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Unsteady heat transfer in capillary zone electrophoresis

I. A mathematical model

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ABSTRACT

A solution to the problem of unsteady heat transfer in capillary zone electrophoresis is presented. A general set of partial differential equations for conjugated heat transfer in a capillary is formulated. An approximate analytical solution is obtained for a limiting case of a "thin-walled" capillary and for different regimes of a power supply (voltage-stabilized, power-stabilized or current-stabilized). An exact analytical solution is derived for transient times in the voltage-stabilized regime. It is shown that temperature evolution in a capillary can be described by the only eigenfunction with a corresponding exponential factor.

INTRODUCTION

Steady-state heat transfer in capillary zone electrophoresis (CZE) has been the subject of a number of publications [1–5]. However, unsteady phenomena such as transition of temperature and electric current to a steady-state were not considered previously. Experimental observations have shown that an increase in the power generation within a capillary and/or an increase in capillary radius lead to an increase in the time necessary to achieve stationary current values. Under certain conditions, current and temperature can increase substantially [4,5]. In order to study theoretically the transient heat transfer in a capillary, we formulated a set of partial non-linear integro-differential equations for unsteady heat transfer in a capillary cross-section taking into account the temperature dependence of electric conductivity [6].

In this paper an equation and its solution are derived for the average temperature in the capillary lumen. The exact solution of the equations for the case of the voltage-stabilized regime is obtained by using an expansion in eigenfunction series.

GOVERNING EQUATIONS

We consider a cross-section of a cylindrical structure consisting of an inner cylindrical lumen that contains an electrolyte solution (buffer), its wall, having different thermal properties, and the outer wall coating, with properties different from those of the electrolyte solution and the wall.

The temperature in the domain is governed by a set of equations [6] which can be represented in dimensionless form as follows:

$$\frac{\partial \vartheta}{\partial t} = \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial \vartheta}{\partial r}\right) + F \qquad 0 \leqslant r < 1 \qquad (1)$$

$$\frac{\partial \vartheta}{\partial t} = \kappa_{\mathrm{WL}} \cdot \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial \vartheta}{\partial r}\right) \qquad 1 \leqslant r < r_{\mathrm{W}} \qquad (2)$$

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$$\frac{\partial \vartheta}{\partial t} = \kappa_{\mathrm{PL}} \cdot \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial \vartheta}{\partial r}\right) \qquad r_{\mathrm{W}} \leqslant r < r_{\mathrm{P}} \tag{3}$$

$$\vartheta = \text{finite at } r = 0 \tag{4a}$$

$$\vartheta^{-} = \vartheta^{+}, \frac{\partial \vartheta^{-}}{\partial r} = \beta_{\mathrm{WL}} \cdot \frac{\partial \vartheta^{+}}{\partial r} \text{ at } r = 1 \tag{4b}$$

$$\vartheta^{-} = \vartheta^{+}, \frac{\partial \vartheta^{-}}{\partial r} = \beta_{\mathrm{PW}} \cdot \frac{\partial \vartheta^{+}}{\partial r} \text{ at } r = r_{\mathrm{W}} \tag{4c}$$

$$-\beta_{\mathrm{PL}} \cdot \frac{\partial \vartheta}{\partial r} = Bi(\vartheta - \vartheta_{\mathrm{C}}) \text{ at } r = r_{\mathrm{P}} \tag{4d}$$

$$\vartheta(r, t = 0) = \vartheta_{\mathrm{C}} \tag{5}$$

where r is the dimensionless radius measured in units of inner capillary diameter, ϑ is the dimensionless temperature, F the dimensionless heat source, t the dimensionless time, Bi the Biot number, κ_{WL} and κ_{PL} are the relative thermal diffusivities (temperature conductivities) of the wall and coat measured in units of the electrolyte thermal diffusivity and $\beta_{\mathrm{WL}} = \chi_{\mathrm{W}}/\chi_{\mathrm{L}}$, $\beta_{\mathrm{PW}} = \chi_{\mathrm{P}}/\chi_{\mathrm{W}}$, $\beta_{\mathrm{PL}} = \chi_{\mathrm{P}}/\chi_{\mathrm{L}}$ are the relative thermal conductivities (χ_{L}, χ_{W} and χ_{P} being the thermal conductivities of the electrolyte, wall and coating, respectively).

