

Column Preconcentration and Determination of Cobalt(II) Using Silica Gel Loaded with 1-Nitroso-2-naphthol

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A sensitive technique for the determination of trace Co(II) in various samples after column preconcentration by adsorbing onto silica gel loaded with 1-nitroso-2-naphthol was developed. Several experimental conditions, such as pH of sample solution, the amount of silica gel loaded with 1-nitroso-2-naphthol, the flow rate for adsorption and so forth, were optimized. The interfering effects of diverse concomitant ions were investigated. Fe(III) interfered with more than any other ions, but the interference by Fe(III) was completely eliminated by adjusting the amount of silica gel loaded with 1-nitroso-2-naphthol to 0.30 g. The dynamic range, the correlation coefficient (R^2), and the detection limit obtained by the proposed technique were 3.0-140.0 ng mL⁻¹, 0.9942, and 1.81 ng mL⁻¹, respectively. For validating the technique, the aqueous samples (tap water, reservoir water, stream water, and wastewater) and the plastic samples were used as real samples. Recovery yields of 93.0-107.0% were obtained. These measured data were not different from ICP-MS data at the 95% confidence level by F test. Based on the results of the experiment, it has been found that the proposed technique can be applied to the determination of Co(II) in various real samples.

Key Words: Cobalt, 1-Nitroso-2-naphthol, Silica gel, Preconcentration

Introduction

Cobalt is an important element, not only for industry but also for biological systems. It is present in vitamin B₁₂ and is an essential micro nutrient for all living systems. However, in larger amounts it is toxic and causes pulmonary disorders, dermatitis, nausea and vomiting.¹

In the determination of trace cobalt, various methods including ICP-MS,² spectrofluorometry,³ ICPAES,⁴ differential pulse voltammetry,⁵ anodic stripping voltammetry,⁶ and GFAAS⁷ have been used. Among these techniques, GFAAS, ICP-MS, and anodic stripping voltammetry can be directly applied to the determination of Co at the ng mL⁻¹ level. However, some of these methods are time-consuming and require complicated and expensive instruments. They also have complex operational conditions, are not free from various types of interference, and have high maintenance costs. Therefore, other methods that can determine the low concentrations of cobalt conveniently in real samples were required.

UV-Vis spectrophotometers, FAAS, and polarographic analyzers are commonly available in laboratories. However, their main problem is their low sensitivity to trace metal ions at the ng mL⁻¹ level. This limitation can be overcome by the use of some preconcentration techniques.

For the preconcentration and separation of Co(II), various solid adsorbents such as Amberlite XAD-2 resin,⁸ activated carbon,⁹ and alumina¹⁰ have been used. These adsorbents have good preconcentration yields and high recovery yields for some cobalt(II) complexes. These techniques are generally troublesome and time-consuming because of slow sorption and desorption process, but they have many advantages, including the availability and the easy recovery of the solid phase, the attainability of large preconcentration factors, the facility for separation and enrichment using systems with continuous

flow, and the needlessness of toxic organic solvents.¹¹ Solid phase extraction procedures based on adsorption of metal complexes on silica gel have also applied.¹²⁻¹³

The use of silica-based ion exchangers in preconcentration and separation of trace heavy metal ions from different media has been of particular interest. The modified silica gel generally exhibits sorption capacities higher than those of organic polymer based resins. Silica gel has many adsorption sites, and therefore, the number of chelating agents adsorbed is high, which results in good adsorption capacity for metal ions.¹⁴

The aim of this work is to develop and validate a method for the preconcentration and separation of ng mL⁻¹ levels of Co(II) from matrix constituents of real samples such as aqueous solutions and plastic samples using a glass column packed with silica gel loaded with 1-nitroso-2-naphthol.

