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ANALYTICAL APPLICATIONS OF CHRONOPOTENTIOMETRY

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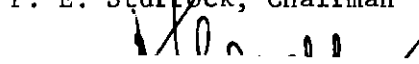
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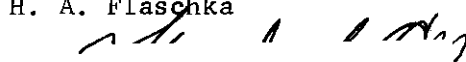
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SYMBOLS

Latin

<u>a</u>	electrode area
erfc	complementary error function, $1-\text{erf}$, where $\text{erf} = \int_0^y \exp(-z^2) dz$
i	applied current
i_d	diffusion controlled current
i_o	current density, i/a
m	flow rate of mercury, milligrams/second
n	number of electrons involved in an electrochemical reaction
r	a radial distance from center of electrode
r_o	radius of electrode
t	a time
t_d	drop time
x	a distance from an electrode surface
A	chronopotentiometric constant
B	$i\tau$ intercept of a Bard plot
C	a formal concentration in the bulk of a solution
C_{dl}	differential double-layer capacitance
D	a diffusion coefficient
DME	dropping mercury electrode
E	a potential
F	the Faraday constant
<u>F</u>	formal, a measure of concentration
$F_{(x,t)}$	flux

SYMBOLS (Concluded)

Latin

N	number of moles
R	gas constant
SCE	saturated calomel electrode
T	absolute temperature
T_c	time during which prebias is applied in the potential step--current step technique
X	a parameter relating T_c and τ in the potential step--current step technique

Greek

α	transfer coefficient
τ	transition time
Γ	relative surface excess in moles/cm ²

Units of Measure

cm	centimeters
g	grams
ml	milliliters
msec	milliseconds
sec	seconds
μA	microamperes
$\mu coul$	microcoulombs
μf	microfarads
Ω	ohms

CHAPTER I

INTRODUCTION

The electrochemical technique known as chronopotentiometry was described by Sand¹ in 1901, a quarter century before Heyrovsky developed the more widely known technique of polarography. Yet chronopotentiometry remained unexplored for many years, due in part to a technological lag in developing suitable instrumentation, and later due to the overwhelming attention paid to polarography. It was not until 1950 that Gierst and Julliard² pointed out chronopotentiometry's potential for use as an analytical tool.

In chronopotentiometry one applies a constant current to a cell containing an electroactive substance in solution and measures the time it takes for the concentration of that substance at the electrode surface to drop essentially to zero. The square root of the transition time is proportional to the concentration of the electroactive substance in the bulk of the solution. Chronopotentiometry can thus be used as an analytical tool for the quantitative determination of electroactive substances in solution.

Until recently there have been several significant drawbacks to the analytical use of chronopotentiometry: 1) difficulty in the graphical evaluation of transition times; 2) interference from capacitative double layer charging, especially in dilute solutions; and 3) in multi-component systems, interference from species which are reduced or oxidized

more readily than the one being determined. A variety of techniques has been proposed to overcome these difficulties. The purpose of this research is to simplify the techniques and develop instrumental compensations so that the data obtained from an experimental chronopotentiogram are immediately applicable to analytical determinations.

The usual chronopotentiogram displays potential, E , as a function of time, t . At the end of the transition when the substance of interest is depleted at the electrode, there occurs a sudden increase in E . This change in E is not so abrupt as to be unequivocal and many graphical constructions have been proposed to obtain a "good" value of τ , the transition time. Peters and Burden³ described the use of derivative chronopotentiometry in which one records the derivative of the potential with respect to time. They derived the equations relating the value of the dE/dt minimum to the value of the transition time. This value can be read directly and eliminates the need for oftentimes ambiguous graphical evaluation of transition time.

Chronopotentiometry is especially plagued by complications due to double-layer capacitance because the potential changes over the course of an experiment. A certain portion of the applied current must go to charge the double layer to the new potential. Neither of the functions, potential versus time nor double-layer capacitance versus potential, is linear, thus the fraction of the applied current used for this purpose is not constant. The effect is greatest for low concentrations of electroactive species and for short transition times.

Bard⁴ reported a method for evaluating and correcting for the influence of double-layer charging. Sturrock et al.⁵ have applied derivative

methods and Bard type double-layer corrections to the determination of submicroformal concentrations of a single electroactive substance. Bard corrections can be tedious if applied to routine analytical work. Other methods based on theoretical considerations offer means to evaluate and correct for double-layer charging, but they too are too complicated for routine use. An instrumental method of compensating for double-layer effects is preferable; such a method is developed in the course of this investigation.

When there is more than one electroactive species in a solution, a residual diffusion controlled current from the more active species interferes with a simple quantitative relationship between bulk concentration and transition time for a second or subsequent component. Sturrock et al.⁶ developed a complex mathematical solution for the relationship. By using a table of constants calculated with the assistance of a computer, they were able to correlate transition time and concentration for two and three component systems. Bowman and Bard⁷ have used a potential step-current step sequence to decrease the effect of preceding waves and were able to obtain the transition time for the second component by an extrapolation technique. A purpose of the present investigation is to develop a more direct method of obtaining quantitative relationships from chronopotentiometric data on multicomponent systems.