The dimensionless heat source term (volumetric power generation) is represented as follows:

$$F = 1 + k^2\vartheta \tag{6a}$$

for the voltage-stabilized mode of operation,

$$F = (1 + k^2\vartheta)/(1 + k^2\bar{\vartheta})^2 \tag{6b}$$

for the current-stabilized mode and

$$F = (1 + k^2\vartheta)/(1 + k^2\bar{\vartheta}) \tag{6c}$$

for the power-stabilized mode, where $\bar{\vartheta}$ is the average dimensionless temperature, given by

$$\bar{\vartheta} = 2 \int_0^1 \vartheta r \mathrm{d}r \tag{6d}$$

and k^2 is the autothermal parameter defined in ref. 6.

The average temperature of the buffer $\bar{\vartheta}$ is of great importance for CZE, as it influences the characteristics of an analyte and the buffer electric conductivity. The dimensionless electric current i is related to $\bar{\vartheta}$ as follows:

$$i = I/I_0 = 1 + k^2\bar{\vartheta} \tag{6e}$$

where I is the electric current at time t and I_0 is its initial value.

APPROXIMATE SOLUTION FOR AVERAGE TEMPERATURE

In this part we shall derive an approximate equation for the average temperature of the buffer and its solution in an analytical form.

We are mainly interested in the case of poor cooling conditions, as we assume the Biot number to be small in comparison with unity:

$$Bi \ll 1$$

This assumption allows us to assume that the temperature profile within the capillary is flat and close to a constant. In this case the possibility of finding an average temperature would be enough to describe the heat-conduction process. For deriving an equation for the average buffer temperature defined by eqn. 6d, we multiply eqn. 1 by $2r$ and integrate it from 0 to 1. The result is

$$\frac{\partial \bar{\vartheta}}{\partial t} = 2 \cdot \left.\frac{\partial \vartheta}{\partial r}\right|_{r=1} + \bar{F} \tag{7}$$

$$\bar{F} = 2 \int_0^1 F r \mathrm{d}r \tag{8}$$

By substituting eqns. 6a–c in eqn. 8, one obtains

$$\bar{F} = 1 + k^2\bar{\vartheta} \tag{8a}$$

for the voltage-stabilized mode of operation and

$$\bar{F} = 1/(1 + k^2\bar{\vartheta}) \tag{8b}$$

for the current-stabilized mode. For the power-stabilized mode, the integration gives

$$\bar{F} = 1 \tag{8c}$$

For deriving the approximate equation, we assume the capillary wall and coating to be thin in the sense that the characteristic times of temperature conduction through the wall and coating are much shorter than the characteristic time of temperature conduction in the lumen. This means validity of the following relationships:

$$p_{\mathrm{W}} \equiv r_{\mathrm{W}}(r_{\mathrm{W}} - 1)/\kappa_{\mathrm{WL}} \ll 1; \qquad p_{\mathrm{P}} \equiv r_{\mathrm{P}}(r_{\mathrm{P}} - r_{\mathrm{W}})/\kappa_{\mathrm{PL}} \ll 1 \tag{9}$$

where p_{W} and p_{P} are dimensionless parameters representing ratios of the characteristic times for temperature conduction in the wall and coating to the characteristic time of the lumen temperature conduction.

Assumption 9 allows us to neglect temporal derivatives on the left-hand sides of eqns. 2 and 3 and to consider them as quasi-steady. By seeking their solutions in the form

$$\begin{aligned} \vartheta &= B\ln(r) + C \qquad 1 \leqslant r < r_W \\ \vartheta &= D\ln(r) + E \qquad r_W \leqslant r < r_P \end{aligned} \tag{10}$$

where B, C, D and E are constants, and by applying boundary conditions 4b–d, one obtains

$$-\frac{\partial\vartheta}{\partial r}\bigg|_{r=1} = Bi_{OA}(\bar{\vartheta} - \vartheta_C) \tag{11}$$

$$Bi_{OA} = \beta_{WL}\left\{\ln(r_W) + \frac{1}{\beta_{PW}}\left[\ln(r_P/r_W) + \frac{\beta_{PL}}{r_P\, Bi}\right]\right\}^{-1} \tag{12}$$

By substituting eqn. 11 into eqn. 7 we can derive an approximate equation for the average temperature $\bar{\vartheta}$:

$$\frac{d\bar{\vartheta}}{dt} = -2Bi_{OA}(\bar{\vartheta} - \vartheta_C) + \bar{F} \tag{13}$$

Note that the coefficient Bi_{OA} given by eqn. 12 is exactly the overall Biot number [4].