Experimental

Instrumentations and apparatus. For the determination of preconcentrated Co(II), a GBC model 903 flame atomic absorption spectrophotometer was used. Co(II) in real samples was determined directly with an HP 4500 ICP-MS spectrometer. A Bantex model 300A digital pH meter with a combined glass and calomel electrode was used to adjust the pH of all sample solutions. To pulverize plastic samples, Vibratory Micro Mill (Model Pulverisette 0, Taemyoung Co., Korea) was used. ACEM microwave oven (Mars 5 model, vessel type XP 1500 plus) was used to change the plastic powder samples to the solution samples. To determine what amount of 1-nitroso-2-naphthol adsorbed on silica gel, a Hewlett-Packard 8453 UV-Vis spectrophotometer was used. In order to control the flow rate of sample solution, a peristaltic pump (Micro tubing pump MP-1000, EYELA Tokyo Rikakikai, Japan) was used. A glass column (10 cm × 10 mm i.d.) consisting of a glass

filter(1-G-1) and a Teflon stopcock at the bottom was used to preconcentrate Co(II).

Reagents and solutions. All chemicals used in this experiment, such as $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich Co., U. S. A) and 1-nitroso-2-naphthol (Merck Co., Germany) were of analytical grade and guaranteed grade reagents unless otherwise specified. Silica gel 60 (70-230 mesh) as adsorbent support was supplied by Merck Co.(Germany). A Co(II) standard solution was prepared from $1000 \mu\text{g mL}^{-1}$ stock solution by a suitable dilution. The concentration of the stock solution of various species used for investigating the interfering effects was $1000 \mu\text{g mL}^{-1}$. The deionized water obtained with a Barnstead E-Pure 3-module deionization system was used throughout all experimental procedures.

Preparation of adsorbent. Silica gel was purified with 2 M hydrochloric acid and washed with deionized water until the washings contained no acidity. Then, silica gel was dried at 110°C for a day. A 1.0 g of the cleaned silica gel was shaken in 20% ethanol (50 mL) containing 0.2 g of 1-nitroso-2-naphthol for three hours. Thereafter, the modified silica gel was filtered, washed with deionized water, dried at 60°C and stored in a desiccator. When the actually loaded amount of 1-nitroso-2-naphthol ($\lambda_{\text{max}} = 376 \text{ nm}$) was measured by UV-Vis spectrophotometry, it was 0.0132 g of 1-nitroso-2-naphthol per 1.0 g silica gel.

Preconcentration of cobalt(II) in a column. A 0.20 g of silica gel loaded with 1-nitroso-2-naphthol was packed in a glass column. Next, 1000 mL of the Co(II) sample solution was taken into a 1000 mL Erlenmeyer flask, and adjusted to pH 6.0. In order to adsorb Co(II), the Co(II) sample solution was passed through the column filled with silica gel loaded with 1-nitroso-2-naphthol at a flow rate of 20 mL min^{-1} . The flow-rate was controlled by peristaltic pump. The desorption of Co(II) retained on silica gel was carried out by treating with 10 mL portion of 4 M HNO_3 in ethanol at a flow rate of 3 mL min^{-1} . The desorbed Co(II) solution was collected in a 10 mL volumetric flask. The Co(II) content in the collected solution was measured on the basis of a Co-free blank solution at 240.7 nm with a flame atomic absorption spectrophotometer.

Calibration curve and detection limit. A calibration curve was prepared in the concentration range of $3.0\text{-}140.0 \text{ ng mL}^{-1}$ Co(II) according to the procedure described earlier by using several columns simultaneously. The regression equation and the correlation coefficient (R^2) of the calibration curve were obtained using the least squares method. The detection limit was obtained from the signals of 25 blank samples and the slope of the calibration curve. The detection limit is defined as the sample concentration giving signals that equal to three times the standard deviation of the blank signal.¹⁵

Preparation of aqueous samples. The 1000 mL aliquots of tap water (The University of Suwon, Korea), reservoir water (Botongri, Hwaseong, Korea), stream water (Hwangguchi-cheon, Suwon, Korea), and untreated wastewater (Suwon Environmental Production Office, Korea) were taken after the suspended matters or particles were filtered out with a glass filter(1-G-4) and used as real samples.

