

Review

Electrochemical properties of columns in capillary electrochromatography I. Ohm's law, resistivity and field strength

Michael P. Henry*, Chitra K. Ratnayake

Beckman Coulter Inc., Advanced Technology Center, 4300 North Harbor Boulevard, Fullerton, CA 92834, USA

Available online 19 March 2005

Abstract

The most commonly used type of column in capillary electrochromatography (CEC) consists of a packed segment and an open (but buffer-filled) segment. The two segments differ importantly in two respects: firstly, their electrical resistivity; and secondly, their zeta potentials at a multitude of solid–liquid interfaces. Determination of the magnitude of these properties for each segment cannot be made using only results from the column as a whole. Instead, measurements of resistivity and zeta potentials of an entirely open, unpacked column can be used in conjunction with those of the CEC column to determine the electrochemical nature of both segments. This review of basic electrochemical properties will describe simple procedures that can be used to determine resistance, resistivity, conductivity, conductance, and field strength in each segment. In addition, it will be shown how the properties of each segment add together to give the same properties of the CEC column as a whole. The equations so derived will be applied to data from the literature and conclusions drawn from the results.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Capillary electrochromatography; Resistivity of buffers; Electrochemical properties of packed capillaries

Contents

1. Introduction	70
1.1. Ohm's law	70
1.2. Mobile phase velocity	70
1.3. Resistivity	70
1.4. Duplex structure	70
1.5. Constant current	71
1.6. Segmental field strengths	71
1.7. Resistivities, conductivities and conductances	71
1.8. Additivities of electrochemical properties	71
1.8.1. Resistance (R)	71
1.8.2. Resistivity (ρ)	72
1.8.3. Conductivity (σ)	72
1.8.4. Conductance (λ)	72
1.8.5. Field strength (E)	72
1.8.6. Electrochemical properties of the stationary phase in packed segments	72
1.8.7. Contribution of stationary phase and mobile phase electrochemical properties to total CEC column properties	73
1.9. Summary	73
2. Published data	73
2.1. Data source and column properties	73
2.2. Columns and segments	73

* Corresponding author. Tel.: +1 714 773 8221; fax: +1 714 773 8512.
E-mail address: mphenry@beckman.com (M.P. Henry).

2.3.	Total porosity and bonded phase resistivity	74
3.	Discussion	74
3.1.	Ohm's law (Eq. (1)) in CEC	74
3.2.	Resistivities	74
3.3.	Duplex structures—total versus segmental electrochemical properties	75
3.4.	Field strength and L_e	75
3.5.	Resistivities, resistances, conductivities and conductances	75
3.6.	Electrochemical properties of the stationary phase in packed segments	75
3.7.	Other CEC column configurations	75
4.	Conclusions	75
	Acknowledgements	76
	References	76

1. Introduction

1.1. Ohm's law

The application of an electromotive force (emf, V in V) across the ends of a packed capillary in capillary electrochromatography (CEC; shown schematically as column B or C in Fig. 1) generates a current (I in A) that flows against a resistance (R in Ω). Ohm's law, given in Eq. (1), is an expression of the relationship among these three variables:

$$V = IR \quad (1)$$

1.2. Mobile phase velocity

The electrical current in a CEC system is simply the flow rate of ions through the column and is therefore primarily related to mobile phase flow rate, a critical parameter of any chromatographic system. An additional contributor to current is the movement of ions in the surface of the capillary, which may be different to ion flow in the bulk mobile phase. However, this paper (Part I) will not, in general, go into any details regarding the origins or mechanism of ion flow. These aspects will be reviewed in future (Parts II and III).

The movement of liquid through the capillary occurs by the process of electro-osmosis (eo) generated by the applied emf [1]. How fast the liquid moves by this mechanism, whether measured as a volumetric flow rate or linear velocity, depends upon the dielectric constant of the medium (ϵ), the bulk mobile phase viscosity (η), the electric field strength

(E , V/cm) and the zeta potential (ζ) expressed as the Smoluchowski [2] Eq. (2):

$$u_{eo} = \frac{\epsilon E \zeta}{\eta} \quad (2)$$

where u_{eo} = linear velocity of the mobile phase and E = voltage change per unit length.

[The linear velocity is determined by dividing the length of the segment by the time taken for an unretained, neutral marker to pass through it.]

Thus, the set voltage and the induced current in a CEC capillary are clearly major electrochemical properties of the system, related through resistance (R).

