

# การแยกโลหะบางชนิดด้วยเครื่องไอออนโครมาโทกราฟี

## Separation of Some Metals by Ion Chromatography

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### บทคัดย่อ

ศึกษาความเป็นไปได้ในการแยกทองแดง แคดเมียม โคบอลต์ สังกะสี และนิกเกิล ด้วยไอออนโครมาโทกราฟีโดยใช้ 8-ไฮดรอกซีควิโนลีน-5-ซัลโฟนิกแอซิด เป็นสารโพสต์คอลัมน์และอาศัยการแลกเปลี่ยนแบบประจุบวก สารประกอบที่เกิดขึ้นละลายน้ำได้และตรวจวัดการดูดกลืนคลื่นแสงที่ 370 นาโนเมตร พบว่าสามารถตรวจวัดสารได้ในช่วงความเข้มข้นระดับนาโนกรัม โดยมีค่าความสามารถตรวจวัดต่ำสุดระหว่าง 0.005-0.050 นาโนกรัมของโลหะ และให้ผลการตรวจวิเคราะห์ซ้ำดีโดยมีค่าการเบี่ยงเบนมาตรฐานสัมพัทธ์ร้อยละ 2.2-4.2

### Abstract

The possibility of separation of copper(II), cadmium(II), cobalt(II), zinc(II) and nickel(II) by ion chromatography using 8-hydroxyquinoline-5-sulfonic acid as a post column reagent and cation exchange separation has been studied. The water soluble complexes were formed and their UV detection was made at 370 nm. The calibration curve was linear for the concentration range in nanogram levels, the detection limit of the metal ranged 0.005-0.050 ng and showed good reproducibility with the relative standard deviation of 2.2-4.2%.

คำสำคัญ : โลหะ ; ไอออนโครมาโทกราฟี

Keywords : Metal ; Ion chromatography

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## Introduction

Modern ion chromatography(IC) was introduced by Small et al in 1975 [Small; Steam and Bauman, 1975] and as originally conceived was used for anion determination with suppressor and without suppressor. Post column derivatization is now the most commonly applied detection mode for the determination of trace amounts of transition metals by non suppressed cation chromatography [Timerbaev and Bonn, 1993]. Complexing agent used as post column reagent such as: Alizaline Red S, arsenazo(III), chlorophosphonazo(III) quinalizarin, 4-(2-pyridylazo)-resorcinol (PAR), 4-(2-thiazolylazo)resorcinol (TAR) and xylenol orange. PAR is the most common reagent for many metals that have been reported [Roston, 1984]. Eriochrom Black-T [Jones; Barron and Ebdon, 1985] and the mixture of PAR and zinc diethylaminetetraacetic acid [Jones, Challenger and Hill, 1992] have also been used as post column reagent for spectrophotometric detection. A post column system was developed using the water soluble reagent 8-hydroxyquinoline-5-sulfonic acid (8-HQS) [Jone; Barron and Ebdon, 1985].

8-hydroxyquinoline-5-sulfonic acid reacts with most metal ions to form water soluble complexes and has been widely used for the spectrophotometric and the fluorometric determination of trace metals. An investigation of metal-8HQS complexes on the fluorescence properties employing 8-HQS as a post column reagent with cation exchange separation of metals has been reported [Soraka; et. al. 1987]. The investigation of metal-8HQS based on spectrophotometric properties on the reversed phase HPLC first reported in 1989 [Shijo, Saitoh and Suzuki, 1989]. In this paper the possibility for analysis of some metals with 8-HQS as a post column reagent with cation exchange column and subsequent spectrophotometric detection is described.

## Methodology

### Chemicals

Lithium hydroxide, oxalic acid and ammonium acetate (Fluka, A.G., Switzerland), 8-hydroxyquinoline-5-sulfonic acid (Aldrich, U.S.A.) were of analytical reagent grade.

Standard 1000 ng/ $\mu$ l of metal solutions were prepared by dissolving copper(II) nitrate, cadmium(II) sulfate, cobalt(II) nitrate, zinc(II) sulfate and nickel(II) nitrate in water. Working standards were made by diluting the stock solution with water. The prepared water was deionized distilled water.

### Instrumental

A Dionex DX 300 Ion chromatograph (Dionex Co., U.S.A.) consisting of injection valve with a 25  $\mu$ l sample loop (Rheodyne, U.S.A.), IonPac CS5 separating column, CG5 guard column, post column IonPac membrane reactor, and ultraviolet-visible detector (Dionex Co., U.S.A.) was used.