Preparation of plastic sample. A 0.5 g finely ground plastic sample was taken to a high-pressure digestion vessel. Then, 9

Table 1. Decomposition conditions of microwave digestion system for plastic powder sample

Step	Ramping time (min.)	Temperature ($^\circ\text{C}$)	Holding time (min.)
1	3.0	120	0.0
2	3.0	150	0.0
3	3.0	180	10.0
4	5.0	200	25.0
Cooling		room temperature	60.0

mL of concentrated HNO_3 and 2 mL of H_2O_2 were added and mixed well. The plastic powder sample was decomposed in a CEM microwave oven using the digestion program given in Table 1. The dissolved sample solution and the solution washing the digestion vessel were collected in a 1000 mL volumetric flask and diluted with deionized water to the mark.

Results and Discussion

pH. The pH of the sample solution was investigated to evaluate its effect on the adsorption degrees of Co(II) in a column. When a specific metal ion was separated and preconcentrated by silica gel loaded with a chelating agent at the optimum pH, the selectivity and the efficiency of silica gel loaded with chelating agent could be maximized. After 0.20 g of silica gel loaded with 1-nitroso-2-naphthol was added to each glass column, 1000 mL of a 60 ng mL^{-1} Co(II) solution varied in pH from 4.0 to 11.0 by using 0.1 M HCl or 0.1 M NaOH was passed. We investigated at which pH was preconcentrated quantitatively and the results are represented in Figure 1. We found that Co(II) was adsorbed quantitatively at pH ranging from pH 5.0 to 7.0. Co(II) was not preconcentrated quantitatively above pH 7.0. It was assumed that the adsorption process competed with the process forming the hydroxide precipitate, and that in alkaline solution, Co(II) is readily oxidized to Co(III) by the dissolved oxygen present in aqueous solution.¹⁶ At lower pH than 5.0, it is guessed that not only the oxygen atom in the chelate site of 1-nitroso-2-naphthol has more affinity power with hydrogen ion, but also peeling of 1-nitroso-2-naphthol loaded on silica gel is possible. When the pH of the Co(II) solution was adjusted to 6.0, a buffer solution was not used. The concentrated phosphate buffer ($\text{KH}_2\text{PO}_4 + \text{NaOH}$) used to prepare the buffer solution with pH 6.0 might interfere with the preconcentration of Co(II). Therefore, pH 6.0 was selected as the optimum pH and it was adjusted using 0.1 M HCl or 0.1 M NaOH.

Amount of silica gel loaded with 1-nitroso-2-naphthol. It is known that Co(II) combines stoichiometrically with 1-nitroso-2-naphthol to form 1:2 complex.¹⁷ To separate metal complex quantitatively, chelating agent was generally used more than its stoichiometric amount. So, the quantitative retention can only be obtained with an appropriate amount of silica gel loaded with 1-nitroso-2-naphthol. An insufficient amount of silica gel may induce the loss of analytes. A reasonable excess amount of silica gel can prevent the desorption of the retained metal chelates and metal ions when an appropriate volume of desorption solvent is used. For this reason, the amount of

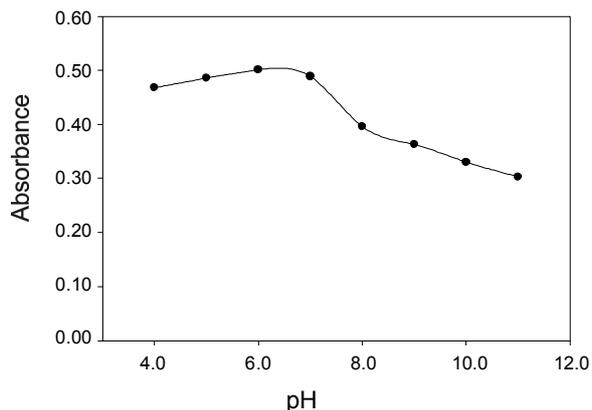


Figure 1. Effect of pH on the adsorption of Co(II) (60 ng mL^{-1}) on silica gel loaded with 1-nitroso-2-naphthol.

