

## Theory of Differential Staircase Voltammetry

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Staircase voltammetry in differential mode, applied to spherical electrodes of different sizes, is analyzed theoretically. Dependences of peak currents on the sampling times, the potential step increment, the charge transfer coefficient and the electrode radius are investigated. Criteria of reversibility are proposed. Differential responses of reversible redox reactions are independent of the sphericity parameter  $Y = (D/f)^{1/2}/r$ .

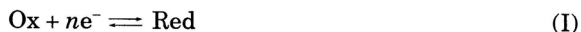
### INTRODUCTION

Differential staircase voltammetry<sup>1–3</sup> is a newly proposed variation of the well known electroanalytical technique.<sup>4,5</sup> Its novelty consists of sampling the currents twice on each tread of the staircase potential–time waveform, after the charging current has decayed to a negligible value. The difference between the two sampled currents is amplified and recorded as the function of electrode potential, resulting in a bell-shaped current–potential curve with a maximum that is proportional to the concentration of an analyte. By this procedure, the background current, which remains nearly constant, but very noisy, after the decay of the capacitive component, can be successfully suppressed.

A theory of this method, if it is applied to virtually planar electrodes, can be derived from the theories of the staircase<sup>6,7</sup> and the differential pulse voltammetry.<sup>8,9</sup> However, all these theories require numerical calculations of the relationships between the current responses and the signal parameters. Besides, the method has been developed to be used, primarily, with the hanging or the static mercury drop electrodes. So, in this paper, the theory is developed assuming a spherical semiinfinite diffusion towards the surface of both micro- and macro-electrodes. The experimentally observed relationship between the differential peak currents and the square-roots of the potential step durations<sup>1</sup> is re-examined and confirmed. It is demonstrated that there are no sphericity effects in this technique, or that they are very small, which means that the method is very useful at conventional mercury drop electrodes, but should not be applied to microelectrodes because the differential peak currents decrease proportionally to the reduction of the electrode surface area.

## THEORY

A simple redox reaction



is considered assuming spherical diffusion of a soluble reactant and soluble product. If only the oxidized species is initially present in the solution, and if the diffusion coefficients of the reactant and the product are equal, reaction (I) can be mathematically represented by the well-known integral equation:<sup>10</sup>

$$\phi = X \exp(-\alpha \varphi) \left[ 1 - f^{1/2} (1 + \exp(\varphi)) I^\circ \right] \quad (1)$$

where:

$$\phi = i(nFS c_o^*)^{-1} (Df)^{-1/2},$$

$$I^\circ = \int_0^t \phi(\pi(t-u))^{-1/2} du - a \int_0^t \phi \exp(a^2(t-u)) \operatorname{erfc}(a(t-u)^{1/2}) du,$$

$\varphi = nF(E - E^\circ)/RT$ ,  $a = D^{1/2}/r$ ,  $X = k_s(Df)^{-1/2}$  and  $f = \tau^{-1}$  is the frequency of the staircase excitement signal. The other symbols are defined in the list of symbols.

For numerical integration, Eq. (1) can be transformed to a system of recursive formulae:<sup>11,12</sup>

$$\phi_1 = Y \left[ (Y/X) \exp(\alpha \varphi_1) + (1 + \exp(\varphi_1)) S(1) \right]^{-1}$$

$$\phi_m = \left[ Y - (1 + \exp(\varphi_m)) \sum_{i=1}^{m-1} \phi_i S(m-i+1) \right] \left[ (Y/X) \exp(\alpha \varphi_m) + (1 + \exp(\varphi_m)) S(1) \right]^{-1}$$

where  $Y = (D/f)^{1/2}/r$ ,  $\varphi_m = nF(E_m - E^\circ)/RT$ , and  $\phi_m$  and  $E_m$  are the dimensionless current density and electrode potential, respectively, at time  $t_m = m d$ . The ratio  $X/Y = r k_s/D$  is the dimensionless standard charge transfer rate constant of redox reaction (I). Partial integrals are:

$$S(1) = 1 - \exp(Y^2/N) \operatorname{erfc}(Y/N^{1/2})$$

$$S(k) = \exp(Y^2(k-1)/N) \operatorname{erfc}(Y(k-1)^{1/2}/N^{1/2}) - \exp(Y^2k/N) \operatorname{erfc}(Y(k/N)^{1/2})$$

where  $N$  is the number of time increments  $d$  in each staircase period  $N = \tau/d$ . In this work, the increment  $d = (50 f)^{-1}$  and the potential step increment  $\Delta E = -5 \text{ mV}$  were used. A scan rate of the staircase signal is defined as  $v = \Delta E f$ . Functions of the type  $\exp(z^2) \operatorname{erfc}(z)$  were calculated using Oldham's algorithm.<sup>13</sup>

If  $Y \rightarrow 0$ , the mass transfer can be interpreted by the planar diffusion model and the current can be calculated by means of the following set of recursive formulae:<sup>11</sup>

$$\phi_1 = Z \left[ (Z/X) \exp(\alpha \varphi) + 1 + \exp(\varphi) \right]^{-1}$$

$$\phi_m = \left[ Z - (1 + \exp(\varphi_m)) \sum_{i=1}^{m-1} \phi_i S_p(m-i+1) \right] \left[ (Z/X) \exp(\alpha \varphi_m) + 1 + \exp(\varphi_m) \right]^{-1}$$

where  $Z = (\pi N)^{1/2}/2$  and  $S_p(k) = k^{1/2} - (k - 1)^{1/2}$ . At a certain fraction of each tread ( $\tau/2 < \tau_1 < \tau$ ) and at its end ( $\tau_2 = \tau$ ), the instantaneous currents were sampled and subtracted:  $\Delta\phi_{(\tau_1/\tau_2)} = \phi_{(\tau_1)} - \phi_{(\tau_2)}$ . Five different values of the ratio  $\tau_1/\tau$  were used: 0.52, 0.62, 0.72, 0.82 and 0.92. Besides, the realistic current sampling procedure was simulated by averaging the currents sampled in five subsequent time increments;  $\bar{\phi}_{(\tau_1)} = \sum_{i=1}^5 \phi_{j+i} / 5$ . These average currents were calculated for five average sampling times ( $\bar{\tau}_1/\tau = 0.56, 0.66, 0.76$  and  $0.86$  and  $\bar{\tau}_2/\tau = 0.96$ ) and subtracted:  $\Delta\phi_{(\tau_1/\tau_2)} = \bar{\phi}_{(\tau_1)} - \bar{\phi}_{(\tau_2)}$ . The maximum value of each differential response  $\Delta\phi_{(\tau_1/\tau_2)}$ , is reported as a dimensionless peak current density  $\Delta\phi_p$  for the chosen ratio  $\tau_1/\tau_2$ , and the reported peak potential  $E_p$  is equal to the corresponding potential of the working electrode. For this reason the minimum change in  $E_p$  equals  $\Delta E$ .

## RESULTS AND DISCUSSION

Direct staircase voltammograms resemble the well-known current-potential curves of linear scan voltammetry.<sup>4-7</sup> If the redox reaction (I) is strictly reversible for all frequencies and electrode radiuses, the maximum dimensionless current sampled at  $\tau_1 = \tau$  is a function of the inverse value of dimensionless electrode size  $Y = (D/f)^{1/2}/r$ . The relationship is not linear but can be satisfactorily approximated by two straight lines:

$\phi_{\max(1)} = 0.170 + 0.900 Y$  (for  $Y \leq 0.6$ ) and  $\phi_{\max(1)} = 0.135 + 0.985 Y$  (for  $0.6 < Y \leq 2$ ). The result applies to  $n \Delta E = 5$  mV. If the current is sampled at  $\tau_1/\tau = 0.52$ , the difference appears only in the planar component of the dimensionless maximum current:  $\phi_{\max(0.52)} = 0.185 + 0.900 Y$  (for  $Y \leq 0.6$ ) and  $\phi_{\max(0.52)} = 0.135 + 0.985 Y$  (for  $0.6 < Y \leq 2$ ). The currents are independent of  $Y$  if  $Y < 10^{-3}$ . This condition can be satisfied at macro-sized electrodes, such as the hanging and the static mercury drop electrodes, if the frequency is high enough. However, the possible influence of the sphericity must be taken into consideration under most other conditions, and generally at microelectrodes. If a semispherical electrode ( $S = 2\pi r^2$ ) is extremely small ( $Y > 0.6$ ), the real maximum current can be expressed as:  $i_{\max} = 0.85 n F c_o^* r D^{1/2} (r f^{1/2} + 7.3 D^{1/2})$ . Theoretically, if  $r f^{1/2} \ll 7.3 D^{1/2}$ , a steady-state, frequency-independent maximum current appears:  $(i_{\max})_{SS} = 6.2 n F c_o^* r D$ . This condition can be satisfied with more than 5% accuracy if, for instance,  $D = 10^{-5}$  cm<sup>2</sup>/s,  $f = 1$  Hz and  $r < 10$   $\mu$ m. It seems that the staircase voltammetric measurements are not generally performed under rigorously established steady-state conditions. Potentials of the maxima also depend on parameter  $Y$ . Their non-linear relationship is characterized by the asymptotes:  $E_{\max} = -0.035 V$  vs  $E^\circ$ , for  $Y < 10^{-2}$ , and  $E_{\max} = -0.100 - 0.084 \log(Y)$ , for  $0.5 < Y \leq 2$ .

A differential dimensionless response  $\Delta\phi_{(\tau_1/\tau_2)} = \phi_{(\tau_1)} - \phi_{(\tau_2)}$ , is a bell-shaped current-potential curve with the maximum at  $-0.010 V$  vs  $E^\circ$  if  $n\Delta E = 5$  mV. Both the peak current  $\Delta\phi_p$  and the peak potential  $E_p$  of the differential response are independent of the parameter  $Y$ , regardless of the ratio  $\tau_1/\tau_2$ . The direct dimensionless currents measured at the peak potential  $-0.010 V$  are linear functions of  $Y$  and the slopes of these proportionalities are independent of the sampling times  $\tau_1$  and  $\tau_2$  (e.g.:  $\phi_{E_p, (0.52)} = 0.169 + 0.596 Y$  and  $\phi_{E_p, (1)} = 0.150 + 0.596 Y$ , where  $E_p = -0.010 V$  vs  $E^\circ$ ).

Consequently, their differences do not depend on the electrode sphericity. It has been shown previously<sup>1</sup> that the real differential peak currents  $\Delta i_p$  depend linearly