### Procedure

A solution of Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) with the concentration range 0-100 ng/ $\mu$ l was injected directly onto the cation exchange column with 50 mM oxalic acid eluent that has been adjusted to the desired pH by using 1 M lithium hydroxide. 8-HQS as a post column reagent diffused under helium gas pressure into the column effluent through a permeable fiber membrane. The detector was set to an appropriate wavelength at 370 nm.

## Results and conclusion

The relationship between pH of eluent and retention time and peak area are illustrated in Fig.1 and Fig.2, respectively. The results showed the appropriated pH of eluent was 5.0 giving low retention time and high sensitivity. The relationship between pH of the post column

reagent and peak area is shown in Fig.3, the optimized pH of post column reagent was 7.0. The optimized conditions are summarized in Table1.

It was found that the linearity range of Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) were 0.2-40, 0.4-40, 0.4-200, 0.4-200 and 0.4-40 ng/ $\mu$ l, respectively, with the correlation coefficient in the range of 0.996-0.999. The chromatogram obtained with the optimized condition is shown in Fig.4. The calibration data and detection limits for metal ions are presented in Table 2. The detection limits of Cu(II), Cd(II), Co(II), Zn(II) and Ni(II) were 0.005, 0.010, 0.008, 0.050 and 0.007 ng, respectively, which defined by using the values corresponding to twice the background noise. The reproducibility obtained for five injections are presented in Table 3. The percentage of relative standard deviation (%RSD) for each metal ranges from 2.2-4.20.

The application of ion chromatography in trace metal analysis offers new possibilities for the separation and determination at nanogram levels by using 8-HQS as post column reagent for spectrophotometric detection. There are also several advantages in common such as large linear range, rapidity and ability to detect simultaneously.

## References

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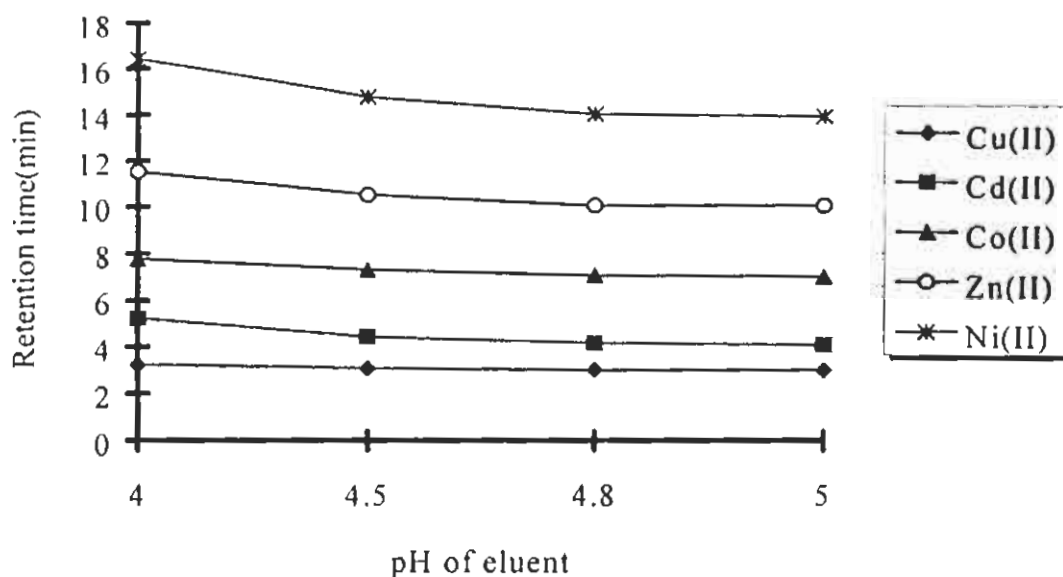


Fig. 1 Effect of the pH of eluent on retention time obtained with IonPac CS5 column, 50 mM oxalic acid as eluent, 50 mM 8-HQS as post column reagent, at 370 nm, Cu(II) 2 ng/ $\mu$ l, Cd(II) 50 ng/ $\mu$ l, Co(II) 20 ng/ $\mu$ l, Zn(II) 50 ng/ $\mu$ l, Ni(II) 10 ng/ $\mu$ l, respectively.