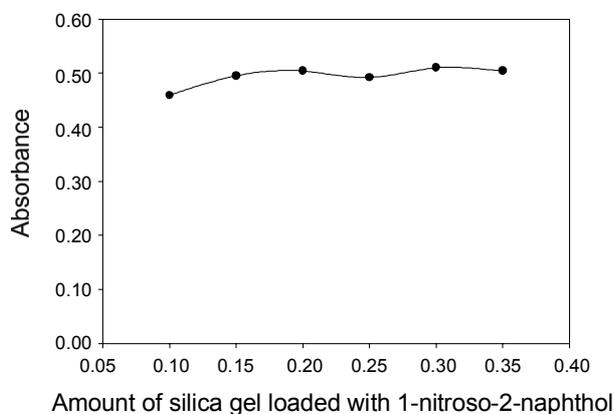


Figure 2. Effect of the amount of silica gel loaded with 1-nitroso-2-naphthol on the preconcentration of Co(II) (60 ng mL^{-1}) at pH 6.0.

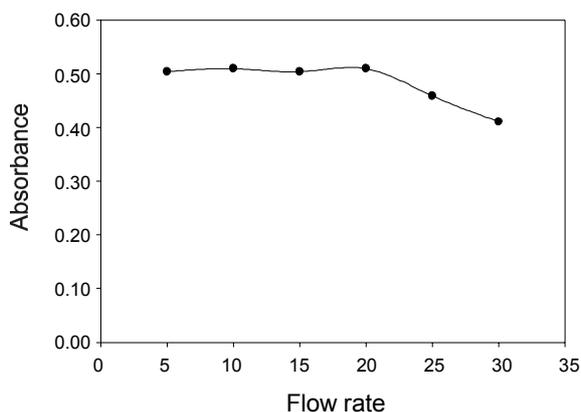


Figure 3. Effect of the flow rate of Co(II) solution (60 ng mL^{-1}) on the preconcentration yield of Co(II) at pH 6.0.

silica gel should be optimized. The amount of silica gel loaded with 1-nitroso-2-naphthol added to each glass column was varied from 0.05 to 0.40 g, then 1000 mL of 60 ng mL^{-1} Co(II) solution adjusted to pH 6.0 was passed through the glass column. We investigated what amount of silica gel loaded with 1-nitroso-2-naphthol was appropriate to enrich Co(II), and the result is represented in Figure 2. We found that when

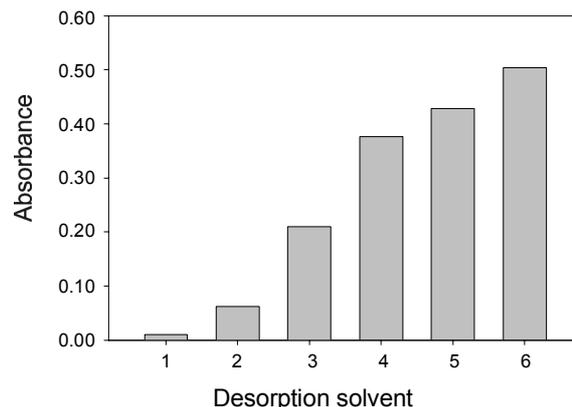


Figure 4. Effect of various solvents on the desorption of preconcentrated Co(II) (60 ng mL^{-1}) at desorption flow rate 3.0 mL min^{-1} . 1. $0.1 \text{ M CH}_3\text{COOH}$; 2. 1 M NaOH ; 3. ethyl alcohol; 4. 4 M HNO_3 ; 5. 1 M HNO_3 in ethyl alcohol; 6. 4 M HNO_3 in ethyl alcohol.

