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Measurement of Packing Tortuosity and Porosity in Capillary Electrochromatography

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The application of conductivity measurements for packing structure characterization has been extended to a column consisting of a packed section and an open section as typically used in capillary electrochromatography (CEC). Because of the difference in electric conductivity between the packed and open sections, the electric fields applied across the two sections vary, depending on the length of the packed section relative to that of the total column. On the basis of mass conservation law, it can be shown that the ratio of the electric current measured in such a duplex column to that without packing is a function of the length and the geometric structure of the packing bed. Thus, knowing the lengths of the packed section and the whole column, we can readily calculate the obstructive factors, such as the porosity and the tortuosity factor, from the measured conductivity ratio. An example is given to demonstrate the application of this method, with experimental data taken from published work.

Capillary electrochromatography (CEC) is an emerging separation technique that combines the separation power of high-performance liquid chromatography (HPLC) with the high efficiency of capillary zone electrophoresis (CZE).[1−10] In this technique, the capillary column used is typically packed with conventional HPLC packing materials, and a high electric field is applied across the column to induce electroosmotic flow. The presence of the packing may have some significant effects on the electroosmotic flow occurring in CEC. First, the electroosmotic velocity in the fused-silica capillary column with the packing is generally reduced in comparison to that without the packing. As we have shown previously,[11] this reduction is largely accounted for by two geometric factors of the packing, namely, the column's porosity and tortuosity. Second, because of the heterogeneous nature of the packing, over-heating and double-layer overlap are liable to occur in column sections of high packing density, causing a drastic loss in column efficiency or bubble formation during the operation of CEC.[3,11,12] Thus, for developing CEC into a viable high-efficiency separation technique, it is essential to ensure that the packing structure in both frits and column is made as homogeneous as possible.

Previously, we described a method for characterization of the columns used in CEC that is based on measurements of relative electric conductivity, defined as a ratio of the electric conductivity in a column with packing to one without packing.[11] Several groups have since performed more comprehensive studies on the relative conductivities for columns of varying inner wall charges packed with charged and uncharged stationary phases and on the effect of mobile phase pH on the relative conductivities.[13,14] The results from these studies have confirmed the general usefulness of the method. In connection with the current practice of CEC in which the column consisting of a packed section and an open section is typically used, we report an improved method to measure packing structure characteristics for this type of column. In this method, the electric current is measured with a packed column connected to an open column of the same diameter. The current is then correlated with the obstructive factors and the length of the packing. The obstructive factors, such as the porosity and the tortuosity factor, are readily determined on the basis of this correlation.

RESULTS AND DISCUSSION

The electric current, I_o, generated at the electric field strength, E, in a capillary tube filled with electrolyte obeys Ohm's law, as shown in the following,

$$I_o = AkcE \qquad (1)$$

where A is the cross-sectional area of the capillary, k is the molar conductivity of the electrolyte, and c is the concentration of the electrolyte.

In a capillary column packed with nonconducting materials, such as porous, spherical silica particles as prevalently used in CEC, the electric current can be transported through the flow

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channels formed between and within the particles. The effective electric conductivity in the packed column is reduced, as compared to that in an open-tubular capillary column. Two geometrical obstructive effects are incurred to account for this reduction.[11] First, the tortuous flow channels in the porous media increase the path lengths and alter the directions, thus reducing the effective field strength. Second, the particles occupy some free space within the column, causing a reduction of the effective cross-sectional area available to the current. Allowing for these two effects, the electric current, I_p, in the packed capillary column is given by

$$I_p = AkcE\epsilon\gamma = I_o\epsilon\gamma \tag{2}$$

where ϵ and γ refer to the effective column porosity and the tortuosity factor of the packing bed, respectively. Thus, the product of the obstructive factors can be determined by measuring the currents in the packed and open columns of the same diameter, as shown by the following equation.

$$\epsilon\gamma = \frac{I_p}{I_o} \tag{3}$$

To date, the majority of CEC columns have consisted of a packed section and an open section through which on-line optical detection is usually performed. As a result of the difference in electric conductivity between the packed and open sections, the electric fields applied across the two sections are varied, depending upon the packed length fraction, $\lambda = L_p/L$, which is defined as a ratio of the length of the packed section to that of the whole column. As required by the mass conservation law, the current, I_{po}, passed through the duplex column must be the same in both sections of the column,

$$I_{po} = AkcE_{ps}\epsilon\,\gamma = AkcE_{os} \tag{4}$$

where the subsripts ps and os refer to the packed and open sections of the column.

