

## Amberlite XAD-7 비이온성 수지로 분리후 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone을 이용한 철의 분광학적 정량

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### Spectrophotometric Determination of Iron with 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone after Separation with Amberlite XAD-7 Nonionic Resin

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**요 약.** 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone(2HB-5NPH)를 합성하여 철의 분광학적 정량에 응용하였다. 이 시약은 pH 6.0~7.5 범위에서 철과 반응하여 메탄올 용액에서 매우 안정한 노란색의 1:2 킬레이트를 형성한다. 철의 농도범위가 0.05~2.0  $\mu\text{g mL}^{-1}$ 일 때 Beer's law에 적용되고 미량의 철을 분광학적으로 정량하기 위하여 Amberlite XAD-7 비이온성 킬레이트 수지로 채워진 짧은 컬럼을 사용하여 분리과정에 적용하였다. 몇가지 이온들의 방해 효과를 연구하였다. 혼합용액으로부터 철이온의 분리는 완충용액(pH 5.0)과 용리액으로서 0.25M HCl을 가지고 수행하였다.

**ABSTRACT.** 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone (2HB-5NPH) was synthesized and its application to the spectrophotometric determination of iron was studied. The reagent reacts with iron in the pH range 6.0~7.5 to form a yellow colored 1:2 chelate which is very stable in methanol solution. Beer's law is obeyed in the concentration range 0.05~2.0  $\mu\text{g mL}^{-1}$  iron and separation procedure using a short column filled with Amberlite XAD-7 nonionic chelating resin is proposed for the spectrophotometric determination of traces of iron. The influence of several ions as interference was discussed. The separation of Fe(III) ion from the mixture solution were carried out with the buffer solution (pH 5.0) and 0.25M HCl as eluents.

## INTRODUCTION

Hydrazones were used in detection, determination and isolation of compounds containing carbonyl group and hydrazones act as multidentate ligands with metals forming coloured chelates. These hydrazones (characterized by the grouping C=N-N, and related to Schiff's bases) have been used as photometric and fluorimetric analytical reagents for the determination of metal.<sup>1-5</sup> Chelating resins are frequently used in analytical chemistry for pre

concentration of metal ions and their separation from interfering constituents prior to their determination by an instrumental method.<sup>6-10</sup> Fe(III) is widely distributed in foods, plant tissue and animal organ. For this reason, several methods have been developed for the determination of iron including the use of hydrazones.<sup>11-13</sup>

In the previous work,<sup>14</sup> the author synthesized 2-hydroxybenzaldehyde-5-nitropyridylhydrazone (2HB-5NPH), and showed it showed a sensitive spectropho-

tometric reagent for Co(II). This paper describes the spectrophotometric determination of Fe(III) by 2HB-5NPH with separation of Fe(III) using Amberlite XAD-7 nonionic chelating resin. The present paper gives the adsorption capacities for Fe(III) and some metal ions between XAD-7 nonionic chelating resin and buffer solution and applies the results to quantitative separation of metal ions. It is a highly sensitive and simple method for separation and spectrophotometric determination of Fe(III).

## EXPERIMENTAL

### Apparatus and Reagents

Absorption spectra and absorbances were measured with a spectrophotometer. Perkin-Elmer Model 552S, using 1 cm quartz cell. A Shimadzu AA-670 atomic absorption spectrometer was used for metal ions determination. All pH measurements were made with a NOVA-310 pH meter. The resin used in the column was Amberlite XAD-7, 20-60 mesh. The resin was washed successively with 2 M HCl, water, 1 M NaOH, water, 1 M HCl and water in order to remove organic and inorganic contaminants.

Amberlite XAD-7 nonionic chelating resin was obtained from Aldrich Co. Analytical-reagent grade chemicals and distilled, deionized water were used throughout. An iron(III) stock solution (100 mg/L) was prepared by dissolving appropriate amounts of analytical grade  $\text{FeCl}_3$  in doubly distilled water and standardized with EDTA.<sup>15</sup> Working solutions were prepared by suitable dilutions of the stock solution with water. The following buffers were used to control the pH of the solutions: hydrochloric acid-glycine (pH 1-3), sodium acetate-acetic acid (pH 3-6), ammonium acetate-ammonia (pH 7-8).

