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INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

CLASSIFICATION AND NOMENCLATURE OF ELECTROANALYTICAL TECHNIQUES

(RULES APPROVED 1975)

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At the XXVth Conference of the International Union of Pure and Applied Chemistry in 1969, Commission V.5 on Electroanalytical Chemistry requested Profs. L. Meites, H. W. Nürnberg and P. Zuman to revise and up-date the recommendations on electroanalytical classification and nomenclature made by P. Delahay, G. Charlot and H. A. Laitinen [*Anal. Chem.*, **32** (6), 103A (1960)].

Almost without exception, the recommendations made here are descriptive rather than prescriptive, in the sense that they reflect what seem to be the best—the most accurate, informative, and logical—of the names that have gained some currency in the prior literature. Many of these techniques, probably including polarography itself, would be unlikely to be given the names here recommended if they were just being developed now. Nevertheless their prior histories provide ample proof that those names are much too firmly established, both in the literature and in the minds of their users, to be dislodged. An attempt to develop a completely systematic and consistent nomenclature *ab initio* therefore seems futile and has not been made.

This report follows the general lines of its predecessor, but deviates from it in a number of details. A slightly different classification is given in Table 1, and the other tables are differently arranged accordingly. Many techniques that have been developed, or that have become important in analysis or fundamental research, since 1960 have been added, and a few older or less important techniques are also included for the sake of completeness.

As much of the nomenclature recommended by Delahay, Charlot, and Laitinen has been retained as seemed possible, but several deviations therefrom are to be noted. The term "polarographic titration" has not been accepted in place of either "amperometric titration" or "polarometric titration" and is accordingly withdrawn. The terms "biamperometric" and "bipotentiometric" are withdrawn, although they have been more widely used than "polarographic titration", because most of the colleagues we consulted thought them objectionable on the ground that they seemed to denote measurements of two currents or potential differences, respectively. Their replacements, "amperometry with two indicator electrodes" and "potentiometry with two indicator electrodes," contain more syllables, but it is hardly possible to suppose that both conciseness and reasonable accuracy can be achieved for any but a few of the techniques covered here.

Table 1. Classification of electroanalytical techniques

1. Techniques in which neither the electrical double layer nor any electrode reaction need be considered (Table 2)
2. Techniques that involve double-layer phenomena but in which any electrode reactions need not be considered (Table 3)
3. Techniques involving electrode reactions
   - A. Techniques involving electrode reactions and employing constant excitation signals (Table 4)
   - B. Techniques involving electrode reactions and employing variable excitation signals
     1. Variable excitation signals of large amplitude (usually considerably larger than $2 \times 2{,}3\,RT/F$ volt, approximately 0·12 V at 25°C) (Table 5)
     2. Variable excitation signals of small amplitude (usually considerably smaller than $2{,}3\,RT/F$ volt, approximately 0·06 V at 25°C) (Table 6)

It is recommended that the term "polarography" be used to denote the study of relationships between electric current and applied e.m.f. or electrode potential with a liquid electrode whose surface is periodically or continuously renewed. The most common polarographic indicator electrode is the classical dropping mercury electrode, but this definition also comprises the use of dropping electrodes of other metals or liquid conductors; of variants such as multiple dropping electrodes and fritted discs from which droplets of the liquid conductor emerge into the solution being investigated; and streaming metal (or other liquid conductor) electrodes. It excludes the use of all stationary and solid electrodes, such as hanging drops and pools, regardless of the material from which these are made; it is recommended that the term "voltammetry" be used to denote the study of relationships between electric current and applied e.m.f. or potential with indicator electrodes of these types.

Electroanalytical techniques have had some problems of symbology in recent years. Recommended symbols for quantities peculiar to individual techniques—such as the diffusion current constant in polarography and the transition time in chronopotentiometry—are not included here; they will be the subject of a separate report. However, IUPAC has recently published the second edition of *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (Butterworths, London: 1975) prepared by the Physical Chemistry Division. Some of the symbols therein prescribed—such as V for volume, c for concentration of a solute, and G

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for electric conductance—are used here without comment. Others, which conflict with traditional usage, must be the subject of further discussion with the object of achieving as high a degree of conformity between different disciplines as possible. For example, the symbol I for current, recommended in the Manual and by other international organisations, has been added in parentheses after each i, which is the symbol far more generally used in the electroanalytical literature. In addition, the quantity E (potential difference) is often called simply "potential" by electroanalytical chemists.

The tables are generally self-explanatory; it need only be remarked that graphical representations of typical measured responses and of all variable excitation signals are given for ease of classification and comparison. In general, only those techniques are included that have achieved reasonable analytical significance or that seemed to present special problems of nomenclature. Similar representations have been given by many authors, of whom C. N. Reilley was to our knowledge the first.