1.3. Resistivity

More useful than resistance, however, is the property of resistivity (ρ in Ω cm), defined in Eq. (3):

$$\rho = \frac{RA}{L} \quad (3)$$

where A = cross-sectional area of the capillary (in cm^2) and L is its length (in cm).

In other words, resistivity determines how rapidly resistance increases with capillary length and how rapidly it decreases with increasing cross-sectional area. The electrical resistivity of a solid or liquid medium in a capillary is a fundamental intrinsic property of the CEC column, being independent of voltage, current, resistance and column dimensions. It depends only upon temperature and the nature of the liquid and solid in the capillary. In other words, for a given CEC system (fixed capillary size, packing type, mobile phase and temperature), ρ values of the stationary and mobile phases are constants.

1.4. Duplex structure

The duplex nature of the usual column type in CEC means that the open and packed segments have different voltage drops, resistances, resistivities and zeta potentials, which cannot be obtained from measurements of these electrochemical properties of the column as a whole. For although the voltage drops (V_{pack} , V_{open}), for example, across each segment type

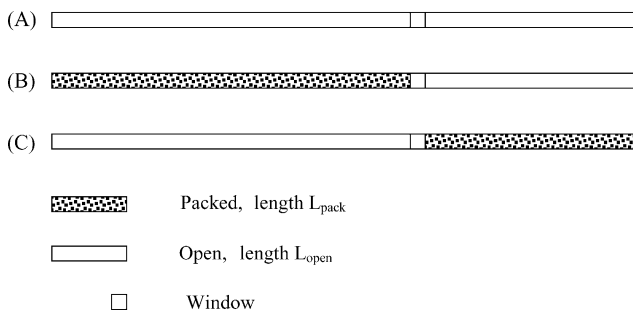


Fig. 1. Schematic illustration of the packed and open lengths in a CE and CEC column.

add up to give the total voltage drop for the whole column (V_T) (see Eq. (4)), the individual values are unknown. It is important to know the values of

$$V_T = V_{\text{pack}} + V_{\text{open}} \quad (4)$$

segmental voltage changes since field strengths (E) are determined from these properties.

1.5. Constant current

While the most of the electrochemical properties of CEC columns are different for the packed and open segments, current flowing at any point in the column (denoted I_T) is constant, since there is usually no accumulation of charge at any point. This simplifies the methods of calculating various electrochemical properties of CEC column as will be shown further.

1.6. Segmental field strengths

The determination of V_{open} for the CEC column can be made simply from measurements of ρ_{open} of a fully open capillary (as used in capillary electrophoresis (CE)) containing the same buffer, by applying a voltage V_{CE} , measuring the current I_{CE} , length L_{CE} , and internal cross-sectional area A_{CE} , as shown in Eq. (5):

$$\rho_{\text{open}} = \frac{V_{\text{CE}} A_{\text{CE}}}{I_{\text{CE}} L_{\text{CE}}} \quad (5)$$

Since ρ_{open} will be the same for the CEC column, V_{open} for this column will be given by Eq. (6):

$$V_{\text{open}} = \frac{\rho_{\text{open}} I_T L_{\text{open}}}{A} \quad (6)$$

where all values refer to the CEC column and its dimensions.

R_{open} can be calculated from ρ_{open} as shown in Eq. (7):

$$R_{\text{open}} = \frac{\rho_{\text{open}} L_{\text{open}}}{A} \quad (7)$$

Subtraction of V_{open} from both sides of Eq. (4) gives the result for V_{pack} .

Calculation of field strengths, E_{open} and E_{pack} (in V/cm), are made using Eqs. (8) and (9):

$$E_{\text{open}} = \frac{V_{\text{open}}}{L_{\text{open}}} \quad (8)$$

$$E_{\text{pack}} = \frac{V_{\text{pack}}}{L_e} \quad (9)$$

where L_e is the “equivalent” length (in cm) of the packed segment as defined by Rathore and Horváth [3].

L_e is the total length traveled by the unretained, neutral marker, and can be calculated from Eq. (10), using electrochemical properties only:

$$L_e = L \left[\frac{I_{\text{open}}}{I_{\text{pack}}} \right]^{1/2} - L_{\text{open}} \quad (10)$$

where L is the total capillary length, and I_{open} and I_{pack} are the currents through the column in the absence and presence of packing, respectively.