The initial condition for eqn. 13 follows directly from eqn. 5:

$$\bar{\vartheta}(t = 0) = \vartheta_C \tag{14}$$

If the autothermal parameter k^2 is small (or, more strictly, $k^2\bar{\vartheta} \ll 1$), eqn. 8b, representing the heat source term for the current-stabilized mode, can be linearized as follows:

$$\bar{F} = 1 - k^2\bar{\vartheta} \tag{15}$$

and the governing equation for the average temperature of the buffer for all the modes of operation can be written in the following general form:

$$\frac{\partial\bar{\vartheta}}{\partial t} = -2Bi_{OA}(\bar{\vartheta} - \vartheta_C) + 1 + fk^2\bar{\vartheta} \tag{16}$$

where the factor f is

$$f = \begin{cases} 1 & \text{for the voltage-stabilized mode} \\ -1 & \text{for the current-stabilized mode} \\ 0 & \text{for the power-stabilized mode} \end{cases}$$

The solution of eqn. 16 with initial condition 14 is given by

$$\bar{\vartheta} = \bar{\vartheta}_s + [\vartheta_C - \bar{\vartheta}_s]\exp(-t/\tau) \tag{17}$$

$$\bar{\vartheta}_s = \frac{2Bi_{OA}\vartheta_C + 1}{2Bi_{OA} - fk^2} \tag{17a}$$

$$\tau = (2Bi_{OA} - fk^2)^{-1} \tag{17b}$$

where $\bar{\vartheta}_s$ is the steady-state (*i.e.*, independent of time) part of the solution and τ is the characteristic time of the transient process.

The linearization 15 of the heat source 8b is used only to show clearly the difference between the three modes of power supply operation. The exact solution of eqn. 13 with eqn. 8b can be obtained as this is an ordinary differential equation of first order with separable variables. The solution has the following form:

$$G(\bar{\vartheta}) - G(\vartheta_C) = -t \tag{18}$$

$$G(x) = \frac{1}{4Bi_{OA}}\cdot\ln(X) + d^{-1}\left(1 - \frac{b}{4Bi_{OA}}\right)\ln\left(\frac{2cx + b - d}{2cx + b + d}\right)$$

$X = a + bx + cx^2$, $a = -\vartheta_C - 1$, $b = 2Bi_{OA} - \vartheta_C k^2$, $c = 2Bi_{OA}k^2$, $d = 4c + (2Bi_{OA} + \vartheta_C k^2)^2$.

Solution 18 is not restricted by the condition $k^2\bar{\vartheta} \ll 1$ as is eqn. 15 but it is too complex; therefore, we shall use eqns. 17–17b wherever possible.

SOLUTION FOR THE EQUATION OF UNSTEADY HEAT TRANSFER

This part aims at finding a solution of eqns. 1–5 for the case of the voltage-stabilized mode of operation.

The solution of eqns. 1–5 can be represented as the sum of the temperature-independent function $\vartheta_s(r)$ (steady-state) and the function $\vartheta_u(r,t)$, the latter vanishing as time increases:

$$\vartheta(r,t) = \vartheta_s(r) + \vartheta_u(r,t) \tag{19}$$

The solution for $\vartheta_s(r)$ is straightforward (see ref. 7). In Appendix I we present this solution in our notation and for $\vartheta_C \neq 0$.

The solution for ϑ_u is found in the following form [8]:

$$\vartheta_u = \sum_{n=1}^{\infty} a_n \exp(-\lambda_n^2 t)\, g_n(r) \tag{20}$$

where a_n are constants and λ_n and $g_n(r)$ are the nth eigenvalue and eigenfunction of the differential operator $\boldsymbol{L}$ defined by the right-hand sides of eqns. 1–4 and the appropriate boundary conditions.