Some general recommendations and comments deserve special mention:

1. There is widespread, but unfortunately not quite universal, agreement that the term "differential" should be used to denote measurement of a difference while "derivative" should be used to denote measurement of a rate of change, and these meanings are generally employed here. Thus a "differential potentiometric titration" is a titration that involves monitoring the difference between the potentials of two indicator electrodes (in different solutions), while a "derivative potentiometric titration" is a titration that involves measuring, recording, or computing the first derivative of the potential of a single indicator electrode with respect to the volume or otherwise added amount of reagent. As the term "differential" has occasionally been given the meaning here reserved for "derivative," some authors have been driven to use "subtractive" in its place. It is recommended that the term "subtractive" be dropped, that "differential" be used in its place, and that derivative techniques be so designated.

2. Some techniques, including polarography, have variants in which three-electrode configurations (including the indicator or working electrode, the auxiliary or counter electrode, and a reference electrode) are employed and in which some instrumental compensation for the ohmic potential drop is applied. In principle these techniques are equivalent to the corresponding ones with two-electrode configurations when proper corrections are made to the values of the applied e.m.f. in the latter. We have therefore drawn no distinction between them in these tables, but would encourage the use of terms like "controlled-potential polarography" when the difference of instrumentation or configuration is to be emphasized. In general, variants of other techniques should be similarly named. For example, the application of a constant current to a rotating disc electrode and the observation of the dependence of potential on time should not be called "chronopotentiometry" without qualification because, contrary to what is specified under 4.12 below, it does not involve the use of a stationary electrode in an unstirred solution. It should instead be called "rotating-disc-electrode chronopotentiometry," thereby conveying the natures of the excitation signal and the dependence observed and also the difference between its mathematical foundations and those of ordinary chronopotentiometry. For reasons of space, only a few illustrations (e.g. 4.20 and 4.22) are given below.

3. Different techniques for reagent addition are not distinguished below, but terms like "potentiometric weight titration" are available when needed.

4. Among the family of techniques based on cathodic or anodic stripping of (usually) previously deposited compounds or elements, only electrography is individually distinguished below. Other techniques of this family are best designated by names like "anodic stripping voltammetry (*or* anodic stripping chronoamperometry with linear potential sweep)", "anodic stripping controlled-potential coulometry," and the like. The term "stripping analysis" is widely used in the literature to denote the first of these, but would better be reserved as a generic name for the entire family of electroanalytical techniques based on stripping procedures.

5. As applied to triangular-wave and related techniques, the ungainly term "multicyclic" is avoided by recommending the use of "triangular-wave polarography (or triangular-wave voltammetry)" to denote the examination of only a single cycle, and prefixing this with the word "cyclic" to denote iteration or reiteration of the cycle.

6. In most electroanalytical techniques there is one electrode that serves as a transducer, responding to the excitation signal and the composition of the solution being investigated but without effecting any appreciable change of bulk composition over the ordinary duration of a measurement. This electrode is the "indicator electrode" or "test electrode", only the former term being used below to save space. When, however, the technique depends on effecting significant changes of bulk composition by the flow of current through the cell, this electrode is called the "working electrode". It is immaterial whether the change of bulk composition occurs in the solution phase or in the liquid metal constituting the working electrode. For example, a stirred mercury-pool electrode used for voltammetry (5.9) is considered to be an indicator electrode, but if it is used for controlled potential coulometry (4.27) it is considered to be a working electrode regardless of whether the electroreducible or -oxidizable substance under study is initially dissolved in the solution or in the mercury.

7. Throughout these tables the term "alternating" (current or voltage) denotes the use of a sinusoidal waveform.

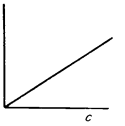
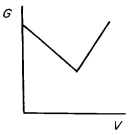
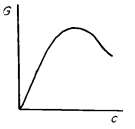
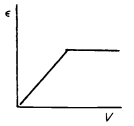
8. Several recently proposed techniques may be regarded as close descendants of others appearing below but differ from them in the nature of the data-handling involved (as, indeed, may be said of amperometry and coulometry). In choosing names for these and others of the same sort, we recommend deriving them from names given below. Two typical examples would be "semi-integral polarography" and "convolution-integral linear-sweep voltammetry".

9. Some techniques, like conductometry (2.1) and differential potentiometry (4.2) employ two indicator electrodes, but more often the second electrode is more or less non-polarizable and is used merely to complete the measuring circuit and to provide a suitably constant potential. An electrode serving these purposes is called a "reference electrode". Sometimes these functions of the reference electrode are separated by using a three-electrode configuration. This comprises (1) an indicator (or test) or working electrode; (2) a reference electrode, through which no significant current is allowed to flow and

which serves to permit observation or control of the potential of the first electrode; and (3) an "auxiliary electrode" or "counter electrode", which serves to carry the current that passes through the first electrode.

