Derivative and Differential Voltammetry and Reciprocal Derivative Chronopotentiometry
Identical Behavior Verification for Electrode Reversible Processes

Joaquín Gonzalez, Angela Molina,* Manuela López-Tenéz, and Carmen Serna

Departamento de Química Física. Facultad de Química, Universidad de Murcia, Espinardo, 30100 Murcia, Spain

In the present paper, we carry out the experimental verification of the analogy between the responses obtained in derivative and differential voltammetric techniques and those corresponding to a new modality of the reciprocal derivative chronopotentiometric techniques using a programmed current of the form \( i(t) = I_0 e^u \), with \( u \geq -1/2 \). Identical information can be obtained from derivative voltammetry and reciprocal derivative chronopotentiometry although the experimental application of the latter is simpler and signals obtained are less noise influenced due to the use of programmed current. In order to show the above mentioned analogy in the case of reversible electrode processes, we have carried out an experimental study of the systems \( \text{Fe}([C_2O_4]^{3-}) \) in 0.2 M \( K_2[C_2O_4] \) (pH 4.49) at a static mercury drop electrode and ferrocene in \( \text{CH}_3\text{CN}0.25 \) M \( \text{PF}_6\text{NBu}_4 \) at a Pt electrode.

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Voltammetric differential-pulse techniques are very useful electrochemical techniques for characterizing electrode processes.1-3 The response obtained in these techniques can be considered as an approximation of the successive derivatives of the \( I \) vs. \( E \) curve, and it presents one or two peaks which are characteristic of the process analyzed. Thus, for example, differential pulse voltammetry (DPV) is a double-pulse technique whose response emulates the first derivative of the \( I \) vs. \( E \) curve,4,6 while double differential pulse voltammetry (DDPV) is a recently designed triple-pulse technique whose response emulates the second derivative of the \( I \) vs. \( E \) curve.9,11 The signals obtained in these differential and double differential pulse techniques coincide with the first and second derivative of the \( I \) vs. \( E \) curve, respectively, when the difference between the applied potential pulses, \( \Delta E \), tends to zero.

The true derivatives of the \( I \) vs. \( E \) curve are the responses corresponding to derivative voltammetry (DV), a potentiostatic technique which has received little attention in the literature due to the problems of the differentiation of digitally acquired signals, in particular the low signal-to-noise ratio.12 However, modern digital filtering techniques can alleviate to a great extent the problems associated with the differentiation of the \( I \) vs. \( E \) signal,13 and, therefore, we can use differential and double differential voltammetry together with the derivative voltammetry technique in order to study electrode processes.

Another derivative technique which has been much used in recent years for the study of different electrode processes is reciprocal derivative chronopotentiometry,14-18 due to the fact that this technique, based on the plotting of the reciprocal of the time derivative of the chronopotentiogram vs. the measured potential (\( dI/dE \) vs. \( E \)), presents a characteristic peak that is quantitatively related to the kinetic and thermodynamic parameters of the electrode process and is scarcely affected by the capacitative effects on account of the fact that it has been obtained from the central zone of the \( E \) vs. \( t \) curve. This derivative technique is very simple to apply, and it presents high reproducibility in the measure of the peak potentials and peak heights, affording simple diagnosis criteria for the electrode processes analyzed.17

In a recent paper we gave the conditions under which it is possible to establish a total analogy between the potentiostatic response when a constant potential \( E \) is applied and the chronopotentiometric response when a programmed current of the general form \( i(t) = I_0 e^u \), \( u \geq -1/2 \) is applied, in the case of a reversible electrode process.19 This analogy was extended to the potentiostatic technique DPV at the limit in which its response is analogous to that of derivative voltammetry technique (\( \Delta E \to 0 \)), and to a new reciprocal derivative chronopotentiometric technique with programmed current proposed in the above mentioned paper which consists of the analysis of the \( dI/dE \) vs. \( E \) curve when a programmed current of the form \( i(t) = I_0 e^u \), \( u \geq -1/2 \), is applied to a planar electrode. Thus, for example, in the case of the application of a constant current \( i(t) = I_0 \) (\( u = 0 \)), we should obtain the \( dI/dE \) vs. \( E \) curve, while in the case of a current which varies with the square root of time, \( i(t) = I_0 t^{1/2} \) (\( u = 1/2 \)), we should obtain the traditional \( dI/dE \) curve.

