

Treatment of Polarographic Data by the Method of Least-squares. II. Simultaneous Estimation of the Diffusion Current and the Half-wave Potential*

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By applying the method of least squares it is possible to estimate simultaneously the diffusion current and the half-wave potential with precision which exceeds that of the usual graphical methods. The method described in this paper is particularly suitable for analysing composite current-voltage curves. An example is given of the analysis of the composite curve obtained with a solution containing thallos and lead ions in 0.1 N KCl.

INTRODUCTION

In a previous communication from our laboratory¹ it has been shown how the method of least squares may be successfully applied if precise values of half wave potentials are needed. This method is, however, limited to cases where the diffusion current can be estimated with sufficient precision by graphical methods. The method described in this paper enables precise estimation of both the half wave potential and the diffusion current, if approximate values of these parameters are available.

METHOD

Suppose we have N pairs of observed values (x, y) and we want to fit the equation

$$y = f(x, A, B) \quad (1)$$

to these points; A and B are constants the approximate values (A_0, B_0) of which are known so that

$$A = A_0 + a; \quad B = B_0 + b \quad (2)$$

where a and b are small correction terms. Using the method of least squares² the correction terms a and b can be calculated by solving the normal equations

$$\begin{aligned} \sum (\varphi - af_A - bf_B) f_A &= 0 \\ \sum (\varphi - af_A - bf_B) f_B &= 0 \end{aligned} \quad (3)$$

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where φ , f_A , f_B are known, and a and b unknown quantities. φ , f_A and f_B are calculated as follows:

$$\varphi = y (\text{obs.}) - f(x, A_o, B_o); \quad (4)$$

$$f_A = \frac{\partial f(x, A_o, B_o)}{\partial A} \quad (5)$$

$$f_B = \frac{\partial f(x, A_o, B_o)}{\partial B}$$

Partial derivatives f_A and f_B are calculated from eq. (1) and evaluated for each observed value x using A_o and B_o . N values of f_A , f_B and φ are thus obtained which are used in solving the normal equations (3).

We shall apply this procedure to the equation of Heyrowsky and Ilikovič³.

$$E_{d.e.} = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \quad (6)$$

where $E_{d.e.}$ is the potential of the dropping electrode at any point on the wave, $E_{1/2}$ is the half wave potential, i is the current at any point on the wave and i_d is the diffusion current; symbols R , T , n and F have their usual meaning. In order to simplify the notation we shall write $E_{d.e.} = y$, $i = x$, $E_{1/2} = A$, $i_d = B$ and $k = RT/nF$; $2.303 k = k'$. In terms of this notation equation (6) reads:

$$y \equiv f(x, A, B) = A - k \ln [x/(B_o - x)] \quad (7)$$

Hence

$$f_A = 1; f_B = k/(B_o - x) \text{ and } \varphi = y (\text{obs.}) - A_o + k \ln [x/(B_o - x)] \quad (8)$$

and the normal equations (3) reduce to

$$\begin{aligned} aN + b \sum f_B &= \sum \varphi \\ \alpha \sum f_B + b \sum f_B^2 &= \sum \varphi f_B \end{aligned} \quad (9)$$

from which it is easy to calculate a and b , if we compute $\sum f_B$, $\sum f_B^2$, $\sum \varphi$ and $\sum \varphi f_B$. Approximate values A_o and B_o can always be obtained by graphical methods.

ANALYSIS OF CURRENT-VOLTAGE CURVES

As an example of the application of this method we give the analysis of current voltage curves obtained with aqueous $0.1 N$ KCl solutions containing $4.0 \times 10^{-4} N$ thallium nitrate (Fig. 1, curve 3), $4.0 \times 10^{-4} N$ lead acetate (Fig. 1, curve 2) and $4.0 \times 10^{-4} N$ thallium nitrate + $4.0 \times 10^{-4} N$ lead acetate (Fig. 1, curve 1), respectively.

Approximate values for the diffusion current (B_o) and the half wave potential (A_o) were obtained graphically. The value of the current (x) corresponding to a given dropping electrode potential (y) was determined by measuring the distance between the extrapolated residual current and the corresponding point on the wave (see for instance fig. 1, curve 3). This method

was used with curve (2) and (3) and with the first part of the curve (1). For the second part of the curve (1) the difference was measured between the extrapolated diffusion current and the corresponding point on the current voltage curve, and the value for the current (x) calculated from the difference $B_0 - (B_0 - x)$. (See Fig. 1, curve 1) It should be pointed out that only those parts of the composite curve (Tl + Pb) were used in the analysis which were not distorted by the interference of Pb and Tl-ions, that is, the current values corresponding to a potential not greater than -400 mV (for Pb^{++}) and not less than -440 mV (for Tl^+) were taken.

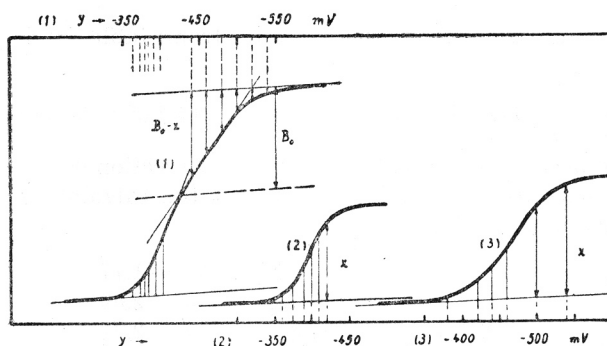


Fig. 1. Current voltage curves obtained with solutions of thallous and lead ions in $0.1 N$ KCl . 1) $4.0 \times 10^{-4} N$ thallium nitrate + $4.0 \times 10^{-4} N$ lead acetate; 2) $4.0 \times 10^{-4} N$ lead acetate; 3) $4.0 \times 10^{-4} N$ thallium nitrate.