1.7. Resistivities, conductivities and conductances

Once V_{open} and V_{pack} are known, calculation of other major electrochemical properties of the CEC column is straightforward. For example, Eq. (11) gives a means of calculating ρ_{pack} :

$$V_{\text{pack}} = \frac{\rho_{\text{pack}} I_T L_{\text{pack}}}{A} \quad (11)$$

The simple reciprocal of resistivity is conductivity (σ in $\Omega^{-1} \text{cm}^{-1}$). Thus,

$$\sigma_{\text{pack}} = \frac{1}{\rho_{\text{pack}}} \quad (12)$$

and

$$\sigma_{\text{open}} = \frac{1}{\rho_{\text{open}}} \quad (13)$$

Conductivity is therefore an intrinsic property of CEC columns, although conductance (λ in Ω^{-1}) like resistance, depends upon column dimensions as shown in Eq. (14):

$$\lambda = \frac{\sigma A}{L} \quad (14)$$

Or simply,

$$\lambda = \frac{1}{R} \quad (15)$$

1.8. Additivities of electrochemical properties

It is instructive to observe how individual segmental electrochemical properties contribute to the corresponding property of the CEC column as a whole. The relationships below give the property for the column as a whole in terms of the corresponding properties of the packed and open segments.

1.8.1. Resistance (R)

In Eq. (4), it was shown that voltages of the individual segments add along the CEC column. Replacing V with IR , and since current throughout both segments is the same, we obtain Eq. (16):

$$I_T R_T = I_T R_{\text{pack}} + I_T R_{\text{open}} \quad (16)$$

Therefore,

$$R_T = R_{\text{pack}} + R_{\text{open}} \quad (17)$$

Individual resistances can be calculated from values of resistivities for the appropriate segments.

1.8.2. Resistivity (ρ)

Eq. (17) can be expressed in terms of resistivities and measured parameters, as follows:

$$\frac{\rho_T L}{A} = \frac{\rho_{\text{open}} L_{\text{open}}}{A} + \frac{\rho_{\text{pack}} L_{\text{pack}}}{A} \quad (18)$$

Multiplying both sides by A and rearranging segment lengths:

$$\rho_T = \rho_{\text{open}} \left\{ \frac{L_{\text{open}}}{L} \right\} + \rho_{\text{pack}} \left\{ \frac{L_{\text{pack}}}{L} \right\} \quad (19)$$

Putting $L_{\text{pack}}/L = r$, Eq. (19) can be written as:

$$\rho_T = (1 - r)\rho_{\text{open}} + r\rho_{\text{pack}} \quad (20)$$

The ratio r is introduced here primarily to improve the visual appearance of Eq. (19) and those that follow, so that the contributions of the electrochemical properties of the open and packed segments may be more clearly seen.

1.8.3. Conductivity (σ)

Since conductivity is the simple reciprocal of resistivity, substitution into Eq. (20) gives Eq. (21):

$$\frac{1}{\sigma_T} = (1 - r) \left(\frac{1}{\sigma_{\text{open}}} \right) + r \left(\frac{1}{\sigma_{\text{pack}}} \right) \quad (21)$$

Taking reciprocal of both sides and rearranging:

$$\sigma_T = \frac{\sigma_{\text{open}} \sigma_{\text{pack}}}{(1 - r)\sigma_{\text{pack}} + r\sigma_{\text{open}}} \quad (22)$$

1.8.4. Conductance (λ)

Conductance is the simple reciprocal of resistance, therefore Eq. (23) follows directly from Eq. (17):

$$\frac{1}{\lambda_T} = \frac{1}{\lambda_{\text{open}}} + \frac{1}{\lambda_{\text{pack}}} \quad (23)$$

Taking the reciprocal of both sides and rearranging gives Eq. (24):

$$\lambda_T = \frac{\lambda_{\text{open}} \lambda_{\text{pack}}}{\lambda_{\text{open}} + \lambda_{\text{pack}}} \quad (24)$$

1.8.5. Field strength (E)

Here, the equivalent length (L_e) is used in place of L_{pack} , throughout. Capillary length L is taken as the sum $L_e + L_{\text{open}}$. The ratio L_e/L is put as r , and therefore L_{open}/L is $1 - r$ and L_e/L_{open} becomes $r/(1 - r)$.

