# Resolution of Differential Pulse Polarography: Comparison with a. c. Polarographic Techniques

T. GARAI*, Z. NAGY*, F. FAGIOLI** and C. LOCATELLI**

*Research Laboratory for Inorganic Chemistry of the Hungarian Academy of Sciences, H-1502 Budapest, P. O. Box 132
**Department of Analytical Chemistry, Institute of Chemistry, University of Ferrara, 44100 Ferrara, Italy

A relationship was derived for the resolution of differential pulse polarography as a function of the pulse amplitude and various parameters of the electrode reaction of the simultaneously present components(number of electrons exchanged in the electrode reaction, half-wave potentials). The resolution was found to be higher at small pulse amplitudes and large difference in the half-wave potentials. Resolution is higher when the number of electrons involved in the electrode reaction of both the measured and the interfering species are larger and it is mainly affected by the latter. The resolution of differential pulse polarography was found to be inferior to that of fundamental harmonic and second harmonic a.c. polarography.

Keywords Resolution, a.c. polarography, differential pulse polarography

Differential pulse voltammetry and polarography is considered one of the best among the modern electroanalytical techniques as far as sensitivity and resolution are concerned.[1]

The resolution of voltammetric techniques exhibiting a current–potential relationship similar to the derivative of the d.c. polarographic curve (such as fundamental harmonic a.c. voltammetry, square-wave polarography) can be characterized by the half-width of the peak. In their studies related to differential pulse polarography Osteryoung and his coworkers[2] derived a relationship between the pulse amplitude and peak half-width. The latter was found to tend to $W_{1/2}=3.52RT/zF$ (where $z$ is the number of electrons exchanged in the electrode process, and $R$, $T$ and $F$ are the gas constant, the temperature and the Faraday constant respectively) when the pulse amplitude approaches zero, while $W_{1/2}$ increases by increasing pulse amplitude. Thus a better resolution of overlapping peaks is obtained when a small pulse amplitude is used, however, the sensitivity of the measurement is improved by increasing pulse amplitudes.[3] In view of these counteracting factors a pulse amplitude of 20 to 100 mV is generally selected in practical analysis.

The effect of the pulse amplitude on the resolution of differential pulse polarography were not quantitatively studied yet.

Reports on the resolution of various polarogarphic and voltammetric techniques assumed identical conditions to prevail in derivative d.c., fundamental harmonic a.c., square-wave polarography and differential pulse polarography (and voltammetry), since the current potential relationship in these techniques is proportional to $\cosh^{-2}(U/2)${where $U=(zF/RT)(E-E_{1/2})$, $E$ being the potential, and $E_{1/2}$ the polarographic half-wave potential in the case of small perturbations $(\Delta E \rightarrow 0)(e.g.$ ref. 4,5)}. Since the formula reported in literature did not take into account the broadening of the peak observed at increasing pulse amplitude, in this paper a relationship is derived between resolution and pulse amplitude and the effect of some other parameters ($e.g.$ $z$, difference in the half-wave potentials) is also taken into account. The resolution of differentical pulse polarography and that of a.c. polarography is compared as well.

Since the resolution of the various polarographic techniques depends on several parameters, and the relationship relating them is not easily evaluated, an Apple 2 minicomputer has been used for the calculations.

## Resolution of Differential Pulse Polarography

The interference of species "i" on the determination of species "m" is defined by

$$\Delta I_i = 0.01\, p\; \Delta I_m \quad\quad\quad\quad\quad (1)$$

where $\Delta I_m$ is the peak current corresponding to the

measured species, $\Delta I_i$ is the current of species "i" at the peak potential of species "m" and $p$ is the percentage of the interference.