As an example of the computation procedure, the analysis of the first part of curve (1) is given in full:

$A_0 = -395$ mV, $B_0 = 25$ mm (from curve (2) estimated graphically)

$k' = 29.578$ mV (calculated from R , T and $n = 2$); $N = 6$

a) computation of $f_0 = A_0 - k \ln [x/(B_0 - x)]$

x	y_{obs}	$B_0 - x$	$x/(B_0 - x)$	$\log [x/(B_0 - x)]$	f_0
1.3	-360	23.7	0.0549	-1.26081	-357.71
3.2	-370	21.8	0.1468	-0.83326	-370.35
4.9	-375	20.1	0.2438	-0.61297	-376.87
5.8	-380	19.2	0.3021	-0.51985	-379.62
10.0	-390	15.0	0.6667	-0.17612	-389.79
15.0	-400	10.0	1.5000	-0.17609	-400.21

b) Computation of φ , $f_B = k/(B_0 - x)$ and the necessary sums.

φ	f_A	φ	f_B
— 360	— 357.71	— 2.29	0.542
— 370	— 370.35	0.35	0.589
— 375	— 376.87	1.87	0.639
— 380	— 379.62	— 0.38	0.669
— 390	— 389.79	— 0.31	0.856
— 400	— 400.21	0.21	1.285
sums		— 0.45	4.580

The following sums are calculated directly from table b) by means of a calculating machine:

$$\Sigma f_B^2 = 3.880528; \quad \Sigma f_B = 0.00423; \quad (\Sigma f_B)^2 = 20.9764$$

c) Determinants necessary for calculating the correction terms a and b (see equation 9) were also obtained by means of the calculating machine from the values given under b):

$$\begin{aligned} \Sigma \varphi \Sigma f_B^2 - \Sigma \varphi f_B \Sigma f_B &= -1.77 \\ N \Sigma \varphi f_B - \Sigma f_B \Sigma \varphi &= 2.09 \\ N \Sigma f_B^2 - (\Sigma f_B)^2 &= 2.31 \end{aligned}$$

$$a = -1.77/2.31 = -0.8; \quad b = 2.09/2.31 = +0.9$$

Corrected values A and B are thus:

$$A = A_0 + a = -395.8 \text{ mV}; \quad B = B_0 + b = 25.9 \text{ mm.}$$

Curves (2) and (3) and second part of curve (1) were analysed in a similar way. Table I compares the half wave potentials (in mV) and the wave heights (in mm) obtained with solutions containing Pb^{++} and Tl^+ alone with those calculated from the composite curve (1) obtained with a solution containing both thallous and lead ions. The agreement is very good. It is obvious that curve (1) could not have been analysed by the usual graphical methods.

In order to see to what extent the first order corrections a and b can improve the approximate values A_0 and B_0 , we tried to analyse curve (1) starting with $A_0 = -400$ mV and $B_0 = 28$ mm, and we obtained $A = A_0 + a = -395.73$ mV and $B = B_0 + b = 25.74$ mm which is in excellent agreement with the results shown in table I.

These examples show the usefulness of the described method for the analysis of composite current voltage curves exhibiting marked interference of the constituents of the polarographed solution. There are many other instances where this method of analysis might be successfully applied, particularly in analytical applications of polarography.

EXPERIMENTAL

A Cambridge Polarograph, Pen Recording Type, and a standard polarographic cell with external saturated calomel electrode were used. Dissolved oxygen was displaced by bubbling purified hydrogen through the solution for 15 minutes prior to the polarographic determination. The dropping time was approximately 3 seconds.

TABLE I

	Measured from	Curve No.	Half-wave potential mV	Difference		Wave height mm	Difference	
				mV	%		mm	%
Pb	composite curve	1	-395.74	+0.07	0.02	25.8	+0.4	1.6
	single curve	2	-395.67			25.4		
Tl	composite curve	1	-464.39	-1.01	0.22	31.5	-0.1	0.32
	single curve	3	-465.40			31.6		

The potential readings on the bridge were checked against a standard Weston element. The rate of change of the potential was 18.8 mV/min.; damping 4, range 0.5/0; 1 cm on the potential axis of the polarogram thus corresponded to 50 mV; sensitivity 1/20 of the maximal, i. e. 52.65×10^{-9} A/mm.

Analytical grade chemicals and redistilled water were used for preparing the solutions. The solutions to be analysed were prepared by dilution from stock solutions containing 0.002 N TlNO₃, in 0.1 N KCl and 0.002 N Pb(CH₃COO)₂ in 0.1 N KCl; 0.002% of gelatin was added as maximum suppressor.

Computations were performed with a Friden Automatic Calculator.

REFERENCES

1. O. A. Weber, *Arhiv kem.* **25** (1953) 231.
2. See e. g. H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, Van Nostrand Co., New York, 1943, p. 500.
3. J. Heyrowsky and D. Ilkovič, *Collection Czechoslov. Chem. Commns.* **7** (1935) 198.

IZVOD

**Obrađivanje polarografskih podataka metodom najmanjih kvadrata
II. Simultano određivanje difuzione struje i poluvalnog potencijala***

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Primjenom metode najmanjih kvadrata može se simultano odrediti difuziona struja i poluvalni potencijal. Preciznost tog određivanja premašuje preciznost, koja se može postići uobičajenim grafičkim metodama. Opisana metoda osobito je prikladna za analizu složenih polarografskih krivulja. Kao primjer dana je složena polarografska krivulja, koja je dobivena analizom otopine talijevih i olovnih iona u 0.1 N otopini KCl.

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