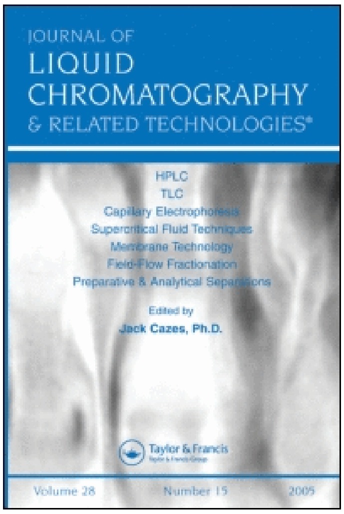

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Liu Mancang[a]; Fan Biwei[a]; Hu Zhide[a]
[a] Department of Chemistry, Lanzhou University, Gansu, China

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THE HPIEC SEPARATION OF SOME HEAVY METAL IONS IN THE SUCCINATE MEDIA

Liu Mancang, Fan Biwei and Hu Zhide
Department of Chemistry,
Lanzhou University.
Gansu, China

ABSTRACT

A flow coulometric detector was applied to a study of the separation of heavy metal ions by cation exchange chromatography using succinate as an eluent. The separation of Fe, Cd, Zn and Co was carried out within 20 minutes under suitable conditions. The IEC behavior of the ions was discussed and the following formula was obtained:

$$V_R = \frac{1}{a + b\frac{Z}{r}}$$

where V_R, $\frac{Z}{r}$ are the retention volume and ion-potential of the ion, a and b are constants. The formation constants of three ions were determined with HPIEC method. The suitable working voltage of the detector was selected from theory and reported in the experimental part. The amount of Zn, Cu and Fe in samples was determined.

INTRODUCTION

Several organic acids have been successfully used for the HPIEC separations of metal ions(1-4). However, it seems that reports on using succinate as an eluent in HPIEC have not appeared, though it was used in the classical IEC(5).

In this paper, the HPIEC separation of some heavy metal ions in succinate media is reported, the chromatographic behavior of the ions is discussed. The working condition of coulometric detector was investigated, four ions - Fe^{3+}, Cd^{2+}, Zn^{2+} and Co^{2+} were separated within 20 minutes by using a

HPIEC apparatus and a strong acid type cation-exchanger, the contents of Fe, Cu and Zn in several samples were determined.

EXPERIMENTAL

Apparatus

SY-202 type high performance ion exchange chromatograph. The set was made in the Sichuan Ninth Instrument Factory(China, Chongqing). It has a flow coulometric detector. Carbon clothes are used as material of electrods in the experiment. Its structure and principle could be seen in the reference(6). The column is a glass tube with an i.d. of 8 mm.

Reagents

YSG-SO_3Na type cation-exchange resin made in the Tianjin Second Reagent Factory(China, Tianjin). Its size is 10-15μm and 20-25μm.

Succinate eluent was prepared freshly by mixing the solutions of succinic acid and sodium hydroxide of various concentrations.

The reaction solution and opposite electrode solution for the detector was prepared according to the reference(7).

The standard solutions of the various ions. They were prepared from nitrate salts and standardized by suitable methods.

All the reagents are analytical grade.

Procedure

The resin is packed into the column by the balanced slurry packing technique. Operations follow common practice of HPLC while applying direct injection. When pre-column is used, samples are pumped through the pre-column by another plunger reciprocal pump. Then the pre-column is connected to the separation column by hand.

RESULTS AND DISCUSSION

The retention of the ions at various pH values.

The various pH values of eluent are obtained by changing the ratio between succinic acid and sodium hydroxide.The total concentration of acid and salt is 0.5 M. The logarithm values of the retention volumes (log V_R) of Fe^{3+},Cu^{2+},Pb^{2+},Cd^{2+}, Zn^{2+},Ni^{2+} and Co^{2+} at various pH values are shown in Fig.1.

As shown in Fig.1, the retention of metal ions decreases with increase of pH, because under the experimental condition with the increase of pH, not only the concentration of sodium cation used as the eluate ion but also the concentration of succinate anion used as the complexing anion increase.

So long as the retention and the peak width at half-height are measured in the short column at the given pH, the length of the column and pH for certain separation can be estimated according to following formulae:

$$X_R \propto L \qquad (1)$$

$$\Delta X \propto \sqrt{L} \qquad (2)$$

$$R = \frac{X_{R2}-X_{R1}}{\Delta X_2+\Delta X_1} \qquad (3)$$

where X_R, ΔX, L and R are retention distance,peak width at half-height, column length and resolution, respectively. It was estimated by the method mentioned above, that 40-57 mm is the necessary column length for the separation of Fe^{3+}, Cd^{2+}, Zn^{2+} and Co^{2+}. The experimental results prove that the column of length of 57 mm is just good for satisfactory separation of the ions(See Fig.2).