In the present paper, we carry out the experimental verification of the analogy between the responses obtained in derivative voltammetry for the first and second derivatives of the \( I \) vs. \( E \) curve (\( dI/dE \) vs. \( E \) and \( d^2I/dE^2 \) vs. \( E \)), as well as with DPV and DDPV, and those corresponding to the first and second reciprocal derivatives of the \( E \) vs. \( t^{1/2} \) curves in chronopotentiometry programmed current (\( d^{n+1/2}I/dE^{n+1/2} \) vs. \( E \) and \( d^{n+1/2}I/dE^{n+1/2} \) vs. \( E \) curves).

The information obtained from derivative voltammetry and reciprocal derivavtive chronopotentiometry (RDCP) is identical, although the experimental application of the latter is simpler due to the fact that it requires only a source of constant or programmed current and recording of the \( E \) vs. \( t \), \( E \) vs. \( t \), or \( E \) vs. \( t^{1/2} \) vs. \( E \) response in a single experiment, while voltammetric techniques such as DV, DPV, and DDPV require many experiments as different potentials are applied in order to obtain the \( I \) vs. \( E \) curve and its derivatives. Moreover, we have confirmed experimentally that the signal \( n^{n+1/2} \) vs. \( E \) obtained in chronopotentiometry is less noise influenced than the \( I \) vs. \( E \) curve and presents a greater versatility due to the great ease with which we can vary the heights and positions of the curves \( d^{n+1/2}I/dE^{n+1/2} \) and \( d^{n+1/2}I/dE^{n+1/2} \) vs. \( E \), simply by changing the amplitude, \( I_0 \), or the time exponent, \( u \), in the applied current \( i(t) = I_0 e^u \).

In order to show the above mentioned analogy in the case of reversible electrode processes, we have carried out the experimental study of the system \( \text{Fe}([C_2O_4]^{3-}) \) in 0.2 M potassium oxalate (pH 4.49) at a static mercury-drop electrode (SMDE) by using DV and RDCP, with a total concordance between the results obtained with the two techniques. Likewise, we have used RDCP to characterize the ferrocene system in \( \text{CH}_3\text{CN}0.25 \) M \( \text{PF}_6\text{NBu}_4 \) at a Pt electrode.

We choose the ferrocene-ferriicium system because it is of great interest in electrochemistry since it has been proposed as an internal standard for use in instrumental and reference-potential calibration in organic solvents and it is often chosen as a model system in electrochemical studies.20-22

For all these reasons, we believe that this new chronopotentiometric technique is of great interest in the study of different electrode processes together with differential multipotential step techniques and derivative voltammetric techniques.
Experimental

Apparatus.—Computer-driven potentiostat-galvanostat was designed and constructed by Quiceltron (Spain).

Pulse and waveform generation and data acquisition were performed using a SBX6D4 and DAS16-3364 (ComputerBoards, USA) boards, respectively. All computer programs were written in our laboratory.

Data acquisition and waveform generation were independent tasks which have been carried out using two different time scales and different but connected routines. For waveform generation we have used an interrupt service routine programmed for this purpose and triggered by the 8254 counter in the personal computer. Data acquisition was under the control of the on-board pacer which usually runs at the maximum sampling rate, and data were stored in the on-board first in first out (FIFO) buffer. The interrupt service routine was called a variable number of times in each potential step and was responsible for changes in the potential values and for reading of the acquisition counter and status. Hence, the use of appropriate programming techniques allows large data oversampling (very useful for digital filtering) and almost complete versatility in the selection of time and amplitude for potential pulses with a very good acquisition synchronization.