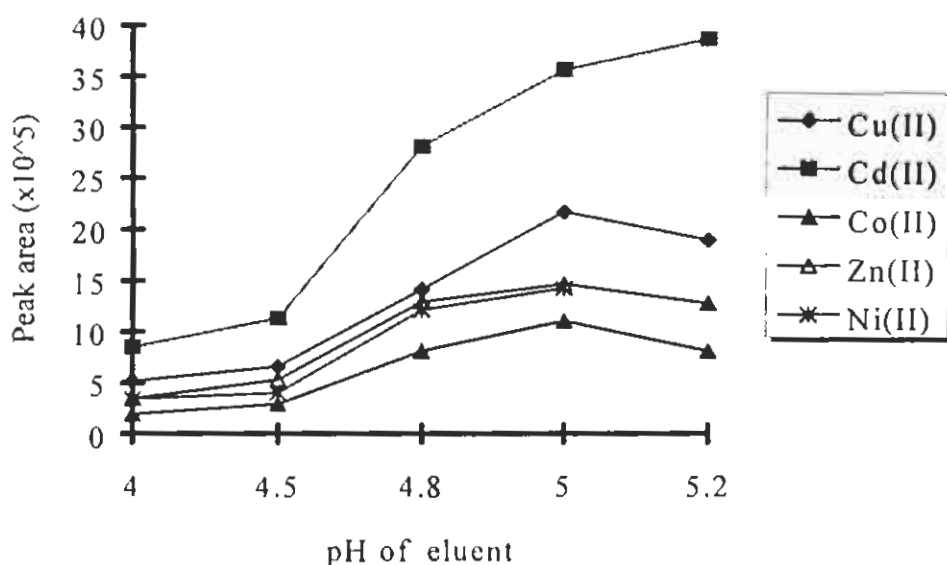


Fig. 2 Effect of the pH of eluent on peak area, obtained with IonPac CS5 column, 50 mM oxalic acid as eluent, 50 mM 8-HQS as post column reagent, at 370 nm, Cu(II) 2 ng/ $\mu$ l, Cd(II) 50 ng/ $\mu$ l, Co(II) 20 ng/ $\mu$ l, Zn(II) 50 ng/ $\mu$ l, Ni(II) 10 ng/ $\mu$ l, respectively.

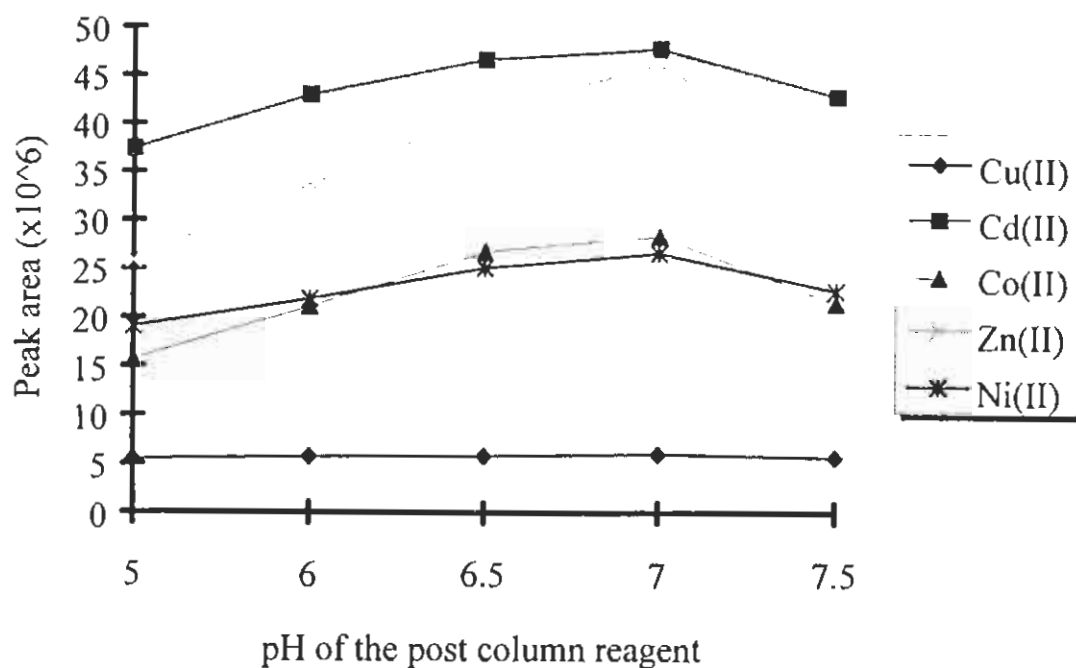


Fig. 3 Effects of pH of the post column reagent obtained with an IonPac CS5 column, 50 mM oxalic acid pH 5.0 as eluent, flow rate 1.0 cm<sup>3</sup>/min, 50 mM 8-HQS as post column reagent, at 370 nm, Cu(II) 2 ng/ $\mu$ l, Cd(II) 50 ng/ $\mu$ l, Co(II) 20 ng/ $\mu$ l, Zn 50 ng/ $\mu$ l and Ni(II) 10 ng/ $\mu$ l, respectively.