The operator $\boldsymbol{L}$ is given by

$$\boldsymbol{L}y = \begin{cases} \boldsymbol{L}_r y + k^2 y & 0 \leqslant r < 1 \\ \dfrac{\partial y^-}{\partial r} = \beta_{\mathrm{WL}} \cdot \dfrac{\partial y^+}{\partial r},\ y^- = y^+, & r = 1 \\ \kappa_{\mathrm{WL}}\, \boldsymbol{L}_r y & 1 < r < r_{\mathrm{W}} \\ \dfrac{\partial y^-}{\partial r} = \beta_{\mathrm{PW}} \cdot \dfrac{\partial y^+}{\partial r},\ y^- = y^+, & r = r_{\mathrm{W}} \\ \kappa_{\mathrm{PL}}\, \boldsymbol{L}_r y & 1 < r < r_{\mathrm{W}} \\ -\beta_{\mathrm{PL}} \cdot \dfrac{\partial y}{\partial r} = Biy & r = r_{\mathrm{P}} \end{cases} \tag{21}$$

where $\boldsymbol{L}_r \equiv \frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial}{\partial r}\right)$ is the radial part of the Laplace operator in the cylindrical coordinates.

The details of the solution for eigenvalues and eigenfunctions are given in Appendix II. The characteristic times of decay of the exponents 20 and, therefore, of the transition to the steady-state are given by

$$\tau_i = 1/\lambda_n^2 \tag{22}$$

where $\tau_1 > \tau_2 > \ldots > \tau_n$.

It is worth noting that if $\tau_1 \gg \tau_n$ and $a_1 \gg a_n$ then the temporal behaviour of the process is determined by τ_1, which should be considered as the transient time in general. It will be shown below that this is indeed the case.

CALCULATIONS OF TRANSIENT TIMES AND IMPROVEMENT OF THE APPROXIMATE SOLUTION FOR AVERAGE TEMPERATURE

In the following calculations we shall use the dimensionless parameters listed in Table I. These parameters correspond to physical parameters of the buffer, fused silica and polyimide [6].

TABLE I

DIMENSIONLESS PARAMETERS USED FOR COMPUTER SIMULATIONS

Parameter	Value	Parameter	Value
κ_{WL}[a]	4.78	β_{PL}	0.262
κ_{PL}	0.71	β_{PW}	0.107
β_{WL}[b]	2.46		

[a] Relative thermal diffusivity.

[b] Relative thermal conductivity.

The ratio of two first characteristic times τ_1/τ_2 as a function of the Biot number Bi is shown in Fig. 1 for $r_{\mathrm{W}} = 2.125$, $r_{\mathrm{P}} = 2.28$ and $k^2 = 0.05$. It can be seen that the first characteristic time τ_1 is considerably greater than the second. This allows us to leave in the expansion 20 only the first term and to describe approximately the evolution of the temperature of the buffer by the following equation:

$$\vartheta(r,t) = \vartheta_s(r) + a_1 J_0(\sqrt{\lambda_1^2 + k^2}r)\exp(-t\lambda_1^2) \tag{23}$$

where $J_0(x)$ is the Bessel function of the zeroth order of the first kind and a_1 and λ_1^2 are given by the procedure described in Appendix II. These results also permit the identification of the characteristic time of the heat transfer process with the time τ_1.

By substituting eqn. 23 into eqn. 6d and inte-

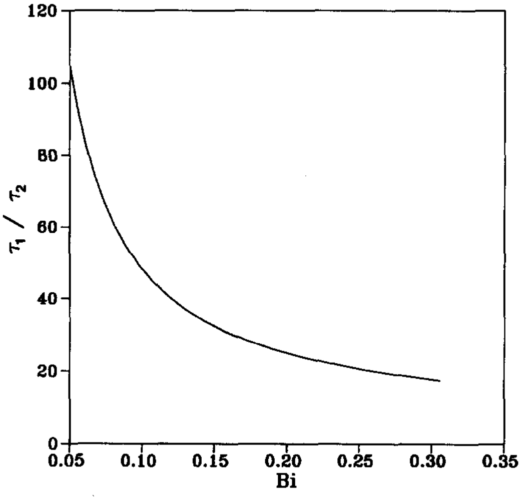

Fig. 1. Ratio of two first characteristic times τ_1/τ_2 as a function of the Biot number; $r_{\mathrm{W}} = 2.125$, $r_{\mathrm{P}} = 2.28$, $k^2 = 0.05$. Note that the Biot number represents the ratio between the thermal conductivity of the wall (in this case the fused-silica capillary) and the product of the thermal conductivity of the liquid contained therein times its dimensionless thickness. The relevant equations for the Biot number are given in Part II (eqns. 4e and 7e).

grating the Bessel function [9], one obtains for the average temperature $\bar{\vartheta}$

$$\bar{\vartheta} = \bar{\vartheta}_s + 2a_1 \cdot \frac{J_1(\sqrt{\lambda_1^2 + k^2})}{\sqrt{\lambda_1^2 + k^2}} \exp(-t/\tau_1) \qquad (24a)$$

$$\bar{\vartheta}_s = 2A \cdot \frac{J_1(k)}{k} - 1/k^2 \qquad (24b)$$

where $J_1(x)$ is the Bessel function of the first order of the first kind and the coefficient A is given by eqn. A1.5b.