E_T is then defined as shown in Eq. (25):

$$E_T = \frac{V_T}{L} = \frac{V_{\text{open}} + V_{\text{pack}}}{L_{\text{open}} + L_e} \quad (25)$$

Dividing numerator and denominator by L_{open} and putting the ratio L_e/L as r and rearranging:

$$E_T = \frac{V_{\text{open}}/L_{\text{open}} + V_{\text{pack}}/L_{\text{open}}}{1 + L_e/L_{\text{open}}} \quad (26)$$

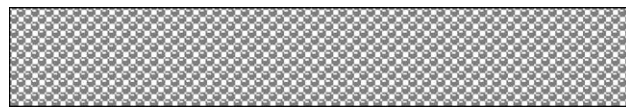


Fig. 2. Schematic illustration of the structure of the packed segment in a CEC column, where the small spheres represent the solid elements of the stationary phase and mobile phase is present amongst the spheres.

Therefore,

$$E_T = \left[E_{\text{open}} + E_{\text{pack}} \left\{ \frac{r}{1 - r} \right\} \right] [1 - r] \quad (27)$$

This relationship is correct whether L_e or L_{pack} are used to calculate E_T and E_{pack} .

1.8.6. Electrochemical properties of the stationary phase in packed segments

Any packed segment consists of mobile phase and solid stationary phase (support plus bonded layer), each of which will have different electrochemical properties (represented in Fig. 2).

These electrochemical properties will add in the same way as described above in Eqs. (16)–(27) for separated segments. Both phases essentially fill the complete interior cross-sectional area, so Eqs. (18)–(20) apply in the case of resistivity.

Each phase will occupy a specific volume within the packed segment. Thus, if $\text{Volume}_{\text{phase}}$ is the volume of the solid and $\text{Volume}_{\text{mobile}}$ is the volume of the liquid in the packed segment, then their sum is the volume of the packed segment ($\text{Volume}_{\text{pack}}$). It also follows that the ratio $\text{Volume}_{\text{mobile}}/\text{Volume}_{\text{pack}}$ is the proportion of the total packed volume that is void, i.e. the total column porosity (ε_{tot}). Thus, $1 - \varepsilon_{\text{tot}}$ is the proportion of the packed segment that is solid.

The role played by ε_{tot} in determining resistivity of the stationary phase can be explained as follows.

Consider the stationary phase and mobile phase shown schematically in Fig. 2 to be separated and formed into two segments as shown in Fig. 3. This is simply a two-segment column, whose total resistivity, for example, can be obtained from Eq. (19).

Therefore, substituting L_{open} and L_{phase} into Eq. (19) instead of L_{open} and L_{pack} , we obtain Eq. (28):

$$\rho_T = \rho_{\text{open}} \left\{ \frac{L_{\text{open}}}{L} \right\} + \rho_{\text{phase}} \left\{ \frac{L_{\text{phase}}}{L} \right\} \quad (28)$$

But since the cross-sectional area of the above capillary, is assumed the same throughout, the volume of each segment will be proportional to its length. Thus, L_{open}/L and L_{phase}/L will be equal to $\text{Volume}_{\text{open}}/\text{Volume}_{\text{total}}$ and $\text{Volume}_{\text{phase}}/\text{Volume}_{\text{total}}$, or ε_{tot} and $1 - \varepsilon_{\text{tot}}$, respectively.

Thus, Eq. (19) can be written for the packed segment alone as shown in Eq. (29):

$$\rho_{\text{pack}} = \varepsilon_{\text{tot}} \rho_{\text{open}} + (1 - \varepsilon_{\text{tot}}) \rho_{\text{phase}} \quad (29)$$

where ρ_{pack} , ρ_{open} and ρ_{phase} are the resistivities of packed segment, the mobile phase and the solid stationary phase in the packed segment, respectively.

Eq. (29) can be rearranged to give Eq. (30):

$$\rho_{\text{phase}} = \frac{\rho_{\text{pack}} - \varepsilon_{\text{tot}}\rho_{\text{open}}}{1 - \varepsilon_{\text{tot}}} \quad (30)$$

Thus, Eq. (30) can be employed to calculate ρ_{phase} from known values of ρ_{pack} , ε_{tot} and ρ_{open} . Other electrochemical properties of the stationary phase may be calculated in a similar fashion using other equations.

