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RETENTION OF IONS IN A MAGNETIC CHROMATOGRAPH USING HIGH-INTENSITY AND HIGH-GRADIENT MAGNETIC FIELDS

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ABSTRACT

The control of the retention and separability of samples to be analyzed with high performance liquid chromatography systems is difficult, and usually requires exchanging of the mobile phase and/or the column. We developed a magnetic chromatography (MC) system, which does not require regular exchanging of the mobile phase and/or the column, and uses a continuous-flow system to separate multiple ionic species with different magnetic properties.

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To demonstrate experimentally the feasibility of such an MC system, we measured the retention of ions in the MC system for aqueous solutions of either pure NaI, $CuSO_4$, $NiCl_2$, $CrCl_3$, or $CoCl_2$. We applied magnetic fields varying from 0 to 3 T to the aqueous solution of transition element cations and anions flowing in an MC system, and demonstrated that the retention time was delayed by about 20 min, and that for Co(II) the chromatogram broadened with increase in the applied magnetic field intensity (H). Furthermore, our results suggest that for ionized transition elements with a larger Bohr magneton number, the retention time in MC systems becomes longer.

We derived experimentally a retention factor, k, that can be simply expressed in terms of an MC parameter, p_{MCH}, which is the product of the Bohr magneton number, the concentration of the cations, and H. The MC parameter can be used to correlate all experimental data in terms of k, as $k = 0.0014p_{MCH}^{1.47}$. Hence, k is proportional to about 3/2 power of the MC parameter. We therefore confirmed that there is a significant effect of high-intensity, high-gradient magnetic fields on the behavior of paramagnetic cations in water.

Key Words: Magnetic chromatography; High-intensity and high-gradient magnetic field; Superconducting magnet; Ion retention factor; MC parameter

INTRODUCTION

To simplify chromatographic processes, for example, to control retention and separability of a sample without exchanging the mobile phase and/or the column, efforts are being made to remotely control the stationary phase characteristics of high performance liquid chromatography (HPLC). Systems have been developed where outside thermal,[1] electric,[2] centrifugal, and light field intensities[3] were varied. Remote control of the stationary phase is a simple method for regulating the retention and/or separation factors without replacing multiple conventional mobile phases and/or columns used in HPLC systems.

We proposed a magnetic chromatography (MC) system controlled with a magnetic field,[4,5] and also developed a numerical model[6–8] (referred to as the MC simulator) to evaluate the performance of this MC system. But to date no experimental verification of such proposed MC systems has been made. Therefore, in this work we made experimental measurements to demonstrate the feasibility of using MC systems, and clarified the basic characteristics of MC retention using aqueous solution of transition element cation.

Figure 1 shows a conceptual model about our MC systems. MC systems use 30 μm thin ferromagnetic wires in a high-intensity magnetic field to create high-intensity magnetic field gradients. These magnetic field gradients create forces between the wires and the suspended ions. The magnetic force increases with increase in ion magnetism, and decrease in distance between the ions and the wires. For ions of varying magnetism, the magnetic force creates an ion concentration distribution near the wires. The fluid containing the ions flows parallel to the wires, and because the wires are either embedded in or attached to the walls of the flow channel, where the fluid velocities are low, MC systems are therefore designed so that the fluid velocity is low near the wires. This causes the ions, which are attracted to the wires, to move through the system slower than ions attracted less strongly to the wires. This creates an ion velocity gradient between ions with high magnetism (those drawn near the wires) and ions with low magnetism (those remaining farther from the wires), causing the particles with low magnetism to separate from the ions with high magnetism, and exit the MC system first, as shown in Fig. 1.

We used the MC simulator to design a prototype MC column[8] that uses a dipole superconducting magnet to create high-intensity magnetic fields. We evaluated to what extent the magnetized ions can be held in the MC column. This behavior is called retention, and the retention factor is defined as the flow ratio of