Table 7 is an index to Tables 2–6. For each of the techniques included in Tables 2–6, Table 7 lists all of the names under which it may be sought, including both names that are recommended and others that are not. Each entry in Table 7 includes a reference in the form $x.y$, where x is the number of the table in which the technique appears and y is its ordinal number in that table. These key numbers appear in the first columns of Tables 2–6, to facilitate both finding techniques sought through Table 7 and occasional cross references within tables.

Table 2. Techniques in which neither the electrical double layer nor any electrode reaction need be considered

Key no.	Excitation signal	Independent variable	Measured response	Recommended name of technique	Typical response curve	Remarks
2.1	Alternating voltage; frequency $f <$ *ca.* 0·1 MHz	Concentration c	Conductance G	Conductometry		Dc conductometry is rarely employed but should be so designated. The spelling "conductimetry" is not recommended.
2.2		Volume V (or otherwise measured amount) of a reagent	Conductance G	Conductometric titration		
2.3	Alternating voltage, frequency $f >$ *ca.* 0·1 MHz	Concentration c	Conductance G, susceptance B, or admittance Y	High-frequency conductometry		The recommended term is inexact when B or Y is measured, but names like "susceptometry" cannot be encouraged.
2.4		Volume V (or otherwise measured amount) of a reagent	Conductance G, susceptance B, or admittance Y	High-frequency conductometric titration		
2.5	—	Concentration c	Relative permittivity ϵ†	Dielectrometry		The name "dielcometry" is found in the literature, but is not recommended.
2.6		Volume V (or otherwise measured amount) of a reagent	Relative permittivity ϵ†	Dielectrometric titration		

†Generally, though incorrectly, considered to be the dielectric constant.

Table 3. Techniques that involve double-layer phenomena but in which any electrode reactions need not be considered

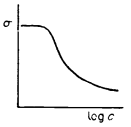
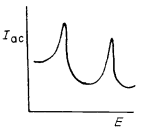
Key no.	Excitation signal	Independent variable	Measured response	Recommended name of technique	Typical response curve	Remarks
3.1	Potential difference (potential, see p. 84) E	Concentration c	Interfacial tension σ between an electrode and solution (or a related parameter such as the drop time at a dropping electrode or the relative height of a polarographic maximum)	No recommendation		
3.2	Alternating voltage or potential E_{ac}, typically 1–5 mV	Direct potential E	Alternating current i_{ac} (I_{ac})	Measurement of nonfaradaic admittance		"Tensammetry," the name most widely used, is but imperfectly analogous to "voltammetry" and is therefore not recommended.

Table 4. Techniques involving electrode reactions and employing constant excitation signals

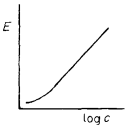
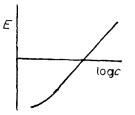
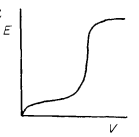
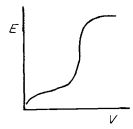
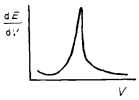
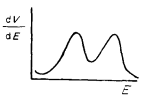
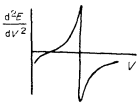
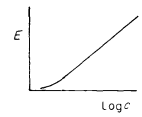
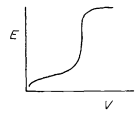
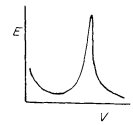
Key no.	Excitation signal (constant)	Independent variable	System	Measured response	Recommended name of technique	Typical response curve	Remarks
4.1	Current $i(I)$ $(=0)$	Concentration c	One indicator electrode and one reference electrode, (or two indicator electrodes) in the same solution	Potential $E = f(c)$	Potentiometry		The terms "zero-current potentiometry" and "null-current potentiometry" are not recommended. No special terminology is recommended for measurements of pH and similar quantities.
4.2			Two indicator electrodes in separate solutions joined by an ionic conductor	Potential $E = f(c, c')$	Differential potentiometry		The term "precision null-point potentiometry" is not recommended.
4.3		Volume V (or otherwise measured amount) of added reagent	As for potentiometry (4.1)	Potential $E = f(V)$	Potentiometric titration		The terms "zero-current potentiometric titration" and "null-current potentiometric titration" are not recommended; see 4.10.
4.4			As for differential potentiometry (often with one of the indicator electrodes in the titrant solution)	Potential $E = f(V)$	Differential potentiometric titration		
4.5			As for potentiometry (4.1)	$\frac{dE}{dV} = f(V)$	Derivative potentiometric titration		
4.6				$\frac{dV}{dE} = f(E)$	Inverse derivative potentiometric titration		
4.7				$\frac{d^2E}{dV^2} = f(V)$	Second-derivative potentiometric titration		
4.8	Current $i(I)$ $(\neq 0)$	Concentration c	One indicator electrode and one reference electrode in same solution	Potential $E = f(c$ or $\log c)$	Controlled-current potentiometry		
4.9			Two indicator electrodes in same solution	Potential $E = f(c$ or $\log c)$	Controlled-current potentiometry with two indicator electrodes		The term "bipotentiometry" is no longer recommended.
4.10		Volume V (or otherwise measured amount) of added reagent	As for controlled-current potentiometry (4.8)	Potential $E = f(V)$	Controlled-current potentiometric titration		
4.11			As for controlled current potentiometry with two indicator electrodes (4.9)	Potential $E = f(V)$	Controlled-current potentiometric titration with two indicator electrodes		The term "bipotentiometric titration" is no longer recommended.