The differential pulse polarographic current $(\Delta I)$ as the function of potential[1-4] is given by

$$\Delta I = \frac{zFAD^{1/2}c}{\pi^{1/2}(\tau-\tau_1)^{1/2}} \frac{\{\exp[(zF/RT)(E-E_{1/2})]\}(1-\sigma^2)}{\{1+\exp[(zF/RT)(E-E_{1/2})]\}\{1+\sigma^2\exp[(zF/RT)(E-E_{1/2})]\}} \quad\quad\quad (2)$$

where $\sigma=\exp[(zF/RT)(\Delta E/2)]$ and $z$, number of electrons exchanged in the electrode reaction; $A$, area of the electrode; $D$, diffusion coefficient; $c$, concentration; $\tau-\tau_1$, time between pulse application and current sampling; $E$, potential; $E_{1/2}$, half-wave potential; $\Delta E$,

pulse amplitude; $F$, $R$, $T$, Faraday number, gas constant, and absolute temperature, respectively, in the case of polarographically reversible reaction. The peak current is given as

$$\Delta I_{max} = \frac{zFAD^{1/2}c}{\pi^{1/2}(\tau-\tau_1)^{1/2}} \frac{1-\sigma}{1+\sigma} \quad\quad\quad\quad\quad\quad\quad\quad\quad (3)$$

The ration of concentration of the interfering species $(c_i)$ and the measured species $(c_m)$ is thus obtained by

substituting Eqs. 2 and 3 in Equation 1,

$$\frac{c_i}{c_m} = 0.01\,p\,\frac{z_m}{z_i} \frac{(1-\sigma_m)/(1+\sigma_m)}{\dfrac{\{\exp[(z_iF/RT)\Delta E_{1/2}]\}(1-\sigma_i^2)}{\{1+\exp[(z_iF/RT)\Delta E_{1/2}]\}\{1+\sigma_i^2\exp[(z_iF/RT)\Delta E_{1/2}]\}}} \quad\quad\quad (4)$$

where $\Delta E_{1/2}$ is the difference of the half-wave potential of the two species and suffixes "i" and "m" refer to the interfering and measured species respectively.

Equation 4 can be simplified if the exponential terms in brackets in the denominator of the equation are large as compared to unity, i.e. $\sigma_i^2\exp[(z_iF/RT)\Delta E_{1/2}] \gg 1$ as in this case $\exp[(z_iF/RT)\Delta E_{1/2}]\gg 1$ also, since $\sigma_i^2 < 1$. Whence we obtain

$$\frac{c_i}{c_m} = 0.01\,p\,\frac{z_m(1-\sigma_m)\sigma_i^2}{z_i(1+\sigma_m)(1-\sigma_i^2)}\exp[(z_iF/RT)\Delta E_{1/2}] \quad\quad\quad\quad (5)$$

thus $c_i/c_m$ depends exponentially on $\Delta E_{1/2}$.

The effect of the various parameters such as pulse amplitude, difference of half-wave potentials, etc. can be calculated on the basis of Equation 4.

It is apparent in Equation 4 that the pulse amplitude plays an important role as far as resolution is concerned, although the effect of other parameters—mainly the number of electrons exchanged in the eleactrode reaction of the species—cannot be neglected either.

The formula relating the half-width of the peak and the pulse amplitude was derived by Osteryoung and co-workers[2,3]:

$$W_{1/2} = \frac{RT}{zF} \ln \frac{(\sigma^2+4\sigma+1)+\sqrt{(\sigma^2+4\sigma+1)^2-4\sigma^2}}{(\sigma^2+4\sigma+1)-\sqrt{(\sigma^2+4\sigma+1)^2-4\sigma^2}}.$$

$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (6)$$

The broadening of the peak with increasing pulse amplitude is shown in Fig. 1, where the ratio of $W_{1/2}$ at
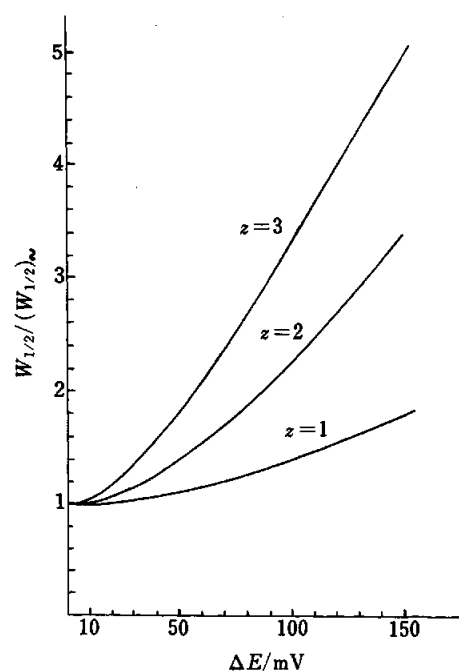