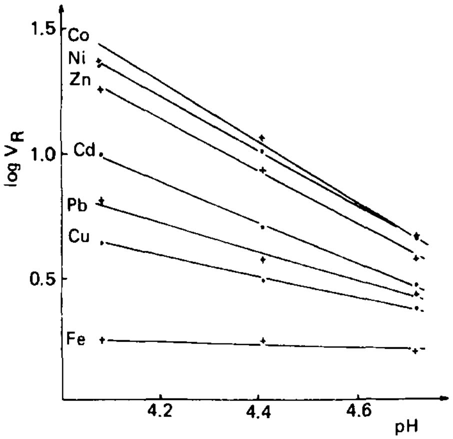

FIGURE 1 The retention at various pH

Resin: YSG-SO_3Na, 20-25 μm; Column: 8mm i. d.x20mm; Eluent: succinic acid and NaOH; Flow rate: 1.3 ml/min.

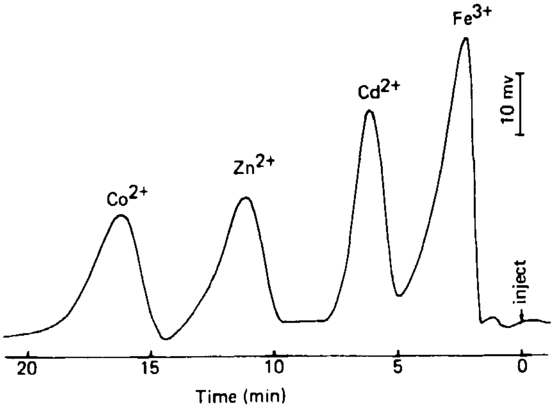

FIGURE 2 The chromatogram of Fe^{3+}, Cd^{2+}, Zn^{2+}, Co^{2+}

Resin: YSG-SO_3Na, 10-15 μm; Column: 8mm i.d.x 57mm;
Eluent: succinic acid and NaOH, pH 4.7; Flow rate:1 ml/min;
Voltage of cell: -0.45v; Amount of sample: 0.25 μgmol.

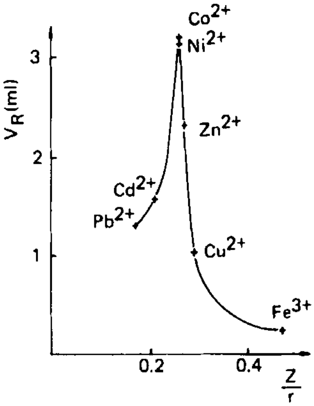

FIGURE 3 The relation between V_R and $\frac{Z}{r}$

pH 4.7; the other conditions: See Fig.1.

As shown in Fig.2, the four ions are separated within 20 minutes under the experimental conditions.

The relation between the retention volume and the ion-potential of the ions.

When complexing reagent is used as eluent, the effect of the ion-potential ($\frac{Z}{r}$) on eluation is complicate. It affects simultaneously exchanging, hydration and complexing of the ion. The relation between $\frac{Z}{r}$ and retention volume (V_R) of the ions is shown in Fig.3.

It is discovered that the curve in Fig.3 agrees with following experimental formula:

$$V_R = \frac{1}{a + b\frac{Z}{r}} \tag{4}$$

when $\frac{Z}{r} \leq 0.26$, a=1.65 , b= -0.57 ;

when $\frac{Z}{r} > 0.26$, a= -4.70 , b= 19.3 .

The determination of the formation constant of succinate complexes.

When the concentration of the eluate ion is constant, the following relations are held:

$$\alpha_M = \frac{D_2}{D_1} \tag{5}$$

$$V_R = \alpha\, Vc + (1 - \alpha)\, D\, Vc \tag{6}$$

Therefore

$$\alpha_M = \frac{V_{R2} - \alpha V_c}{V_{R1} - \alpha V_c} \tag{7}$$

where D_2 is the distribution coefficient of an ion in noncomplexing eluent, and D_1 in complexing eluent. V_{R2}, V_{R1} are the retention volume in noncomplexing and complexing eluent, respectively. α is the porosity coefficient of the column. α_M is the complexing effect coefficient of the metal ion.

