



# Automatic solution of integral equations pertinent to diffusion with first order homogeneous reactions at cylindrical wire electrodes

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## ABSTRACT

The application of the integral equation method to the modelling of controlled-potential transient experiments at cylindrical wire or fibre electrodes under conditions of diffusion coupled with (pseudo-) first order homogeneous reactions, was not attempted thus far. One of the reasons is the lack of simple closed-form formulae for the relevant integral transformation kernels. The algorithm presented in this work allows one to compute accurately (at least 13–15 significant digits) moment integrals of the kernel that most frequently occurs in such cases. It is assumed that the cylinder length to radius ratio is very large. The algorithm is combined with the recently developed adaptive Huber method for solving electrochemical integral equations. The resulting method is tested on example integral equations, including the equations of cyclic voltammetry for the catalytic mechanism, for which no former simulation reports have been available. The method provides automatic solutions with an accuracy that can be effectively achieved by choosing an appropriate value of the error tolerance parameter. Errors as small as  $10^{-6}$  (relative to the maximum solution value) or even smaller, are obtainable, at a moderate computational cost. In this way, a variety of integral equations pertinent to cylindrical wire electrodes can now be solved easily and reliably.

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## 1. Introduction

The present work is a continuation of the long-term research program [1] devoted to the development of automatic digital simulation methods [2] and problem solving environments [3,4] for the modelling of electrochemical transient experiments [5]. The general objective of this program is to extend the contemporary ideas of laboratory automation in electroanalytical chemistry [6–8] onto the activities of theoretical modelling and simulation [2,9]. The particular objective of the present paper is to describe an extension of the recently elaborated [10–16] adaptive Huber method for automatically solving electrochemical Volterra integral equations (IEs) arising in electroanalytical chemistry. The extension refers to solving the IEs characteristic of diffusion coupled with homogeneous reactions at cylindrical wire (or fibre) electrodes. Although the recent addition [17,18] to the method allowed one to simulate diffusion at such electrodes, homogeneous reactions could not be handled.

The usefulness of cylindrical wire electrodes is well known [19,20]. Theoretical modelling of transient experiments at such

electrodes is therefore of interest. The modelling has been accomplished thus far almost exclusively by means of the digital simulation based on the direct numerical solution methods for partial differential equations describing the experiments [2]. The method of the IEs has been rarely used. Very few former examples of the IEs for cylindrical wire electrodes, pertinent to diffusion without homogeneous reactions, have been listed in Ref. [18]. To the knowledge of the present author, there are no published examples of IEs representing diffusion coupled with homogeneous reactions at cylindrical wire electrodes. This has to be contrasted with other standard types of electrodes (planar and spherical), for which the literature contains numerous examples of the IEs, both for the pure diffusion, and for the homogeneous reaction–diffusion systems (see, in particular, the seminal paper of Nicholson and Shain [21]). One reason why theoreticians choose the method of the IEs, whenever it can be applied, is its semi-analytical character. The method offers a possibility of formula manipulation and deduction of various properties of the solutions in an analytical way, without relying exclusively on numerical results, although the numerical solution of the IEs is also involved in most of the cases. Hence, the theoretical modelling based on the IEs can be a remedy against blind uses of the contemporary black-box digital simulation software, which may easily lead to misinterpretations and wrong understanding [22].

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The main problem with using the IE method for cylindrical electrodes is that the integral transformation kernel function for diffusion in cylindrical geometry cannot be expressed by a simple closed-form formula. In order to facilitate the modelling, a highly accurate and computationally inexpensive procedure for computing the kernel function (and related moment integrals) has been elaborated by the present author [17], and incorporated into the adaptive Huber method [18]. This opened a way to convenient applications of the IE method, since the IEs corresponding to the pure diffusion to cylindrical wires can now be solved reliably and automatically. The approximate formulae for the kernel function can also be manipulated analytically, if the need arises. An alternative way of approximating the kernel function for diffusion at cylindrical wire electrodes has also been recently described by Phillips and Mahon [23]. The present work builds upon Refs. [17,18], to allow one to simulate homogeneous reactions as well.

Similar to Refs. [17,18], throughout this paper we assume that the cylinder length to radius ratio is very large, so that there are no significant end effects. The consideration of such effects would require a solution of a spatially two-dimensional model. There have been no reports of the simulation of the end effects at cylindrical wire electrodes by the IE method, but it is expected that in such cases one does not obtain the Volterra IEs that are the subject of the present study, but a different type of the IEs. Readers interested in the end effects are referred to the paper by Britz et al. [24] where finite-difference simulations of the chronoamperometric current were performed, and from which some clues can be obtained, regarding the conditions under which the end effects are significant.

## 2. Theory

Let us consider a reaction mechanism involving  $S$  species  $X_1, X_2, \dots, X_S$  distributed in a semi-infinite electrolyte volume adjacent to the wire electrode. If the reaction mechanism does not include homogeneous reactions, then under conditions of pure diffusion transport the concentration  $c_j(r, t)$  of any  $j$ -th of these species ( $j = 1, 2, \dots, S$ ) obeys the diffusion equation:

$$\frac{\partial c_j(r, t)}{\partial t} = D_j \left[ \frac{\partial^2 c_j(r, t)}{\partial r^2} + r^{-1} \frac{\partial c_j(r, t)}{\partial r} \right]. \quad (1)$$

In Eq. (1)  $D_j$  is the diffusion coefficient of the species,  $r$  is the distance from the electrode symmetry axis, and  $t$  is time. Equation (1) is usually accompanied by a uniform initial condition:

$$c_j(r, 0) = c_j^*, \quad (2)$$

which is consistent with the boundary condition at  $r \rightarrow \infty$ :

$$c_j(\infty, t) = c_j^* \quad (3)$$

where  $c_j^*$  is the constant bulk concentration. The system (1)–(3) must also be completed with boundary conditions at  $r = r_0$ , where  $r_0$  is the electrode radius. The actual form of these boundary conditions depends on the heterogeneous reactions in the reaction mechanism, and on the type of the transient experiment. However, the knowledge of the boundary conditions at the electrode surface is not needed for the present discussion.