Fig. 1   Ratio of the half-width of the differential pulse polarographic waves vs. the pulse amplitude at various values of the number of electrons exchanged in the electrode reaction $(z)$.
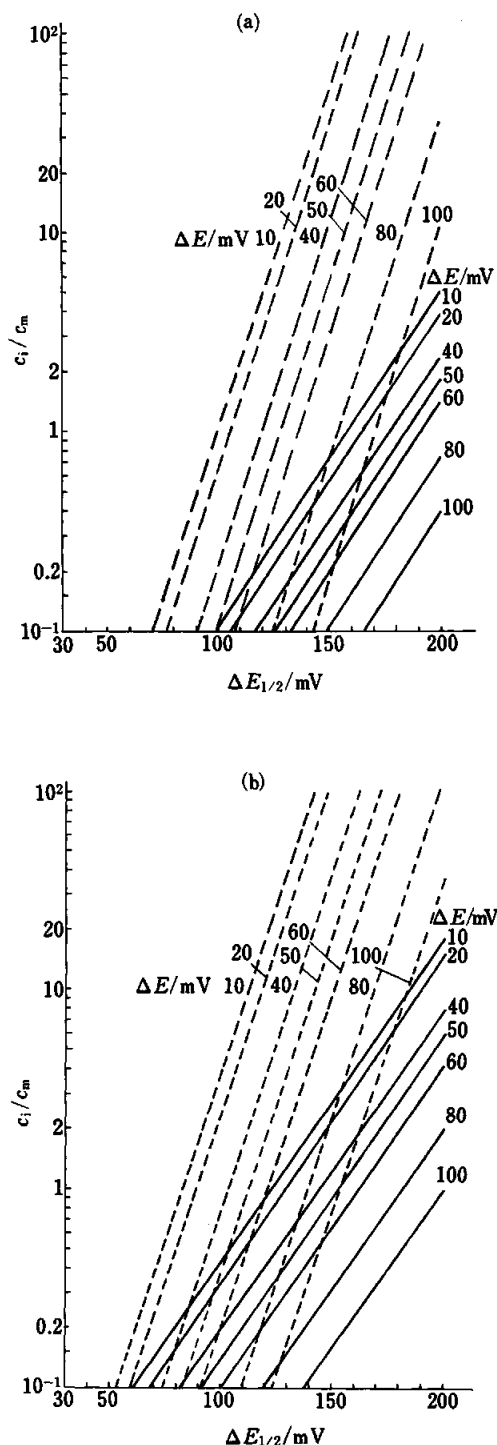
Fig. 2 Effect of pulse amplitude ($\Delta E$) on the resolution of differential pulse polarography. The ratio of the concentration of the interfering ion and of that of the measured ion (on logarithmic scale) vs. the difference in the half-wave potentials of the ions at various pulse amplitudes. The number of electrons exchanged in the electrode reaction of the interfering ion, $z_i$=1(—); 2(---). (a) Valence of the measured ion, $z_m$=1; (b) $z_m$=2.
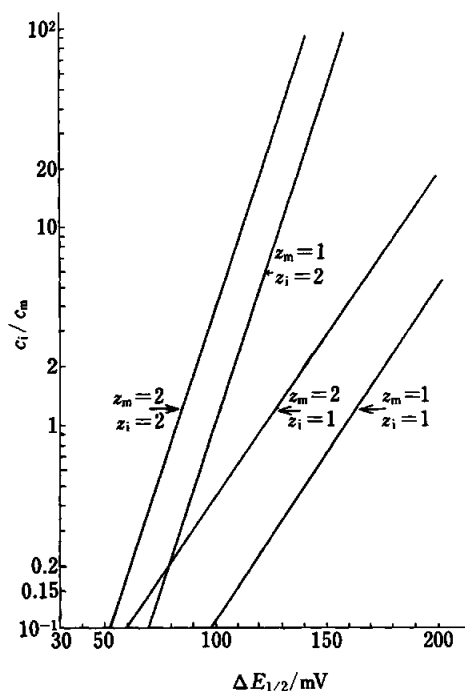