However

$$\alpha_M = 1 + \beta\,[L] \tag{8}$$

where β is the formation constant, [L] is the concentration of the free complexing anion. The concentration can be calculated at a known pH by using following formula:

$$L = C\frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (9)$$

where K_1, K_2 are the first and second ionization constants of succinic acid, C is the total concentration of the anion.

It is thus clear that the formation constant can be calculated after having measured V_{R1}, V_{R2} and α. The constants of three ions were determined by the method. The results are shown in Table 1. In the experiment 0.54 M $NaNO_3$ was used as a noncomplexing eluent, 0.27 M $Na_2C_4H_4O_2$- 0.23 M $H_2C_4H_4O_2$(pH 4.7) was used as the complexing eluent.

Selection of the working voltage of the coulomb-cell.

When complexing agent is used as an eluent, the principle of the second Coulomb detection is based on following reactions:

$$MA + CuDTPA \rightarrow MDTPA + CuA \qquad (10)$$

$$CuA + 2e \rightarrow Cu\downarrow + A^{2-} \qquad (11)$$

where A^{2-} is complexing eluent anion, M is assumed to be a bivalent metal. The reactions indicate that the voltage of cell must be just enough to allow the CuA to be electrolyzed and to keep CuDTPA not to be electrolyzed. H_2A and H_5DTPA are **weak** acids, therefore their acid effect coefficients and the complexing effect coefficients (α_M) vary with changing of pH. So the reduction voltage which is decided by following formulae also changes:

$$E_1 = E^\circ - 0.059\ lg\,\alpha_{M1} \quad \text{(for the CuDTPA/Cu)} \qquad (12)$$

$$E_2 = E^\circ - 0.059\ lg\,\alpha_{M2} \quad \text{(for the CuA/Cu)} \qquad (13)$$

E_1 and E_2 were calculated at varied pH values in succinate system. The results are listed in Table 2.

TABLE 1 The values of the formation constants

Ion	V_{R1}	V_{R2}	lg β (determined)	lg β* (in literatures)
Cu^{2+}	1.13	19.0	3.21	3.3
Zn^{2+}	2.45	18.2	2.58	2.5
Cd^{2+}	1.68	17.0	2.81	2.2

* See reference (8)

From the formulae (12) and (13) it can be concluded that if voltage of the cell $Vc < E_1$, the CuDTPA is reduced, a large amount of copper precipiate on the cathode, the background current increases, if $Vc > E_2$,reduction of CuA does not occur, the electrolysis efficiency equals almost zero. The experimental results are in agreement with the conclusion mentioned above. It is shown in Fig.4. It is more noted that the reaction solution is basic, but the flow rate is slow, therefore the effect on the pH value of the system is unnotable.

As shown in Fig.4, when $Vc < -0.6$ v the background current is too large, when $Vc > -0.4$ v the electrolysis efficiency is too low, therefore we decided that Vc is -0.45 v.

TABLE 2$^{\bullet}$ The E_1 and E_2 at various pH

pH	3	4	5	6	7	8	9	10
$\lg \alpha_{M1}$	4.95	7.95	10.3	12.4	14.4	16.3	17.8	18.9
E_1	-0.52	-0.69	-0.83	-0.95	-1.07	-1.18	-1.27	-1.34
$\lg \alpha_{M2}$	0.57	1.01	2.25	2.87	3.01	3.03	3.03	3.03
E_2	-0.23	-0.28	-0.36	-0.39	-0.40	-0.40	-0.40	-0.40

$^{\bullet}$v.s. $K_3Fe(CN)_6/K_4Fe(CN)_6$

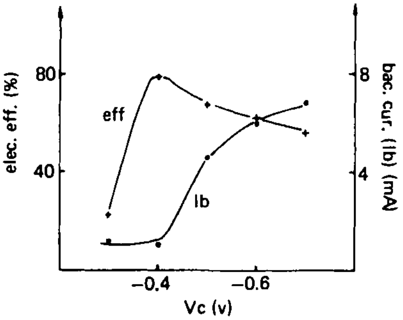

FIGURE 4 The background current and electrolysis efficiency at various voltage of cell

pH 4.1; Sample: Zn^{2+}, 1 μgmol; Other conditions: See Fig.1.

Quantitative determination of Cu, Zn, Fe in samples.

a) The calibration curves. Mixed standard solution of Fe^{3+}, Cu^{2+}, Zn^{2+} was injected into the column. Plots of the amount of Cu and Zn against the peak area were drawn. It is shown in Fig.5.