on the difference  $(\tau_1)^{-1/2} - (\tau_2)^{-1/2}$ , as well as on the potential step increment. Dimensionless peak current is a function of a complex variable  $\rho = (\tau/\tau_1)^{1/2} - (\tau/\tau_2)^{1/2}$ , or  $\rho = (\tau/\tau_1)^{1/2} - 1$ , if  $\tau_2 = \tau$ . Calculations show that  $\Delta\phi_p = 5.125 \cdot 10^{-2} \rho$ , if  $\rho \leq 0.2$  in agreement with experimental data.<sup>1</sup> However, in a wider range of variable  $\rho$ , the non-linear relationship is more accurate:  $\Delta\phi_p = 4.645 \cdot 10^{-2} \rho^{0.955}$ . The dependence of  $\Delta\phi_p$  on  $\Delta E$  is similar:  $\Delta\phi_p = k \Delta E^{0.876}$ . The factor of proportionality also depends on variable  $\rho$ :  $k = 1.135 \cdot 10^{-2} \rho^{0.955}$ . Thus, these two relationships can be integrated into:  $\Delta\phi_p = 1.135 \cdot 10^{-2} \rho^{0.955} \Delta E^{0.876}$ , or  $\Delta i_p = 1.135 \cdot 10^{-2} n F S c_o^*(Df)^{1/2} \Delta E^{0.876} \rho^{0.955}$  (where  $\Delta E$  is expressed in mV). The formula applies to all stationary electrodes, irrespective of their sphericity and size. However, this means that microelectrodes cannot be used for differential staircase voltammetry of reversible redox reactions since the peak current decreases proportionally to the reduction of the electrode surface area. The peak potentials change slightly with the increasing of the potential step increment: from  $E_p = -0.006$  V for  $\Delta E = 2$  mV, to  $E_p = -0.010$  V for  $\Delta E = 10$  mV. A half-peak width depends slightly on both  $\Delta E$  and  $\rho$ , and changes inside the narrow range  $\Delta E_{p/2} = (99.5 \pm 1.0)/n$  mV.

Differential staircase responses of totally irreversible redox reactions are somewhat different. Under the conditions of small sphericity ( $Y \leq 0.1$ ), the dimensionless peak currents are linearly proportional to parameter  $Y$ , but as  $Y$  increases, its influence on  $\Delta\phi_p$  gradually diminishes and if  $Y \geq 1$  (for  $\tau_1/\tau_2 = 0.52/1$ ) and even if  $Y \geq 0.4$  (for  $\tau_1/\tau_2 = 0.92/1$ ), it totally vanishes. Hence, if  $\alpha = 0.5$  and  $n\Delta E = 5$  mV,  $\Delta\phi_p = 1.22 \cdot 10^{-2} \rho^{0.895} + 1.245 \cdot 10^{-2} \rho^{1.035} Y$  for  $Y \leq 0.1$ , and  $\Delta\phi_p = 1.6 \cdot 10^{-2} \rho^{0.935}$  for  $Y \geq 1$ . The influence of the charge transfer coefficient was investigated for  $Y = 0$  and  $Y = 1$ . If  $Y = 0$ ,  $\Delta\phi_p = 2.95 \cdot 10^{-2} \rho^{0.895} \alpha^{1.263}$ , and if  $Y \geq 1$ ,  $\Delta\phi_p = 3.255 \cdot 10^{-2} \alpha^{1.014} \rho^{0.935}$ . Thus, if  $Y \leq 0.1$ ,  $\Delta\phi_p = 2.95 \cdot 10^{-2} \alpha^{1.263} \rho^{0.895} + 1.245 \cdot 10^{-2} \rho^{1.035} Y$ . Again, the method is not applicable to microelectrodes but at macroelectrodes the sphericity effects

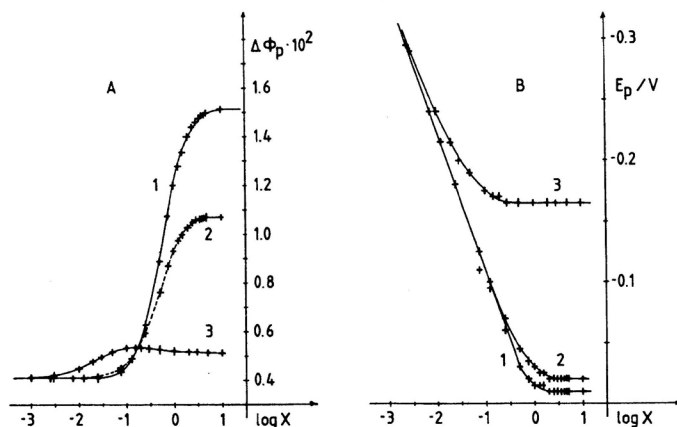


Figure 1. Dependences of (A) dimensionless differential staircase peak currents  $\Delta\phi_p = \Delta i_p (n F S c_o^*)^{-1} (Df)^{-1/2}$  and (B) peak potentials of quasireversible redox reaction on the kinetic parameter  $X = k_s(Df)^{-1/2}$ . Stationary planar (1) and spherical diffusion models:  $X/Y = 2.5$  (2) and 0.1 (3). Sampling times  $\tau_1/\tau = 0.56$  and  $\tau_2/\tau = 0.96$ ;  $n = 1$ ,  $\alpha = 0.5$  and  $\Delta E = -5$  mV.