Fig. 3 Effect of the number of electrons transferred in the electrode reaction on the resolution. The ratio of the concentration of the interfering ion and that of the measured ion vs. the difference in half-wave potentials. Pulse amplitude $\Delta E$=10 mV, $z_i$ and $z_m$: number of the electrons transferred in the electrode reaction of the interfering species and the measured one, respectively.

apparent that the broadening of the peak is lerger when the number of electrons exchanged in the electrode process is larger.

Figure 2 shows the effect of the peak broadening on resolution in terms of the ratio of the concentration of the interfering and the measured species. The logarithm of the latter is plotted vs. the difference in the half-wave potentials at various pulse amplitudes, assuming the error caused by the interference to be $p$=1 per cent. It is apparent that the interference is considerably increased by larger pulse amplitudes. E.g. an interfering ion with one electron transferred in the reduction causes 1 per cent error in the measurement of an ion with $z_m$=2 and 1 : 1 ratio of the concentrations in the case of a pulse amplitude of 20 mV when the difference in helf-wave potentials is 130 mV while with $\Delta E$=80 mV, the same error can already be expected when $\Delta E_{1/2}$=180 mV (Fig. 2b).

If $z_i$=2 for the interfering ion, and the concentration ratio is e.g. 1:1, an 1 per cent error is observed in the measurement of an ion with $z_m$=1 at $\Delta E_{1/2}$=100 mV when $\Delta E$=10 mV and at $\Delta E_{1/2}$=155 mV when $\Delta E$=80 mV (Fig. 2a).

The effect of the number of electrons exchanged in the electrode reaction on the interference is shown in Fig. 3. It is apparent in Fig. 3 that the slope of the $c_i/c_m$ vs. $\Delta E_{1/2}$ function depends on the value of $z_i$ of

a given pulse amplitude ($\Delta E$) and the limiting value of $W_{1/2}$ when $\Delta E$ tends to zero is plotted vs. $\Delta E$. It is
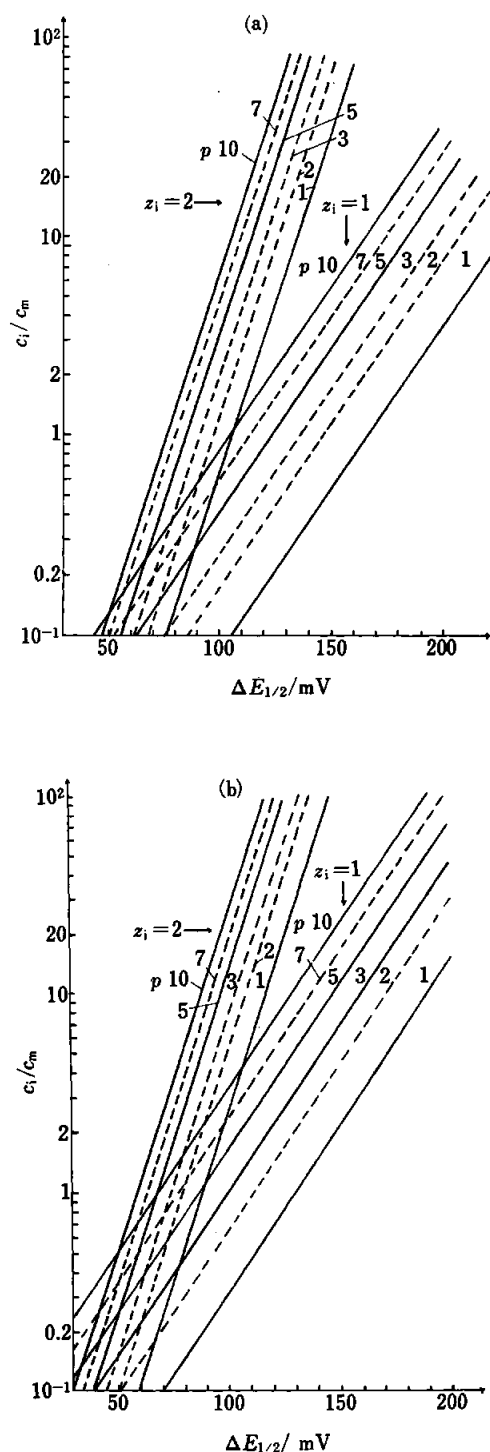
Fig. 4  Error percentage at various concentration ratios of the measured species and the interfering species vs. the difference in the half-wave potentials. $\Delta E$=20 mV; (a) $z_m$=1, (b) $z_m$=2.