1.8.7. Contribution of stationary phase and mobile phase electrochemical properties to total CEC column properties

Through relationships like those expressed in Eqs. (20) and (28) for resistivity, it is possible to derive equations for electrochemical properties of the CEC column as a whole in terms of the same property of the open segment and the stationary phase. The mobile and stationary phases after all, are the two major elements that comprise any CEC column.

For conductivity as an example of an electrochemical property, we select Eqs. (22) (conductivity) and (29) (resistivity) for convenience:

$$\sigma_{\text{T}} = \frac{\sigma_{\text{open}}\sigma_{\text{pack}}}{(1 - r)\sigma_{\text{pack}} + r\sigma_{\text{open}}} \quad (22)$$

$$\rho_{\text{pack}} = \varepsilon_{\text{tot}}\rho_{\text{open}} + (1 - \varepsilon_{\text{tot}})\rho_{\text{phase}} \quad (29)$$

Since conductivity (σ) is the simple reciprocal of resistivity (ρ), Eq. (29) can be written as shown in Eq. (31):

$$\frac{1}{\sigma_{\text{pack}}} = \varepsilon_{\text{tot}} \left(\frac{1}{\sigma_{\text{open}}} \right) + (1 - \varepsilon_{\text{tot}}) \left(\frac{1}{\sigma_{\text{phase}}} \right) \quad (31)$$

Rearranging the right-hand side and taking the reciprocal of both side, gives Eq. (32):

$$\sigma_{\text{pack}} = \frac{\sigma_{\text{open}}\sigma_{\text{phase}}}{\varepsilon_{\text{tot}}\sigma_{\text{phase}} + (1 - \varepsilon_{\text{tot}})\sigma_{\text{open}}} \quad (32)$$

This expression for conductivity (σ_{pack}) can now be substituted into Eq. (22) to give Eq. (33):

$$\sigma_{\text{T}} = \frac{\sigma_{\text{open}}\sigma_{\text{open}}\sigma_{\text{phase}}/[\varepsilon_{\text{tot}}\sigma_{\text{phase}} + (1 - \varepsilon_{\text{tot}})\sigma_{\text{open}}]}{[(1 - r)\sigma_{\text{open}}\sigma_{\text{phase}}]/[\varepsilon_{\text{tot}}\sigma_{\text{phase}} + (1 - \varepsilon_{\text{tot}})\sigma_{\text{open}}] + r\sigma_{\text{open}}} \quad (33)$$

Eq. (33) can be simplified by bringing each segment to a common denominator, and multiplying throughout, giving

the final expression as shown in Eq. (34):

$$\sigma_{\text{T}} = \frac{\sigma_{\text{open}}\sigma_{\text{phase}}}{\sigma_{\text{phase}}(1 - r + r\varepsilon_{\text{tot}}) + r\sigma_{\text{open}}(1 - \varepsilon_{\text{tot}})} \quad (34)$$

Thus, Eq. (34) is the expression for the total conductivity of the CEC column in terms of the conductivities of the mobile (σ_{open}) and stationary (σ_{phase}) phases.

Similar relationships can be derived for other electrochemical properties of the mobile and stationary phases.

1.9. Summary

The above explanations and set of Eqs. (1)–(15) enable the calculation of many basic electrochemical properties of CEC columns. Eqs. (16)–(27) illustrate how the individual segmental properties add to give the corresponding property for the column as a whole. Eq. (20) can be utilized in the forms of Eqs. (28) and (29) to determine the resistivity of the stationary phase alone in the packed segment when total column porosity is known. Other electrochemical properties of the stationary phase may be determined in the same way. Eqs. (31)–(34) illustrate how electrochemical properties of the mobile and stationary phases combine together to give the same property of the CEC column as a whole.

In the next section, we take data from the literature to see how some of this mathematics is applied to actual CEC systems.

2. Published data

2.1. Data source and column properties

Ratnayake et al. [4,5] have measured several electrochemical properties of sol-gel monolithic columns (B and C) that they have prepared. The 75 μm I.D. columns were packed with 3 μm C18 bonded particles embedded in a silica gel and fitted into cartridges compatible with a Beckman Coulter's P/ACE MDQ capillary electrophoresis system. The columns were equilibrated with 70:30 (v/v) acetonitrile/morpholinoethanesulfonic acid (25 mM, pH 6.2). This choice of organic/aqueous mobile phase was made by Ratnayake et al. [4,5] in order to allow the column to function as a standard reversed-phase packing in their chromatographic work.