The electric field strength in both sections can be expressed as a function of the packed length fraction, λ, as follows:

$$E = \frac{V_{ps} + V_{os}}{L} = \lambda E_{ps} + (1-\lambda)E_{os} \tag{5}$$

Rearranging eq 4 yields

$$E_{os} = E_{ps}\epsilon\gamma \tag{6}$$

We substitute eq 6 for E_{os} in eq 5 and then solve the equation to give

$$E_{ps} = E\frac{1}{(1-\lambda)\epsilon\gamma + \lambda} \tag{7}$$

and

Table 1. Packing Structure Characteristics of the CEC Columns Based on Measured Electric Currents[a]

parameters	column A	column B	column C
L_{ps}, cm	0	10	20
L_{po}, cm	30	20	10
λ	0	1/3	2/3
I_{po}, μA	6.6	3.9	2.6
$\epsilon\gamma$	1	0.32	0.30
ϵ	1	0.44	0.42
γ	1	0.72	0.71

[a] Conditions: column packing, 3.5-μm Zorbax ODS, 80 Å; mobile phase, acetonitrile + 10 mM borate, pH 8.0 (1:1, v/v); applied voltage, 18 kV.

$$E_{os} = E\frac{\epsilon\gamma}{(1-\lambda)\epsilon\gamma + \lambda} \tag{8}$$

Accordingly, the electric current passed through the column of two sections is given by

$$I_{po} = AckE\frac{\epsilon\gamma}{(1-\lambda)\epsilon\gamma + \lambda} = I_o\frac{\epsilon\gamma}{(1-\lambda)\epsilon\gamma + \lambda} \tag{9}$$

Rearranging eq 9, we obtain

$$\epsilon\gamma = \frac{\lambda}{\frac{I_o}{I_{po}} - (1-\lambda)} \tag{10}$$

By measuring I_{po} at a given λ, we can determine the product of the obstructive factors ϵ and γ for the packed section of the column. The product can be further resolved into individual items. Since the tortuosity factor is related to the porosity by the Slawinski equation,[15]

$$\gamma = \frac{1}{(1.3219 - 0.3219\epsilon)^2} \tag{11}$$

Rearranging eq 11, we arrive at

$$\gamma^2 - [0.572 + 0.487(\epsilon\gamma)]\gamma + 0.0593(\epsilon\gamma)^2 = 0 \tag{12}$$

Substituting experimental data for $\epsilon\gamma$ and solving eq 12 yields a value of γ. Knowing the value of γ, we can readily calculate the value of ϵ from $\epsilon = (\epsilon\gamma)/\gamma$.

Choudhary and Horvath[13] reported current measurements on columns consisting of a packed section and an open section. With their experimental data, we calculated the porosity and the tortuosity factor for the packed column. As shown in Table 1, the products of obstructive factors, $\epsilon\gamma$, measured at varying λ are ~0.31, which is quite close to 0.33, the value measured for $\lambda = 1$.[11] The porosity and tortuosity factors are ~0.43 and 0.71, respectively. For columns packed with porous particles, the total porosity, ϵ_T, is related to interparticle, ϵ_{inter}, and intraparticle, ϵ_{intra}, porosities by

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$$\epsilon_T = \epsilon_{inter} + \epsilon_{intra}(1 - \epsilon_{inter}) \quad (13)$$

Assuming $\epsilon_{inter} = \epsilon_{intra} = 0.4$,[16] the total column porosity is 0.64. The measured porosities are lower than the total column porosities, but are in good agreement with the interparticle porosities for this kind of stationary phase that are in the range 0.4−0.45. It would appear that pores in chromatographic stationary phase are not all through pores and cannot contribute to current transport. Thus, the porosities measured by the method described here are actually corresponding to the interparticle porosities rather than the total column porosities.

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