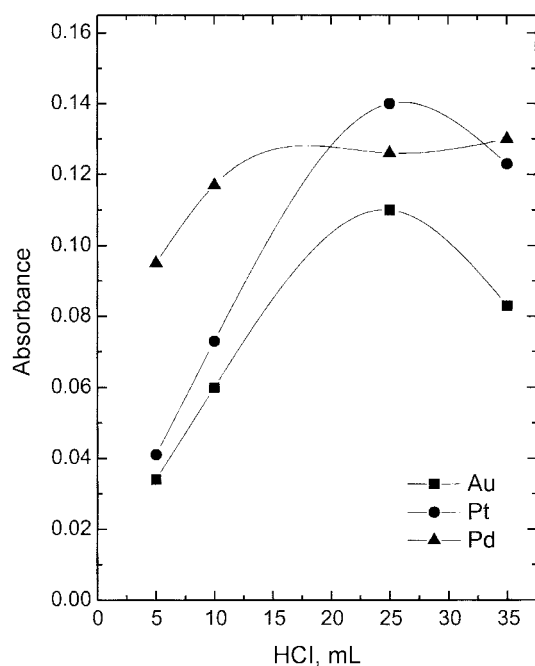


Figure 1. Optimum volume of 2M HCl for the effective formation of metal-MBT complexes. Au(III): 1.0 ng/mL, Pt(IV): 72.0 ng/mL, Pd(II): 30.0 ng/mL.

involved in the complex, the extent to which depends on the concentration of Cl^- . Thus, Cl^- ion could be involved in the complexes of Au(III) and Pt(IV) in a high concentration of HCl.³⁴

In accordance with the above descriptions, 2 M HCl was added to a 1.0 L sample solution of 1.0 ng/mL Au(III), 72.0 ng/mL Pt(II) and 30.0 ng/mL Pd(II), ranging in amounts from 5.0 to 35.0 mL to form their perfect complexes (Figure 1). The different concentrations were taken for each analyte, considering their different sensitivities in the absorbance measurement by GF-AAS.

Pd(II) formed the complex well across a whole range of pH values. The maximum formation for Au(III) and Pt(IV) appeared at the addition of 25.0 mL. The decrease over 25.0 mL was due to the formation of chlorocomplex.¹

On the other hand, as shown in Diamantatos' work, MBT and other ligands exhibited a low reactivity with Pt(IV) at room temperature, so that the solution was heated to 80 °C on a hot plate.

Amount of MBT. A sufficient ligand is needed for the complex formation of trace metal ions under optimum other conditions. To determine the amount of MBT for the effective formation of complexes of all analyte ions in HCl acidic solution, the 0.4 (w/v)% MBT solution was added to 1.0 L aqueous solution of the given concentrations of analyte ions as in the section "**HCl acidic solution**", changing the volume after heating for 30 minutes. The absorbances of floated elements in MIBK were measured and plotted against the MBT concentration (Figure 2). The absorbance of Pd(II) became a plateau at the addition of more than 20.0 mL MBT solution, and Au(III) and Pt(IV) showed constant absorbances after the addition of 30.0 mL. Therefore, 30.0 mL of

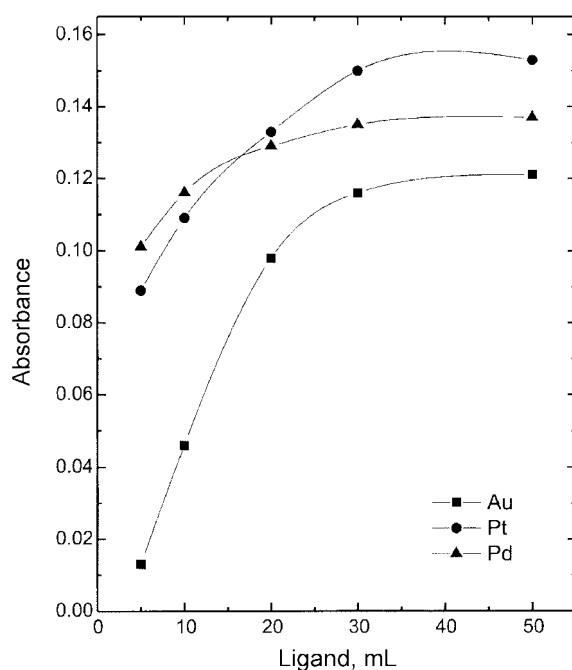


Figure 2. Optimum volume of 0.4%(w/v) MBT-ethanol solution as a ligand added to form the complexes for the effective solvent sublation.

0.4 (w/v)% MBT solution were added to 1.0 L solution to form the complexes simultaneously. The amount of MBT added was equivalent to more than 1000 times all the analyte ions as a mole ratio. The solution was kept for 10 minutes at 80 °C after added the ligand.