Electrodes.—A three-electrode cell was employed in the experiments. A platinum disk electrode (disk radius, r0 = 0.05 cm) and a static mercury-drop electrode (SMDE, electrode radius, r0 = 0.0497 cm), served as working electrodes. The SMDE was constructed using a DME, EA 1019-1 (Metrohm) to which a homemade valve was sealed. The electrode radius of the SMDE was determined by weighing a large number of drops. The counter electrode was a Pt foil and the reference electrodes were a Ag/AgCl/KCl 1.0 M electrode and a saturated calomel electrode (SCE).

In the case of the SMDE, the errors due to the electrode sphericity in the measurement of the peak currents and peak heights were, in all cases less than 4%. In order to evaluate these errors, we have used Eq. 1 and 5 of Ref. 19 corresponding to the i vs. E and E vs. t curves, respectively, for an SMDE and considered spherical diffusion. The influence of the electrode sphericity on the peak potentials was negligible.

Signal processing.—Experimental IE and E(t) curves were smoothed by applying the moving-average smoothing procedure proposed by Savitzky and Golay.25 The obtained curves were fitted with a sigmoidal regression by using the program SigmaPlot,26 and numerically differentiated by using a finite-difference formula of the fifth degree27 to give the dE/dE’ and dl/dE’ curves. The second-order differentiated curves di2E/dEi2 and d2l/dE2, were obtained by numerically differentiating the first-order differentiated curves.

For the determination of peak potentials in DPV and DDPV we have used a second order polynomial fitting, taking the eight points nearest to the maximum and minimum. Peak potentials and peak heights in DV and RDCPM were measured from the fitted differentiated curves without further analysis. Cross potentials were obtained from a linear regression of the central zone of the derivative and differential curves.

Chemical reagents.—FeCl3 and K2C2O4 were of Merck reagent grade while ferrocene, CH3CN, and PF6NBu4 were of Aldrich reagent grade. All chemical reagents were used without further purification. Water was distillated, and nitrogen gas was used for deaeration.

Working solutions containing Fe(OCO2)3 were freshly prepared in order to avoid possible oxidation of the oxalate anion by the Fe3+.

The diffusion coefficients of Fe(OCO2)3 and of benzocarbazole were determined by chronocoulometric measurements, obtaining the following values: DFe(OCO2)3 = (7.30 ± 0.10) × 10-6 cm2 s−1 and DBenzocarbazole = (2.28 ± 0.03) × 10-5 cm2 s−1, which are in agreement with the reported values in the literature.20,26,28

Derivative and Double-Derivative Voltammetry (DV and DDPV), Differential Pulse Voltammetry (DPV), and Double Differential Pulse Voltammetry (DDPV)

The current-potential response obtained in voltammetric techniques corresponding to a reversible E process when only one oxidized species is initially present in the electrolytic solution at a concentration cA presents the following features:

\[ I_N = \frac{I_A}{I_0} = \frac{1}{1 + e^{-\frac{t}{\tau}}} \]  

where \( I_A \) is the diffusion current for a plane electrode given by Cottrell’s equation

\[ I_A = nFAD_A \frac{D_A}{\xi} \]  

with A being the electrode area, \( D_A \) the diffusion coefficient of the oxidized species, n the number of electrons transferred, and \( t \) the time at which the current is measured. Moreover

\[ \delta = \frac{nF}{RT} \left[ E + E_1/2 \right] \]  

\[ E_1/2 = E_0 + \frac{RT}{nF} \ln \left( \frac{D_A}{D_A} \right) \]  

where \( E_0 \) being the formal potential of the electroactive couple and \( D_A \) (with i = A or B) the diffusion coefficient of species i.

The first and second derivatives of the \( I_A \) vs. E response are given by

\[ \frac{dI_A}{dE} = \frac{nF}{RT} \left[ e^\frac{E}{RT} \right] \]  

\[ d^2I_A \]  

The characteristics of the \( I_A \) vs. E, dI/dE vs. E, and d2I/dE2 vs. E curves have been commented on exhaustively, e.g., Ref. 13 for the particular case in which the diffusion coefficients of both species are equal (\( D_A = D_B \)).