Table 4. (*Contd*)

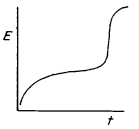
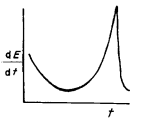
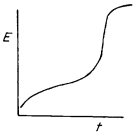
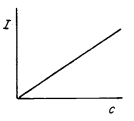
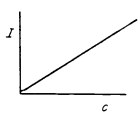
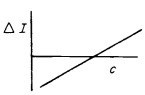
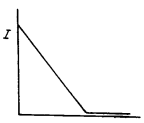
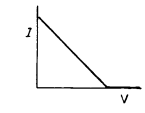
Key no.	Excitation signal (constant)	Independent variable	System	Measured response	Recommended name of technique	Typical response curve	Remarks
4.12		Time t	Indicator electrode stationary in unstirred solution	Potential $E = f(t)$	Chronopotentiometry		
4.13				Rate of change of potential $\frac{dE}{dt} = f(t)$	Derivative chronopotentiometry		
4.14			Convective mass transfer to working electrode	Potential E of an indicator electrode, absorbance A, or some other composition-dependent property of the bulk of the solution electrolyzed $= f(t)$	Coulometric titration (controlled-current coulometry)		Terms like "potentiometric coulometric titration" or "controlled-current coulometry with potentiometric end-point detection" are recommended when the technique of end-point location is to be specified.
4.15	Applied e.m.f. or potential E	Concentration c, time t, or any other independent variable	One indicator electrode and one reference electrode	Current $i(I) = f(c)$	Amperometry		Terms like "stirred-mercury-pool amperometry" and "rotating-platinum-wire-electrode amperometry" are recommended to denote the indicator electrode employed.
4.16			Two indicator electrodes in same solution	Current $i(I) = f(c)$	Amperometry with two indicator electrodes		The term "biamperometry" is no longer recommended.
4.17			Two indicator electrodes in separate solutions joined by an ionic conductor	Current difference $\Delta i(\Delta I) = f(c, c')$	Differential amperometry		
4.18		Volume V (or otherwise measured amount) of added reagent	As for amperometry (4.15)	Current $i(I) = f(V)$	Amperometric titration		The term "amperometric titration with a dropping mercury electrode" is recommended in preference to "polarometric titration" or "polarographic titration."
4.19			As for amperometry with two indicator electrodes (4.16)	Current $i(I) = f(V)$	Amperometric titration with two indicator electrodes		The term "biamperometric titration" is no longer recommended.

Table 4. (*Contd*)

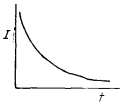
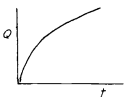
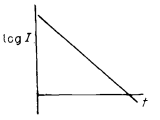
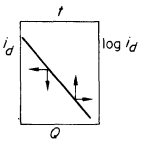
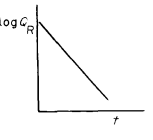
Key no.	Excitation signal (constant)	Independent variable	System	Measured response	Recommended name of technique	Typical response curve	Remarks
4.20		Time t	Stationary indicator electrode in unstirred solution	Current $i(I) = f(t)$	Chronoamperometry		The term "polarographic chronoamperometry" is recommended to denote the technique in which measurements are made during the lifetime of a single drop at a dropping electrode.
4.21				Quantity of electricity $Q = f(t)$	Chronocoulometry		The commonly used term "potential-step chronocoulometry" is redundant and is not recommended.
4.22			Convective mass transfer to working electrode	Current $i(I) = f(t)$	Convective chronoamperometry		
4.23			Dropping mercury (or other liquid metal) electrode as working electrode	Diffusion current $i_d(I_d) = f$ (quantity of electricity Q) or $f(t)$	Polarographic coulometry		The terms "microcoulometry" and "millicoulometry" are not recommended. The term "dropping electrode coulometry" is more specific than the recommended one and may be used when appropriate.
4.24			Convective mass transfer to working electrode	Mass m of material deposited on the working electrode	Electrogravimetry		The terms "internal electrogravimetry" and "spontaneous electrogravimetry" are recommended to denote spontaneous deposition.
4.25				Separation	Electroseparation		
4.26	Applied e.m.f. E or current $i(I)$		Cathodic or anodic stripping from a solid electrode into an electrolyte in a porous medium	Identification or determination of material stripped	Electrography		
4.27	Potential E	Time t	Convective mass transfer to working electrode	Quantity of electricity Q $\left(= \int_0^\infty i\,dt\right)$	Controlled-potential coulometry		The term "controlled-potential coulometric titration" is inappropriate and is not recommended.
4.28				Quantity of electricity $Q = f(t)$ or $Q_R\left[= \int_0^\infty i\,dt - \int_0^t i\,dt\right] = f(t)$	Convective chronocoulometry		

