

## Treatment of Polarographic Data by the Least-Squares Method I. Estimation of the Half-wave Potential

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The application of the half-wave potential in polarographic investigations is reviewed. In view of the fact that the methods currently used for computation of the half-wave potential do not give very reliable values and do not allow the estimation of experimental errors, an attempt is made to apply the least-squares method to the computation of the half-wave potential from the current-voltage data.

Prior to the introduction of the half-wave potential in polarographic literature<sup>1</sup> several attempts were made to characterize electroreducible and electrooxidizable substances by arbitrary points on the current-voltage curve. In this connexion the deposition potential<sup>2, 3</sup>, the reduction potential<sup>4, 5</sup> and the characteristic potential obtained by applying Le Blanc's procedure<sup>6</sup> should be mentioned. However, none of these arbitrarily selected points could be used for characterization of the processes at the dropping electrode and consequently they had little practical significance.

The half-wave potential is best defined using the equation of Heyrowsky and Ilkovič<sup>6</sup>:

$$E_{de} = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \quad (1)$$

This function has an inflexion point at  $i = \frac{i_d}{2}$ . The potential corresponding

to this point is the half-wave potential. Reversible electrode processes are well characterized by this potential, which is independent from the concentration of the reacting substance, the sensitivity of the recording instrument, the drop time, the rate of flow of mercury, the spacing of the abscissa and the value of the diffusion current provided the concentration of the supporting electrolyte and the temperature are constant. The influence of the concentration of the supporting electrolyte on the half-wave potential was investigated by Lingane<sup>7</sup>, who found that increase in concentration of the supporting electrolyte makes the half-wave potential more negative. The half-wave potential of a given substance does not depend on the concentration of other oxidizable or reducible substances which might be present in the solution. The temperature coefficient of the half-wave potential of simple metal ions is  $-0.7 \text{ mV}/^\circ\text{C}$  if the reduction at the dropping electrode is reversible<sup>8</sup>. The same temperature coefficient has been obtained with some organic irreversible systems<sup>9</sup>.

The half-wave potential has a well defined thermodynamic meaning being in a simple way related to the normal potential<sup>7, 10</sup>. The thermodynamic

equation of a reversible polarographic wave becomes identical with the equation of the potentiometric titration, if the volume of the titrating solution is substituted for the current; and the half-wave potential corresponds to the potential obtained when exactly one half of the equivalent amount of the titrating solution is added.

Recently it has been observed that the half-wave potential is influenced by the drop time<sup>18</sup> and the rate of flow of mercury<sup>19</sup> in such a way that

$$\frac{\Delta E_{1/2}}{\Delta \log m} \approx \frac{0.030}{n}$$

( $m$  is the rate of flow of mercury in  $\text{mg sec}^{-1}$ ;  $n$  is the number of equivalents involved).

The knowledge of the half-wave potential is important in studying the formation of complex metal ions. The half-wave potential of complex metal ions is usually shifted towards negative values. The composition of the complex and the complexity constant can be calculated from the magnitude of this shift<sup>6, 11, 12</sup>.

The half-wave potential is also used in organic polarography in connexion with the study of redox potentials, of structural problems, of Raman- and absorption spectra<sup>14, 15, 16</sup> as well as a criterion of reversibility<sup>17</sup>.

Graphical methods are usually employed for determination of the half-wave potential. Tomeš<sup>10</sup> has proposed an indirect method for determination of the half-wave potential based on graphical solution of the Heyrowsky-Ilkovič<sup>6</sup> equation. Linear interpolation was applied by Meites<sup>21</sup> to a series of pairs of measurements of current and potential in the neighbourhood of the half-wave potential, while the symmetry of the polarographic wave was used in a method published by Monnier and Rusconi<sup>22</sup>. By applying a geometrical method they found the centre of symmetry and calculated the corresponding potential, which was identical with the half-wave potential. Recently, Heyrowsky<sup>23</sup> determined the half-wave potentials from the maximum of the function:  $\Delta I/\Delta E = f(E)$ . The oscilloscope has also been used for this purpose<sup>24-27</sup>.

Although the methods are numerous, little is known about their precision and reliability. If very small differences of the half-wave potential are involved (for instance when studying the influence of the rate of flow of mercury on the half-wave potential<sup>19</sup>) it is most important to know the experimental errors and to be able to test the significance of such differences. In such cases the usual procedures do not seem satisfactory<sup>28</sup>. Therefore, an attempt was made to apply the least-squares method to this problem.

#### ESTIMATION OF THE HALF-WAVE POTENTIAL BY THE LEAST-SQUARES METHOD

The purpose of the present paper is to show the method of least-squares can be applied in estimating the half-wave potential from the current-voltage data.

By rearranging equation (1) and using logarithms to base 10 we obtain:

$$\log \frac{i}{i_d - i} = \frac{0.4343 nF}{RT} E_{1/2} - \frac{0.4343 nF}{RT} E_{de}. \quad (2)$$

By setting

$$\log \frac{i}{i_d - i} = y; \quad - \frac{0.4343 nF}{RT} = b \text{ and } \frac{0.4343 nF}{RT} E_{1/2} = a$$

we can write equation (2) as

$$y = a + b \cdot E_{de} \quad (3)$$

For  $y = 0$ ,  $E_{de} = - \frac{a}{b} = E_{1/2}$

By comparing  $1/b$  with its theoretical value  $0.0591/n$  (at  $25^\circ\text{C}$ ) an estimate of  $n$  can also be obtained.

Since both  $y$  and  $E_{de}$  can be measured, the problem of estimating the half-wave potential reduces to a linear regression analysis of  $y$  upon  $E_{de}$ .