The use of eqns. 23 and 24 instead of the series given by eqn. 20 leads to an error at the very beginning of the transient process, at times of the order of τ_2 which are much less then the duration of the transient process as a whole. With the same degree of accuracy we can simplify eqn. 24a as follows:

$$\bar{\vartheta} = \bar{\vartheta}_s[1 - \exp(-t/\tau_1)] \qquad (25)$$

Fig. 2 compares the exact characteristic time τ_1 and approximate solution given by eqn. 17b for $p_W = p_P = 0.1, k^2 = 0.1$ ($r_W = 1.353, r_P = 1.404$). It can be seen that the approximate and exact characteristic times agree qualitatively. Our calculations show that for smaller values of p_W and p_P the agreement is better, in accord with assumption 9.

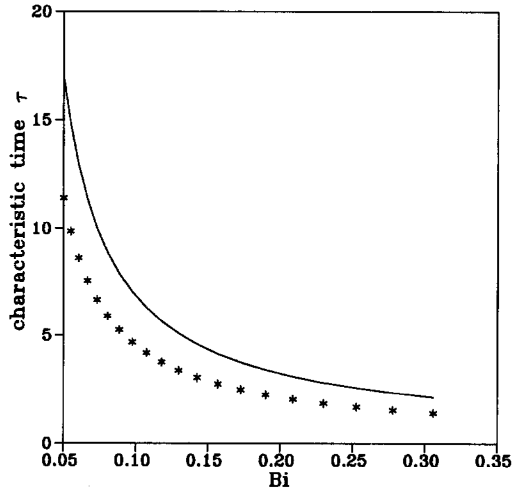

Fig. 2. Comparison of an exact characteristic time τ_1 (solid line) and the approximate solution (symbols) given by eqn. 17b, $p_W = p_P = 0.1$, $k^2 = 0.1$ ($r_W = 1.353$, $r_P = 1.404$).

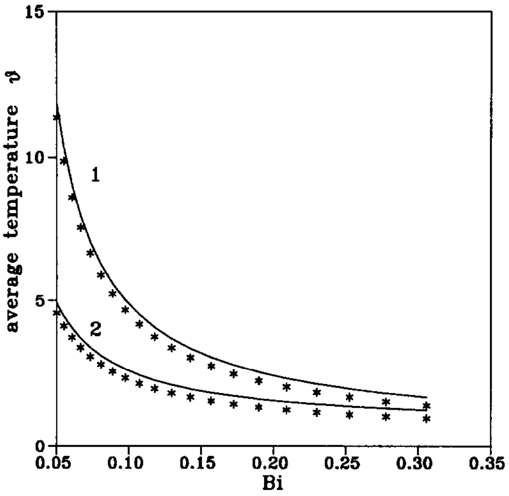

Fig. 3. Comparison of the exact average stationary (solid lines) (eqn. 24b) and approximate (symbols) (eqn. 17a) temperatures; $p_W = p_P = 0.1$, $k^2 = 0.05$ (curves 1); $p_W = p_P = 1$, $k^2 = 0.05$ (curves 2).

A comparison of the exact (eqn. 24b) and approximate (eqn. 17a) average stationary temperatures is given in Fig. 3 for $p_W = p_P = 0.1$, $k^2 = 0.05$ (curves 1) and for $p_W = p_P = 1, k^2 = 0.05$ (curves 2). It is seen from Fig. 3 that the curves corresponding to the approximate and exact solutions are in good agreement for different Biot numbers. Therefore, it is possible to use a simple approximate expression for temperature evaluation (eqn. 17a). By substituting eqn. 17a into eqn. 6e, one obtains for a stationary electric current in the voltage-stabilized mode

$$i_s = \frac{2Bi_{OA}(\vartheta_C k^2 + 1)}{2Bi_{OA} - k^2} \qquad (26)$$

This equation can be used for estimations of the overall Biot number of a given capillary and cooling system or, otherwise, to determine the properties of the buffer.

