



Interrupted amperometry: An ultrasensitive technique for diffusion current measuring



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ABSTRACT

One of the key aims of electroanalytical methods development is the increase in sensitivity of measurements. This communication reports about a new amperometric technique called "interrupted amperometry" that is based on periodic interruption of the measuring electrical circuit. The main feature of this method is that capacitive current is analytically useful as well as faradaic current. This enables a dramatically higher sensitivity compared to the conventional amperometry. Theoretical consideration of the proposed method as well as the design of the home-made instrumentation is presented. Iron (III) was chosen as a model analyte in this preliminary study in order to demonstrate analytical possibilities of interrupted amperometry. The theoretical limit of detection of iron (III) at a carbon rotating disk electrode was found to be 3 nM. The calibration curve is linear in the whole investigated concentration range from 0.02 to 0.38 μM and gave a value of $1.22 \mu\text{A} \mu\text{M}^{-1}$ for the sensitivity. These results were compared with the values obtained in conventional direct-current amperometry mode other conditions being the same: 0.2 μM and 0.81 $\text{nA} \mu\text{M}^{-1}$ for the limit of detection and sensitivity, respectively. The proposed technique can be useful for titration, flow injection analysis, HPLC, amperometric sensors, potentiostatic coulometry and for amperometric measurements with ultramicroelectrodes.

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1. Introduction

Since Jaroslav Heyrovský introduced polarography as analytical method in 1922, the development of voltammetry is generally related with increase in sensitivity [1–3]. In amperometry and voltammetry sensitivity is defined by the signal-to-noise ratio. In quantitative measurements, the analytically relevant part of the current, i.e. the signal, is the diffusion controlled faradaic current, arising from the charge transfer reaction of the analyte. The noise is usually associated with residual current which consists of the capacitance or charging current and the faradaic currents produced by the reduction or oxidation of electroactive impurities [1,4]. The latter contribution can be made insignificant by using high purity reagents and solvents. Thus, the capacitance current appears to be the main interference. The great variety of

approaches to enhancing the signal-to-noise ratio can be roughly divided into two groups – mathematical and instrumental methods. Various mathematical techniques, such as derivative voltammetry [5–8], Fourier [9–12] and wavelet [13–15] transformations, effectively eliminate noise-like signals thus improving sensitivity and resolution. However, these methods operate with experimentally collected data and don't improve the analytical signal physically. Moreover, signal processing can result in the loss of the useful part of the current in some cases. Most commonly used instrumental methods of enhancing sensitivity are based on time- and phase-selective current measurements that allow separating the capacitive and faradaic currents. The former approach is pulse voltammetry [16–18], differential pulse [19,20] and square-wave [21–23] versions being the most effective. Current selection by phase is implemented in alternating current voltammetry [24–27], and sinusoidal voltammetry [28–30] in particular. Various stripping techniques are also powerful tools for sensitivity enhancing as the faradaic current is increased due to analyte preconcentration [31–34]. However, the variety of analytes that can be determined by these techniques is limited.

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Additionally, the preconcentration step makes the automation of the analysis more complex, as this step often leads to the electrode contamination, especially in the case of solid working electrodes. As a result, there is a need in the subsequent cleaning step, which is undesirable under the conditions of automatic measurements.

All the mentioned methods are directed to the reducing of the capacitance current or to the gain in the faradaic current. We report about the method that receives both capacitive and faradaic currents as analytically useful [35]. The method is based on periodic interruption of the measuring electrical circuit and thus was called “interrupted amperometry”. It should be noted that similar approach has been already used for ohmic resistance measurements [36–38]. However, here we present the use of “interruption mode” for diffusion current measurements for analytical purposes for the first time. Theoretical consideration of the proposed method as well as experimental data demonstrating the possibilities of the new technique are presented. Determination of iron (III) in water was chosen as an example of possible applications. This is still an actual problem in oceanography [39] and nuclear power industry where there is a need for sensitive, rapid and easy-to-automate technique.

2. Theory

The main principle of interrupted amperometry is that both faradaic and capacitive currents are related to the amount of depolarizer. This effect is achieved by periodically opening (or interrupting) and subsequent locking of the measuring electrical circuit.