The Type and Amount of Surfactant. A surfactant helps the flotation of complexes by making the surface of the complexes hydrophobic. According to the literature,³⁵ the surfactant combines with complex or counter ion pair in the aqueous solution, which floats them and separates the complexes into an organic layer. The best surfactant was determined for the flotation of complexes by using cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) as a cationic surfactant, sodium lauryl sulfate (SLS) and sodium oleate (SO) as an anionic surfactant, and triton X-100 (TX-100) as a neutral surfactant. The concentration of each surfactant was 1×10^{-3} M.

As shown in Figure 3, even when a surfactant was used, the flotation efficiencies were not significantly improved compared with the flotation without surfactants. But the cationic CTAB was selected as a surfactant because the flotation of Pt(IV) was somewhat improved and it is known to decrease the background in the measurement of AAS absorbance.

Also the effect of the amount of CTAB on flotation was investigated, changing the volume of 1×10^{-3} M CTAB solution from 1.0 to 6.0 mL (Figure 3). Pd(II) was not very much influenced by the CTAB. This is considered to be due to the neutral property of the Pd(II)-MBT complex. The flotation of Pt(IV) gradually improved up to the addition of 4.0 mL, and the flotation of Au(III) improved up to the addition of 3.0 mL. Thus, 4.0 mL of 1×10^{-3} M CTAB was added to

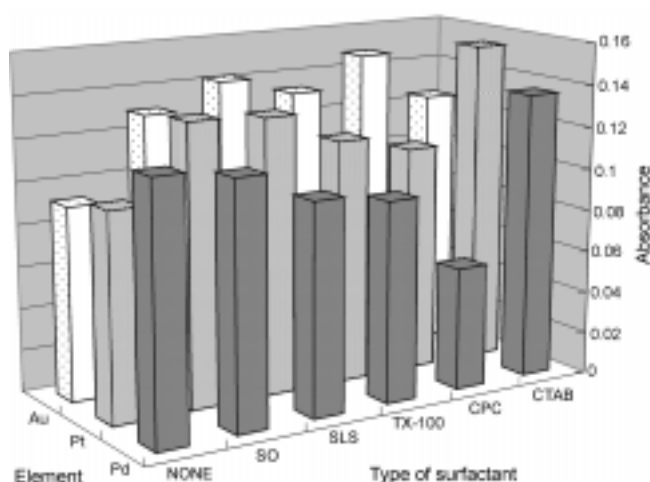


Figure 3. Comparison of flotation efficiencies according to various surfactant. SO: sodium oleate, SLS: sodium lauryl sulfate, TX-100: triton X-100, CPC: cetylpyridinium chloride, CTAB: cetyltrimethylammonium bromide

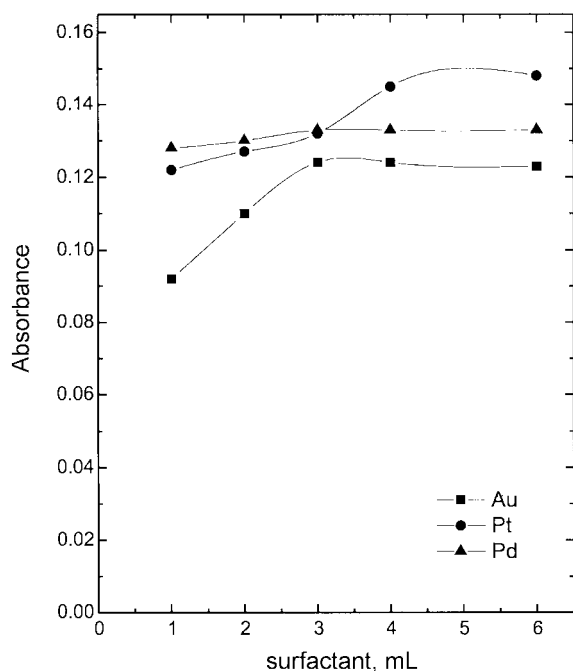


Figure 4. Optimum volume of 1×10^{-3} M CTAB as a surfactant for effective flotation.

1.0 L solution.

After the surfactant was added, the solution was further stirred for 5 minutes and slowly cooled to room temperature by standing for 2 hours to prevent the crystallization of MBT.