These characteristics are of great interest in the study of electrode processes, to such an extent that some potential-pulse techniques have been designed as an approximation of the first derivative, dI/dE vs. E (Eq. 4) and of the second derivative, d2I/dE2 vs. E (see Eq. 5), of the \( I_A \) vs. E curve, as are the cases of DPV and DDPV.

In DV two potential pulses of amplitude \( E_1 \) and \( E_2 \) and duration \( t_1 \) and \( t_2 \) (with \( t_1 > t_2 \)), respectively, are applied to an electrode, with the potential being scanned in the negative direction (\( \Delta E < 0 \), with \( \Delta E = E_2 - E_1 \)) or in the positive direction (\( \Delta E > 0 \)) in such a way that a delay between each pair of pulses is introduced in order for the equilibrium to be re-established.1,3–9 In this technique the difference \( \Delta I = I(E_1) - I(E_2) \) is plotted vs. E. The response \( \Delta I/\Delta E \) vs. \( E \) presents a peak and can be considered as an approximation of the derivative of the normal pulse voltammogram \( [l_{l(t)} \text { vs. } E] \) for a time pulse equal to \( t_2 \) when \( \Delta E = 0 \).

DDPV consists of the application of three potential pulses of amplitude \( E_1 \), \( E_2 \), and \( E_3 \) with \( E_2 - E_1 = E_3 - E_2 = \Delta E = 0 \). The durations of these pulses are \( t_1 \), \( t_2 \), and \( t_3 \), respectively, with \( t_1 > t_2 > t_3 \). The potential is scanned in the negative (\( \Delta E < 0 \)) or in the positive direction (\( \Delta E > 0 \)) with the equilibrium being re-established between each trio of pulses applied. In this technique the signal \( \Delta I = I_1(t_1) - 2I_2(t_2) + I_3(t_3) \) is plotted vs. one of the three potentials applied, for example, \( E_2 \). This signal presents two peaks of identical heights when \( t_3 = 2t_2/3 \) or \( D_A = D_B \) and specie B is soluble in the electrolytic solution.8,11

In these conditions, the signal \( \Delta I/\Delta E^2 \) vs. \( E_2 \) is an approximation of the second derivative of the normal pulse voltammogram for a time pulse equal to \( t_2 \) when \( \Delta E = 0 \).

Table I we give the theoretical expressions corresponding to the characteristic experimental parameters of DV, DPV, DDPV, and DDPV techniques for a reversible electrode process. As can be seen from this table, the peak potentials and peak currents of DPV and
DDPV coincide with those obtained in derivative voltammetry and double derivative voltammetry, respectively, when \( \Delta E \to 0 \).

Reciprocal Derivative and Double Derivative Chronopotentiometry with Programmed Current (RDCP and RDDCP)

The dependence of the potential on time corresponding to a reversible electrode process when a programmed current of the form \( I_p(t) \), with \( u \approx -1/2 \), is applied to the electrode is given by (see Eq. 9 in Ref. 19)

\[
\tau^{n+1/2} = \left( \frac{1}{\tau} \right)^{n+1/2} = \frac{1}{1 + e^{-\delta}}
\]

where \( \tau \) is the transition time given by

\[
a_u^{n+1/2} = \left( \frac{2}{\Gamma(a+1)} \right)^{n+1/2} \frac{nFAc^*_A \Delta \phi}{\Sigma A_p} \]

and

\[
P_{2n+1} = \frac{2\Gamma[2(a+3/2)]}{\Gamma(a+1)}
\]

\[
\delta = \frac{nF}{RT} \left[ E(t) - E'_{1/2} \right]
\]

\( \Gamma \) in Eq. 8 is the Gamma-Euler function.

Note that \( E(t) \) in Eq. 9 is the measured potential at time \( t \) while the potential \( E \) that appears in Eq. 3 corresponding to the \( I_p \) vs. \( E \) response is the constant potential applied.