Table 4. (*Contd*)

Key no.	Excitation signal (constant)	Independent variable	System	Measured response	Recommended name of technique	Typical response curve	Remarks
4.29			Convective mass transfer to working electrode	Mass m of material deposited on the working electrode	Controlled-potential electro-gravimetry		
4.30				Separation	Controlled-potential electro-separation		

Table 5. Techniques involving electrode reactions and variable excitation signals of large amplitude

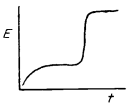
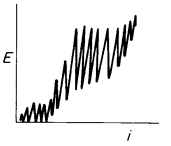
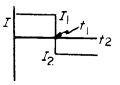
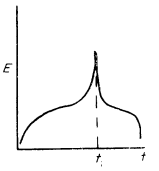
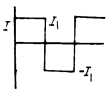
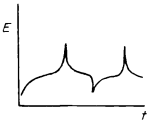
Key no.	Excitation signal	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
5.1	Current $i(I)$	$i = i^0 + at$	Stationary indicator electrode in unstirred solution	Potential $E = f(t)$	Chronopotentiometry with linear current sweep		
5.2			Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Potential $E = f(i$ or $t)$	Current-scanning polarography (or polarography with linear current sweep)		
5.3		$i = f(t)$ (nonlinear but monotonic)	Stationary indicator electrode in unstirred solution	Potential $E = f(t)$	Programmed-current chronopotentiometry		The nature of the current-time dependence must be specified separately. For the special case in which i is a linear function of t see 5.1.
5.4		$i = i_1$ for $t < t_1$, for $t > t_1$ 	Stationary indicator electrode in unstirred solution	Potential $E = f(t)$	Current-step chronopotentiometry		The term "current-reversal chronopotentiometry" is recommended for the special case in which $i_2 = -i_1$. The term "current-cessation chronopotentiometry" is recommended for the special case in which $i_2 = 0$.
5.5		i periodically reversed 	Stationary indicator electrode in unstirred solution	Potential E $E = f(t)$	Cyclic chronopotentiometry		The term "cyclic current-reversal chronopotentiometry" may be used to signify that $i_2 = -i_1$, and the term "cyclic current-step chronopotentiometry" may be used to signify that $i_2 \neq -i_1$. These two terms should not be used except to emphasize the difference between them.

Table 5. (*Contd*)

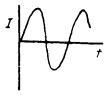
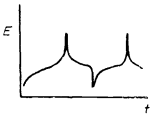
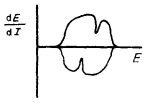
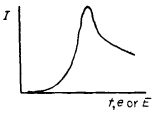
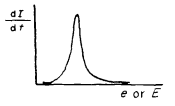
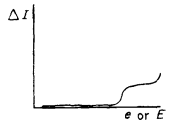
Key no.	Excitation signal	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
5.6		$i = i_{ac} \sin \omega t$ 		Potential $E = f(t)$	Alternating-current chronopotentiometry		
5.7			Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Rate of change of potential $dE/dt = f(E)$	Oscillopolarography		
5.8	Applied e.m.f. or potential E	$E = E^0 \pm at$	Diffusive mass transfer to any indicator electrode whose surface is not renewed	Current $i(I) = f(t)$ or, implicitly, $f(E)$	Chronoamperometry with linear potential sweep, stationary-electrode voltammetry, or linear-sweep voltammetry		Though the name "chronoamperometry with linear potential sweep" is superior in principle because all of the experimental data are dependent on the sweep rate, the alternative "stationary-electrode voltammetry" is also firmly entrenched in the literature. Single-sweep polarography (5.16) is a special case of this technique.
5.9			Convective mass transfer to any indicator electrode whose surface is not renewed	Current $i(I) = f(E)$	Hydrodynamic voltammetry		
5.10				Rate of change of current di/dt (dI/dt) or di/dE, $(dI/dE) = f(E)$	Derivative voltammetry		
5.11			Two indicator electrodes in separate solutions with reference electrode in each	Difference of current $dI(\Delta I) = f(E)$	Differential voltammetry		
5.12			Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed, and a reference electrode	Current $i(I) = f(E)$	Polarography (or dc polarography)		From the viewpoint of systematic nomenclature the term "dc polarography" is a misnomer, and it should be used only when the distinction between this technique and another, such as ac polarography or rf polarography, has to be emphasized.

