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Signifficance of Mathematical Equations in Electroanalytical Techniques

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SIGNIFFICANCEOFMATHEMATICALEQUATIONSINELECTROANALYTICALTECHNIQUES

Strictly as per the compliance and regulations of:

Ref

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Signifficance of Mathematical Equations in Electroanalytical Techniques

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I. INTRODUCTION

Many modern analytical methods are widely employed for determining active ingredient in formulations, and minute quantities of pesticide residues in various environmental samples. Although each pesticide requires a specific procedure, the following techniques are widely used for the detection and determination of pesticides individually or sometimes combinely. These techniques are:

1. Spectrophotometry
2. Fluorescence spectrophotometry
3. Chromatography
4. Radiochemical Methods
5. Electrochemical Methods

In this article application of mathematical formulae in Electrochemical Methods was discussed in this article.

II. DISCUSSION

a) In Measurments

In the standard addition method, the voltammogram of the unknown is first recorded after which a known volume of standard solution of the same electroactive species is added to the cell and second voltammogram is taken. From the magnitude of the peak height, the unknown concentration of species may be calculated using the equation[1].

$$\mathrm{Cu} = \frac{C_s \,\mathrm{x}\, V}{V_t \,\mathrm{x}\, i_2} \,\mathrm{x}\, i_1$$

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where,

i_1=the observed maximum current of voltammogram in microamperes of unknown solution.

i_2=the maximum current of the voltammogram after adding volume of V ml of unknown concentration.

C_s=concentration of the standard solution in mM

C_u=concentration of the unknown solution in mM

V_t=total volume of the solution (V + v)

III. Cyclic Voltammetry

Cyclic voltammetry is one of the most exploited techniques in electrochemical studies. Its primary advantage comes from the fact that it gives insight into both the half-reactions taking place at the working electrode, providing at the same time information about the chemical or physical phenomena coupled to the studied electrochemical reaction. Hence cyclic voltammetry is often considered as electrochemical spectroscopy. Although its usage is relatively minimal in quantitative food analysis, it is important to elaborate the principles of cyclic voltammetry, since every electroanalytical study almost inevitably commences with this technique. In cyclic voltammetry, starting from an initial potential Ei, a staircase potential sweep (or linear sweep in older potentiostats) is applied to the working electrode. After reaching a switching potential Ef, the sweep is reversed and the potential returns to its initial value. The main instrumental parameter in the cyclic voltammetry is the scan rate, since it controls the timescale of the voltammetric experiment. The useful scan rates range from 1 to 1000 mV=s, although scan rates of over 10 V=s are technically achievable. The instrumental output in cyclic voltammetric techniques is a current–potential curve, a cyclic voltammogram . The main features of the cyclic voltammogram are the cathodic and anodic peak potentials, the cathodic and anodic peak currents, and the formal (or half-peak) potential. While the half-peak potential (defined simply as a median between the cathodic and the anodic peak potentials) provides mainly thermodynamics information, the magnitudes of the peak currents reveal the kinetics involved in the electrochemical reaction. The shape of the cyclic voltammogram gives information about the type of the electrode reaction, the number of electrons involved in the elementary step of electrochemical transformation, as well as about the additional phenomena coupled to the electrochemical reaction of interest, like those for coupled chemical reactions or adsorption and crystallization. If the electron transfer process is much faster than the kinetics of the mass transport processes (diffusion), then the electrode reaction is electrochemically reversible. In this case, the peak separation DEp is defined as follows:

$$\mathrm{DEp} \quad = (\mathrm{Ep,c\text{-}Ep,a}) = 2.303\ \mathrm{RT/nF}$$

For example, in a simple reversible and diffusion-controlled electrochemical reaction, where one electron is exchanged in an elementary act, the peak separation should be about 59 mV (at 258C). Moreover, the peak potential separation should not vary by increasing the scan rate, while both cathodic and anodic peak currents should be a linear function of the square root of the scan rate. Every breach of these criteria means deflection of the electrochemical reversibility, caused either by the slow electron transfer (quasi-reversibility or irreversibility) or by additional involvement of the electroactive species in chemical reactions or adsorption phenomena. In this technique, the potential applied between the working electrode and the reference electrode is varied with time in known fashion in a triangular sweep mode. The forward or cathode potential sweep gives a reduction wave where as backward or anodic potential sweep gives an oxidation wave. Generally linear diffusion conditions are employed in cyclic voltammetry. Fast scan rates minimize diffusion problems.