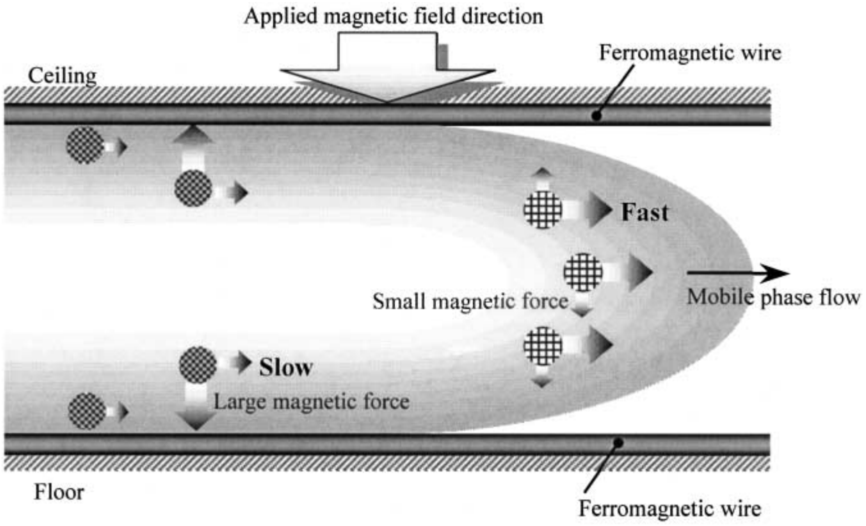

Figure 1. A conceptual model of an MC system.

mobile phase to the magnetized ions in water. We measured this factor experimentally by changing the intensity of the magnetic field applied to the MC column from 0 to 3.0 T.

Compared with conventional HPLC systems, MC systems allow easy control of retention and separation characteristics by simply adjusting the applied magnetic field intensity (H) from outside of the MC column. Furthermore, magnetic forces serve the same function as that of the stationary phase of HPLC systems, so that MC systems do not need packed filter beds for the chromatographic adsorption materials, for example, silica gel. Consequently, MC systems do not produce secondary waste associated with periodic disposal of the packed filter beds, and therefore MC is promising in the analysis of either dangerous or precious substances.

THE PURPOSE OF THIS EXPERIMENT

The degree to which weak magnetic forces in MC systems can be used to separate and analyze ions in water has long been a point of controversy among researchers and engineers.[9–13] The purpose of this study was to verify experimentally the feasibility of achieving an MC device in which magnetic forces play a dominant role to retain ions, while adsorption not caused by any magnetic force has been utilized in the conventional HPLC.

EXPERIMENTAL SETUP AND PROCEDURE

Figure 2 shows the cross section of an MC column. Weakly magnetized SUS-316 was used for the channel, in which a mobile phase flowed normal to the plane of the paper. A relatively high magnetic field of about 3 T was imposed onto ferromagnetic wires made of Co(7%)–Ni(93%) alloy plated on both the channel ceiling and floor, creating high-magnetic field gradients. The column length, width, and thickness were 700, 50, and 10 mm, respectively. The channel length, width, and thickness were 450 mm, 27 mm, and 190 μm, respectively. The magnetic wire length, width, and thickness were 450 mm, 150 mm, and 30 μm, respectively. A total of 33 ferromagnetic wires were plated on both the channel ceiling and floor, and the width between wires was 150 μm. Figure 3 shows the experimental MC system. The magnet was a dipole superconducting magnet, with a room-temperature bore of 62.5 mm in diameter and 2 m long. The maximum vertical magnetic field strength was 3.5 T. The deviation of H along a length of 450 mm in the center the axis of the magnet was less than 1% in the bore, which had a length of 450 mm in the center, where the MC column was placed.

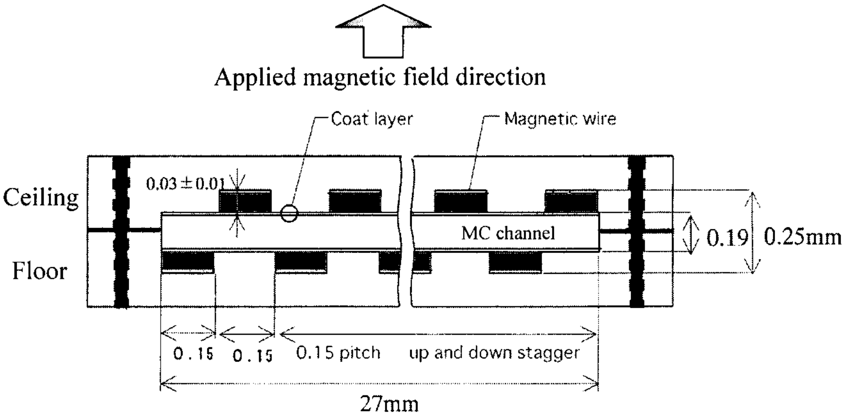

Figure 2. Cross-section of the MC column with flow perpendicular to the plane of the sheet.