Equations 1 and 6 clearly show that the potentiostatic response \( I_p \) vs. \( E \) and the chronopotentiometric one \( I_p^{n+1/2} \) vs. \( E \) have an identical dependence on the potential \( E \) (which is applied in the first case and measured in the second, see Ref. 19). If we differentiate Eq. 6 with respect to the potential \( E \), we deduce for the first and second derivatives of the \( I_p^{n+1/2} \) vs. \( E \) response

\[
\frac{dI_p^{n+1/2}}{dE} = \frac{nF}{RT} \left( \frac{e^\delta}{(1 + e^\delta)^2} \right)^2
\]

\[
\frac{d^2I_p^{n+1/2}}{dE^2} = \frac{nF}{RT} \left( \frac{e^\delta}{(1 + e^\delta)^3} \right)^2
\]

Since the response \( I_p \) vs. \( E \) deduced in voltammetry (see Eq. 1) and the response \( I_p^{n+1/2} \) vs. \( E \) obtained in chronopotentiometry (see Eq. 6) are identical for a reversible process, the total analogy between Eqs. 1, 4, and 5 and Eqs. 6, 10, and 11, respectively, suggests to us the design of a new modality of reciprocal derivative chronopotentiometry based on the representations \( dI_p^{n+1/2}/dE \) vs. \( E \) and \( d^2I_p^{n+1/2}/dE^2 \) vs. \( E \). Instead of the \( dI/dE \) and \( d^2I/dE^2 \) vs. \( E \) curves (or the \( dI_p/dE \) vs. \( E \) and \( d^2I_p/dE^2 \) vs. \( E \) curves) characteristic of the traditional reciprocal derivative chronopotentiometry. The curves \( dI_p^{n+1/2}/dE \) and \( d^2I_p^{n+1/2}/dE^2 \) vs. \( E \) present, independently of the value of the time exponent \( a \), an identical behavior to that of derivative voltammetry (or DPV, see Eq. 4), and function of double derivative voltammetry (or DDPV, see Eq. 5), respectively. Thus, if \( a = 0 \), i.e., if the applied current \( I(t) \) has a constant value \( I_0 \), it is convenient to calculate the reciprocal derivatives of the \( E \) vs. \( I^{1/2} \) curve; if \( a = 1/2 \) \( (I(t) = I_0^{1/2}) \), then the reciprocal derivatives of

---

**Table I. Theoretical expressions for the peak potentials, cross potentials, and peak currents corresponding to DV and DPDV.**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Peak potentials, ( E_p ) (mV)</th>
<th>Cross potential ( E_c )</th>
<th>Peak currents</th>
</tr>
</thead>
<tbody>
<tr>
<td>DV</td>
<td>( E_p = E_{1/2} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPDV</td>
<td>( \frac{\Delta I}{\Delta E} = \left( \frac{I_1 - I_2}{nFAc^*_A \Delta \Phi} \right) ) vs. ( E_1 )</td>
<td>( E_p = E_{1/2} \geq \frac{[\Delta E]}{2} )</td>
<td>( \Delta I_p = \frac{1}{\Delta E} ) tanh ( \frac{nFAc^*_A}{RT} )</td>
</tr>
<tr>
<td>DDPV</td>
<td>( d^2I_p/dE^2 \max = 68n )</td>
<td>( E_p = E_{1/2} \max = \frac{[d^2I_{1/2}/dE^2]}{max} )</td>
<td>( d^2I_{1/2}/dE^2 ) max</td>
</tr>
</tbody>
</table>