2.2. Columns and segments

The structure of these columns, plus the fully open (CE) column, can be illustrated schematically as shown in Fig. 1.

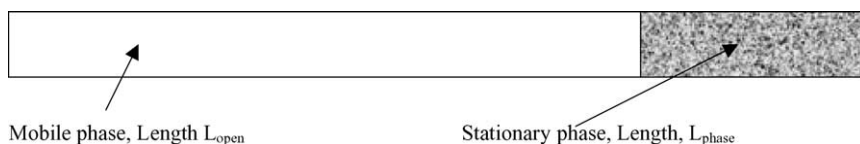


Fig. 3. Schematic illustration of how the mobile phase and stationary phase may be separated into two segments of a hypothetical capillary.

Table 1
Basic electrochemical properties of columns A–C

Column parameter (units, name)	Column A (open)	Column B	Column C
L_{open} (cm)	30	10	20
L_{pack} (cm)	NA	21.5	10
V_{T} (kV)	20	20	20
I_{T} (μA) (current)	5.6	2.6	3.5
ρ_{T} ($\Omega\text{ cm}$) (resistivity)	5.24×10^3	10.74×10^3	8.38×10^3
ρ_{open} ($\Omega\text{ cm}$) (resistivity)	5.24×10^3	5.24×10^3	5.24×10^3
ρ_{pack} ($\Omega\text{ cm}$) (resistivity)	NA	13.3×10^3	14.7×10^3
V_{open} (kV)	20	3.1	8.33
V_{pack} (kV)	NA	16.9	11.67
L_{e} (cm) (equivalent length)	NA	36.2	17.9
E_{T}^{a} (V/cm) (field strength)	667	430	529
E_{open} (V/cm) (field strength)	667	310	417
E_{pack} (V/cm) (field strength)	NA	467	652
R_{T} (Ω) (resistance)	3.57×10^9	7.69×10^9	5.71×10^9
R_{open} (Ω) (resistance)	3.57×10^9	1.19×10^9	2.38×10^9
R_{pack} (Ω) (resistance)	NA	6.50×10^9	3.34×10^9
σ_{T} ($\Omega^{-1}\text{ cm}^{-1}$) (conductivity)	1.9×10^{-4}	9.31×10^{-5}	11.93×10^{-5}
σ_{open} ($\Omega^{-1}\text{ cm}^{-1}$) (conductivity)	1.9×10^{-4}	1.9×10^{-4}	1.9×10^{-4}
σ_{pack} ($\Omega^{-1}\text{ cm}^{-1}$) (conductivity)	NA	7.52×10^{-5}	6.8×10^{-5}
λ_{T} (Ω^{-1}) (conductance)	0.28×10^{-9}	0.130×10^{-9}	0.175×10^{-9}
λ_{open} (Ω^{-1}) (conductance)	0.28×10^{-9}	0.84×10^{-9}	0.42×10^{-9}
λ_{pack} (Ω^{-1}) (conductance)	NA	0.154×10^{-9}	0.3×10^{-9}

$A = 44 \times 10^{-6}\text{ cm}^2$.

^a E_{T} = field strength calculated using values of L_{e} according to Eq. (25).

The basic data of Ratnayake et al. [4,5] have been used to calculate the electrochemical properties of their CEC columns, employing Eqs. (1)–(15). The results are given in Table 1.

2.3. Total porosity and bonded phase resistivity

From Eq. (30), it can be seen that the total porosity (ε_{tot}) of a packed segment is required in order to calculate stationary phase resistivity (ρ_{phase}). Ratnayake et al. [5] have used the relationship shown in Eq. (35) to calculate total porosity. It is not clear how they

$$\varepsilon_{\text{tot}} = \frac{L_{\text{pack}}}{L_{\text{e}}} \quad (35)$$

derived this equation, so instead we shall measure ε_{tot} more directly using data that Ratnayake et al. have included in their *Journal of Chromatography A* paper [4]. These data are the retention time of an unretained marker in both the open and packed segments which allow us to obtain flow rates and therefore void volumes in both types of segment. The data is included for convenience in Table 2.