Table 5. (*Contd*)

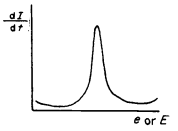
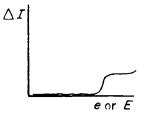
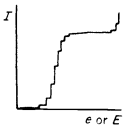
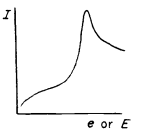
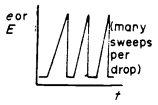
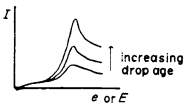
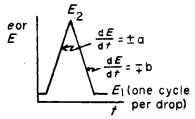
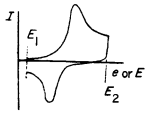
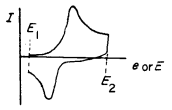
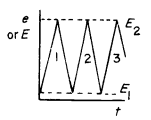
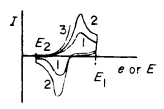
Key no.	Excitation signal	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
5.13				Rate of change of current $\frac{di}{dt}\left(\frac{dI}{dt}\right)$ (or, implicitly, $(di/dE)) = f(E)$	Derivative polarography (or derivative dc polarography)		See the remark about "dc polarography" above.
5.14			Two dropping or streaming mercury (or other liquid conductor) indicator electrodes in separate solutions, with a reference electrode in each	Difference of current $\Delta I(I) = f(E)$	Differential polarography (or differential dc polarography)		See the remark about "dc polarography" above.
5.15			As for polarography (5.12) but with recording of current only during the interval $t_1 \leq t \leq t_1 + \Delta t$ during the drop life, the recording device being disconnected between successive intervals	Current $i(I) = f(E)$	Tast polarography		
5.16			Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Current $i(I) = f(E)$	Single-sweep polarography		In the limiting case where the sweep is so fast that the change of area during the sweep is negligible, the term "dropping-electrode chronoamperometry with linear potential (or voltage) sweep" is recommended. The terms "single-sweep oscillographic polarography" and "cathode-ray polarography" are found in the literature but are not recommended.
5.17			As for single-sweep polarography (5.16)	Current $i(I) = f(E,$ drop age)	Multisweep polarography		
5.18			As for single-sweep polarography (5.16)	Current $i(I) = f(E)$	Triangular-wave polarography		a and b may be equal or unequal.
5.19			As for linear-sweep voltammetry (5.8)	Current $i(I) = f(E)$	Triangular-wave voltammetry		
5.20			As for single-sweep polarography (5.16)	Current $i(I) = f(E)$	Cyclic triangular-wave polarography		

Table 5. (*Contd*)

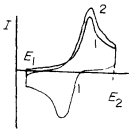
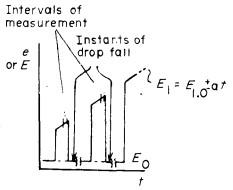
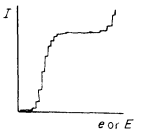
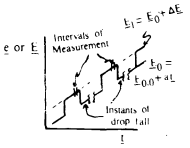
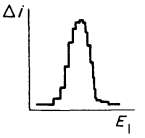
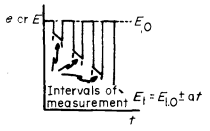
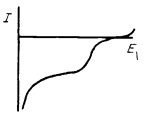
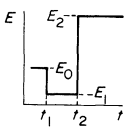
Key no.	Excitation signal	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
5.21			As for linear-sweep voltammetry (5.8)	Current $i(I) = f(E)$	Cyclic triangular-wave voltammetry		
5.22			As for single-sweep polarography (5.16)	Current $i(I) = f(E_1)$	Pulse polarography		It is the difference between the numbers of pulses during the life of one drop that distinguishes this technique from Kalousek polarography (5.24).
5.23	 (one pulse per drop)			Difference of current Δi $(\Delta I) = f(E_1)$; implicitly $\frac{di}{dt}\left(\frac{dI}{dt}\right)$ or $\frac{di}{dE}\left(\frac{dI}{dE}\right)$ $= f(E_1)$	Derivative pulse polarography		The measured response is the difference between the direct current that flows during the interval of measurement and the direct current that flowed during the corresponding interval during the life of the preceding drop. For differential pulse polarography see 6.3.
5.24	 (5–50 pulses per drop)		As for single-sweep polarography (5.16)	Current $i(I) = f(E_1)$	Kalousek polarography		The range of variation of E_1 may be confined to values more positive than E_0, more negative than E_0, or may include E_0. Only the first possibility is shown in the illustrative curve here. Depending on the location of E_0, the range of variation of E_1, and the manner in which the recorder is connected, response curves having several different characteristic shapes may be obtained. Measurements may be made during only the latter portions of the intervals shown.
5.25			Indicator electrode stationary in unstirred solution	Current $i(I) = f[(t - t_1)$ and $(t - t_2)]$	Double-potential-step chronoamperometry		In this and the following technique E_1 must differ from the open-circuit potential; if it does not, the techniques are properly called "chronoamperometry" and "chronocoulometry," respectively.