As shown in Fig.5, the linearity of the calibration curves of Cu and Zn are rather satisfactory, but Fe, because of serious tailing and poor reproducibility, only can be semiquantitatively determined.

b) Dolomite. Weight 1 g of sample, dissolve it by HNO_3. The final volume of the sample solution is 5.00 ml. 50 μl of the sample solution is injected, and peak area is then measured. Amount of Cu and Zn is found on the calibration curves.

c) The waste water. The sample is directly injected into the column without any pre-treatment. The chromatogram is shown in Fig.6.

d) The tap water. The sample is first enriched in the pre-column, then connect the pre-column to the separation column. The sample enriched in the pre-column is then pumped into the separation column. The chromatogram is shown in Fig.7. In the figure the undulations marked by W1, W2, W3 are caused by the operations of transferring and connecting of the pre-column. They are not peaks of the determined substances at all.

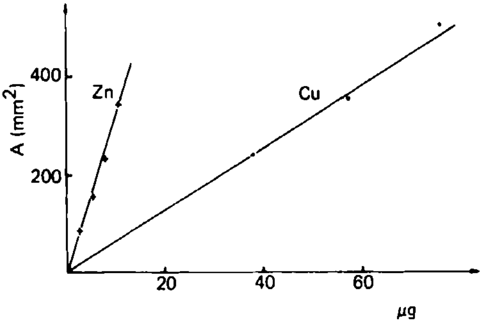

FIGURE 5 The calibration curve of Cu and Zn

Sensitivity of recorder: 250mm/0.1v(for Zn), 250mm/0.5v (for Cu); Speed of paper: 5mm/min; the others: See Fig.2.

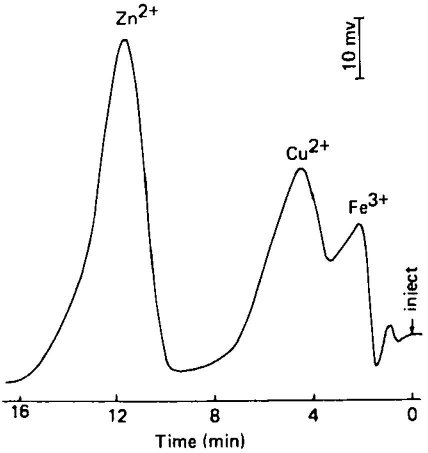

FIGURE 6 The chromatogram of waste water

Size of sample: 45 1; the others: See Fig.2.

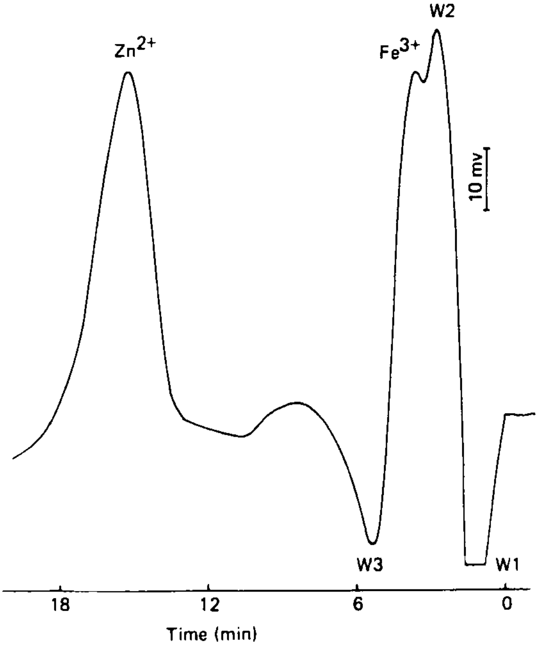

FIGURE 7 Fe^{3+} and Zn^{2+} in tap water

Size of sample: 120 ml; Pre-column: 8mm i.d.x 20mm; Other conditions: See Fig.2.

The results of the determinations are listed in Table 3.

TABLE 3 The results of the determinations

Sample	Size of sample	Element	Known results	Results of determinations		
				Mean	Deviation	Recovery
Dolomite (standard sample)	50 l	Cu	0.48%	0.47%	0.03%	
		Zn	0.064%	0.061%	0.005%	
Waste water	40 l	Cu		0.26 mg/ml	0.026 mg/ml	105%
		Zn		0.76 mg/ml	0.10 mg/ml	109%
Tap water	120 ml	Fe		about 10 ppb		
		Zn		0.52 ppm	0.08 ppm	102%

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