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단 신

Nickel(II)의 분리 및 분광학적 정량에 관한 연구

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Separation and Spectrophotometric Determination of Nickel(II)

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Hydrazones are azomethine characterized by the presence of the triatomic grouping -C=N-N-. In analytical chemistry, hydrazones have been used frequently as ligands in the development of photometric methods[1~9] for determination of cations; for example, 2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminophenol has been used for cobalt,[10] and 2,4-dihydroxy-benzophenone benzoic hydrazone for cerium.[11]

In our previous work, a new hydrazone in which a nitro group was introduced to the 5-position of the pyridine ring in the amine moiety of 2-pyridinecarbaldehyde-pyridylhydrazone (2PC-5NPH) was synthesized and its application to the determination of trace amount of Fe(III) was described 12. This paper describes the spectrophotometric determination of Ni(II) by 2PC-5NPH with separation of Ni(II) using Amberlite IRC-718 resin. The present method is a highly sensitive and simple method for separation and spectrophotometric determination of Ni(II).

EXPERIMENTAL

All chemicals were of analytical-reagent grade. 2-pyridinecarbaldehyde-5-nitropyridylhydrazone (2PC-5NPH) was synthesized as described previously.[12] AAS 1000-ppm standard solutions of Ni(II), Cr(II), Co(II) and Pb(II) were obtained from Junsei Chemical Co. The pH was adjusted with hexamethylenetetramine (HTM) buffer solution. The resin used in the column was Amberlite IRC-718, 16~50 mesh. The resin was washed successively with 6 M HCl, water, 1 M NaOH, water, 1 M HCl and water in order to remove organic and inorganic contaminants. Perkin-Elmer 552S spectrophotometer with a 10-mm quartz cell was used for absorbance measurement. Shimadzu AA-670 atomic absorption spectrometer was used for metal ions determination.

Spectrophotometric determination

An aliquot of metal standard solution was transferred to a 50 mL volumetric flask, and 5.0 mL of the 1×10^{-3} M 2PC-5NPH methanol solution, 3.0 mL of pH 6.5 hexamethylenetetramine (HTM) buffer solution and 7.5 mL of 2×10^{-4} M surfactant solution were added sequentially. The solution was made up to the mark with methanol. The absorbance of the solution was measured at 400~700 nm against a reagent blank as a reference.

Separation

Column. Separateion a glass column (25×150 mm) having a stopcock was packed with 20 g of the resin. The resin was regenerated with 6.0 M HCl and a large volume of water.

Batch procedure. Resin (1.0 g) and 50 mL solution of Co(II), Cr(II), Ni(II) and Pb(II) in a 100 mL beaker were stirred moderately for 24 hr at room temperature. After equilibrium, the solution was filtered through Whatman #2 filter paper. The filtrate was diluted with water and the concen-

tration of metal ions was determined by AAS.

Column procedure. Separation of metal ions in the column system was carried out under the following conditions. A fixed volume of aqueous solution of the metal ions was adjusted to a suitable pH and percolated through the column at a flow rate of 1.0 ± 0.2 mL min^{-1}. Co(II) and Cr(II) was eluted with 0.25 M HCl, Ni(II) with 1.5 M HCl and Pb(II) with 2.0 M HNO_3. Ni(II) was analysed spectrophotometrically.

RESULTS AND DISCUSSION

The absorption spectra of the binary and ternary complexes and the reagent blanks are shown in *Fig.* 1. The Ni(II)-2PC-5NPH complex has an strong absorbance at 473 nm. On addition of cetyltrimethylammonium bromide (CTMAB), the absorption band unchanged except for a slight increase in peak absorption. The effect of pH on the Ni(II)-2PC-5NPH-CTMAB complex formation was studied over the pH range of 4 to 10. The optimal pH range for formation of the complex is 6.5~7.3. The solution pH was adjusted with hexamine buffer solution and hydrochloric acid or sodium hydroxide was used to maintain the optimum pH. It dose not affect the intensity but improves the stability of the colour of the complex.

