Magnetic Chromatography of Magnetic Fine Particles Suspended in a Liquid with a Steel-Bead Column under a Periodically Intermittent Magnetic Field

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The magnetic chromatography of magnetic fine particles has been proposed using a periodically intermittent magnetic field. A separation column packed with magnetically permeable steel beads is inserted into the center hole of an electromagnetic coil. The steel beads are coated with a polytetrafluoroethylene film, and the column is vibrated at *ca.* 10 Hz in order to minimize any irreversible adsorption of the magnetic particles on the beads. Ethanol is used as a mobile phase, and the iron oxide magnetic particles in the mobile phase are continuously monitored by flame atomic absorption spectroscopy. An elution peak for magnetite particles is delayed with increasing coil current and loading ratio of the magnetic field, while that for hematite particles is not influenced by the magnetic field. The effects of various parameters on the retention time for the magnetite particles are discussed from a theoretical viewpoint.

Keywords Magnetic chromatography, magnetic particle, liquid chromatography, magnetite, hematite

Magnetic fine particles are widely used for magnetic recording media (magnetic tape, magnetic card, *etc.*), magnetic paint, magnetic fluids, an image-intensifying agent for nuclear magnetic resonance imaging and so on. Although a further development of these particles with superior magnetic property and higher quality has always been pursued by industries and various research fields, no simple and practical technique has been developed to separate and characterize a mixture of particles having different magnetic properties. Although there have been a few studies¹⁻⁴ concerning the field flow fractionation (FFF) method using a high-gradient static magnetic field to separate the magnetic species chromatographically, the separation of a mixture of particles has not been realized. This method may not be practical, because it requires a large-scale magnetic field and precise fabrication of a flat separation channel. A high-gradient magnetic separator (HGMS) or filter with magnetically permeable steel wires^{5,6} or beads^{7,8} as filter elements has been studied to remove magnetic particles from a water stream. However, all of the magnetic particles in the stream were trapped by the filter in a strong static magnetic field, and the trapped particles could not be easily detached from the filter elements when the magnetic field was released. Thus, the chromatographic separation of particles having different magnetic properties could not be realized by this method. Although an axial HGMS using a single wire has also been studied for the continuous feeding and separation of magnetic particles^{9,10}, an effective isolation of particles is

difficult, even with a strong magnetic field.

In this work, we proposed a new approach for the chromatographic separation of magnetic fine particles suspended in a liquid using a separation column packed with magnetically permeable steel beads under a periodically intermittent magnetic field. When a magnetic field is applied, the magnetic particles are trapped on the magnetized steel beads, while nonmagnetic particles pass through the column along with the liquid stream (mobile phase). When the magnetic field is released, the particles trapped on the steel beads are detached and fed back into the liquid stream. After frequent repetition of their trapping on and detaching from the steel beads under a periodically intermittent magnetic field, the magnetic particles are expected to be eluted with a delay time that depends on their magnetic properties as well as the operating conditions of the magnetic field. Weakly magnetized particles may be eluted with a shorter delay time than that of strongly magnetized ones because of incomplete trapping on the steel beads by the intermittent magnetic field.

In this experiment, we assembled a separation column by packing steel beads into a polytetrafluoroethylene (PTFE) tube, and inserted it into the center hole of an electromagnetic coil. Coating the steel beads with PTFE film and vibrating the column were effective to minimize the irreversible adsorption of magnetic particles on the beads. The elution of magnetite particles from the column was delayed depending on the magnetic field operation, while the elution of weakly

Fig. 1 Schematic diagram of the separation system by magnetic chromatography.

magnetized hematite particles was not influenced by the magnetic field. The retention time of the magnetite particles was related to the coil current and the loading ratio of the intermittent magnetic field. This work demonstrated the chromatographic elution of magnetic particles using a periodically intermittent magnetic field, although irreversible adsorption of particles on the column became inevitable under a stronger magnetic field or a larger loading ratio.