DISCUSSION

A solution of unsteady heat transfer in CZE has been given for the general case of capillary and cooling conditions and approximate equations and their solutions for average temperature have been derived for different modes of power supply operation. The temporal behaviour of temperature in CZE can be described by an exponent for small Biot numbers (poor cooling). A procedure has been given for finding the characteristic time of an unsteady process from a solution of an eigenvalue problem for conjugated heat transfer. The approximate equation for the characteristic time is valid for "thin-walled" capillaries. The approximate equations for stationary temperature and current can be used instead of exact equations for small Biot numbers.

The problem of heat evolution in electrophoretic techniques is not a trivial one. In the particular case of CZE, where this problem has been extensively studied both theoretically and experimentally, the following general conclusions can be drawn.

According to the original equation proposed by Jorgenson [10], the plate number N is directly proportional to the applied voltage gradient (E). In their experiments, N increased linearly with E with a tendency for plateauing at high E values. There is now a general consensus [4,11,12] that this is not the case: at high field strengths (varying according to several experimental parameters, such as molarity of background electrolyte and capillary radius, but in general above 200 V/cm) there exists a maximum in the experimental dependence of N *vs.* E, explained in terms of joule heat.

According to Jones *et al.* [13], at increasing applied potentials, the slope of the peak variance *versus* time plot increases in magnitude. If only molecular diffusion were causing this time-dependent variance, there should be a negligible slope change over the experimental range of applied voltages, as the calculated temperature increase was less than 1°C. According to Jones *et al.*, at high field strengths joule heating is approximately twice as significant than any other "non-ideal" flow contribution to solute band spreading.

As will be indicated in the accompanying Part II, a way to minimize temperature gradients would be to resort to narrow-bore capillaries and/or lower the conductivity of the background electrolyte. However, by decreasing the concentration of the operative buffer one could obtain highly skewed peaks due to a mismatch of the respective conductivities of analyte and buffer. In addition, in very narrow bore capillaries (*e.g.*, 25 μm diameter) zone detection could be problematic.

Perhaps, as suggested by Jansson *et al.* [14], a good solution would be to adopt rectangular cross-section capillaries. When the aspect ratio is increased from 1 (cylindrical) to 25 (highly flattened) capillaries, owing to the strongly increased heat dissipation in the rectangular conduit, the temperature increase is negligible even at E values well above 1000 V/cm. Moreover, if detection is made through the long side of the rectangle, sensitivity is increased even at progressively decreasing channel heights. Jansson *et al.* also proposed the use of rectangular silicon capillaries, as silicon has a *ca.* 100 times higher heat conductivity than fused silica.

According to a recent study [15], the overall column temperature could have a profound impact on protein separation and analysis. For example, on going from 20 to 45°C, myoglobin showed a progressive reduction from the Fe^{3+} form to the Fe^{2+} form. In the same temperature range, α-lactalbumin demonstrated a conformational transition that resulted in asymmetric peaks and sigmoidal mobility *vs.* temperature plots. Hence the importance of cooling the capillary, even below room temperature (at 2–4°C), as is customarily done in other electrophoretic techniques [16], for protein analysis, cannot be over-emphasized.

Another important aspect of operating at varying column temperatures is that the sample volume injected (*e.g.*, by pressure loading) could also vary substantially. Rush *et al.* [15] calculated that in the column temperature range 15–50°C, there will be a 70% increase in the sample volume injected.

SYMBOLS (PARTS I AND II)

a	Temperature coefficient of electric conductivity
β_{PL}	Relative thermal conductivity of polyimide coating
β_{WL}	Relative thermal conductivity of fused-silica wall
Bi	Biot number
C_L	Specific heat capacity of liquid (buffer inside the capillary)
C_P	Specific heat capacity of the capillary polyimide coating
C_W	Specific heat capacity of the capillary fused-silica wall
E	Electric field strength
$\bar{\vartheta}$	Average dimensionless temperature
F	Volumetric power generation
h	Coefficient of external heat transfer