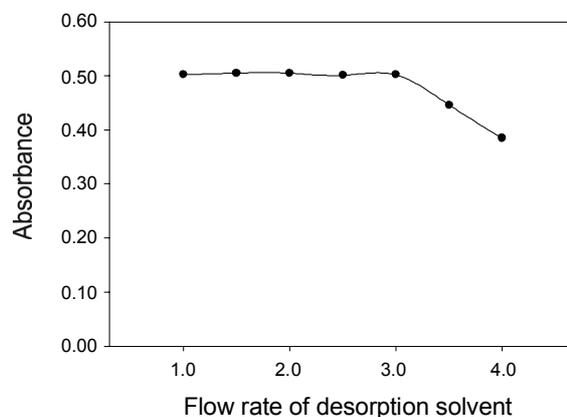


Figure 5. Effect of the flow rate of 4 M HNO_3 in ethyl alcohol on the desorption of preconcentrated Co(II).

the amount of silica gel loaded with 1-nitroso-2-naphthol was above 0.15 g, the degree of adsorption was high and varied slightly. Therefore, the optimized amount of silica gel loaded with 1-nitroso-2-naphthol was 0.20 g.

Flow rate for adsorption. The flow rate of sample solution controls preconcentration time that metal ion is able to be quantitatively adsorbed at a given amount of adsorbent. A 0.20 g of silica gel loaded with 1-nitroso-2-naphthol was taken to each glass column, and 1000 mL of 60 ng mL^{-1} Co(II) solution adjusted to pH 6.0 was passed through. It was compared to the preconcentration efficiency according to the flow rate of the sample solution, and the result is represented in Figure 3. It is shown that Co(II) is preconcentrated quantitatively below 20 mL min^{-1} . As the flow rate was increased above 20 mL min^{-1} , however, the preconcentration yield was slowly decreased. It is assumed because the flow rate was faster than the equilibrium adsorption rate. Therefore, the flow rate controlled at 20 mL min^{-1} with peristaltic pump was used in this experiment.

Solvent and flow rate for desorption. Ethyl alcohol, 4 M HNO_3 , 1 M NaOH , $0.1 \text{ M acetic acid}$, 1 M HNO_3 in ethyl alcohol and 4 M HNO_3 in ethyl alcohol were used to desorb

Table 2. Tolerance limit^a for various species in 60 ng mL⁻¹ Co(II) solution at pH 6.0

Concentration of species (μg mL ⁻¹)	Interfering species
200	Ca ²⁺ , Na ⁺ , NH ₄ ⁺ , Cl ⁻ , NO ₃ ⁻
100	Ni(II), Mg(II), F ⁻ , Br ⁻ , SCN ⁻
50	tartrate ion, citrate ion
10	Cr(III), Zn(II)
5	Cu(II), Ni(II), Al(III), CN ⁻
1	Fe(III)

^aTolerance limit is the maximum concentration in which there is less than 5% effect on absorbance.

Table 3. Determination and recovery yields of Co(II) in several aqueous samples

Samples	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹) ^a		Recovery yield(%)
		This method	ICP-MS	
Tap water	0.0	2.1 (± 0.2)	0.0 (± 0.5)	
	20.0	21.0 (± 1.3)		94.5
	40.0	40.8 (± 2.4)		96.8
Reservoir water	0.0	5.8 (± 0.4)	5.7 (± 0.4)	
	20.0	25.3 (± 1.4)		97.5
	40.0	44.2 (± 2.3)		96.0
Stream water	0.0	6.3 (± 0.4)	6.5 (± 0.5)	
	20.0	24.9 (± 1.8)		93.0
	40.0	45.5 (± 2.7)		98.0
Wastewater	0.0	18.2 (± 1.1)	17.9 (± 1.0)	
	20.0	39.6 (± 2.3)		107.0
	40.0	59.2 (± 3.6)		102.5

^aThe mean values in this method were obtained from 7 samples and those in ICP-MS were obtained from 5 samples.