The experimental conditions were as follows. The mobile phase was ion-exchanged water, the flow rate was 0.3 mL/min, and the injected volume of the sample solution into the MC column was 20 μL. Five different aqueous solutions of transition element were used: NaI, $CuSO_4$, $NiCl_2$, $CrCl_3$, and $CoCl_2$, at concentrations of 2.0, 1.3, 2.1, 3.1, and 3.8 mol/L, respectively. The potential of hydrogen (pH) of $CuSO_4$, $NiCl_2$, $CrCl_3$, and $CoCl_2$ aqueous solutions was 2.4,

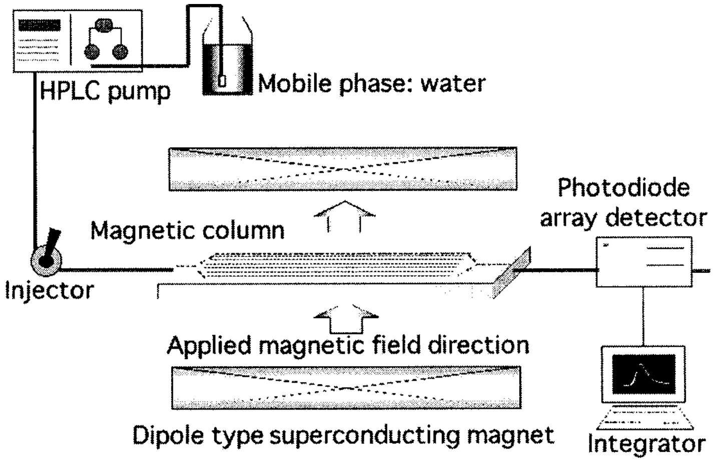

Figure 3. An MC system with a large dipole superconducting magnet.

2.7, 0.6, and 3.6, respectively. To determine time-dependent ion concentrations at the outlet of the MC column for these five ion solutions, we used a photodiode array detector operated at wavelengths of 210, 800, 398, 432, and 516 nm, respectively. For these experimental conditions, we used $0 < H < 3.0\,\mathrm{T}$, and we measured the light absorption vs. elapsed time when the solution flowed out from the MC column outlet.

We defined a retention factor, k, as the difference between retention times without magnetic fields as

$$k = (t_{\mathrm{RT}} - t_{0\mathrm{T}})/t_{0\mathrm{T}} \tag{1}$$

where $t_{0\mathrm{T}}$ and t_{RT} are the time of the maximum peak height for $H = 0$ and for $H > 0\,\mathrm{T}$, respectively.

Because the magnetic force on ions may depend on the effective magnetic moment, on the concentration of the cations or anions in each sample solution, C (mol/L), and on H, we define a parameter called the "MC parameter," p_{MCH} as

$$p_{MCH} = M_{\mathrm{B}}CH\,(\mathrm{mol\,T/L}) \tag{2}$$

where M_{B} is the effective magnetic moment of the ionized element given in units of Bohr magnetons.[14]

RESULTS AND DISCUSSION

Effect of Applied Magnetic Field on Chromatogram

Figure 4 shows the measured chromatogram for Co(II) as a function of H. Figure 4 indicates that the retention time was delayed a maximum of 20 min, and that the chromatogram became broad when Co(II) was injected into the MC column under an applied field of 3 T. With increasing H from 0 to 3 T, although the time delay for the initial detection of Co(II) was the same, and independent of H, the time delay to the maximum Co(II) light absorbance increased and the peak height decreased. Assuming that no ions and particles were trapped in the MC column, the cross-section enclosed each curve and the base line in Fig. 4 must be the same, because this area corresponds to the sample volume injected into the MC system. As the maximum Co(II) absorbance decreases with increase in H, the corresponding width of the Co(II) peak broadens with time. This broadening indicates that increased H caused increased retention time in the MC column.