i	Dimensionless electric current
I	Electric current
J_0	Bessel function of the zeroth order of the first kind
k^2	Autothermal parameter
k_{PL}	Relative thermal diffusivity of polyimide coating
k_{WL}	Relative thermal diffusivity of fused-silica wall
Nu	Nusselt number
Pr	Prandtl number
q_0	Initial dissipated power per unit volume
q	Joule heat generation
ρ_L	Density of the buffer inside the capillary
ρ_P	Density of the capillary polyimide coating
ρ_W	Density of the capillary fused-silica wall
Ra	Rayleigh number
Re	Reynolds number
R_L	Radius of the capillary lumen
R_P	Radius of the capillary polyimide coating
R_W	Radius of the capillary fused-silica wall
r	Dimensionless radius (in units of inner capillary diameter)
σ	Buffer electric conductivity
t	Dimensionless time
T_c	Temperature of coolant
τ	Time of a transient process
Y_0	Bessel function of the zeroth order of the second kind

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APPENDIX I

Steady-state radial temperature distribution

By substituting $\vartheta_s(r)$ in eqns. 8–14a, one obtains

$$\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\cdot\frac{\partial\vartheta_s}{\partial r}\right)+1+k^2\vartheta_s=0 \qquad 0\leqslant r<1 \qquad \text{(A1.1)}$$

$$\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\cdot\frac{\partial\vartheta_s}{\partial r}\right)=0 \qquad 1\leqslant r<r_P \qquad \text{(A1.2)}$$

$$\vartheta_s = \text{finite at } r = 0 \qquad \text{(A1.3a)}$$

$$\vartheta_s^- = \vartheta_s^+,\ \frac{\partial\vartheta_s^-}{\partial r} = \beta_{WL}\cdot\frac{\partial\vartheta_s^+}{\partial r} \text{ at } r = 1 \qquad \text{(A1.3b)}$$

$$\vartheta_s^- = \vartheta_s^+,\ \frac{\partial\vartheta_s^-}{\partial r} = \beta_{PW}\cdot\frac{\partial\vartheta_s^+}{\partial r} \text{ at } r = r_W \qquad \text{(A1.3c)}$$

$$-\beta_{PL}\cdot\frac{\partial\vartheta_s}{\partial r} = Bi(\vartheta_s - \vartheta_C) \text{ at } r = r_P \qquad \text{(A1.3d)}$$

We seek the solution in the form

$$\begin{aligned} \vartheta_s &= AJ_0(kr) - \frac{1}{k^2} && 0 \leqslant r < 1 \qquad \text{(A1.4)}\\ \vartheta_s &= B\ln(r) + C && 1 \leqslant r < r_W\\ \vartheta_s &= D\ln(r) + E && r_W \leqslant r < r_P \end{aligned}$$

where $J_0(x)$ is the Bessel function of the zeroth order of the first kind. The five constants A, B, C, D and E should be determined from the boundary conditions (eqns. A1.3b–d). Substitution of eqn. A1.4 into eqns. A1.3b–d gives the following set of equations for the constants:

$$\begin{aligned} &AJ_0(k) - \frac{1}{k^2} = C\\ &-AkJ_1(k) = \beta_{WL}B\\ &B\ln(r_W) + C = D\ln(r_W) + E \qquad \text{(A1.5a)}\\ &B = \beta_{PW}D\\ &-\beta_{PL}\cdot\frac{D}{r_P} = Bi[D\ln(r_P) + E - \vartheta_C] \end{aligned}$$

where $J_1(x)$ is the Bessel function of the first-order of the first kind.

Solving this set of equations, one obtains

$$A = \frac{Bi_{OA}(1 + k^2\vartheta_C)}{Bi_{OA}J_0(k) - kJ_1(k)} \qquad \text{(A1.5b)}$$

where

$$Bi_{OA} = \beta_{WL}\left\{\ln(r_W) + \frac{1}{\beta_{PW}}\left[\ln(r_P/r_W) + \frac{\beta_{PL}}{r_P\,Bi}\right]\right\}^{-1} \qquad \text{(A1.6)}$$

is the dimensionless coefficient of proportionality of the heat flux from the inner surface of the lumen to the temperature difference between the inner surface and the coolant.

APPENDIX II

Calculation of eigenvalues, eigenfunctions and coefficients for the unsteady solution.