quantitatively Co(II) on the silica gel. Among these reagents, 4 M HNO₃ in ethyl alcohol was the most effective for desorption as shown in Figure 4. It is assumed that Co(II)-1-nitroso-2-naphthol adsorbed on silica gel would be well desorbed by ethanol, and also Co(II) would be dissociated in Co(II)-1-nitroso-2-naphthol chelate by 4 M HNO₃. As the flow rate of 4 M HNO₃ in ethyl alcohol varied from 1.0 mL min⁻¹ to 4.0 mL min⁻¹, the absorbance of desorbed Co(II) was measured. The result is shown in Figure 5. When the flow rate for desorption was less 3.0 mL min⁻¹, the absorbance was high and constant. So, 10 mL of 4 M HNO₃ in ethanol was used at a flow rate of 3.0 mL min⁻¹ for the desorption of Co(II). Unfortunately, silica gel loaded with 1-nitroso-2-naphthol could be used only one time when 4 M HNO₃ in ethanol was utilized as the desorption solvent. However, this was an insignificant problem, because silica gel could be reused several times and 1-nitroso-2-naphthol could be adsorbed on silica gel well and simply.

Effect of coexisting species. Preconcentration procedures for trace metal ions could be strongly affected by the matrix constituents of the samples. The possible interfering effects of concomitant ions by competition for active sites on the determination of Co(II) were investigated under optimum conditions given above. Various species were used for investigation of their interference effects on 60 ng mL⁻¹ Co(II) solution,

Table 4. Determination and recovery yields of Co(II) in plastic sample

Samples	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹) ^a		Recovery yield(%)
		This method	ICP-MS	
Plastic	0.0	0.3 (± 0.2)	0.0 (± 0.4)	
	20.0	20.8 (± 1.2)		102.5
	40.0	39.6 (± 1.9)		98.3

^aThe mean values in this method were obtained from 7 samples and those in ICP-MS were obtained from 5 samples.

because it was assumed that they prevented the Co(II)-1-nitroso-2-naphthol complex from forming. The results of interference studies are summarized in Table 2. Fe(III) interfered with more seriously than any other ions. However the interference by Fe(III) could be overcome sufficiently by adjusting the amount of silica gel loaded with 1-nitroso-2-naphthol to 0.30 g. Under practical point of view, almost possible interferences were tested on concentrations usually found in aqueous samples and plastic sample. So, it is not probable that some problems could arise in determination of cobalt in aqueous samples and plastics by the proposed technique, what can be proved by the accuracy and precision found in analysis of preconcentrated samples.¹⁶

Calibration curve and detection limit. A calibration curve was constructed at optimum conditions according to "Calibration curve and detection limit". The linear range of Co(II) was 3.0-140.0 ng mL⁻¹. The regression equation was $y = 0.0083 (\pm 0.0010)x + 0.0076 (\pm 0.0012)$ (x unit: ng mL⁻¹), and the correlation coefficient (R^2) was 0.9942, showing a good linearity of calibration curve. The detection limit was 1.81 ng mL⁻¹.

Aqueous samples. Co(II) in tap water, reservoir water, stream water, and untreated wastewater samples was determined by the proposed method and the results are shown in Table 3. In this determination, the relative standard deviations were generally less than 10.0%. Co(II) in real aqueous samples was also determined by ICP-MS spectrometry. No difference between the results obtained by the proposed method and ICP-MS had been established at the 95% confidence level by F test.¹⁸ The recovery yields in the real samples spiked with 20.0 and 40.0 ng mL⁻¹ Co(II) were 93.0 ~ 107.0%. Therefore, it has been found that the proposed technique can be applied to the determination of Co(II) in real aqueous samples.

Plastic sample. Co(II) in the plastic samples prepared according to the procedures given in the experimental section was determined by the proposed method and ICP-MS, and the results are shown in Table 4. In the plastic sample, Co(II) was not contained. Recovery yields in the spiked plastic solution were more than 98.0%.

Conclusions

A new silica gel loaded with 1-nitroso-2-naphthol has been prepared. This adsorbent was an effective material for the separation and preconcentration of Co(II) in the aqueous solutions and plastic sample. The preconcentration factor of this method on Co(II) was about 100. The recovery yields obtained with the spiked real samples were about 93 ~ 107%. The results

obtained in the determination of Co(II) with this method and ICP-MS were not different at 95% confidence level.

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