As was shown in Ref. [25], the analytical solution of the (incomplete) initial boundary value problem (1)–(3) leads to the following convolution relationships between the concentrations and their fluxes  $D_j \partial c_j(r, \tau) / \partial r|_{r=r_0}$  at the electrode surface at times  $\tau \leq t$ :

$$c_j(r_0, t) = c_j^* - D_j^{-1/2} \int_0^t \mathcal{K}_j^d(t, \tau) [D_j \partial c_j(r, \tau) / \partial r|_{r=r_0}] d\tau, \quad (4)$$

where  $\mathcal{K}_j^d(t, \tau)$  is the integral transformation kernel specific for the cylindrical diffusion Eq. (1). According to Ref. [17] the kernel can

be conveniently expressed as

$$\mathcal{K}_j^d(t, \tau) = [\pi(t - \tau)]^{-1/2} - \rho_j \text{kcyIw}[\rho_j(t - \tau)^{1/2}] \quad (5)$$

where  $\rho_j = D_j^{1/2} / r_0$ , and  $\text{kcyIw}(\theta^{1/2})$  (with  $\theta$  standing for  $\rho_j^2(t - \tau)$ ) is a special function introduced in Ref. [17]. The function is defined by the formula:

$$\text{kcyIw}(\theta^{1/2}) = \mathcal{L}^{-1} \left\{ \frac{K_1(s^{1/2}) - K_0(s^{1/2})}{s^{1/2} K_1(s^{1/2})} \right\}, \quad (6)$$

where  $s$  is the Laplace variable,  $\mathcal{L}^{-1}\{\dots\}$  denotes the inverse Laplace transform from the  $s$  domain back to the  $\theta$  domain, and  $K_0(z)$  and  $K_1(z)$  are modified Bessel functions [26] of the second kind and orders 0 and 1, respectively. We note that Eq. (4) holds independently for every  $j$ -th species.

Let us discuss now how to take into account the presence of first (or pseudo-first) order homogeneous reactions. The addition of homogeneous kinetic terms into Eq. (1) usually causes couplings between the various concentrations, and the system of thus coupled reaction–diffusion equations has to be solved simultaneously to obtain a vector analogue of Eq. (4). The recent analysis [27] of the applicability of the integral equation method to such systems has shown that the concentration–flux relationships can, in general, be very complicated in such cases. The analysis was limited to planar electrodes, but even more complications are expected for cylindrical wire electrodes. The single integral in Eq. (4) must be replaced by a suitable linear combination of the integrals of the interfacial fluxes of (possibly) all species  $X_1, X_2, \dots, X_S$ , and each integral may involve a different kernel function. Depending on the reaction mechanism, and assumptions regarding the diffusion coefficients (equal or unequal), a variety of situations may arise, ranging from those in which the kernels are simple and easily obtainable, to those in which closed-form expressions for the kernels are impossible to obtain. Out of these many situations, for the present study we choose one, which luckily appears to be the most common. The majority of standard reaction mechanisms (CE, EC, EC', ECE, etc.) corresponds to this situation, either unconditionally, or under additional assumptions (for example, under the assumption of equal diffusion coefficients). In the situation chosen, the set of the concentrations  $c_j(r, t)$  can be replaced by an equivalent set of new variables  $u_i(r, t)$  ( $i = 1, 2, \dots, S$ ). Each of the new variables is a linear combination of the concentrations of the species involved, and is subject to an independent linear reaction–diffusion equation:

$$\frac{\partial u_i(r, t)}{\partial t} = D_i \left[ \frac{\partial^2 u_i(r, t)}{\partial r^2} + r^{-1} \frac{\partial u_i(r, t)}{\partial r} \right] - k_i u_i(r, t). \quad (7)$$

with initial and boundary conditions

$$u_i(r, 0) = u_i^*, \quad (8)$$

$$u_i(\infty, t) = u_i^* \quad (9)$$

where the constant  $u_i^*$  is an analogous linear combination of the bulk concentrations  $c_j^*$ ,  $D_i$  is a diffusion coefficient associated with the  $i$ -th variable  $u_i(r, t)$ , and  $k_i$  is a coefficient that depends on the rate constant(s) of the homogeneous reactions and diffusion coefficients. By using the terminology of Ref. [27], this is the situation when matrix  $\mathbf{B}(s)$  defined by Eq. (12) in Ref. [27] is diagonalizable, so that it possesses a set of  $N$  linearly independent eigenvectors.

The substitution of variables

$$u_i(r, t) = \exp(-k_i t) w_i(r, t) \quad (10)$$

transforms Eqs. (7)–(9) into a purely diffusional initial-boundary value problem, analogous to Eqs. (1)–(3), but for the unknown  $w_i(r, t)$  in the place of  $c_j(r, t)$ . Therefore, a relationship analogous to Eq. (4) can be written for  $w_i(r_0, t)$  and  $D_i \partial w_i(r, \tau) / \partial r|_{r=r_0}$ :

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