Organic Solvent. Solvent sublation depends on the solubility of the metal-complex in an organic solvent. But the solvent should be immiscible with an aqueous phase, non-volatile and lighter than the aqueous solution. It must be kept at the surface of the solution in a stable state.^{5,9,36,37} The sublation efficiencies were compared with several water-immiscible and light solvents such as methylisobutyl ketone (MIBK), diisopropyl ketone (DIPK), cyclohexane, benzene

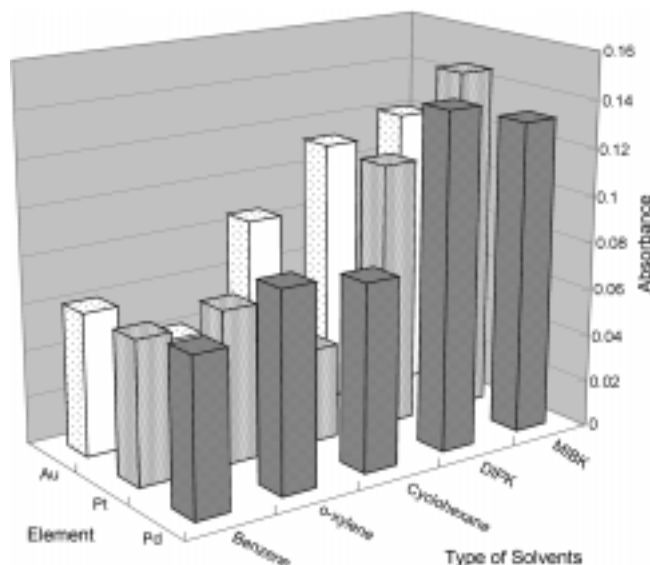


Figure 5. Sublation efficiencies according to the type of solvents. DIPK: diisopropyl ketone, MIBK: methylisobutyl ketone

and o-xylene, having 0.77-0.89 g/mL densities (Figure 5). MIBK and DIPK showed good flotation efficiencies for similar levels, but MIBK was selected as a solvent because of the low background in AAS measurement.

Bubbling Nitrogen Gas. Nitrogen, as an inert gas, does not react with any complexes and also has a active function to float the complexes.⁸ The sublation is also dependent upon the rate of bubbling through a porous fritted disk at the low part of the flotation cell. The fine bubbles have so large a surface area that they can float complexes because of the large area of contact with the complexes.²¹ Because com-

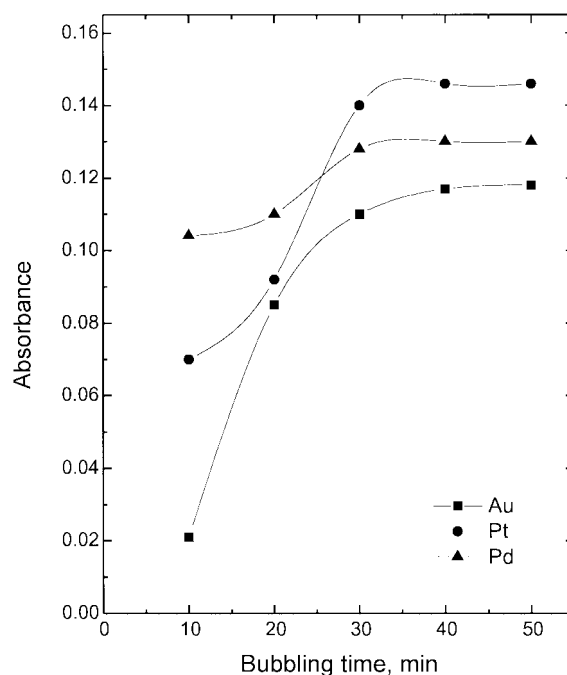


Figure 6. Optimum bubbling time of nitrogen gas at the rate of 40 mL/min for effective sublation.