Previous attempts to correlate transition time and concentration have been focused on correcting measured transition times for the influence of various interfering processes. A new approach is taken in the present investigation. Corrections are applied to the current so that the measured

transition time and the current actually used for the faradaic process can be related directly to the bulk concentration of the electroactive substance. Whenever possible, these corrections are applied instrumentally rather than by calculation so that the measured experimental parameters are immediately useful in establishing quantitative relationships of analytical significance.

CHAPTER II

THEORY

The Sand Equation

The theory of chronopotentiometry derives from the laws of diffusion first worked out by Fick in 1855.⁸ As a constant current is applied to the working electrode of the cell, the electroactive substance is consumed in the vicinity of the electrode surface. A gradient of chemical potential (more commonly called a concentration gradient) develops between the solution at the electrode interface and the solution in the bulk. As a result of this gradient, diffusion of electroactive species occurs from the bulk solution to the region of the electrode, that is, from a region of higher to a region of lower concentration.

To apply Fick's laws of diffusion one must assume certain conditions: a) that the volume of solution and dimensions of the cell are sufficiently large that under experimental conditions one does not deplete the concentration of electroactive species in the bulk of the solution, and b) that the direction of the mass transport is perpendicular to the electrode surface. These are said to be conditions of semi-infinite linear diffusion.

The flux of electroactive substance is defined as the number of moles, N , of the substance which crosses a plane of unit area (1 cm^2) in the time dt . According to Fick's first law, the flux is proportional to the change in concentration of the substance with change in distance from

the electrode. The flux at distance x from the electrode, at time t after the start of the electrolysis is given by Fick's first law.

$$F_{(x,t)} = \frac{dN_{(x,t)}}{adt} = D \left[\frac{dC_{(x,t)}}{dx} \right] \quad (1)$$

a is the electrode area; C is the concentration of the electroactive substance; dC/dx is the concentration gradient; D , a proportionality factor, is called the diffusion coefficient.

Fick's second law relates the rate of change of concentration with time at a given plane to the change in concentration gradient with respect to distance.

$$\frac{\partial C_{(x,t)}}{\partial t} = \frac{\partial \left[D \frac{\partial C_{(x,t)}}{\partial x} \right]}{\partial x} = D \frac{\partial^2 C_{(x,t)}}{\partial x^2} \quad (2)$$

This is the fundamental equation for linear diffusion.

This differential equation can be solved by applying appropriate initial and boundary conditions. In the case of chronopotentiometry, the initial condition assumes homogeneity of solution, that is, the concentration of electroactive species at the electrode equals C , the concentration in the bulk solution.

$$C_{(x,0)} = C \quad (3a)$$

As a boundary condition, the volume of solution is assumed to be sufficiently large so that at any time after the start of the electrolysis

$$C_{(\infty,t)} = C \quad (3b)$$

Furthermore, while the faradaic process is occurring at the electrode, the flux of electroactive substance at the electrode surface is related to the current by Faraday's law,

$$F_{(0,t)} = D \frac{\partial C_{(0,t)}}{\partial x} = \frac{i}{nFa} \quad (3c)$$

Applying these boundary conditions and using LaPlace transforms one obtains the following expression which relates the concentration of electroactive substance at any distance x and time t to the bulk concentration and the applied current:

$$C_{(x,t)} = C - \frac{it^{\frac{1}{2}}}{nFaD^{\frac{1}{2}}\pi^{\frac{1}{2}}} e^{-x^2/4Dt} + \frac{ix}{nFaD} \operatorname{erfc} \left[\frac{x}{2Dt^{\frac{1}{2}}} \right] \quad (4)$$

In chronopotentiometry one is interested in the concentration at the electrode surface ($x=0$). In this case equation (4) reduces to

$$C_{(0,t)} = C - \frac{2it^{\frac{1}{2}}}{nFaD^{\frac{1}{2}}\pi^{\frac{1}{2}}} \quad (5)$$

To evaluate the time at which the concentration of electroactive substance at the electrode is decreased essentially to zero, $C_{(0,t)}$ is set equal to zero and the corresponding value of t is called τ , the transition time.

$$C = \frac{2i\tau^{\frac{1}{2}}}{nFaD^{\frac{1}{2}}\pi^{\frac{1}{2}}} \quad (6)$$

This is the Sand equation and is the basic equation for chronopotentiometry. It relates bulk concentration, current, and transition time, and holds

strictly only for conditions of semi-infinite linear diffusion.