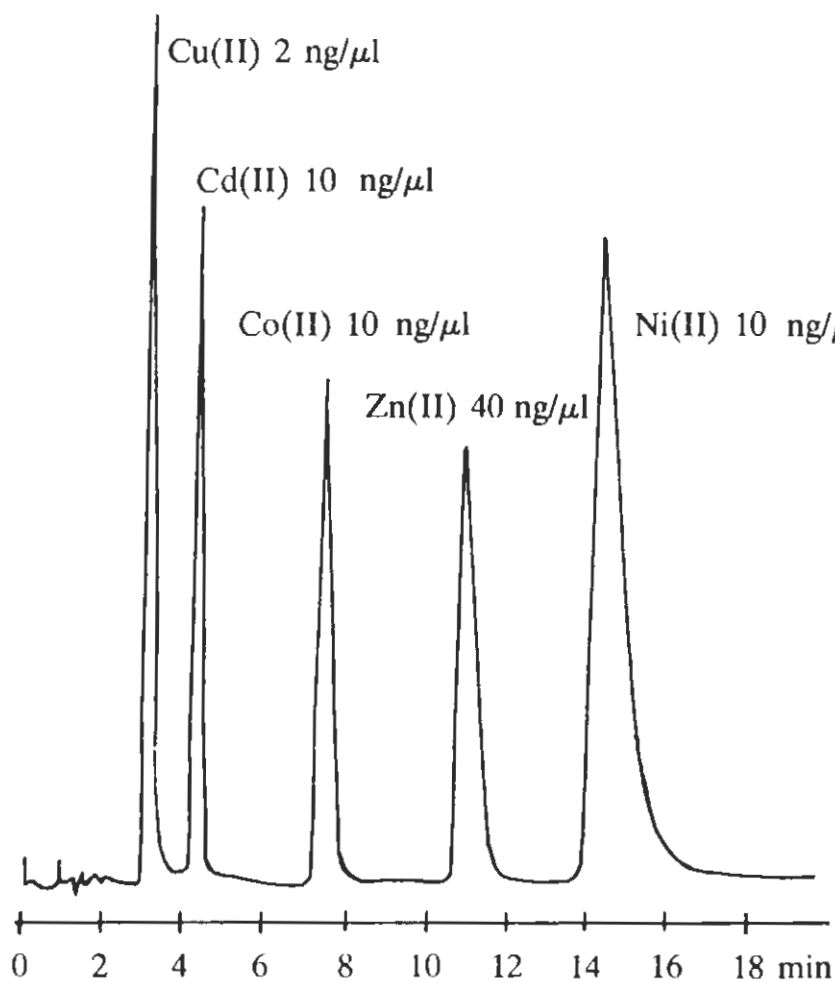


Fig. 4 Chromatogram of Cu (II), Cd(II), Co(II), Zn(II) and Ni(II) obtained with IonPac CS5 column, 50 mM oxalic acid pH 5.0 as eluent, flow rate 1.0cm<sup>3</sup>/min, 50 mM 8-HQS pH 7.0 as post column reagent, at 370 nm.

**Table 1** The optimized operating conditions

column:	IonPac CS5
Eluent:	50 mM oxalic acid pH 5.0
Flow rate (cm <sup>3</sup> /sec):	1.0
Post column reagent :	50 mM 8-HQS pH 7.0
detector wavelength:	370 nm

**Table 2** Linearity range and detection limit for metal ions analysis

metal	linearity range(ng/ $\mu$ l)	slope	correlation coefficient	detection limit(ng)
Cu(II)	0.2-40	$2.808 \times 10^6$	0.999	0.005
Cd(II)	0.4-40	$0.936 \times 10^6$	0.996	0.010
Co(II)	0.4-200	$1.235 \times 10^6$	0.999	0.008
Zn(II)	0.4-200	$0.445 \times 10^6$	0.999	0.050
Ni(II)	0.4-40	$2.575 \times 10^6$	0.999	0.007

**Table 3** Reproducibility of peak areas obtained by five repeated analysis with the optimum operating condition

	Cu(II) 4 ng/ $\mu$ l	Cd(II) 10 ng/ $\mu$ l	Co(II) 10 ng/ $\mu$ l	Zn(II) 10 ng/ $\mu$ l	Ni(II) 10 ng/ $\mu$ l
peak area ( $\times 10^6$ unit)	9.42	6.33	7.70	10.25	27.99
	9.68	6.40	6.73	10.03	27.82
	9.30	6.43	7.24	10.67	27.38
	9.82	6.91	7.34	10.72	28.33
	9.66	6.81	7.54	11.15	29.08
mean of peak area ( $\times 10^6$ unit)	9.58	6.58	7.21	10.56	28.12
SD	0.21	0.26	0.30	0.44	0.64
%RSD	2.20	4.02	4.20	4.12	2.26