Figure 5 shows the relationship between H and k calculated by using Eq. (1) and t_{RT} determined as the time to reach the maximum of the peaks shown in Fig. 4. This experimental result clearly shows that the retention factor, k, depends on the applied magnetic field, H, i.e., application of a high magnetic field causes a strong

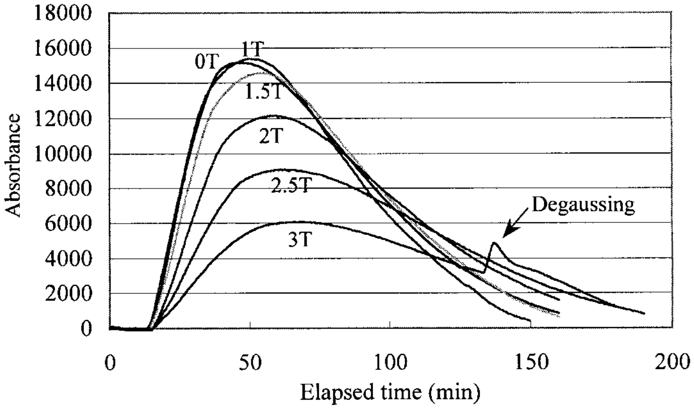

Figure 4. Magnetic chromatogram obtained in experiment for a 3.8 mol/L Co(II).

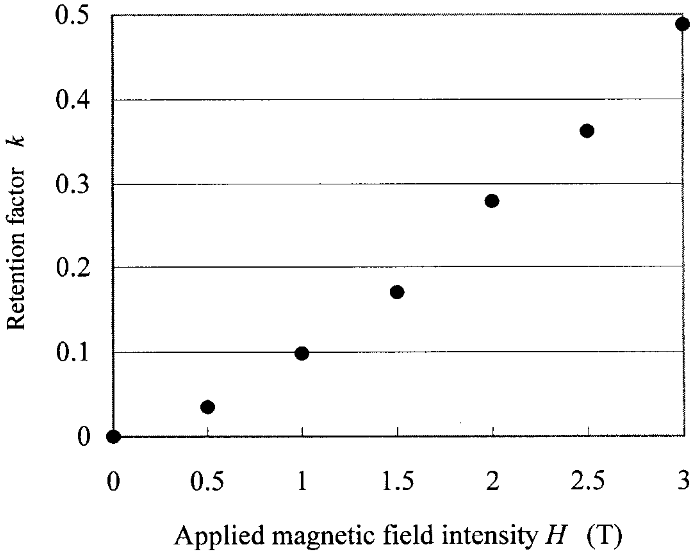

Figure 5. Relationship between retention factor k and magnetic field intensity for Co(II).

magnetic adsorption force between the ions and the wires, and thus the retention time becomes longer.

Retention Factor and Bohr Magneton Number

Figure 6 shows k vs. effective magnetic moment of cations and anions in units of Bohr magnetons for the five ions used in our experiments. Although the concentrations of each element ranged from 1.3 to 3.8 mol/L, and $H = 2.5\,\mathrm{T}$, except for Cu(II) ($H = 3.0\,\mathrm{T}$), the data shown in Fig. 6 indicates that k increases with increase in Bohr magneton number.

Our measurements also show that $k = 0$ for I^-, which has a very weak diamagnetic moment, and this agreement with the simulations confirms that our absorbance measurement system was not influenced by any magnetic-field leakage, and is therefore suitable for these types of measurements.

For our experimental conditions, if pH of these solutions were acidic (pH $0.6 \sim 3.6$), no precipitates were formed, indicating that retention resulted from the influence of the magnetic field on the ion motion.

Figure 7 shows the relationship between the measured values of k and the calculated values of p_{MCH} for the experimental conditions used in this work. The dashed line shows a fitted function to the data, $k = 0.0014p_{MCH}^{1.47}$. This line indicates that the retention of the transition element cations is significantly influenced by high-intensity, high-gradient magnetic fields. Figure 7 also