When the general procedure was followed with varied amounts of the reagent, maximum and constant absorbance was obtained with 4.0~7.5 mL of

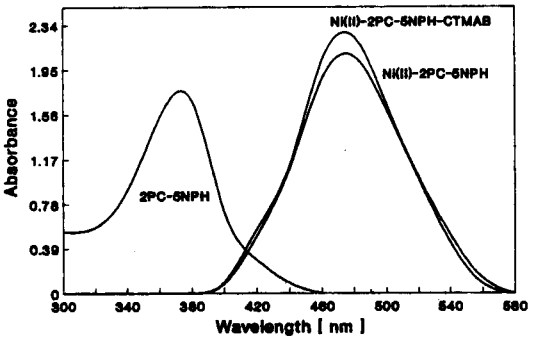

Fig. 1. Absorption spectra of (1) 2PC-5NPH, (2) Ni(II)-2PC-5NPH and (3) Ni(II)-2PC-5NPH with CTMAB. Ni (II): 1.0 mg, 2PC-5NPH: 1.0×10^{-4} M, CTMAB: 1.5×10^{-4} M.

Table 1. Absorption maxima, λ_{max} and apparent molar absorptivities, ε, of metal complex of 2PC-5NPH in MeOH

Metal ion	pH 3.6		pH 6.8		pH 9.9	
	λ_{max} (nm)	ε ($\times10^4$)	λ_{max} (nm)	ε ($\times10^4$)	λ_{max} (nm)	ε ($\times10^4$)
Cr(II)	-	-	-	-	-	-
Pb(II)	-	-	465	2.3	-	-
Cd(II)	-	-	474	6.1	472	10.4
Cu(II)	477	5.0	475	9.0	472	16.2
Co(II)	489	6.9	489	8.9	475	6.3
Ni(II)	472	7.8	473	20.0	477	5.8
V(II)	473	0.1	470	0.8	472	1.1
Mn(II)	-	-	466	0.4	473	1.3
Pt(II)	-	-	-	-	402	6.6
La(II)	-	-	408	1.6	408	0.5
Sc(II)	-	-	-	0	403	0.6
U(II)	402	6.0	408	2.5	402	3.3

[metal: 1 μg/mL, 2PC-5NPH: 1×10^{-4} M].

2PC-5NPH solution and 5.0~10.0 mL of 1×10^{-3} M CTMAB. Thus 5 mL of 2PC-5NPH and 7.5 mL of 1×10^{-3} M CTMAB were respectively selected as optimal volumes. Absorbance of the 2PC-5NPH with metal ions at pH 3.6, 6.8 and 9.8 was investigated. The results are summarized in *Table* 1. 2PC-5NPH forms a stable complexe with various metal ions including transition metal ions. Especially with Fe(II), Ni(II), Pd(II) and Zn(II) reacted 2PC-5NPH to form complexes with large molar absorptivities.

We measured the mole ratio of Ni(II) and 2PC-5NPH in Ni(II)-2PC-5NPH complex with and without CTMAB. The results indicate the formation of a 1:2 complex between Ni(II) and 2PC-5NPH with or without CTMAB. An improvement in detection limit achieved upon the addition of CTMAB. The molar absorptivities in presence of CTMAB found by least-squares analysis of 10 measurments, was 2.0×10^5 $mol^{-1}cm^{-1}L$. Under the optimal conditions explained above, a linear calibration curve obtained over the range 0.02~1.5 μg/mL of Ni(II) ions. The relative standard deviation for 0.5 μg/mL of Ni(II) was 0.6% (n=5). The selectivity in the proposed method was investigated by determining 1.0 μg/mL of Ni(II) in the presence of various oth-