measured ion is smaller. Thus the greatest interference is observed when both the measured and the interfering species are monovalent. E.g at a half-wave potential difference of $\Delta E_{1/2}$=110 mV the presence of about 15 per cent of a monovalent interfering ion already causes 1 per cent error in the determination of a species with $z_m$=1, while in the case of the measurement of an ion with $z_m$=2 the 1 per cent error level is only attained by an amount of 60 per cent of the interfering monovalent ion. The interference caused by an ion with $z_i$=2 is smaller. Thus assuming identical conditions to those mentioned in the previous example 1 per cent error is encountered when the concentration ratio $c_i$:$c_m$=2.2:1 in the case of the determination of a monovalent ion while a 8.5-fold excess of the interfering ion causes the same error in the determination of an ion with $z_m$=2.

A similar trend is observed in the case of various pulse amplitudes, since by increasing the latter the functions shown in Fig. 3 are shifted almost parallelly towards larger values of $\Delta E_{1/2}$.

The above considerations are valid to "reversible" polarographic reactions.  In the case of slower electrode process, the resolution is somewhat impaired since the sensitivity of the technique decreases.[1]

It is apparent from the above considerations that the resolution of differential pulse polarography at a given difference of the half-wave potentials of the species mainly depends on the number of electrons transferred in the electrode reaction of the interfering ion. When the latter is smaller the interference is more pronounced. The interference is also affected by the number of electrons transferred in the reaction of the measured species. Namely it decreases when the latter is larger.

The relative peak-broadening (cf. Fig. 1) can be misleading, since the absolute value of peak-width is the relevant factor in resolution.

The plots shown in Fig. 4 indicate the limits of concentration ratios permitting an analysis with 1 to 10 per cent error in the case of various parameters of the electrode reaction and in various experimental conditions (the computer programme is available on request).

the interfering ion.   Thus the resolution of the polarograms mainly depends on the latter.   The interference is larger when the latter is smaller.   The effect of the interfering ion is larger when the number of electrons exchanged in the electrode reaction of the

## Comparison of the Resolution of Various Polarographic Techniques

It is interesting to compare the resolution of various a.c. polarographic techniques with that of differential pulse polarography.   It has been shown[4,6,7] that the resolution of second harmonic a.c. polarography is better than that of fundamental harmonic a.c. polarography and square-wave polarography.   The shape of the current-potential curve in the latter case is practically identical to the fundamental harmonic a.c. polarographic wave.[8]   The resolution attained with the various techniques is shown in Fig. 5.