The empty volumes of packed segments in columns B and C are 946 and 440 nL, respectively. The flow rate through column B is calculated by multiplying the linear velocity in the open segment (0.08 cm/s) by the capillary cross-sectional

Table 2

Measured values of unretained peak time (t), linear velocities (u) and cross-sectional area^a of CEC columns^b

Column parameter (unit)	Column B	Column C
L_{pack} (cm)	21.5	10
L_{open} (cm)	10	20
t_{open} (s)	128	184
t_{pack} (s)	196	69
u_{open} (cm/s)	0.08	0.11

^a $A = 44 \times 10^{-6}\text{ cm}^2$.

^b Data from ref. [4].

area ($A = 44 \times 10^{-6}\text{ cm}^2$). The result is 3.52 nL/s, which will be the flow rate through the packed segment as well. The unretained marker takes 196 s to move through this packed segment, so the liquid volume in this segment is 3.52×196 or 690 nL. Thus, the value of the total porosity, ε_{tot} , for column B is 718/946 or 0.73.

Similarly, calculations for column C give a value of total porosity (ε_{tot}) of 0.75. Total porosity can therefore be calculated, in general, from Eq. (36):

$$\varepsilon_{\text{tot}} = \frac{L_{\text{open}}t_{\text{pack}}}{L_{\text{pack}}t_{\text{open}}} \quad (36)$$

Stationary phase resistivities, ρ_{phase} , may now be calculated from Eq. (30) using these values of ε_{tot} and values of ρ_{pack} and ρ_{open} from Table 1. Thus, ρ_{phase} is 35 093 $\Omega\text{ cm}$ for column B and 43 080 $\Omega\text{ cm}$ for column C.

3. Discussion

3.1. Ohm's law (Eq. (1)) in CEC

Electrical current in CEC consists of the movement of ions through the open and packed segments of the typical column. The combination of field strength and zeta potential (see Eq. (2)) properties of the packed and open segments drives the mobile phase through the column. Although the impermeability of the packed segment is a factor that provides the major source of physical and therefore electrical resistance, the final current is also determined primarily by the magnitude of the field strength and zeta potential in the two segments. The data in Table 1 show that current is greatest where there is no packing and smallest where there is the greatest amount of packing.

3.2. Resistivities

The resistivities of the packed segments in columns B and C are close, indicating that their preparation is fairly reproducible. This property (ρ_{pack}) is therefore a good indicator of the reproducibility of manufacture in a commercial setting. It is important that packed bed resistivity is consistent from column to column since it is a major determinant of voltage drop in a given segment (Eqs. (6) and (11)) and therefore field strength which determines, in part, mobile phase flow rate.

Resistivities of packed segments are, as expected, significantly greater than those of the open segments (Table 1). Total resistivity of the open column is least (5.24×10^3), and that of the column with the most packing is greatest (10.74×10^3).

3.3. Duplex structures—total versus segmental electrochemical properties

The relationship between the open, packed and total values of the various electrochemical properties depends upon the property. However, the open segments, as predicted, have the lowest resistivity, resistance, voltage drop, and field strength; and the highest conductivity and conductance. The packed segments have the highest resistivity and field strength but only intermediate (between total and open) resistance, conductivity and conductance. The CEC columns have the highest total voltage drop and resistance, but intermediate total resistivity and field strength. Thus, there is a complex relationship amongst the total, open and packed segmental properties, which nonetheless can be expressed precisely in Eqs. (16)–(27).

3.4. Field strength and L_e

Rathore and Horváth's [3] use of the equivalent packed bed length, rather than the true value, to calculate effective field strength is related to the fact that any given element of mobile phase must travel a tortuous path through the stationary phase. Thus, although the actual speed of the element may be greater, the apparent speed, as measured by the linear velocity (u_{eo}) is smaller. The value for L_e is always much larger than L_{pack} and consequently field strengths appear to be smaller, resulting in smaller values of u_{eo} .

3.5. Resistivities, resistances, conductivities and conductances

In qualitative terms, it can be gathered from the fact that if very small currents (I in μA) are generated from large voltages (V in kV), then column resistances must be high (R in billions of Ω) and conductances must be very low (λ in $\text{n}\Omega^{-1}$). Values of resistivity (ρ in $\text{k}\Omega\text{ cm}$) and conductivity (σ in $\text{m}\Omega^{-1}\text{ cm}^{-1}$) are seen to be intermediate between these limits. The reason for this intermediate nature is a direct result of the configuration of the standard capillary used in CEC. In other words, the ratio of the column length to interior cross-sectional area (L/A in cm^{-1}), is very high at about 450 000:1. Thus, when a low conductance is multiplied by this ratio, an intermediate value is obtained for conductivity. Similarly, the intermediate values of resistivity arise when the large column resistances are divided by the L/A ratio.