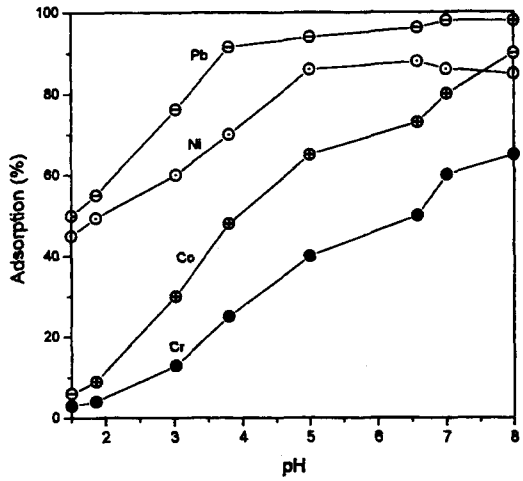

Fig. 2. Adsorption capacities of metal ion on Amberlite IRC-718 chelating resin according to pH change. Metal solution: 2.5 mg/50 mL, Resin taken: 1 g, Shaking time: 24 hr.

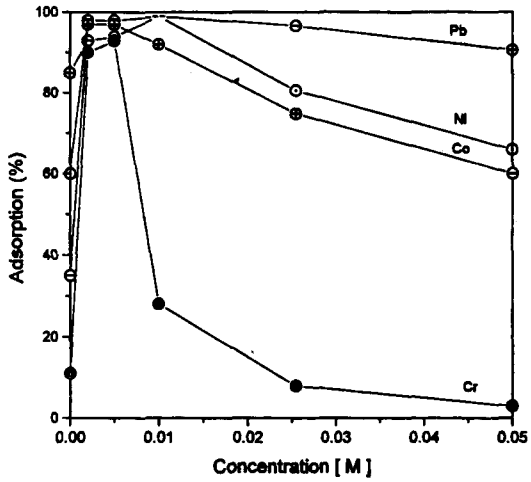

Fig. 3. Adsorption capacities of metal ion on Amberlite IRC-718 chelating resin according to Malic acid concentration. Metal solution: 2.5 mg/50 mL, Resin taken: 1 g, Shaking time: 24 hr, pH: 3.5.

er ions. It was found that the concentration range of 0.1~0.25 μg/mL for Cd(II), Co(II), and Cu(II), and the concentration of 0.7 μg/mL for Pd(II) and Pb(II) are upper limits for interferences. Therefore, it can be understood that the separation of Ni(II) from the matrix is necessary prior to spectrophotometric determination. For this purpose, a column separation method was investigated.

The adsorption capacity to pH (Amberlite IRC-718 resin) profiles for Cr(II), Co(II), Ni(II) and Pb (II) are given in *Fig.* 2. *Fig.* 2 shows that adsorption depends apparently on the pH of the solution due to the competing protonation and complexation reactions of the functional group (iminodiacetic acid) of resin. The order for metal ion's adsorption capacity, as shown by adsorption percent at pH 3.5 (*Fig.* 2), is as follows: Cr(II)< Co(II)<Ni(II)<Pb(II). The metal ions were found to be adsorbed into malic acid over the concentration range of 0.0025~0.0075 M (*Fig.* 3). The adsorption capacities of the resin toward metal ions were found to depend on the HCl and HNO_3 concentration of the sample solutions (*Fig.* 4). For Co(II) ion the capacity decreased gradually with increasing the HCl concentration from 0.1 to 0.5 M. In particular, adsorption capacity of Pb(II) ion did not change over the range 0.25~2.0 M HCl. However, the capacity for Pb(II) ion decreased with increasing HNO_3 concentration (*Fig.* 4).