This technique is based on varying the applied potential at working electrode in both forward and reverse directions (at some scan rate) while monitoring the current for example. The initial scan could be in the negative direction to the switching potential. At the point, the scan would be reversed and run in the positive direction. Depending on the analysis, one or more potential cycles can be performed, hence the term 'Cyclic Voltammetry'. The potential of working electrode is controlled verses a reference electrode such as saturated calomel electrode or silver electrode. The controlling potential, which is applied across these two electrodes, can be considered in excitation signal. The excitation signal for cyclic voltammetry is liner potential scan with triangular wave form. If only a single anodic/cathodic sweep is performed the technique usually called linear potential sweep voltammetry.

Matheson and Nichols[2] established this technique and later Sevcik[3] developed it. A series of papers by Nicholson and Shain[4] did present a detailed development of the theory of cyclic voltammetry. Randles[5] worked out the utility of the technique for reversible processes and Delahay[6] for irreversible processes. A description of triangular wave generator was given by Kaufman et al.[7]The peak current in a reversible process is quantitatively expressed by[8-9]

$$i_p = KACD^{1/2}\, V^{1/2}\, n^{3/2} \tag{1}$$

where,

i_p = peak current in microamperes
K = Randles-Sevcik constant
A = area of working electrode in cm^2
C = concentration of the depolarizer in mM
D = diffusion coefficient of electroactive species in cm^2s^{-1}
V = scan rate in mVs^{-1}
n = number of electrons

Delahay[10] indicated 2.75 x 10^5 as the reliable value for the 'K' in the case of reversible process.

For an irreversible processes[11]

$$i_p = 3.01 \times 10^5\, n\, (\alpha\, n_a)^{1/2}\, AD^{1/2}\, CV^{1/2} \tag{2}$$

where,

α = transfer coefficient.
n_a = number of electrons involved during the rate determining step and other terms have their usual significance.

The above equations (1 and 2) are used for evaluating diffusion coefficient values of reversible and irreversible electrode processes respectively.

The nature of the irreversible process is known from following equations[12]

(i) $E_{p/2} - E_p = 0.0565/n$ volts (3)

(ii) $(E_p)_{anodic} - (E_p)_{cathodic} = 0.058/n$ volts (4)

Ref

2. S.J. Reddy, P. Valenta and H.W. Nurnberg, Fresenius, J. Anal. Chem., 312, 1982, 390.

where, $E_p =$ peak potential in volts

$E_{p\text{“}2} =$ half-peak potential in volts

Any deviation from the above equations (3 and 4) leads to irreversible nature of the electrode process. Absence of anodic signal on the reverse scan indicates irreversible nature of the electrode process.

α_{na} values can be evaluated from the equation[13]

$$E_{p/2} - E_p = 0.048/\alpha_{na} \text{ volts} \tag{5}$$

The forward rate constant values for all irreversible processes can be evaluated using the equation

$$E_p = \frac{-1.14RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{k^0_{f,h}}{D^{1/2}} - \frac{RT}{2\alpha n_a F} \ln(\alpha n_a v) \tag{6}$$

Where, all the terms have their usual significance.

The most useful aspects of cyclic voltammetry is, its application to the qualitative diagnostic of the electrode reactions which are coupled to the homogeneous chemical reactions. Cyclic voltammetry provides a particularly convenient means to study adsorption phenomena in detail. For adsorption controlled waves, the current function (i_p / $Cv^{1/2}$) increased rapidly with an increase in scan rate. Wopschall and Shain[14] have studied the nature of effects of adsorption processes with the aid of cyclic voltammetry. If the product or reactant is strongly adsorbed on the surface of the electrode, a separate adsorption peak will appear prior to or after the normal peak respectively.[15-16] Cyclic voltammetric studies have been useful in deciding EC,CE and catalytic mechanisms. It has several applications in pesticide analysis.

IV. Adsorptive Stripping Voltammetry

For quantitative determination of depolarizer using DPP, AdSV either standard method or calibration method can be employed. The conditions in adsorptive stripping voltammetry are rather complicated as many factors concerning adsorption of the species on the electrode surface are to be taken into account. The factors include the type of adsorption and the respective isotherm, diffusion conditions, type of electrode reaction of the adsorbed species.