The regression equation

$$Y = a + b \cdot E_{de}$$

with  $a = \bar{y} - b \bar{E}$ ,  $b = \frac{N \Sigma E y - \Sigma E \Sigma y}{N \Sigma E^2 - (\Sigma E)^2}$   $\left( \bar{y} = \frac{1}{N} \Sigma y, \bar{E} = \frac{1}{N} \Sigma E_{de} \right)$

is then used for estimating  $E_{de}$  at  $Y = 0$ .

The standard error of  $E_{de}$  at  $Y = 0$  is easily estimated from the equation<sup>31</sup>:

$$s_{E_{1/2}} = \sqrt{\frac{V}{b^2} \left( \frac{1}{N} + \frac{\bar{y}^2}{b^2 \{ \Sigma E^2 - \frac{1}{N} (\Sigma E)^2 \}} \right)} \quad (4)$$

where  $V$  is the variance of  $y$  about the regression  $Y = a + bE$ . For computing  $V$  the following expression<sup>29</sup> may be used:

$$V = \frac{1}{N-2} \left\{ \Sigma y^2 - \frac{1}{N} (\Sigma y)^2 - \frac{(\Sigma E y - \frac{1}{N} \Sigma E \Sigma y)^2}{\Sigma E^2 - \frac{1}{N} (\Sigma E)^2} \right\}$$

$N$  is the number of measured  $E_{de}$ ,  $y$  pairs.

The standard error of  $1/b = RT/0.4343 nF$  can also be estimated from the equation:

$$s_{1/b} = \frac{1}{b^2} s_b$$

where

$$s_b = \sqrt{\frac{V}{\Sigma E^2 - \frac{1}{N} (\Sigma E)^2}}$$

The above procedure has been applied in calculating the half-wave potential of  $+6$  uranium in a supporting electrolyte containing salicylic and sulphuric acid.<sup>30</sup>

## REFERENCES

1. J. Heyrowsky and D. Ilkovič, *Collection Czechoslov. Chem. Commns.* **7** (1935) 198.
2. J. Heyrowsky, *Phil. Mag.* **45** (1923) 303.
3. M. Shikata, *Mem. Coll. Agr. Kyoto Imp. Univ.*, Ser. No 4 (1927) 1.
4. J. Heyrowsky, *Rec. trav. chim.* **44** (1925) 488.
5. G. Semerano, *Gazz. chim. ital.* **62** (1932) 518.
6. A. Winkel and G. Proske, *Ber.* **69** (1936) 693.
7. J. J. Lingane, *J. Am. Chem. Soc.* **61** (1939) 2099.
8. I. M. Kolthoff and J. J. Lingane, *Polarography*. New York 1952. p. 202.
9. O. H. Müller in A. Weissberger, *Physical Methods of Organic Chemistry*, Vol. I, part II. New York 1949. p. 1838.
10. M. von Stackelberg, *Z. Elektrochem.* **45** (1939) 466.
11. M. von Stackelberg and H. von Freyhold, *Z. Elektrochem.* **46** (1940) 120.
12. J. J. Lingane, *Chem. Revs.* **29** (1941) 1.
13. O. H. Müller, *Ann. N. Y. Acad. Sci.* **40** (1940) 91 — see ref. No 9, p. 1829.
14. H. Shikata and I. Tachi, *Collection Czechoslov. Chem. Commns.* **10** (1938) 369.
15. H. Lucas, *J. Am. Chem. Soc.* **48** (1926) 1827.
16. A. Winkel and G. Proske, *Ber.* **69** (1936) 1917.
17. O. H. Müller and J. P. Baumberger, *Trans. Electrochem. Soc.* **71** (1937) 181.
18. H. Strehlow and M. von Stackelberg, *Z. Elektrochem.* **54** (1950) 51.
19. I. Filipović, *Arhiv kem.* **22** (1951) 133.
20. J. Tomeš, *Collection Czechoslov. Chem. Commns.* **9** (1937) 12.
21. L. Meites, *J. Am. Chem. Soc.* **72** (1950) 2293.
22. D. Monnier and Y. Rusconi, *Anal. Chim. Acta* **7** (1952) 567.
23. J. Heyrowsky, *Analyst* **72** (1947) 229.
24. R. H. Müller, R. L. Garman, M. E. Droz and J. Petras, *Ind. Eng. Chem., Anal. Ed.* **10** (1938) 339.
25. L. A. Matheson and N. Nichols, *Trans. Electrochem. Soc.* **73** (1938) 193.
26. J. Boeke and H. van Suchtelen, *Philips' tech. Rundschau* **4** (1939) 243.
27. J. van Cakenberghe, *Bul. soc. chim. Belges* **60** (1951) 3.
28. I. Filipović, private communication.
29. W. J. Youden, *Statistical Methods for Chemists*. New York 1951.
30. O. A. Weber, M. Branica and V. B. Vouk, *Arhiv kem.* **25** (1953) 225.
31. See, for instance, O. L. Davies, *Statistical Methods in Research and Production*. London 1949.

## IZVOD

**Obrada polarografskih podataka metodom najmanjih kvadrata  
I. Izračunavanje poluvalnog potencijala**

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Dan je pregled fizikalno-kemijskog i praktičnog analitičkog značenja poluvalnog potencijala u polarografiji. Istaknuta je potreba poznavanja pouzdanih vrijednosti za tu veličinu. S obzirom na to da metode, koje se upotrebljavaju za izračunavanje poluvalnog potencijala ne daju osobito pouzdane vrijednosti i ne dozvoljavaju određivanje eksperimentalne pogreške, prikazana je primjena metode najmanjih kvadrata na izračunavanje poluvalnog potencijala iz eksperimentalnih podataka.