In order to simplify theoretical consideration of the proposed technique, the following assumptions are to be made:

1. The measurement is performed under stationary diffusion of a depolarizer in the absence of any adsorption phenomena and kinetic limitations, i.e. preceding or subsequent, homogeneous or heterogeneous chemical reactions.
2. The polarizing potential difference is constant and belongs to the limiting current potential region.
3. The measurements are carried out in concentrated solutions of indifferent electrolyte, providing compact structure of the double layer (DL) and low ohmic resistance of the solution.
4. The concentration of a depolarizer is so low, that the current of electrochemical reaction is much lower than the DL charging current.
5. Currents produced by discharge of electroactive impurities are significantly lower than those produced by discharge of the analyte in the fixed potential region.
6. Potentiostat transition time is significantly shorter than the circuit locking time.

The conventional scheme for electrochemical measurements presented on Fig. 1 is supplemented by a switcher, which allows to

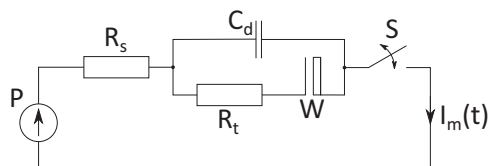


Fig. 1. The measuring electrical circuit for interrupted amperometry. P – potentiostat providing the polarizing voltage; R_s – total ohmic resistance of electrochemical cell; R_t – charge transfer resistance; C_d – double layer capacity; W – Warburg impedance; S – switcher; $I_m(t)$ – measured current.

lock and to open the circuit for short (micro- and milliseconds, respectively) periods of time.

In accordance with the 1st and 2nd assumptions the diffusion flow to the working electrode is constant. Therefore, the circuit part consisting of the serially connected charge transfer resistance (R_t) and the Warburg impedance (W) can be replaced by the value of direct current expressed by the following equation:

$$I_d = nFA\frac{D}{\delta}C_x^0 \quad (1)$$

where n – is the number of electrons, involved in electrochemical reaction; F – is the Faraday constant; A – is the surface area of the working electrode; D – is the diffusion coefficient; δ – is the thickness of the Nernst diffusion layer; C_x^0 – is the bulk concentration of the analyte.

Thus, the circuit from Fig. 1 can be simplified for the case of the locked state (see Fig. 2a) and for the case of the opened state (see Fig. 2b).

The switcher (S) locks the circuit for the period of time t_l and then opens the circuit for the period of time t_o . These two simple actions are repeated periodically during the entire experiment. After several first periods the full charging of the capacitor (C_d) is achieved. Then at every locking of the circuit the capacitor is recharged by the current $I_l(t)$, that emerges in the outer circuit path (see Fig. 2A). At every opening of the circuit the DL discharging supports the current of electrochemical reaction. The process of recharging and discharging of the capacitor is repeated by changing the position of the switcher until a stationary state is achieved. This state is characterised by the current $I_m(t)$ that can be measured.

Following the assumption about stationarity of the process, the charge applied to DL at the locked circuit state (Q_l) is equal to the charge spent by DL on the maintenance of electrochemical reaction at the opened circuit state (Q_o):

$$Q_l = Q_o \quad (2)$$

As the charge is multiplication of the average current value and time, obviously:

$$I_l t_l = I_o t_o \quad (3)$$

where I_l is the average value of the current that charges DL at the locking time t_l and I_o is the average value of the current produced by the discharge of DL during the opening time t_o .

In accordance with Kirchhoff's first law and the circuit presented in Fig. 2A, the following expression is reasonable:

$$I_l(t) = I_d + I_m(t) \quad (4)$$

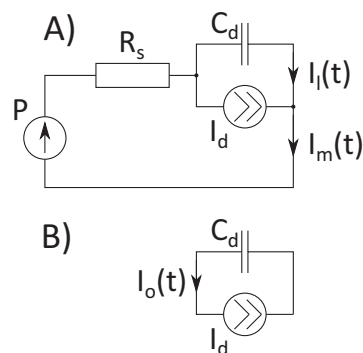


Fig. 2. The simplified measuring electrical circuit for the locked (A) and for the opened (B) states.

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