It can also be noted from Table 1 that conductances of both the packed and open segments are halved when their lengths are doubled. Conversely, resistances of these segments are doubled when segment lengths are doubled.

3.6. Electrochemical properties of the stationary phase in packed segments

Resistivities of the stationary phases (ρ_{phase}) in the packed segments of columns B and C are 35.10×10^3 and $43.1 \times 10^3 \Omega\text{ cm}$, respectively. These are approximately 7–9 times greater than the mobile phase resistivities (ρ_{open} is $5.24 \times 10^3 \Omega\text{ cm}$) and 2.5 times the value of ρ_{pack} for each column. It is to be expected that resistivities of solids are greater than those of liquids. The fact that they are not essentially infinite is due to the fact that the solid stationary phase is extensively solvated and therefore can pass current. There is a significant difference between the two values of ρ_{phase} implying that the preparation of the two packed segments proceeded differently.

It is of course possible to calculate other electrochemical properties of the stationary phase itself, by applying Eqs. (16)–(24) in a similar fashion.

The two porosities of the packed segments in columns B and C (0.73 and 0.75, respectively) are seen to be essentially identical and significantly larger than a typical porosity (0.52) of a packed HPLC column containing the same $3 \mu\text{m}$ particles. This latter value is calculated using the unretained peak time (t_0) and the flow rate under pressure. The greater porosity in the case of the CEC packed segments arises from the sol-gel method of preparing the packed columns. Ratnayake et al. [4,5] have shown that this is a normal result of the technique and is additionally reflected in the much greater specific permeability of their columns.

3.7. Other CEC column configurations

The discussion above concerned only duplex CEC columns (B and C). Similar mathematical treatment of more complex columns, which may consist of open segments separated by packed segments, would follow the same lines of reasoning. In general, the resistivities of open segments, no matter how many are present, are considered to be the same in all columns. Electrochemical properties of the packed segments are obtained essentially by subtraction.

In those cases where there are several packed segments of different chemical makeup (for example, a reversed-phase and an ion-exchange length) together in a given CEC column, it will be necessary to prepare duplex columns containing the open segment and one of the packed segments. This will enable the determination of the fundamental property of any segment type, its resistivity.

4. Conclusions

This article has essentially been a short presentation of the basics of electrochemistry applied to CEC columns. Because the typical CEC column consists of a packed and an open segment, their individual electrochemical properties are

quite different. The application of basic principles of electricity (Ohm's law) and knowledge of the lengths of the segments and I.D. of the capillary, are all that is necessary to calculate most electrochemical properties of the CEC column. These include voltage (V), current (I), resistance (R), resistivity (ρ), conductivity (σ), conductance (λ) and field strength (E) for each segment type, for the stationary phase itself and for the column as a whole. It has also been shown how the individual segment properties can be added together to produce the total column property. Voltages and resistances add simply but other properties are more complex in the way they add and involve reciprocal functions and ratios of segment lengths. The principles of additivity can be applied further to determine electrochemical properties of the bonded phase in the packed segment.

The equations above can be applied to any type of CEC column with any type of structure.

Acknowledgements

It is a pleasure to acknowledge the inspiration of Dr. Chan Oh, and the research environment at Beckman Coulter Inc.,

which encourages publications such as these. We wish to thank Dr. James C. Osborne, Dr. Stephen Pentoney and Dr. Michael Simonian, who show unfailing support of our writing. Finally, it is an honor to have the opportunity to contribute our work to the memory of Professor Csaba Horváth, whose rigorous development of CEC fundamentals expanded our horizons of understanding so immeasurably.

References

- [1] V. Pretorius, B.J. Hopkins, J.D. Schieke, *J. Chromatogr.* 99 (1974) 23.
- [2] C.L. Rice, R.J. Whitehead, *J. Phys. Chem.* 69 (1965) 4017.
- [3] A.S. Rathore, Cs. Horváth, *Anal. Chem.* 70 (1998) 3069.
- [4] C.K. Ratnayake, C.S. Oh, M.P. Henry, *J. Chromatogr. A* 887 (2000) 277.
- [5] C.K. Ratnayake, C.S. Oh, M.P. Henry, *J. High Resolut. Chromatogr.* 23 (2000) 81.