Experimental

A schematic diagram of the experimental system is shown in Fig. 1. To make a separation column, a PTFE tube (2.4 mm i.d. $\times$ 2.5 mm o.d., 100 mm long) was packed with steel beads, and a pair of tube connectors with nylon screen (50 mesh) were fitted at both ends. The column was inserted into a polyethylene tube (6 mm i.d. $\times$ 8 mm o.d.) placed in the center hole of an electromagnetic coil (5 cm outer diam. $\times$ 10 cm long, 1500 turns) which was made by winding 1-mm enameled copper wire. As a column packing material, carbon-steel beads (0.7 mm diam.) coated with PTFE film were selected. The film was coated on the beads by spraying PTFE powder suspensions (Fine Chemical Japan) and heating them in an electric furnace at 250°C for 10 min. After seven repetitions of the coating, the thickness of the coated PTFE film was estimated to be *ca.* 5–10 μ m using a scanning electron microscope (Hitachi S-9000).

The column was mechanically vibrated along the direction of the column length with a stroke of 7 mm and a frequency of *ca.* 10 Hz by connecting the column to a tunable touch mixer (300 to 3000 rpm., Iuchi Inc., Japan) through a brass rod. Direct current to the electromagnetic coil was provided by a rectifier (KR-N103, Kanetec Co. Ltd., Japan) controlled with a 16-bit personal computer (NEC PC9801-UX). The polar of the direct current was alternatively switched, as shown in a typical

current profile illustrated in Fig. 1, although the polar switching did not improve the chromatogram compared with that without switching.

Ethanol was used as a mobile phase because of less irreversible adsorption of magnetic particles on the column than that in an aqueous system. A programmable HPLC pump (Model 576, GL Sciences Inc., Tokyo, Japan) was utilized to feed ethanol at a flow rate of 1 ml/min. The sample liquid (0.1 ml) was injected into the carrier stream through a 6-way rotary valve. The effluent from the column was fed into a pneumatic nebulizer of a flame atomic absorption spectrometer (Nippon Jarrell-Ash AA-1 Mark II), and the absorbance of iron at a wavelength of 248.3 nm was continuously measured using an acetylene–air flame. A PTFE tube (1.5 mm o.d. $\times$ 0.5 mm i.d.) was employed for tubing.

Magnetite (Fe_3O_4) particles were prepared by a homogeneous precipitation method¹¹, in which an 800 ml mixed aqueous solution containing 0.025 mol iron(II) chloride, 0.05 mol iron(III) chloride, 0.5 mol urea and 0.016 mol sodium dodecyl sulfate (SDS), was hydrolyzed by heating at 100°C for 5 h in a nitrogen-gas atmosphere. Hematite (Fe_2O_3) particles were prepared by heating a 0.018 M iron(III) chloride aqueous solution containing 0.001 M hydrochloric acid at 100°C for 24 h.¹² The mean diameters of the magnetite and hematite particles were 20 nm and 0.2 μ m, respectively, which were estimated from their electron micrographs, as shown in Fig. 2. The sample liquids, magnetite and hematite particle suspensions were finally adjusted to 10 μ g Fe/ml (in ethanol) in concentration. Since the magnetite particles prepared in this experiment tend to aggregate (Fig. 2a), they may be separated in the column as aggregates, but not as individually dispersed particles.

Theoretical

Based on the principle of liquid chromatography, the

Fig. 2 Electron micrographs of (a) magnetite and (b) hematite particles.

retention time of the analyte (t_R) is related to the capacity factor (k') and the partition coefficient (K) of the analyte as follows:¹³

$$\begin{aligned} K &= c_s/c_m, \\ t_R &= t_0(1 + k') \\ &= t_0(1 + K(V_s/V_m)), \end{aligned} \quad (1)$$

where c_s and c_m are the molar concentrations of the analyte in the stationary and the mobile phases, respectively, t_0 is the time required for an average molecule of the mobile phase to pass through the column, and V_s and V_m are the stationary and mobile phase volumes, respectively.