The effect of flow rate of the sample loading through the column was studied over the range 0.5~2.0 mL min^{-1}. The adsorption of metal ions re-

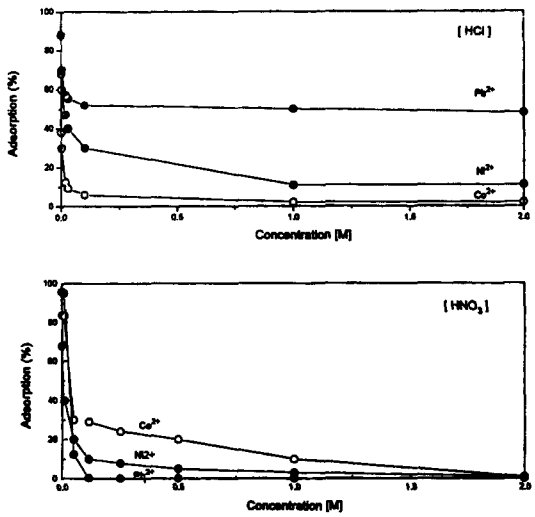

Fig. 4. Adsorption capacities of metal ion on Amberlite IRC-718 chelating resin according to HCl and HNO_3 concentration. Metal solution: 2.5 mg/50 mL, Resin taken: 1 g, Shaking time: 24 hr.

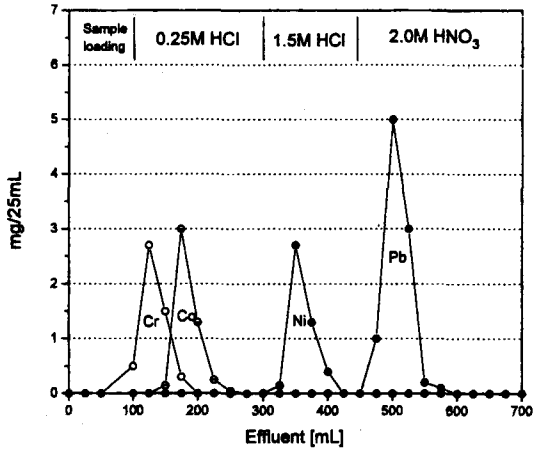

Fig. 5. Elution curve of Cr(II), Co(II), Ni(II) and Pb(II). Loading: 5 mg of Cr(II), Co(II), Ni(II) and 10 mg of Pb (II)+0.005 M Malic acid in 100 mL, Elution: 0.25 M HCl, 1.5 M HCl and 2.0 M HNO_3 solution.

mains almost unchanged regardless of any change in the flow rate. In subsequent experiments a flow rate of 1.0 ± 0.2 mL min^{-1} was maintained for both adsorption and elution. From the results presented in *Fig.* 3 and 4, HCl and HNO_3 solution have been considered as an eluent for the separation of the synthetic metal solution. The column was equilibriated with acetic acid buffer of pH 3.5. 100 mL of a 0.05 M malic acid containing 5.0~10 mg of each metal ion was loaded onto the column (*Fig.* 5). Ni(II) was eluted with 150 mL of 1.5 M HCl after elution with 200 mL of 0.25 M HCl. Then 200 mL of 2.0 M HNO_3 was used to elute Pb(II). The effluent of 150 mL of 1.5 M HCl was used directly for the spectrophotometric determination of Ni(II) as the 2PC-5NPH complex at 473 nm and Cr(II), Pb(II) and Co(II) concentration were analyzed by atomic absorption spectrophotometry.

CONCLUSION

The spectrophotometric determination method of Ni(II) has been investigated after separation of Ni (II) from the mixed ions using Amberlite IRC-718 resin. The complex between 2PC-5NPH and Ni(II) in the presence of CTMAB is very stable and more sensitive than that in the absence of surfactant. The Ni(II)-2PC-5NPH complex in CTMAB has an absorption maximum at 473 nm and obeys the Beer's law in the range of 0.02~1.5 μg/mL. Molar absorptivity is 2.0×10^5 $mol^{-1}cm^{-1}L$. Ni(II) was separated as run 150 mL of 1.5 M HCl after elution with 200 mL of 0.25 M HCl.

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