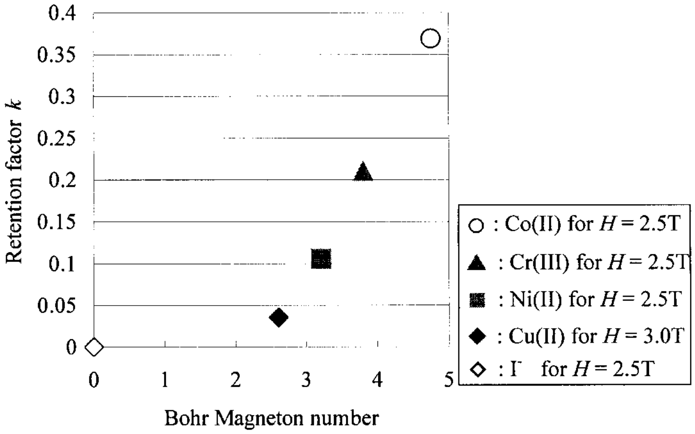

Figure 6. Retention factor k vs. effective magnetic moment of cations and anions (units of Bohr magneton).

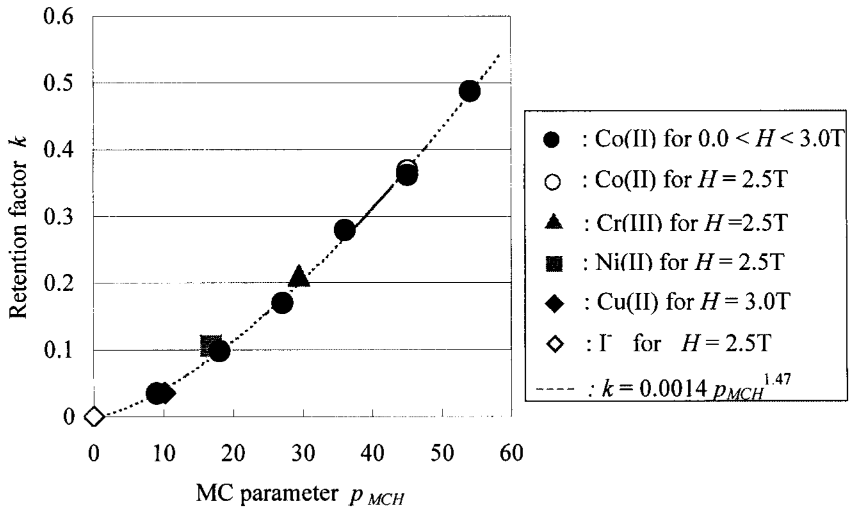

Figure 7. Relationship between measured retention factor k and the MC parameter p_{MCH}.

indicates that k can be used to correlate all of the experimental data, and that k is proportional to 1.47 (about 3/2) power of the MC parameter defined as in Eq. (2) (a product of M_B,C, and H).

Figure 7 suggests that for a given H, MC systems can be used to separate transition element cations with different magnetic properties, because for a given H, p_{MCH}, depends on the transition element cation magnetic properties, and therefore k differs for two transition element cations with different magnetic properties.

The phenomenon caused by applying a magnetic force directly onto ions has been frequently studied,[9–13] however, the experiments often produced only qualitative data, where colors and shapes of ion solutions were observed. Our method provides a quantitative assessment of the transport of ions through magnetic fields, and also confirmed the feasibility of using MC to separate a mixture of ions with different magnetic properties.

CONCLUSIONS

We confirmed that there is a significant effect of high-intensity, high-gradient magnetic fields on the behavior of transition element cations in water. For magnetic fields varying from $0 < H < 3\,\mathrm{T}$ and applied to aqueous ion solutions flowing in an MC system, and demonstrated that the retention time delayed about 20 min. For $H = 3\,\mathrm{T}$, the chromatogram broadened when Co(II) was injected into the MC column. Furthermore, our results suggest that for ionized transition elements with a larger Bohr magneton number, the retention time in MC systems becomes longer. We defined an MC parameter, p_{MCH}, which is the product of M_B, C, and H [see Eq. (2)], and can be used to correlate all of the experimental data in terms of the retention factor, k, as $k = 0.0014 p_{MCH}^{1.47}$, i.e., k is proportional to 1.47 (about 3/2) power of the MC parameter. This means that k depends not only on the effective magnetic moment of the elements in solution, but also on the H and on the concentration of the cations in solution.

This also indicates that MC is feasible only when the difference between p_{MCH} for each cation to be separated is sufficiently large. The determination of the required difference in p_{MCH} for separation of multiple ions is the subject of our ongoing research in this area.

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