### Procedure

The synthesis of 2-Hydroxybenzaldehyde-5-nitro-pyridylhydrazone has been described previously.<sup>11</sup>

### Spectrophotometric determination

Transfer an appropriate amount of sample solution or standard Fe(III) solution a 50 mL volumetric flask. Add 10 mL of the  $1 \times 10^{-3}$  M 2HB-5NPH methanol solution, and 3.0 mL of hexamethylenetetramine buffer solution (pH 6.5), then adjust the volume to 50 mL with methanol. The absorbance of the solution was measured at

300–600 nm against a reagent blank as a reference.

### Separation

**Batch procedure.** Resin (1.0 g) and 50 mL solution of Fe(III), Zn(II), Co(II), Cu(II) and Ni(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 concentrations of metal ions were determined by AAS.

**Column procedure.** Glass column (25×150 mm) having a stopcock was packed with 10 g of the resin. 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  $1.0 \pm 0.2$  mL  $\text{min}^{-1}$ . Cu(II), Ni(II), Zn(II) and Co(II) was eluted with pH 5.0 buffer solution and Fe(III) with 0.25 M HCl. 0.25M HCl fractions were collected and were analyzed for Fe(III) ion concentration by spectrophotometry.

## Result and Discussion

### Absorption spectra of Fe(III)-2HB-5NPH complex

The reaction of 2HB-5NPH with Fe(III) was investigated as a function of pH. The absorption spectra of the binary and the reagent blanks are shown in Fig. 1. The absorption spectra of the Fe(III)-2HB-5NPH complex is a symmetric curve with maximum absorbance at 470–475 nm and that of the reagent blank is at 375–385 nm. In all instances measurements were made at 472 nm against a reagent blank. The molar ratio of 2HB-5NPH

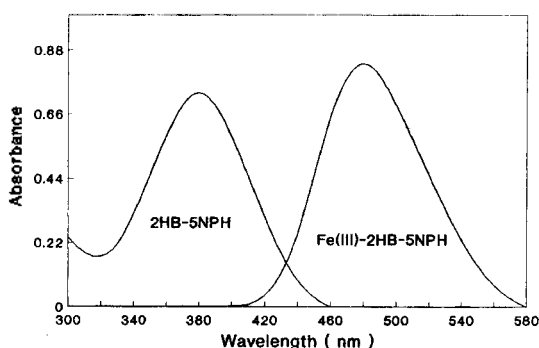


Fig. 1. Absorption spectra of 2HB-5NPH and Fe(III)-2HB-5NPH. Fe(III): 1.0 mg/L, 2HB-5NPH:  $2.0 \times 10^{-3}$  M, pH 7.0

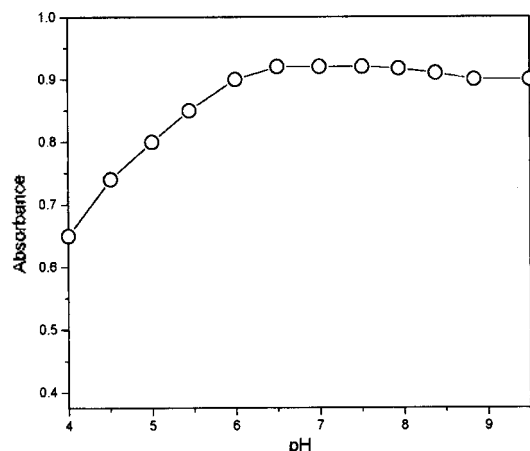


Fig. 2. Effect of pH on Fe(III)-2HB-5NPH complex. Fe(III): 1.0 mg/L, 2HB-5NPH:  $2.0 \times 10^{-4}$  M.

to Fe(III) in the complex formed at pH 7.0 has been found to be 1:2 by continuous-variation method, the absorbance being monitored at 472 nm.

#### Influence of experimental variables

The influence of the pH on the absorbance of the Fe(III)-2HB-5NPH complex is shown in Fig. 2. A maximum and constant absorbance were obtained over the pH range 6.5~7.3. Hence all the solution of pH were carried out at  $\text{pH } 6.8 \pm 0.2$ .