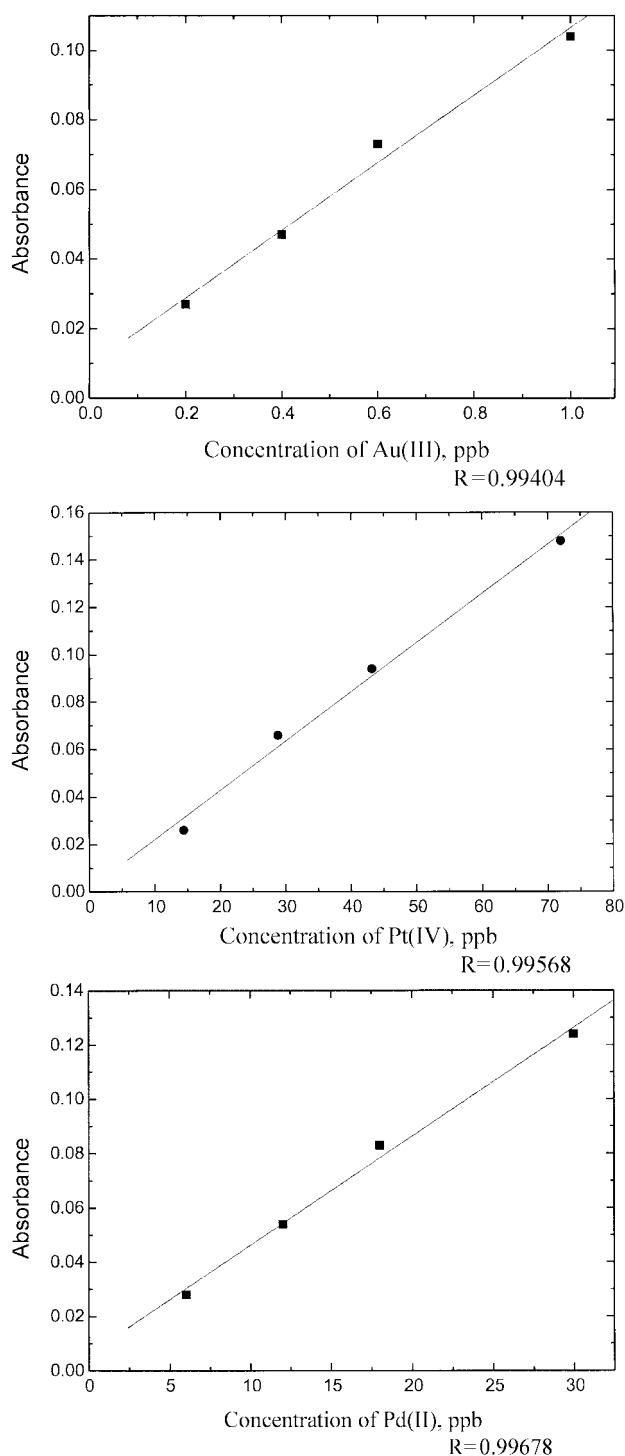


Figure 7. Calibration curves of analytes by a solvent sublation.

plexes are directly floated into an organic layer by the support of the bubbles, the extraction efficiency is better than common solvent extraction.⁹ Too high a rate of bubbling causes turbulent mixing and convection of the complexes decreasing the extraction efficiency.

Considering such phenomena, the introduction rate of nitrogen was fixed at 40.0 mL/min. At a higher rate, the complexes were not effectively floated and the size of the bubbles were too large to redistribute the complexes into the

Table 2. Analytical results of waste water samples by the solvent sublation (Unit : ng/mL)

Sample*	Elements	Spiked	Measured	Recovered	RSD (%)	Recovery (%)
# 1	Au(III)	0.00	0.00			
		1.00	1.07	1.07	2.65	107.0
	Pt(IV)	0.00	0.00			
		72.00	70.04	70.04	2.49	98.2
	Pd(II)	0.00	0.00			
		30.00	31.96	31.96	1.69	106.5
# 2	Au(III)	0.00	0.68		1.13	
		1.00	1.81	1.13	2.00	113.0
	Pt(IV)	0.00	0.00			
		72.00	73.89	73.89	1.88	105.6
	Pd(II)	0.00	0.00			
		30.00	30.46	30.46	0.57	101.5
# 3	Au(III)	0.00	0.98		0.97	
		1.00	2.18	1.20	0.75	120.0
	Pt(IV)	0.00	0.00			
		72.00	66.68	66.68	1.11	95.3
	Pd(II)	0.00	0.00			
		30.00	29.71	29.71	2.08	99.0

*# 1: Original water in the treatment field of waste water at Cheongju. # 2: Final washed water of plating industry at Banweol No. 1. # 3: Final washed water of plating industry at Banweol No. 2.

aqueous solution. Bubbling was investigated after 10 minutes to 50 minutes at the flow rate of 40.0 mL/min (Figure 6). All three analyte ions were effectively floated by bubbling of more than 30 minutes. Sublation was performed for 35 minutes.

Analytical Results. The usefulness of this procedure was evaluated by applying this method to real samples. Calibration curves were prepared with a series of standard solutions under the above conditions (Figure 7).

Analytical data are shown in Table 2 for three kinds of waste water. Au(III) was determined as 0.68 ng/mL and 0.98 ng/mL for the final washed water from the two plating industries. Pd(II) and Pt(IV) were not detected in any of the three samples. Recoveries of 95-120% were obtained for given amounts of analytical elements in samples.

Trace amounts of Au(III), Pt(IV) and Pd(II) in waste waters were determined with GF-AAS by floating and extracting as metal-MBT complexes. Stable complexes of Au(III) and Pt(IV) were formed under HCl acidic conditions and at 80 °C. Flotation efficiency was somewhat improved with CTAB by bubbling nitrogen for 35 minutes at 40 mL/min. Based on the results of the present study, this procedure can be applied to determine trace elements in many other kinds of samples.

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