As for the magnetic chromatography in our system, frequent repetition of trapping and detaching of magnetic particles on the steel beads under an intermittent magnetic field may result in a constant distribution of the analyte particles between the mobile phase (ethanol) and the stationary phase (steel beads). Based on this hypothesis and analogy, the retention time (t_R) of our magnetic chromatography may be written as

$$t_R = t_0(1 + f(T_{on}/T_{off})), \quad (2)$$

where f is the partition factor, and T_{on} and T_{off} are the applied and interval times of the magnetic field, respectively. The partition factor (f) may depend

Fig. 3 Optical micrographs of (a) the carbon-steel beads and (b) the stainless-steel beads used for packing materials (without PTFE coating).

inherently on the magnetic property of the analyte particles, and may also be influenced by other factors, such as the strength of the magnetic field and the flow rate of the mobile phase. The loading ratio of the magnetic field (T_{on}/T_{off}) may also directly affect the retention time. Equation (2) is rearranged to

$$t'_R = t_R - t_0 = t_0 f(T_{on}/T_{off}), \quad (3)$$

$$t'_R/t_0 = f(T_{on}/T_{off}), \quad (4)$$

where t'_R is referred to as the adjusted retention time. From the above equation, t'_R and t'_R/t_0 are expected to be linearly related to the loading ratio of the magnetic field (T_{on}/T_{off}).

Results and Discussion

Selection of packing materials

Two types of steel beads were tested as packing materials of the separation column. Figure 3a shows spherical steel beads made of martensite carbon steel (ca. 0.7 mm diam. TSH-70), which were donated by Itoh Metal Abrasive Co. (Nagoya, Japan). They were

Fig. 4 (a) Typical magnetic chromatograms for magnetite particles with varying the coil current and (b) the relationship between the adjusted retention time (t'_R) and the coil current ($T_{on}=0.6$ s, $T_{off}=0.3$ s and flow rate=1.0 ml/min).

Table 1 Magnetic properties of carbon-steel and stainless-steel beads

	Carbon-steel bead		Stainless-steel bead	
Saturation Magnetization, M_s	188	emu/g	83.3	emu/g
Residual Magnetization, M_r	1.21	emu/g	1.91	emu/g
Coercive force, H_c	43.4	Oe	34.8	Oe
Permeability, χ	0.0422		0.0382	

originally steel shot beads to be used for descaling of castings or peening of steel plates with a shot blast machine. Figure 3b shows ellipsoidal steel beads made of SUS-430 stainless steel, which were donated by Nippon Yakin Kogyo Co., Ltd. (Tokyo, Japan). They were experimentally made as filter elements of a high-gradient magnetic filter. The magnetization curves for the two types of beads were measured with a vibrating-sample magnetometer (Toei-Kogyo VSM-5, Tokyo, Japan); their magnetic properties are listed in Table 1. The carbon-steel beads were finally chosen in this experiment because of their large magnetic permeability and small residual magnetization as well as reproducible elution behavior derived from their spherical shape. After testing three groups of beads with mean diameters of 0.4, 0.7 and 1.00 mm, the diameter of 0.7 mm was selected.

Effect of a coil current on the magnetic chromatogram for magnetite particles

Typical magnetic chromatograms in Fig. 4a show that the magnetite particles were eluted with a delay time depending on the direct current supplied to the

electromagnetic coil surrounding the separation column. Compared with conventional liquid chromatography, the elution-peak widths are quite broad because of the large dead volume in the column caused by packing large spherical beads. Figure 4b shows the relationship between the coil current and the adjusted retention time (t'_R) at the elution peak; t_0 was defined as the time at the elution peak of sample particles under no magnetic field. At a higher coil current than 1.5 A, the width of the elution peak became broader, and the peak area significantly decreased, probably due to the sticking of magnetite on the steel beads. Thus, a coil current of 1.0 A was adopted. The magnetic field strength at the center hole of the electromagnetic coil with the separation column was 65 G, which was measured with a handy Gauss-meter (F. W. BELL Model 4048, USA).

Although hematite particles may be weakly magnetized, their elution peak was not delayed at all, even with a coil current of 3 A (at the maximum in the system). Schunk *et al.* showed by a magnetic field flow fractionation (FFF) method that although an elution peak of 0.8 μ m non-flocculated hematite particles could not be delayed, even using a magnetic field of 300 G, that of the flocculated particles portion could be delayed.^{2,3} Since the flocculation condition is not clear, it is difficult to simply compare the separation ability of our system with the magnetic FFF.