The influence of the amount of 2HB-5NPH on the absorbance of solution containing 1.0 ppm of Fe(III) was studied under the conditions established above. The absorbance increased with increase in the amount of 2HB-5NPH up to 5 mL ( $1.0 \times 10^{-4}$  M), remained constant from  $1.0 \times 10^{-4}$  M to  $2.5 \times 10^{-4}$  M and decreased slowly thereafter. Thus,  $2.0 \times 10^{-4}$  M was selected to ensure a sufficient excess of the reagent throughout the experimental work. The Fe(III)-2HB-5NPH complex was found to be stable for 3hr.

#### Beer's law and sensitivity

The calibration graph was constructed according to the usual procedure (see Spectrophotometric determination). The Fe(III)-2HB-5NPH complex complied with Beer's law, the calibration graph being linear over the range  $0.05\text{--}2.0 \mu\text{g mL}^{-1}$  Fe(III) methanol solution. The molar absorptivity of the system was found to be  $5.5 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$ . The detection limit ( $s/n=2$ ) was found to be  $0.01 \mu\text{g/mL}$ . The relative standard deviation for  $1.0 \mu\text{g/mL}$  of Fe(III) was 2.0% ( $n=5$ ).

Table 1. Effects of interfering ions on determination of  $1 \mu\text{g/mL}$  of Fe(III)

Foreign ion	Tolerance( $\mu\text{g/mL}$ )
Ni(II)	0.5
Cr(III)	10
Mo(II)	5
Cu(II)	0.5
Al(III)	25
Zn(II)	1
Mg(II)	100
Zr(IV)	50
Pt(II)	10
Pb(II)	5
U(II)	5
La(III)	10
Sc(III)	10
Sm(III)	15
Ge(IV)	5
Co(II)	0.1

#### Effect of foreign ion

The selectivity in the proposed method was investigated by determining  $1.0 \mu\text{g/mL}$  of Fe(III) in the presence of various ions. Interference was regarded as significant when it produced the difference of more than  $\pm 3\%$  in absorbance from that found with Fe(III) ion alone. The results are given in Table 1.

The results indicated that the concentration range of  $1.0\text{--}0.1 \mu\text{g/mL}$  for Co(II), Ni(II), Cu(II) and Zn(II) are upper limits for interference. Therefore, it can be understood that the separation of Fe(III) from the matrix is necessary prior to spectrophotometric determination. For this purpose, a column separation method was investigated.

#### Separation of metal ions

In order to determine the optimum conditions of the sorption of metal ions by the loaded resin, the optimum pH ranges were investigated by the batch method. A sample solution (50 mL) containing 1mg metal ions was adjusted at optimum pH of sorption with buffer solution and shaken with 1 g of resin for 24 hr. After equilibrium, the solution was filtered and the concentration of metal ions was determined by AAS. The sorption capacity to pH (Amberlite XAD-7 resin) profiles for Co(II), Zn(II), Ni(II), Cu(II) and Fe(III) are given in Fig. 3. Fig. 3 shows that adsorption depends apparently on the pH of the solution due to the competing protonation and com-

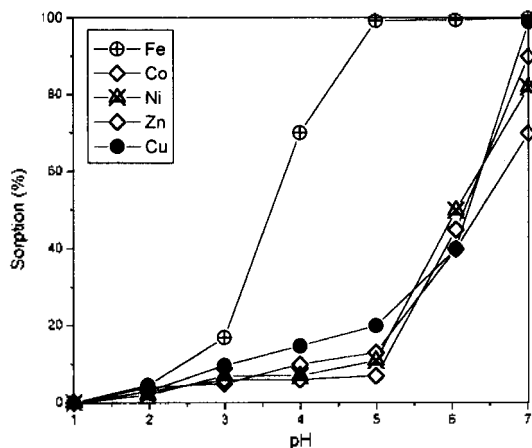


Fig. 3. Sorption capacities of metal ions on Amberlite XAD-7 nonionic chelating resin according to pH change. Metal solution: 2.5 mg/50 mL, Resin taken: 1 g, Shaking time: 24 hr.