\( ^a \) The expressions for \( E_p^{max} \) and \( E_p^{min} \) in DDPV have been obtained for the case \( n = 1 \).
Table II. Theoretical expressions for the peak potentials, cross potentials, and peak heights corresponding to RDCP with programmed current (RDCP, $d_{\text{N}}^2\Delta E / dE^2$ vs. $E$) and to RDDCPC with programmed current (RDDCPC, $d_{\text{N}}^2\Delta E / dE^2$ vs. $E$ response), see Ref. 19 and Eq. 6, 10, and 11. $l(t) = I_d t$, $a \geq -1/2$. $t_d$ is the dimensionless time ($= t / n$).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Peak potentials, $E_p$ (mV)</th>
<th>Cross potential, $E_c$</th>
<th>Peak heights</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDCP</td>
<td>$d_{\text{N}}^2\Delta E / dE^2$ vs. $E$</td>
<td>$E_p = E_{1/2}^{\text{p}}$</td>
<td>$[1]$</td>
</tr>
<tr>
<td>RDDCPC</td>
<td>$d_{\text{N}}^2\Delta E / dE^2$ vs. $E$</td>
<td>$E_{p}^\text{max} = -E_{p}^\text{min} = E_{1/2} + 34/a$</td>
<td>$[3]$</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^{\text{p}}$</td>
<td>$E_{p}^\text{max} = 68/a$</td>
<td>$[4]$</td>
</tr>
</tbody>
</table>

The traditional $E$ vs. $t$ curve should be carried out, while if, for example, $a = 1$, $l(t) = I_d t$, we must plot the two first reciprocal derivatives of the $E$ vs. $t^{3/2}$ curve vs. the measured potential $E(t)$.

In Table II we have summarized the peak parameters (peak potentials and peak heights) and the cross potentials corresponding to this new modality of reciprocal derivative and double-derivative chronopotentiometry with programmed current. If we compare these characteristic parameters with those corresponding to derivative and double-derivative voltammetry (see Table I), the total analogy between the peak and cross potentials is evident, as is also that between the peak currents and peak heights obtained in both potentiostatic and chronopotentiometric derivative techniques, respectively.

**Results and Discussion**

We have experimentally verified the total analogy between the responses obtained in derivative voltammetry and reciprocal derivative chronopotentiometry with programmed current with the system Fe(C$_6$H$_5$CO$_2$)$_3$$^-$ in 0.2 M K$_2$C$_6$H$_5$O$_2$ (pH 4.49) at an SMDE.

Thus, Fig. 1 shows the behavior indicated in Tables I and II for the experimental system mentioned above. The broken line corresponds to the normal pulse voltammogram ($I_N$ vs. $E$ curve, Fig. 1a), along with its first ($dI_N/dE$ vs. $E$ curve, Fig. 1b) and second derivatives ($d^2I_N/dE^2$ vs. $E$ curve, Fig. 1c). The solid line corresponds to the $I_{p}^{3/2}$ vs. $E$ curve (Fig. 1a) obtained for the application of a current ramp of the form $l(t) = I_d (a = 1)$, and also to its first ($dI_{p}^{3/2}/dE$ vs. $E$ curve, Fig. 1b) and second derivatives ($d^2I_{p}^{3/2}/dE^2$ vs. $E$ curve, Fig. 1c). We have superimposed these curves showing the total agreement between the curves $I_N$ vs. $E$ and $I_{p}^{3/2}$ vs. $E$ (Fig. 1a), as well as that found between their first (Fig. 1b) and second (Fig. 1c) derivatives. We have observed in all the cases that the differences between the peak potentials obtained in both techniques are lower than 3 mV while the difference between the peak currents and the peak heights is less than 4%.

We have also experimentally verified the validity of the theoretical expressions of Tables I and II. Thus, in Fig. 2 the behavior of the differential pulse voltammograms ($\Delta I_N/\Delta E$ vs. $E$ responses, see curves a, b, and c) is shown for the experimental system Fe(C$_6$H$_5$CO$_2$)$_3$$^-$ 2 mM in 0.2 M K$_2$C$_6$H$_5$O$_2$ (pH 4.49) obtained at different values of the difference $\Delta E$ between the two applied potential steps. Also included in this figure is the first derivative of the voltammetric curve (see curve d) and the reciprocal derivative chronopotentiogram corresponding to the application of a programmed current of the form $l(t) = I_d$ (curve e).

