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Separation technique based on electrophoresis, chromatography and magnetism phenomena: the migration time and peak broadening

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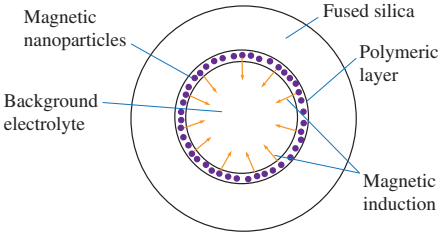
Magnetic nanoparticles incorporated into the surface layer of a capillary column can produce an electromagnetic field upon applying the electric field, which would affect the separation of charged analytes. The main peak parameters, migration time and width at half height were evaluated, which are important to development of a novel separation technique based on the electrophoresis, chromatography, and magnetism.



An idea to employ magnetic nanoparticles (MNPs) in electromigration techniques of the separation is not a new one.[1,2] Main applications of MNPs involve producing open-tubular[3–9] or monolithic columns[10–12] for the capillary electrochromatography (CEC). Due to the incorporation of MNPs into a layer of the polymeric sorbent covering the inner surface of a fused-silica capillary and to the application of an electric field across the capillary length, the electromagnetic field is generated on the surface or in the bulk of the sorbent.[13] However, the effect of this filed on the analyte migration and separation is still remaining unknown.

There are several reasons why a 'magnetic' approach to the CEC gained insofar no momentum. Along with anything but simple producing nonporous polymeric sorbent layers containing MNPs distributed orderly, the theoretical explanation of a fundamental element of magnetic CEC, the magnetic field, has not been established yet. We have previously developed[13,14] a mathematical model for the magnetic CEC in an open-tubular column, simulated the effect of MNPs on the mass-transfer rate upon the application of combined electroosmotic and electrophoretic flows, and demonstrated that the MNPs greatly affect the dielectric constant of near-wall polymeric layer. Consequently, the magnitude of axial electric field strength would be increased upon the increased absolute number of nanoparticles (*e.g.*, at higher particle loadings) and hence, the rate of electroosmotic flow (EOF) as well. This has been confirmed using linearized Poisson–Boltzmann (PB) equation.

The present work was aimed at the calculations of rate of the integrated convectional mass transfer caused by the electroosmosis and electrophoresis in order to estimate the migration time and peak half-width for a model analyte.

The separation capillary was assumed as a rectangular cross-sectional channel of its width of 100 μm and its effective length of 40 cm. It should be noted that the channel was considered as an ensemble of flat slots of the equal width in order to simplify the calculations. The thickness of a polymeric layer was set to 2.5 μm, and the fraction of MNPs was varied in the range of 0–30 vol%. At this step of developing the theory of magnetic CEC, we did not define the exact shape, size, type and magnetic properties of the nanoparticles. It has been only assumed that they are electrically conductive (while not all the magnetic particles are conductive). This assumption is important since there are electric (not magnetic) characteristics of the particles, which can affect the EOF. Polystyrenesulfonic acid selected as the material for the polymeric coating was demonstrated to maintain the required magnitude of cathodic EOF.[15] The molecular size of a model analyte was adopted as 1.5 nm, which corresponds to the size of many biomolecules, *e.g.*, basic proteins. The latter are distinguished by their positive charge and consequently, by the electrophoretic mobility co-directed with EOF (this fact facilitates the calculations).

The following parameters of considered CEC system were selected: the maximum (axial) rates of electrophoretic and electroosmotic flows were 0.3 and 1.0 mm s^{-1}, respectively, at the applied voltage of 200 V s^{-1}. Under these conditions, the convectional mass transfer becomes dominating one, and the Peclet number falls in the range of 350–380. Although this seems as an oversimplification, we disregard at this step the chromatographic effects, which could be substantial and even determining the CEC separation.

The calculation algorithm was based on the moment method[16] working efficiently in the case of domination of one of the geometrical dimensions of separation channel (in our case, the length) and of uniformity of the overall convectional rate of analyte migration during the analysis. Thus, the electroosmotic rate was calculated, and the overall migration rate was obtained by adding the electrophoretic rate. The peak center of gravity (PCG) and channel-averaged peak dispersion $\langle\sigma^2\rangle$ were consequently calculated by assigning the ratio of electroosmotic and electrophoretic rates to the analyte parameters according to equations (1) and (2).

$$\mathrm{PCG} = U^*B^0t, \quad (1)$$

where $U^* = U/H$ is the total migration rate normalized to the channel half-width, B^0 is the constant term of expansion in eigenfunctions [*i.e.*, $\cos(\pi jz)$] of total electrophoretic and

electroosmotic profiles at the convectional rate, and t is the migration time.