Effect of the loading ratio of the magnetic field

Figure 5a shows chromatograms of the magnetite particles depending on the applying time (T_{on}) of the magnetic field under a fixed interval time (T_{off}) of 0.3 s, a coil current of 1 A and a mobile-phase flow rate of 1 ml/min. Figure 5b shows plots of the adjusted retention time against the loading ratio for fixed interval times at 0.2, 0.3 and 0.4 s. The measurement of the adjusted

Fig. 5 (a) Typical magnetic chromatograms for magnetite particles while varying the applying time (T_{on}) of the magnetic field at the fixed interval time ($T_{off}=0.3$ s) and (b) the relationship between the adjusted retention time (t'_R) and the loading ratio (T_{on}/T_{off}) at various interval times.

retention time at a larger loading ratio became imprecise because of peak broadening and a decreased peak height. A curved relationship was observed between the adjusted retention time and the loading ratio, although a linear relationship was expected from the theoretical prediction (see Eq. (3)). One reason is that the applied magnetic field may not fully work on the steel beads during the applied time (T_{on}).

Effect of the mobile-phase flow rate and separation column length

Although t'_R or t_0 is inherently affected by the mobile-phase flow rate, the value of t'_R/t_0 would not be changed by it according to Eq. (4) if the partition factor (f) is not influenced by the flow rate. Figure 6 shows plots of the value of t'_R/t_0 against the loading ratio (T_{on}/T_{off} ; $T_{off}=0.3$ s) at two flow rates of 1.0 and 2.0 ml/min. The higher flow rate may cause a shortening of the retention time by reducing the magnetic interaction between the magnetic particles in the mobile phase and the steel beads. At a lower flow rate than 1.0 ml/min, reproducible elution profiles could not be obtained.

With keeping 10 cm of the electromagnetic coil length, the length of the separation column with steel beads was compared (Fig. 7). Obviously, the same length of the separation column as the coil length was the most effective to obtain a large adjusted retention time (t'_R).

Fig. 6 Relationship between the normalized retention time (t'_R/t_0) and the loading ratio (T_{on}/T_{off}) at the different mobile-phase flow rates.

Irreversible adsorption of particles on the steel beads and reliability of the system

At the beginning of this work, particles trapped on the steel beads could not easily be desorbed when the PTFE film was not coating on the steel beads and the column

Fig. 7 Effect of the packing column length on the retention time.

was not vibrated. These modifications in the operation could realize the chromatographic elution of the magnetite particles with an intermittent magnetic field. The desorption of particles, however, became insufficient at the higher coil current, the higher loading ratio and the lower mobile-phase flow rate. The longer or stronger trapping of particles on the PTFE coated steel beads may enhance the interaction between the particles and the steel beads along with an additional contribution of residual magnetization of the steel beads. An alternate switching operation of the DC current polar did not improve the problems.

The physical strength of the PTFE film coated on the steel beads was not so large that the chromatograms became unstable after around 20 runs of sample injection. Mechanical vibration of the column may accelerate the deterioration of the film. The condition of the mechanical vibration of the column must carefully be adjusted to obtain reproducible results.

In conclusion, we could demonstrate that magnetic chromatography is realized with a separation column containing magnetically permeable steel beads under a periodically intermittent magnetic field. The chromatography can be controlled by the strength and loading ratio of the magnetic field. The system has an advantage that the separation of magnetic particles can be realized with a relatively weak magnetic field because the magnetic field effectively works on the particles near to the steel beads. During operation, the coil current and the loading ratio can be easily changed by computer

programming in magnetic chromatography. However, applying mechanical vibration to the column induces signal fluctuation and reduces the reliability of the system. To remove mechanical vibration, spherical beads with no irreversible adsorption or superior polymer coating must be either found or developed. After overcoming these problems, the system may be extended to a practical one using a larger magnetic field for separating mixed particles with different magnetic properties. At present, it is difficult to evaluate whether the separation ability of our system is prior to that the magnetic FFF because of fewer characteristic studies concerning the magnetic FFF for magnetic particles as well as several problems to be solved in our system.

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