We seek an eigenfunction of the operator **L** in the following form:

$$g_\lambda(r) = \begin{cases} AJ_0(r\sqrt{\lambda^2+k^2}) & 0 \leqslant r < 1 \\ BJ_0(\lambda r/\sqrt{\kappa_{\mathrm{WL}}}) + CY_0(\lambda r/\sqrt{\kappa_{\mathrm{WL}}}) & 1 < r < r_{\mathrm{W}} \\ DJ_0(\lambda r/\sqrt{\kappa_{\mathrm{PL}}}) + EY_0(\lambda r/\sqrt{\kappa_{\mathrm{PL}}}) & 1 < r < r_{\mathrm{W}} \end{cases} \tag{A2.1}$$

where $Y_0(x)$ is the Bessel function of the zeroth order of the second kind.

Substitution of eqn. A2.1 into the boundary conditions included in the definition of the operator **L** leads to the set of equations for the determination of unknown constants A, B, C, D and E:

$$\begin{aligned} &AJ_0(\sqrt{\lambda^2+k^2}) - BJ_0(\lambda/\sqrt{\kappa_{\mathrm{WL}}}) - CY_0(\lambda/\sqrt{\kappa_{\mathrm{WL}}}) = 0 \\ &A\sqrt{\lambda^2+k^2}J_1(\sqrt{\lambda^2+k^2}) - B\sqrt{\beta_{\mathrm{WL}}}\lambda J_1(\lambda/\sqrt{\kappa_{\mathrm{WL}}})/\sqrt{\kappa_{\mathrm{WL}}} - C\sqrt{\beta_{\mathrm{WL}}}\lambda Y_1(\lambda/\sqrt{\kappa_{\mathrm{WL}}})/\sqrt{\kappa_{\mathrm{WL}}} = 0 \\ &BJ_0(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{WL}}}) + CY_0(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{WL}}}) - DJ_0(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{PL}}}) - EY_0(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{PL}}}) = 0 \qquad \text{(A2.2)} \\ &\frac{1}{\sqrt{\kappa_{\mathrm{WL}}}}[BJ_1(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{WL}}}) + CY_1(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{WL}}})] - \frac{\beta_{\mathrm{PW}}}{\sqrt{\kappa_{\mathrm{PL}}}}[DJ_1(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{PL}}}) + EY_1(\lambda r_{\mathrm{W}}/\sqrt{\kappa_{\mathrm{PL}}})] = 0 \\ &\lambda\beta_{\mathrm{PL}}[DJ_1(\lambda r_{\mathrm{P}}/\sqrt{\kappa_{\mathrm{PL}}}) + EY_1(\lambda r_{\mathrm{P}}/\sqrt{\kappa_{\mathrm{PL}}})]/\sqrt{\kappa_{\mathrm{WL}}} - Bi[DJ_0(\lambda r_{\mathrm{P}}/\sqrt{\kappa_{\mathrm{PL}}}) + EY_0(\lambda r_{\mathrm{P}}/\sqrt{\kappa_{\mathrm{PL}}})] = 0 \end{aligned}$$

The linear uniform system of eqns. A2.2 has a non-trivial solution when the determinant of the system is equal to zero. This condition gives an equation for eigenvalues the solution of which is obtained numerically. The Bessel functions are computed by using programs from ref. 17. For calculating the eigenfunctions corresponding to the found eigenvalues, the coefficient A is set equal to 1 and the remaining coefficients are determined from the set of equations obtained from eqns. A2.2 by setting $A = 1$ and omitting the last equation.

In order to find the coefficients a_n we substitute eqns. 19 and 20 into the initial condition 5, thus obtaining

$$\vartheta_{\mathrm{C}} - \vartheta_{\mathrm{s}} = \sum_{n=1}^{N} a_n g_n(r) \tag{A2.3}$$

where N is the number of eigenfunction used in the expansion. Multiplying eqn. A2.3 by $rg_m(r)$ ($m = 1, \ldots, N$) and integrating with respect to r, one obtains a set of N linear algebraic equations for N unknowns a_n:

$$\sum_{n=1}^{N} a_n(g_n g_m) = \vartheta_m, \quad m = 1, \ldots, N \tag{A2.4}$$

$$(g_n g_m) = \int_0^{r_{\mathrm{P}}} g_n g_m r\mathrm{d}r, \quad \vartheta_m = -\int_0^{r_{\mathrm{P}}} \vartheta_{\mathrm{s}} g_m r\mathrm{d}r$$

The set of eqns. A2.4 was solved by Gauss–Jordan elimination with pivoting [17].

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