$$\langle\sigma^2\rangle = \left(2 + Pe^2 \sum_{j=1}^{+\infty} \frac{B^{j2}}{(\pi j)^2}\right) D^* t + \left(\frac{\Delta_0^2}{3} - \frac{3}{2} Pe^2 \sum_{j=1}^{+\infty} \frac{B^{j2}}{(\pi j)^4}\right), \quad (2)$$

where $D^* = D/H^2$ is the diffusion coefficient normalized to the channel half-width, Δ_0 is the normalized length of analyte zone, $Pe = VH/D$ is the Peclet number (one of the key characteristics of convective-diffusive mass transfer under the given conditions), V is the maximum rate of convective movement, and B^j are the coefficients of expansion in the eigenfunctions of convective rate profile.

First, it was necessary to confirm the applicability of linearized PB equation for the calculations of EOF rate. For this purpose, we have taken experimental data on the EOF rate acquired for open-tubular columns possessing different surface chemistry.[15] In the case of equation validity, the ratio of electroosmotic mobilities (μ_{eo}) at different pH of the background electrolyte (in the considered example, the pH values are 4, 7, and 9) should meet the following constancy condition (the pH values are given in parentheses):

$$[\mu_{eo}(7)–\mu_{eo}(4)]/[\mu_{eo}(9)–\mu_{eo}(4)] = \text{const} \quad (3)$$

and if so, the mobilities would vary only due to the variations in the zeta potential. The respective sets of pH-variable μ_{eo} values are 2.41, 4.80, 6.43 (fused-silica capillary) and 1.86, 2.57, 3.05 ($\times 10^{-4}$ cm^2 V^{-1} s^{-1}) (polystyrene-coated capillary). Ratio (3) is 0.594 for the first set of μ_{eo}, while for the second one, it is almost the same (0.597). Thus, the constancy of ratio (3) seems to be confirmed or at least, the used data[15] do not invalidate the suitability of linearized PB equation for estimating the EOF rate.

Figure 1 shows a schematic representation of the modelled CEC system. The polymeric layer thickness and the fraction of nanoparticles are the variables [see Figure 1(*b*,*c*)], while the other CEC conditions were constant. The calculated peak parameters are summarized in Table 1. It is evident that the effect of MNPs is fairly noticeable at their content of 20% in the layer of 2.5 μm, the migration time decreases for *ca.* 6% accompanied by a reduced peak broadening (the plate number increases up to 1220 as compared to 940 in the case of non-magnetic CEC). At the constant applied voltage and background electrolyte composition, it is due to the EOF, whose rate increases upon

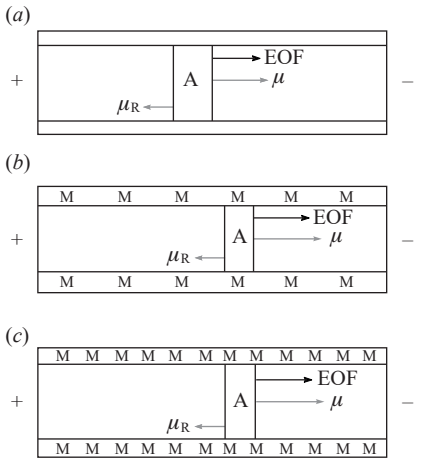


Figure 1 (*a*) Common and (*b*, *c*) magnetic modes of the CEC. Legend: A is a positively charged analyte, M is MNPs (within the polymeric sorbent layer). Vectors μ and μ_R designate the effective mobility and the retardation by the stationary phase (the latter is neglected), respectively. The length of EOF vector and the position and width of analyte zone reflect the effects of layer thickness and the fraction of nanoparticles.

Table 1 Peak parameters in conventional and magnetic CEC.

Layer thickness/μm	Fraction of particles (%)	t^a/s	Peak half-width/s
2.5	0	502	38.5
2.5	20	474	32.0
1.0	30	459	31.3

[a] Migration time.

implementing MNPs responsible for the indicated alterations in peak parameters. It should be noted that the layer thickness of 2.5 μm is quite large (the inner diameter of capillary does not exceed 100 μm). However, its decrease down to 1 μm along with increasing in the fraction of nanoparticles (up to 30%) has resulted in the same outcome (see Table 1).

In summary, we have demonstrated that the magnetic CEC, as compared to the common CEC, is characterized by a broader range of factors allowing one to control the separation, including the geometric parameters of surface layer and the content of MNPs. However, the potential of magnetic CEC as a separation technique is supposed to be more wide-ranging. It is expected that the MNPs would influence the separation selectivity, especially for analytes possessing different magnetic properties, by generating the magnetic field upon the applied voltage. This effect can only be experimentally proven, and our efforts are the first steps in this direction.

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