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A highly accurate, inexpensive procedure for computing integral transformation kernel and its moment integrals for cylindrical wire electrodes

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ABSTRACT

Cylindrical wire or fiber electrodes are attractive for electro-analytical applications, but the theory of transient methods at such electrodes is complicated, necessitating approximate expressions or procedures for computing various special functions occurring in the theory. One of such functions is the integral transformation kernel function corresponding to semi-infinite pure diffusion conditions. In the present work a highly accurate and computationally inexpensive procedure for computing the cylindrical contribution to this kernel function is presented. The procedure relies on local polynomial approximations covering the entire argument domain, and it provides at least 14–15 significant digits. The procedure also computes qth order moment integrals of the kernel function (where $q \geqslant 0$ is a real number). The relative accuracy of 14–15 digits, of the moment integrals, has been verified for $q = 0$, 1 and 2. The procedure can be used in conjunction with numerical algorithms for the solution of integral equations or for the convolution analysis of experimental transients. It can also be used for the computation of chronopotentiometric responses to the programmed current density following the power-time dependence $i(t) = i_0 t^q$ with integer $q \geqslant 0$, which is shown as an example application.

1. Introduction

Cylindrical wire or fiber macro- and micro-electrodes [1–3] are attractive for kinetic or electro-analytical applications [4,5]. Unfortunately, the theory of transient experiments [6] for such electrodes is more complicated than in the case of planar or spherical electrodes, necessitating some kind of numerical approximations in almost all theoretical considerations. Contemporary digital simulation methods [7] based on the direct numerical solution of partial differential equations present one possible approach to obtaining such numerical approximations. Methods of this kind are increasingly often utilised with the help of relevant commercial software packages. However, voices can be heard, from prominent theoreticians [8], that the electrochemists "being content to rely on commercial packages based on obscure algorithms (···) may come to have only a shallow understanding of the processes taking place in their cells", and that "the advent of commercial software is now leading to rapid data interpretation, but at the price of deeply misconstruing the underlying mathematics". For this reason, theoretical approaches based on analytical or semi-analytical solutions of the electro-analytical models should be preferable over direct simulations whenever possible, as they necessitate more intellectual commitment than the blind uses of the black-box software, and thereby ensure a more satisfactory level of scientific insight and understanding. However, in order to make the analytical or semi-analytical approaches feasible, a need arises for accurate and efficient procedures of computing various special functions that occur in the analytical theory of transient methods at cylindrical wire electrodes.

In the present paper we describe a highly accurate and inexpensive procedure for computing a few special functions related to the integral transformation kernel specific for cylindrical wire electrodes under pure diffusion transport in semi-infinite medium. As was shown by Aoki et al. [9], the relationship between the concentration $c_i(r_0, t)$ of any ith species and its flux $D_i \partial c_i(r,t)/\partial r|_{r=r_0}$ at the surface of a wire electrode with radius r_0 and at time t, is given by the convolution formula:

$$c_i(r_0,t) = c_i^* - D_i^{-1/2} \int_0^t K_i(t,\tau)[D_i \partial c_i(r,\tau)/\partial r|_{r=r_0}]d\tau. \quad (1)$$

Here c_i^* is the initial/bulk concentration of the species, D_i is its diffusion coefficient, and $K_i(t, \tau)$ is the aforementioned integral transformation kernel:

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$$K_i(t,\tau) = \rho_i \phi(\rho_i^2 (t-\tau)), \tag{2}$$

where $\rho_i = D_i^{1/2}/r_0$, and $\phi(\theta)$ (with θ standing for $\rho_i^2(t-\tau)$) has the following Laplace transform $\hat{\phi}(s)$:

$$\hat{\phi}(s) = \mathscr{L}\{\phi(\theta)\} = \frac{K_0(s^{1/2})}{s^{1/2} K_1(s^{1/2})}. \tag{3}$$

In Eq. (3) s is the Laplace variable (the Laplace transformation $\mathscr{L}\{\cdots\}$ is from the θ domain to the s domain), and $K_0(z)$ and $K_1(z)$ are modified Bessel functions of the second kind and orders 0 and 1, respectively. The transform $\hat{\phi}(s)$ cannot be inverted analytically, so that an approximate procedure for computing $\phi(\theta)$, and hence $K_i(t,\tau)$, is necessary. Such a procedure is described in this work, together with provisions for computing qth order moment integrals $\int_0^\theta \phi(\vartheta)\vartheta^q \, d\vartheta$ of $\phi(\theta)$, where $q \geqslant 0$ is a real number (the 0th order moment integral is just the ordinary integral of $\phi(\theta)$).