In Fig. 3 we have plotted the DDP voltammograms for the same system ($\Delta^2I_{p}/\Delta E^2$ vs. $E$ responses, see curves a, b, and c) at different values of $\Delta E$ also including the second derivative of the voltammetric curve (see curve d) and the reciprocal double derivative chronopotentiogram for the above mentioned programmed current (see curve e). Note that curves d and e in Fig. 2 and 3 are practically coincident.

The values obtained for the peak parameters in both derivative and differential techniques appear in Fig. 2 and 3.

As can be seen from these figures, the experimental results are in very good agreement with the theoretical expressions shown in Tables I and II. Thus, the peak current of the DPV curves decreases in absolute value with $\Delta E$ according to Eq. 4 of Table I (see curves a, b, and c in Figure 2). We have calculated the theoretical values of

![Figure 1](image1.png)

**Figure 1.** (---) Experimental $I_N$ vs. $E$ (a), $dI_N/dE$ vs. $E$ (b), and $d^2I_N/dE^2$ vs. $E$ (c) curves corresponding to the system 2 mM Fe(C$_6$H$_5$CO$_2$)$_3$$^-$ in 0.2 M K$_2$C$_6$H$_5$O$_2$ (pH 4.49) on a SMDE. Time pulse $t = 0.050$ s, $I_d = 40.77$ µA. (---) Experimental $I_{p}^{3/2}$ vs. $E$ (a), $dI_{p}^{3/2}/dE$ vs. $E$ (b), and $d^2I_{p}^{3/2}/dE^2$ vs. $E$ (c) curves corresponding to the system 6 mM Fe(C$_6$H$_5$CO$_2$)$_3$$^-$ in 0.2 M K$_2$C$_6$H$_5$O$_2$ (pH 4.49) on a SMDE. $l(t) = I_d$, $u = 1$, $t_d = 70$ µA s$^{-1}$, $r = 1.006$ s, $r_0 = 0.4966$ cm, $n = 1$, $D_{\text{Fe(C}_6\text{H}_5\text{CO}_2)_3} = 7.30 \times 10^{-5}$ cm$^2$ s$^{-1}$, $T = 298$ K.
the peak currents according to Eq. 2 and 4 of Table I obtaining in all the cases values in agreement with the experimental ones (errors less than 2%). Moreover, the peak potential in DPV is shifted toward more negative values when $\Delta E$ increases, showing a linear dependence on this parameter according to the expression: $E_p = 0.237 - 0.506\Delta E$, with $E_p$ and $\Delta E$ being given in volts. From this expression we have obtained the following value for the reversible half-wave potential for the experimental system studied (see Eq. 1 and 3 in Table I): $E_{1/2} = E^0 = (-0.237 \pm 0.001) V$.

In Fig. 3 it is shown that the maximum and minimum currents for the DDPV (curves a, b, and c) decrease in absolute value when $\Delta E$ increases, in accordance with Eq. 13 in Table I, and that the ratio between the maximum and the minimum currents remains practically independent of $\Delta E$ and is very close to the unity in all the cases, in agreement with Table I (see Eq. 14). In curves a, b and c of Fig. 3 it can be also observed that, when $\Delta E$ increases, the maximum and minimum potentials are shifted toward more positive and negative values, respectively. From the measured values of the peak potentials we have deduced the following dependence on $\Delta E$ for the difference between both peak potentials valid for the DDPV technique (curves a, b and c)

$$E_p^{\text{max}} - E_p^{\text{min}} = 68 + 6.75 \times 10^{-3} \Delta E^2 - 1.08 \times 10^{-7} \Delta E^4$$

with $E_p^{\text{max}}$, $E_p^{\text{min}}$, and $\Delta E$ in mV, which is very close to Eq. 11 of Table I. In this triple-pulse technique we have obtained the following expression for the reversible half-wave potential from the measurement of the cross potentials $E_{1/2} = E^0 = (-0.237 \pm 0.001) V$.

The obtained values for the half-wave potentials are in agreement with the values reported in the literature.