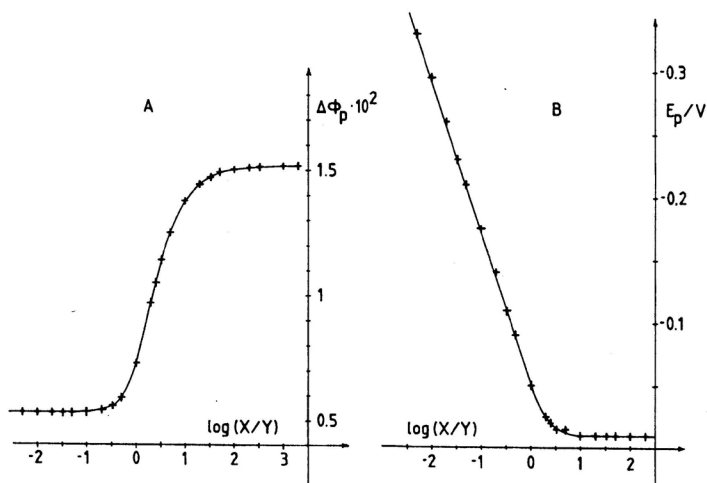


Figure 2. Dependence of (A)  $\Delta\phi_p$  and (B)  $E_p$  on the kinetic ratio  $X/Y$  for  $Y = 1$ . All parameters as in Figure 1.

have to be considered. Under the same experimental conditions, the response of irreversible reactions are from three to five times lower than the responses of reversible redox reactions.

The responses of quasi-reversible redox reactions are functions of two interdependent parameters:  $Y = (D/f)^{1/2}/r$ , which is related to electrode size, and  $X = k_s(Df)^{-1/2}$ , which is related to electrode kinetics. Increasing of the frequency causes a simultaneous decrease of both parameters,  $X$  and  $Y$ , but their ratio  $X/Y = r k_s/D$  remains constant. If sphericity is negligible ( $Y < 10^{-3}$ ), the apparent reversibility of redox reaction depends solely on the kinetic parameter  $X$ . The dimensionless peak current increases with an increase of  $\log(X)$  in the well-known sigmoidal way, as it can be seen in Figure 1, curve 1. The reaction appears reversible if  $X \geq 10$ , and totally irreversible if  $X \leq 0.01$ . At spherical electrodes, the ratio  $X/Y$  is the additional kinetic parameter,<sup>12</sup> as demonstrated by curves 2 and 3 in Figure 1. The relationship between  $\Delta\phi_p$  and  $\log(X/Y)$ , calculated for  $Y = 1$ , is shown in Figure 2. The limits of reversible and totally irreversible reaction are  $X/Y > 300$  and  $X/Y < 0.1$ , respectively. If the variation of frequency causes a decrease of  $X$  and  $Y$  values below 0.1 and 0.01, respectively, the influence of sphericity on the peak potential vanishes and  $E_p$  depends only on the kinetic parameter:  $E_p - E^\circ = 0.010 + 2.3(RT/anF)\log(X)$ . If the value of  $X$  is higher than 2, the peak potential is independent of  $X$ , but depends on the ratio  $X/Y$ . If  $X/Y > 10$ , the reaction is reversible and  $E_p - E^\circ = -0.010$  V. If  $X/Y < 1$ , the reaction is irreversible and  $E_p - E^\circ = -0.059 + 2.3(RT/anF)\log(X/Y)$ . The last equation also defines the constant value towards which the peak potentials of totally irreversible reaction tend if the sphericity is very high ( $Y > 1$ ). For this reason, the slope  $\partial E_p/\partial \log(f)$  measured in the restricted frequency range may suggest an inaccurate value of the product  $an$ . The dimensionless peak currents become independent of the frequency when  $X > 10$  but still remain dependent on the ra-