For fast, diffusion controlled adsorption, which occurs must often in adsorptive accumulation, where during the accumulation period the mass transport is assumed under the limiting current condition. The following relationship was derived for the peak current for the reduction of the compound at working electrode assuming that I_p is a function of the surface concentration:

$$I_p = kAT \tag{7}$$

$$I_p = KAC/(D/r)\ t_{acc} + 2\ (D/\Lambda)^{1/2}\ t_{acc}{}^{1/2} \tag{8}$$

where, k=proportionality constant

A=electrode area

I=surface concentration of the compound

C=concentration of the compound

D=diffusion coefficient

Ref

14. P. Zuman and M. Brezina "D.C. Polarography in Der. Medizein, Biochemic and Pharamazie" AkademicSche, Leipig, 1956.

r=radius of working electrode

t_{acc}=accumulation period

at large values of C and / or t_{acc}, I_p approaches a limiting value, for which it is assumed that

$$I_{p\ max} = KA\Gamma m \tag{9}$$

for complete coverage eq. has derived by Koryta[17]

$$\Gamma m = 7.36 \times 10^{-4}\ CD^{1/2}\ t^{1/2} \tag{10}$$

where, 't' is the time required for complete electrode coverage. It has been found that I_p increase linearly with $t_{acc}{}^{1/2}$ (assuming that there is no interaction between the adsorbed molecules). I_p is proportional to the product of C and $t_{acc}{}^{1/2}$, when neither of these two values is too large. The linear dependence of I_p on scan rate is predicted by the equation.

$$I_p = n^2\ F^2\ \Gamma v/4RT \tag{11}$$

That was derived by Brown and Amson[18] this is a proof of adsorption, in contrast to the $v^{1/2}$ dependence valid for pure Faradic process. Concerning adsorption parameters, for the concentration dependence of the voltammetric signal in the region of small concentration levels, Novotny[19] derived the equation.

$$I = K_2\ \Gamma m\ \beta c - K_3\ \Gamma \beta c^2 \tag{12}$$

and thus, for the slope I/C

$$I/C = K_2\beta\ \Gamma m - K_3\ \Gamma m\ \beta c \tag{13}$$

where, K_2 and K_3 are proportionality constants and Γm denotes the maximum coverage of the electrode. The slope I/C can be considered therefore as a function of the adsorption coefficient β,

$$I/C = F(\beta) \tag{14}$$

and the adsorptivity expressed by the slope as a parameter typical for the compound under study.

Wenrui Jin[20] has derived equations for the dependence of I_p on parameters such as concentration of the analyte and accumulation time for application of micro electrode. These electrodes due to their large edge effect have a uniquely enhanced mass transport characteristic and exhibit lower iR drop. It has been found that the dependences of the peak current on voltage scan rate, accumulation time in quiescent solution, electrode radius (mercury ultramicro electrode) and bulk concentration of adsorbed substances were in agreement with theoretical prediction.

Thus, for a reversible process, equation was derived

$$I_p = (n^2\ F^2\ /\ 4RT)\ ADv\ t_{acc}\ c/r \tag{15}$$

and for an irreversible process

$$I_p = (n^2\ F^2/e\ 4RT)\ \alpha\ ADv\ t_{acc}\ c/r \tag{16}$$

Where, e is the base of natural logarithms, r is the radius of the working electrode. V is the scan rate and α is the transfer coefficient.

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18. T. Devries and T.L. Kroon, J. Amer. Chem. Soc., 75, 1953, 2484.

V. MILLICOULOMETRY

There is a growing interest regarding the number of electrons 'n' involved per molecule during the reaction at the carbon nano tubes paste electrode.[21] The evaluation of number of electrons 'n' by the quantitative reduction of a known amount of electroactive species may be served by incomplete reduction of a voltammetric indicator electrode.

Devries and Kroon[21-22] employed this technique containing a known volume of a standard solution of a substance for which 'n' is known. When current is passed through two voltammetric cells in series, an equivalent amount of electrochemical reaction will occur in each cell. The change in concentration in each cell can be determined from the decrease in wave height and a comparison of these changes leads to determination of the number of electrons used in a unit of reaction for an unknown substance in terms of known 'n' in one of the cells. The amount of a material, which is reduced or oxidised, is given by

$$\Delta w = \left[1 - \frac{i_2}{i_1} \left[\frac{t_1}{t_2} \right]^{1/6} \right] N \qquad (17)$$

by evaluating Δw for the two cells under consideration and taking into account of the known 'n' of the unknown electrode process can easily be calculated. By using the equation (17) the number of electrons participated in the electrode process is evaluated.

VI. CONCLUSION

This Work Is Very Useful for Instrumental Interpretations For one who Deals With Electro analytical Measurements based on oxidation and reduction process takes place at electrodes and electrodynamics.

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