We have also applied the reciprocal derivative chronopotentiometric technique with programmed current to the study of the oxidation of the ferrocene at platinum electrode. Figure 4 shows the $d\alpha^{1/2}/dE^2$ and $d\alpha^{1/2}/dE^2$ vs. $E$ curves (Fig. 4a and b, respectively) and also the $d^{2}u^{1/2}/dE^2$ and $d^{2}u^{1/2}/dE^2$ vs. $E$ curves (Fig. 4c and d, respectively) corresponding to the system 5,33 mM ferrocene in acetonitrile/0.25 M PFP,NBu4 for which we have applied a time-dependent current of the form $i(t) = I_0$, $u = 1$, $I_0 = 70 \mu A s^{-1}$, $\tau = 1.008 s$. Other conditions as in Fig. 1.

![Graph of E vs. Ag/AgCl, KCl 1 M](image)

![Graph of E vs. Ag/AgCl, KCl 1 M](image)
These values correspond to a series of five essays with a programmed current of the form \( I_d \) (\( u = 1 \)) of amplitude \( b_0 = -10 \mu A \) s\(^{-1}\). The potential is the mean of the five experimental values, while the error corresponds to the standard deviation.

**Conclusions**

For reversible electrode processes, the response obtained in reciprocal derivative chronopotentiometry from the curves \( d^2F_N^+ / dE^2 \) vs. \( E \) and \( d^2F_N^+ / dE^2 / \sqrt{2} \) vs. \( E \), when a programmed current of the form...
$I_0^{a}$ with $a \geq -\frac{1}{2}$ is applied to a planar electrode, is identical to that deduced in derivative and double-derivative voltammetry (or its analogue pulse techniques DPV and DDPV), respectively, as is shown in Fig. 1-3, Tables I and II and also in Eq. 1-11.

Although differential pulse and derivative voltammetric methods DPV, DDPV, DV, and DDV are very suitable in the study of electrode processes, it is interesting to emphasize that the great advantage of reciprocal derivative chronopotentiometric methods over voltammetric ones is, the former are much simpler to apply, since through the application of a source of constant or programmed current the complete $E$ vs. $t$ vs. $I$ response is directly registered in one single experiment.

In contrast, to obtaining curves $I$ vs. $E$ and $\Delta I$, $\Delta^2 I$, $dI/dE$, and $d^2I/dE^2$ vs. $E$, in voltammetry it was necessary to renew the electrode surface for each applied potential in order to re-establish the equilibrium in the electrode surface between each potential pulse (i.e., we carried out as many experiments as different potentials are applied). The renewal of the diffusion layer between the application of each potential or sequence of potentials applied and the subsequent ones makes it very difficult to apply these potentiostatic techniques to stationary planar electrodes such as the Pt electrode or the carbon paste electrode. Although there are papers in the literature that deal with potential-pulse techniques applied to stationary planar electrodes, most of them apply the whole potential sweep to the same electrode in the same way as multipulse techniques but allowing a very long time to elapse between each pulse or sequence of pulses applied (see, for example, Ref. 30-32).

These advantages of reciprocal derivative chronopotentiometric techniques, which have been and still are heavily exploited in the study of different electrode processes,15-19 are increased since (as we have confirmed experimentally) in the technique proposed herein, signals are obtained which are less noise influenced than those in the derivative voltammetry, and this effect is even more notorious when programmed current is used. Consequently, the differentiation of these signals has far less error associated with it. Furthermore, the effects of the double layer barely affect the central zone of the chronopotentiogram which corresponds to the peak of the $d^n I/dE^n$ signal, from which all the information of the system under study is taken.

Moreover, the $d^n I/dE^n$ and $d^{n+1} I/dE^{n+1}$ vs. $E$ curves present greater versatility than do the $dI/dE$ and $d^2I/dE^2$ vs. $E$. This is due to the fact that both the heights and the positions of the peaks can be varied by changing the $I_0$ amplitude of the programmed current applied, $I_0^{a}$, or the time exponent $a$. This versatility is highly desirable when obtaining in each case the best experimental conditions under which to study each system.

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