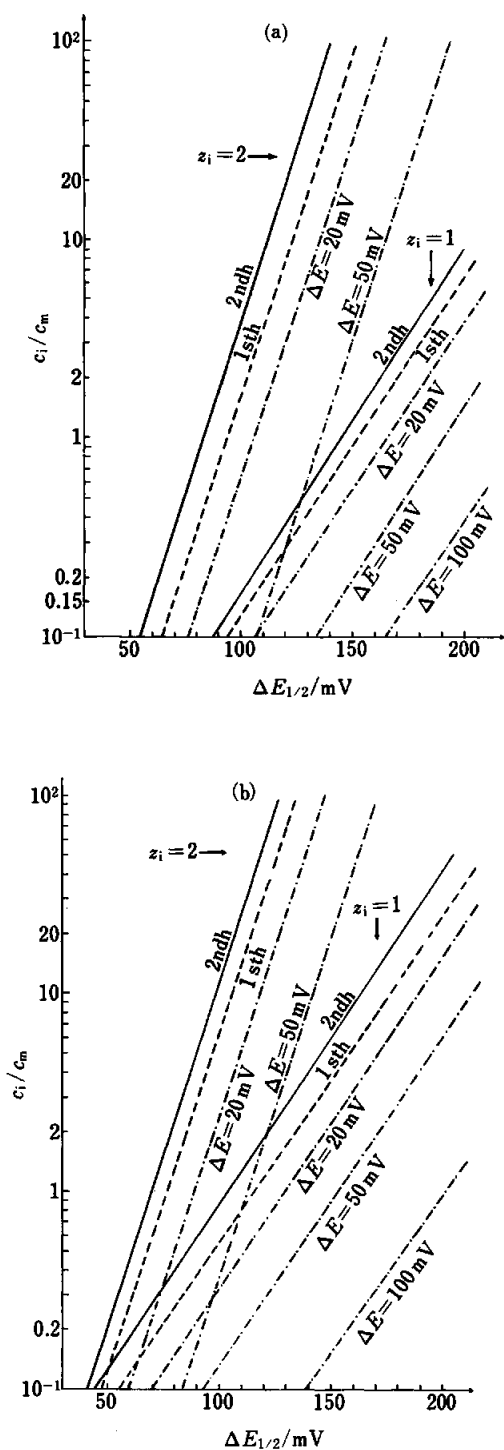The concentration ratio of the interfering ion and the

Fig. 5 The ratio of the concentration of the interfering species and that of the measured one as the function of the difference in half-wave potentials. —, second harmonic a.c. polarography;---, fundamental harmonic a.c. polarography; -·-, differential pulse polarography with various pulse amplitudes ($\Delta E$). The error is assumed to be 1 per cent. $z_i$ and $z_m$ are the number of electrons exchanged in the reaction of the interfering species and the measured one, respectively. (a) $z_m=1$, (b) $z_m=2$. $z_i=1$, 2.

measured one as a function of $\Delta E_{1/2}$ is given by the following formula[6] in the case of fundamental harmonic a.c. polarography

$$\frac{c_i}{c_m} = 0.01\, p\left(\frac{z_m}{z_i}\right)^2 \cosh^2\left(\frac{z_i F \Delta E_{1/2}}{2RT}\right) \quad\quad (7)$$

while in the case of second harmonic a.c. polarography

$$\frac{c_i}{c_m} = 3.8 \times 10^{-3}\, p\left(\frac{z_m}{z_i}\right)^3 \cosh^2\left[\frac{z_i F}{2RT}\left(\Delta E_{1/2}+\frac{0.034}{z_m}\right)\right]$$

$$\quad\quad (8)$$

It is apparent that second harmonic a.c. polarography excells as far as resolution is concerned, since at equal differences of half-wave potentials and given $z_i$ and $z_m$ the concentration ratio of the interfering species and that of the measured one causing the same error (1 per cent in Fig. 5) is always largest for second harmonic a.c. polarography. The sequence of the decreasing concentration ratios is second harmonic, fundamental harmonic a.c., differential pulse polarography. It is to be noted, however, that the somewhat higher sensitivity of differential pulse polarography may counterbalance the disadvantage of lower resolution power.

**References**

1. A. J. Bard, L. R. Faulkner, "Electrochemical Methods", John Wiley, New York (1980).
2. J. Osteryoung, K. Hasebe, Rev. Polarogr., 22, 1 (1976).
3. E. R. Parry, R. A. Osteryoung, Anal. Chem., 37, 1634 (1965).
4. A. M. Bond, R. C. Boston, Rev. Anal. Chem., 2, 129 (1964).
5. A. Bobrowski, Chem. Anal. (Warsaw), 28, 567 (1983).
6. T. Garai, J. Dévay, Hung. Sci. Inst., 25, 27 (1972).
7. F. Fagioli, T. Garai, J. Dévay, Ann. Chim. (Rome), 64, 633 (1974).
8. G. G. Barker, R. L. Faircloth, A. W. Gardner, "Square-wave Polarography". Harwell, Berkshire, "Atomic Energy Research Establishment", (1958).