tio  $X/Y$ , obeying the criteria of reversibility shown in Figure 2. The differential staircase response is strictly reversible and its dimensionless peak current is independent of the electrode size if  $X > 10$  and  $Y < 0.03$ .

A standard reaction rate constant of quasireversible redox reactions can be determined from the dependence of peak potentials on the scan rate, like in the classical linear scan voltammetry.<sup>10</sup> For this purpose, the potential step increment has to remain constant so that  $f = v/\Delta E$ . As shown in Figure 1 B, the intersection of straight lines  $E_p - E^\circ = 0.010 + 2.3 (RT/anF) \log(k_s D^{-1/2}) - (2.3/2)(RT/anF) \log(f)$  (apparently irreversible reactions) and  $E_p - E^\circ = -0.010$  V (apparently reversible reactions) is characterized by a certain critical frequency  $f_{crit}$ . At the planar electrode, this frequency is related to  $k_s$  by the formula:  $k_s = 0.7 (D f_{crit})^{1/2}$ . If the electrode is spherical ( $X/Y = 2.5$ ), this relationship is:  $k_s = 0.6 (D f_{crit})^{1/2}$ . Thus, for the macroelectrode of unknown sphericity, an approximative formula applies:  $k_s = (0.65 \pm 0.05)(D f_{crit})^{1/2}$ . The microelectrodes are not recommendable for this type of measurements for the reasons given above.

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#### LIST OF SYMBOLS

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$\alpha$	charge transfer coefficient
$c_o^*$	bulk concentration of the oxidized species
$D$	diffusion coefficient
$d$	time increment for numerical integration
$E$	potential of the working electrode
$\Delta E$	potential step increment of the staircase potential–time waveform
$E^\circ$	standard potential of reaction (I)
$E_p$	peak potential
$\Delta E_{p/2}$	half-peak width
$f = \tau^{-1}$	frequency of the staircase excitement signal
$F$	Faraday constant
$\phi = i (nFSc_o^*)^{-1} (Df)^{-1/2}$	dimensionless current
$\Delta\phi_{(\tau_1/\tau_2)} = \phi_{\tau_1} - \phi_{\tau_2}$	differential dimensionless current
$\Delta\phi_p$	maximum differential dimensionless current
$i$	real current
$\Delta i$	real differential current
$\Delta i_p$	real differential peak current
$k_s$	standard heterogeneous charge transfer rate constant
$n$	number of electrons
$R$	gas constant
$r$	electrode radius
$S$	electrode surface area
$t$	time
$\tau$	duration of the potential step of the staircase excitement signal
$T$	absolute temperature

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## SAŽETAK

## Teorija diferencijalne stepeničaste voltametrije

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Razvijena je teorija diferencijalne stepeničaste voltametrije na sfernim elektrodama različitim veličina. Istražena je ovisnost vršnih struja odziva o karakteristikama pobude (korak potencijala, trenutci uzorkovanja), svojstvima redoks-reakcije (koeficijent i standardna konstanta prijenosa naboja) te o promjeru elektrode. Postavljeni su kriteriji za procjenu reverzibilnosti redoks-reakcije. Diferencijalni odzivi reverzibilnih redoks-reakcija ne ovise o bezdimenzijskom radiusu elektrode  $Y = (D/f)^{1/2}/r$ . Zbog toga nema sfernog efekta, pa se metoda ne može primijeniti na mikroelektrodama, ali je njezina primjena na velikim sfernim elektrodama olakšana i preporučljiva.