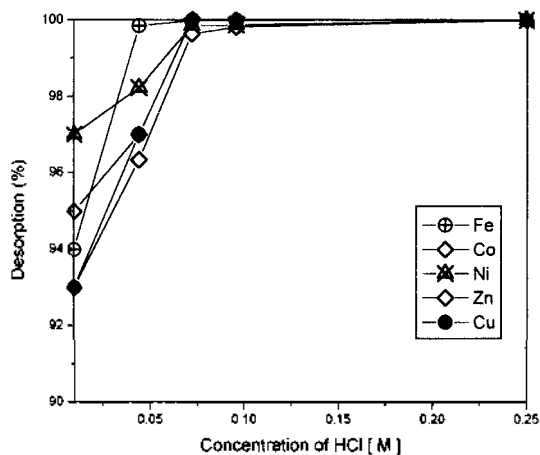


Fig. 4. Sorption capacities of metal ions on Amberlite XAD-7 Nonionic chelating resin according to HCl concentration. Metal solution: 2.5 mg/50 mL. Resin taken: 1 g, Shaking time: 24 hr.

plexation reactions of the functional group of resin. The complete sorption for the metal ions is in the region of pH 4.8-5.2 for Fe(II), 7.0-8.5 for Cu(II), Zn(II), Ni(II) and Co(II). For the quantitative separation of Fe(III) ion from Zn(II) Co(II), Ni(II) and Cu(II) ions, the optimum pH is 5.0. From the results, It was found that the separation of Fe(III) from the other metal ions was possible by varying only the pH of the solution.

The distribution coefficient of the resin toward metal ions were found to depend on the HCl concentration (Fig. 4). The sorption capacity of metal ions decreased

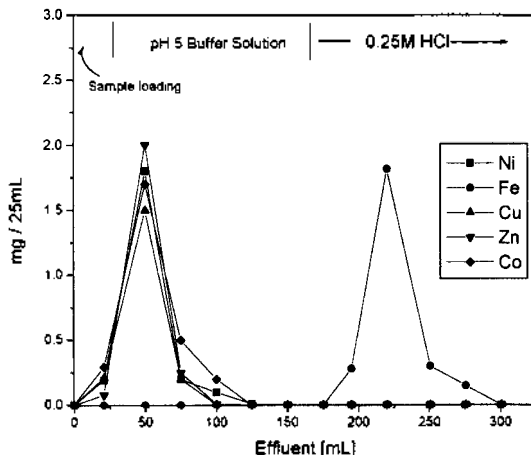


Fig. 5. Elution curves of Cu(II), Co(II), Zn(II), Ni(II) and Fe(III). Loading: 2.5 mg of Cu(II), Co(II), Zn(II), Ni(II), Fe(III) in 25 mL, pH 5.0. Elution: buffer solution (pH 5.0) and 0.5 M HCl solution.

gradually with increasing the HCl concentration from 0.01 to 0.25 M.

From the results presented in Fig. 3 and Fig. 4, pH 5.0 buffer solution and 0.25 M HCl solution have been considered as an eluent for the separation of Fe(III) from the synthetic metal solution. The column was equilibrated with acetic acid buffer of pH 5.0, 25 mL solution containing 2.5 mg of each metal ion was loaded onto the column (Fig. 5). Co(II), Ni(II), Zn(II) and Cu(II) were eluted with 150 mL of pH 5.0 buffer solution after loading with 25 mL of sample solution. Then 100 mL of 0.25 M HCl was used to elute Fe(III). The effluent of 100 mL of 0.25 M HCl was used directly for the spectrophotometric determination of Fe(III) as the 2HB-5NPH complex at 473 nm and Co(II), Ni(II), Zn(II) and Cu(II) concentration were analysed by atomic absorption spectrophotometry.

## CONCLUSION

The spectrophotometric determination method of Fe(III) has been investigated after separation of Fe(III) from the mixed ions using Amberlite XAD-7 resin. The Fe(III)-2HB-5NPH complex has an absorption maximum at 473 nm and obeys the Beer's law in the range of 0.05-2.0  $\mu\text{g/mL}$ . Molar absorptivity is  $5.5 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$ . The Amberlite XAD-7 column provides a simple,

fairly rapid and reliable technique for the separation and determination of Fe(III) from synthetic metal solution.

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