Accurate procedures for the computation of the transformation kernel functions and their moment integrals (for any electrode geometry) are of interest for a number of reasons. First, these functions occur in the algorithms for the numerical solution of electrochemical integral equations [10] resulting from the convolution relationships such as Eq. (1). A number of the algorithms makes use of the following idea: if the unknown species flux $D_i \partial c_i(r,\tau)/\partial r|_{r=r_0}$ in Eq. (1) is expanded into a truncated power series with respect to the variable τ, then the integral in Eq. (1) becomes a certain linear combination of the moment integrals of the kernel function, involving successive, qth powers of τ, with $q = 0, 1, \ldots$ In the case of cylindrical wire electrodes these moment integrals are related to the aforementioned moment integrals $\int_0^\theta \phi(\vartheta)\vartheta^q \, d\vartheta$ by a change of variables. In order to find the solution of the integral equation, the coefficients of the power series must be determined. In particular, the adaptive Huber method recently developed by the present author [11–14] approximates the unknown flux locally by (piecewise) linear functions of τ, which implies that moment integrals for $q = 0$ and 1 are needed for computing the numerical solution for the flux, and additionally the moment integral for $q = 2$ allows estimation of the numerical error. Higher order terms of the power series are neglected. Therefore, in order to extend the method to integral equations specific for the cylindrical wire electrodes, approximations to the moment integrals with $q = 0$, 1 and 2, for the kernel (2) are needed. The approximations must be highly accurate in order to maintain the level of accuracy of the adaptive Huber method, achievable for other kernel functions. This application has been the main motivation for the present work, and the extension of the adaptive Huber method to cylindrical wire electrodes will be presented in a future paper. Second, similar needs arise in the algorithms for performing the generalised convolution analysis of the experimental transients (see, for example, Refs. [15,16] for the discussion of the convolution analysis for cylindrical wire electrodes). The algorithms are largely analogous to those used for solving integral equations, since convolution integrals such as the integral in Eq. (1) have to be computed numerically in both cases. In particular, the convolution algorithm from Refs. [15,16] makes use of the double integral of $\phi(\theta)$, for which the integration by parts gives (in view of the 0th order moment integral tending to zero when the integration interval reduces to zero):

$$\int_0^\theta \int_0^\vartheta \phi(\eta) \, d\eta \, d\vartheta = \theta \int_0^\theta \phi(\vartheta) \, d\vartheta - \int_0^\theta \phi(\vartheta)\vartheta \, d\vartheta, \tag{4}$$

meaning that the double integral can be expressed in terms of the 0th and first order moment integrals of $\phi(\theta)$. Third, the 0th order moment integral of $\phi(\theta)$ occurs in the theory of constant current chronopotentiometry at cylindrical wire electrodes [17–20], and the moment integrals for integer $q = 1, 2, \ldots$ are expected to occur in the theory of chronopotentiometry with the programmed current density following the power-time dependence: $i(t) = i_0 t^q$, in the case of integer exponents q (see Section 3 later). Such a variant of chronopotentiometry has been considered advantageous (over constant current chronopotentiometry) by a number of authors (see, for example, Refs. [21–26]), but the relevant theory for cylindrical wire electrodes still appears unavailable, with the exception of the case of $q = 1/2$ [21].

There have been very few attempts to obtain approximate expressions for $\phi(\theta)$ and its moment integrals. One approximation can be obtained from the asymptotic series for the transform $\hat{\phi}(s)$ in the limit of large s. The inverse Laplace transforms of the $N+1$ successive terms of the series can be obtained analytically, which gives [15,16] the following approximation to $\phi(\theta)$, valid for small θ:

$$\phi(\theta) \approx (\pi\theta)^{-1/2} - \sum_{v=0}^{N} a_v^0 x^v, \tag{5}$$

where $x = \theta^{1/2}$. The first few coefficients a_v^0 are given in Table 1. Analytical integration of Eq. (5) gives a related approximation to $\int_0^\theta \phi(\vartheta) \, d\vartheta$ [17,18,20]. There are also other formulae and approximations to $\int_0^\theta \phi(\vartheta) \, d\vartheta$. One of them is the identity [17,19,20,27]:

$$\int_0^\theta \phi(\vartheta) \, d\vartheta = \frac{4}{\pi^2} \int_0^\infty \frac{1 - \exp(-u^2\theta)}{u^3 \left[J_1^2(u) + Y_1^2(u)\right]} \, du, \tag{6}$$

where $J_1(z)$ and $Y_1(z)$ are the Bessel functions of the first and second kind, respectively, and of order one. The integral in the right-hand side of Eq. (6) can be evaluated numerically. A series expansion valid for large θ is also known:

$$\int_0^\theta \phi(\vartheta) \, d\vartheta = \frac{\zeta}{2} + \frac{\zeta + 1}{4\theta} - \frac{(3+\pi^2)/2 - \zeta - 3\zeta^2}{32\theta^2} + \cdots, \tag{7}$$

where $\zeta = \ln(4\theta) - \gamma$, with γ denoting the Euler gamma constant 0.57722... Carslaw and Jaeger [27] gave the first two terms of this series; the third term was derived by Dornfeld and Evans [28]. Yet another approximation, claimed to have an accuracy of 3% for θ ranging from 0 to 10^4, was proposed in Ref. [20]:

$$\int_0^\theta \phi(\vartheta) \, d\vartheta \approx [2(\theta/\pi)^{1/2} - \theta/2] \exp(-1.44\theta^{1/2}) + 0.484 \ln(\theta + 0.33) + 0.517. \tag{8}$$

Apart from the formulae (5)–(8), approximate values of $\phi(\theta)$ can be computed by the algorithms for the numerical inversion of the Laplace transform, advocated for electrochemical applications by Montella and co-workers [29–31].

Table 1
The first few coefficients a_v^0 of the asymptotic approximation (5). The coefficients have been obtained by invoking the MATHEMATICA program [33] command Series[BesselK[0, z]/BesselK[1, z], {z, ∞, 20}] to find 20 terms of the asymptotic expansion of $K_0(z)/K_1(z)$ for large z, and next by applying the InverseLaplaceTransform[···] command to the successive expansion terms of $\hat{\phi}(s)$, to obtain their inverse transforms.

v	a_v^0
0	1/2
1	$-3/(4\pi^{1/2})$
2	3/8
3	$-21/(32\pi^{1/2})$
4	27/64
5	$-633/(640\pi^{1/2})$
6	27/32
7	$-181161/(71{,}680\pi^{1/2})$
8	10809/4096
9	$-382281/(40{,}960\pi^{1/2})$
10	917541/81,920