Table 5. (*Contd*)

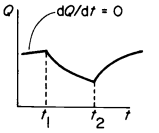
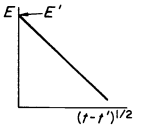
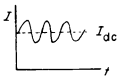
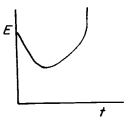
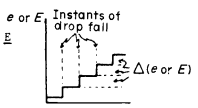
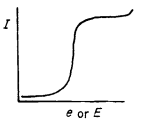
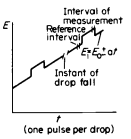
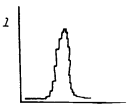
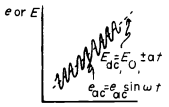
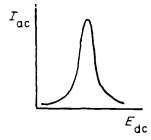
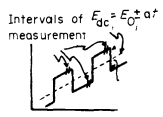
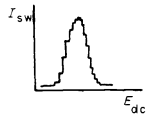
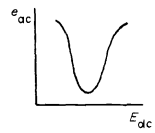
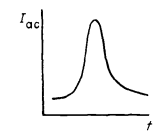
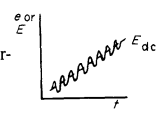
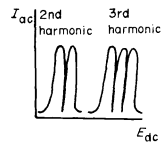
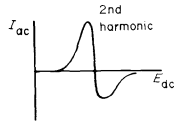
Key no.	Excitation signal	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
5.26				Quantity of electricity $Q = f[(t - t_1)$ and $(t - t_2)]$	Double-potential-step chronocoulometry		See "double-potential-step chronoamperometry" (5.25).
5.27	Quantity of electricity Q	A charge Q', whose magnitude increases uniformly from drop to drop, is rapidly injected at drop age t'	Dropping liquid indicator electrode reference electrode	Potential $E = f(t - t')$ and slope $dE/d(t - t')^{1/2}$ of a plot of E vs $(t - t')^{1/2} = f$ (intercept of that plot)	Incremental-charge polarography		The names "charge-step polarography" and "discharge polarography" are not recommended.

Table 6. Techniques involving electrode reactions and variable excitation signals of small amplitude

Key no.	Excitation signal(s)	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
				A: First-order techniques			
6.1	Current $i(I)$	$i = i_{dc} + \hat{\imath}_{ac} \sin \omega t$ 	Any indicator electrode	Potential $E = f(t)$	Chronopotentiometry with superimposed alternating current		
6.2	Applied e.m.f. or potential	$E = E_0 + \sum_{n=0}^{0} (\Delta E)$ 	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Current $i(I) = f(E)$	Staircase polarography		n = number of steps.
6.3			Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode surface is renewed	Difference of current $i(I) = f(E_0$ or $E_1)$	Differential pulse polarography		The measured response is the difference between the direct current that flows during the interval of measurement and the direct current that flowed during a short interval that just preceded the application of the pulse. This technique has sometimes been termed "derivative pulse polarography," but see 5.23.
6.4			Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Alternating current $i_{as}(I_{ac}) = f(E_{dc})$	Ac polarography†		The frequency of the alternating component of the applied e.m.f. or potential is usually below 1 kHz and is most often 50–60 Hz. The periodic

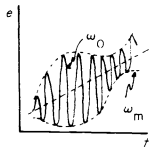
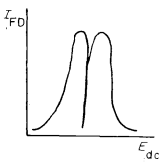
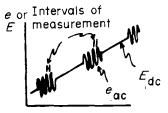
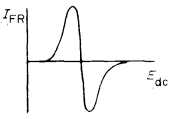
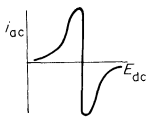
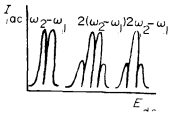
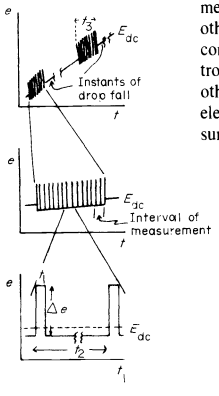
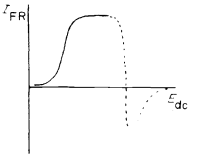
†The names of these techniques, which are dictated by prior usage, are among a very few that are derived from the nature of the measured response rather than from that of the excitation signal.

Table 6. (*Contd*)

Key no.	Excitation signal(s)	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
							component of the excitation signal may be non-sinusoidal (e.g. triangular, sawtooth, etc.), and the technique should then be termed "polarography with superimposed periodic voltage" or, more specifically, "polarography with superimposed triangular voltage," etc. See also square-wave polarography (6.5).
6.5		$E_{dc} = E_0 + at$ 	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Square-wave current $I_{sw}(I_{sw}) = f(E_{dc})$	Square-wave polarography		This technique may be regarded as a small-amplitude analog of one variant of Kalousek polarography (5.24). It is distinguished from differential pulse polarography (6.3) by involving the measurement of a periodic current rather than a direct current.
6.6	Current $i(I)$ and applied e.m.f. or potential E	$i = \hat{i}_{ac} \sin \omega t$ $E_{dc} = E_0 + \pm at$	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Alternating voltage $E_{ac} = f(E_{dc})$	Av polarography†		
6.7		i_{dc} = constant $E_{ac} = \hat{E}_{ac} \sin \omega t$	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Alternating current $i_{ac}(I_{ac}) = f(t)$	Alternating-voltage chronopotentiometry		
			B: Second-order techniques				
6.8	Direct applied e.m.f. or potential E_{dc} with superimposed alternating voltage E_{ac}	$E_{dc} = E_0 \pm at$ $E_{ac} = \hat{E}_{ac} \sin \omega t$ 	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Alternating current $i_{ac}(I_{ac}) = f(E_{dc})$	Higher-harmonic ac polarography		Components of the alternating current due to higher harmonics are filtered out. Typical response curves are shown for the second and third harmonics; second-harmonic ac polarography (which should be so denoted) is the most widely used of the higher-harmonic ac polarographic techniques.
6.9					Higher-harmonic ac polarography with phase-sensitive rectification		

†The names of these techniques, which are dictated by prior usage, are among a very few that are derived from the nature of the measured response rather than from that of the excitation signal.

Table 6. (*Contd*)

Key no.	Excitation signal(s)	Manner of variation	System	Measured response	Recommended name of technique	Typical response curve	Remarks
6.10		$E_{dc} = E_0 \pm at$ $E_{ac} = \hat{E}_{ac} \sin \omega_0 t \times (1 + m \sin \omega_m t)$ 	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Faradaic demodulation current $i_{FD} = f(E_{dc})$	Demodulation polarography		i_{FD} is the faradaic demodulation signal: it has the frequency ω_m and is due to non-linearity of the faradaic admittance of the indicator electrode.
6.11	Direct applied e.m.f. or potential E_{dc} with superimposed high-frequency (f_{ac}) alternating voltage E_{ac} modulated with a square-wave frequency f_s	$E_{dc} = E_0 + at$ $E_{ac} = \hat{E}_{ac} \sin \omega t$ 	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Faradaic rectification current $(I_{FR}) = f(E_{dc})$	Radio-frequency polarography *or* rf polarography		f_{ac} is typically 0·1–6·4 MHz and f_s is typically 225 Hz. i_{FR} is filtered out by a low-pass filter and is recorded only during the last stage of the life of the drop.
6.12	Direct applied e.m.f. or potential E_{dc} with two superimposed periodic voltages E_1 and E_2	$E_{dc} = E_0 \pm at$ E_1 and E_2 may be sinusoidal, triangular, etc.	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Alternating current $(I_{ac}) = f(E_{dc})$	Modulation polarography		$E_1 \neq E_2$; ω_1 and ω_2 usually differ widely. A response curve obtained with phase-sensitive rectification is shown. Components due to combination frequencies are removed by filtering.
6.13	Direct applied e.m.f. or potential E_{dc} with two superimposed alternating voltages E_1 and E_2	$E_{dc} = E_0 + at$ $E_1 = \hat{E}_1 \sin \omega_1 t$ $E_2 = \hat{E}_2 \sin \omega t$	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Alternating current $i_{ac}(I_{ac}) = f(E_{dc})$	Double-tone polarography		E_1 and E_2 are equal and small, typically ≤25 mV; ω_1 and ω_2 are slightly unequal and small; f_i $(=\omega_i/2\pi) < 100$ Hz. Usually responses due to the frequency difference $\omega_2 - \omega_1$, $2(\omega_2 - \omega_1)$, and $2\omega_2 - \omega_1$ are recorded.
6.14	Direct applied e.m.f. or potential E_{dc} with a superimposed train of pulses	$E_{dc} = E_0 \pm at$ 	Dropping mercury (or other liquid conductor) electrode, or any other indicator electrode whose surface is renewed	Faradaic rectification current $i_{FR} = f(E_{dc})$	High-level faradaic rectification	 Only the portion represented by the solid line is used for evaluation.	Typically the pulse amplitude $\Delta e = 0{\cdot}3$–1 V, the pulse duration $t_1 = 1$–30 μs, and the interval between successive pulses $t_2 = 1$ ms.

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