For a given electrode and a given electroactive species, n , a , and D are constants; these and 2 , π , and F are often grouped together into one super constant designated A , and called the chronopotentiometric constant.

$$A = \frac{i\tau^{\frac{1}{2}}}{C} = \frac{nFaD^{\frac{1}{2}}\pi^{\frac{1}{2}}}{2} \quad (7)$$

DME Approximation to Semi-infinite Linear Diffusion

Conditions of semi-infinite linear diffusion can be maintained rigorously at a planar solid electrode only under severe experimental restrictions. The electrode must be shielded to eliminate edge effects and the duration of the electrolysis must be sufficiently short so that convection as a result of density gradients does not develop. The greatest limitation on solid electrodes, however, is the difficulty in obtaining reproducible surface conditions from one experiment to the next.

The dropping mercury electrode (DME) eliminates this complication by presenting a reproducibly renewed surface with each drop. That advantage is not without cost. The area of a DME changes as the drop grows. Early in the drop life the rate of change of surface area is great. Later in the drop life the rate of change is considerably less. From drop to drop at any given time in the drop life, both the rate of increase and the actual area are reproducible and can be calculated from the mercury flow rate. The drop hanging at the tip of the capillary is assumed to be spherical, although in actuality it is not exactly so, and usually one

ignores the area of attachment as insignificant when calculating the surface area. The drop is smooth, so no surface roughness factors need be considered, as would be the case with solid electrodes.

In actual practice, flow rates of mercury are about 0.002 g/sec. This gives a drop time in the range 3-5 sec, and a drop area on the order of $2 \times 10^{-2} \text{ cm}^2$. In order that a chronopotentiogram be run on an electrode of approximately constant surface, the duration of each experiment must be short enough so that drop area growth is but a small fraction of total drop area. This condition is met by applying the current late in the drop life and for a time not exceeding about 50 msec. For a flow rate of .002 g/sec, at 3.5 sec into the drop life, the area of the drop changes by one percent over a 50 msec interval. This is a considerably shorter time gate than is commonly used in solid electrode chronopotentiometry.

While solid electrodes can be shielded and made planar to obey the conditions for linear diffusion, a DME is spherical. Fick's second law as previously stated does not hold under these conditions, but must be worked out in terms of the radius of the sphere and the radial distance from the surface of the sphere. Fick's second law corrected for spherical diffusion is

$$\frac{\partial C(r,t)}{\partial t} = D \left[\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r} \right] \quad (8)$$

Applying the same boundary conditions as for linear diffusion, but in terms of r rather than of x , and using LaPlace transforms, one arrives at the equation for chronopotentiometry at spherical electrodes ⁹

$$C_{(r_o, t)} = C - \frac{i_o r_o}{nFD} \left\{ 1 - \exp \left(\frac{Dt}{r_o^2} \right) \operatorname{erfc} \left[\frac{(Dt)^{\frac{1}{2}}}{r_o} \right] \right\} \quad (9)$$

where r_o is the radius of the electrode, i_o is the current density, i/Area , and other terms are as previously defined. The transition time now is defined as the time at which $C_{(r_o, t)} = 0$. Then the equation analogous to the Sand equation is

$$\frac{CnFD}{i_o r_o} = 1 - \exp \left(\frac{D\tau}{r_o^2} \right) \operatorname{erfc} \left[\frac{(D\tau)^{\frac{1}{2}}}{r_o} \right] \quad (10)$$

For typical values of D , τ , and r_o as used in DME chronopotentiometry, the argument $\frac{D\tau}{r_o^2}$ has a value on the order of 10^{-5} . In this case, $\exp \left(\frac{D\tau}{r_o^2} \right) \approx 1$. The term $\operatorname{erfc} \left[\frac{(D\tau)^{\frac{1}{2}}}{r_o} \right]$ can be expanded for small values of the argument to give

$$\operatorname{erfc} \left[\frac{(D\tau)^{\frac{1}{2}}}{r_o} \right] = \frac{2}{\pi^{\frac{1}{2}}} \frac{(D\tau)^{\frac{1}{2}}}{r_o} \quad (11a)$$

Substituting this into equation (10) and rearranging, the equation reduces to the Sand equation for chronopotentiometry under conditions of semi-infinite linear diffusion. On the other hand, for large values of the argument (that is at a very long transition time or very small electrode radius) expanding the error function term and substituting it into equation (10) gives

$$\frac{i_o \tau^{\frac{1}{2}}}{C} = \frac{nFD}{r_o \left[\frac{1}{\tau^{\frac{1}{2}}} - \frac{r_o}{\pi^{\frac{1}{2}} D^{\frac{1}{2}} \tau} \right]} \quad (11b)$$

As r_0 approaches zero, the product $i\tau^{\frac{1}{2}}$ becomes infinite. For spherical diffusion, it cannot be assumed that the ratio $i\tau^{\frac{1}{2}}/C$ is a constant as it is in the case of semi-infinite linear diffusion. However, if one chooses an appropriate set of conditions to give $\frac{D\tau}{r_0^2} \ll 1$, a linear approximation to spherical diffusion introduces no appreciable error.

In polarography it has been noted that the entire diffusion layer does not fall away with each drop of mercury. There is a residual concentration polarization so that the new drop forms in a region of solution where the concentration of electroactive substance is less than the concentration of the bulk solution.¹⁰

In order to apply this concept to chronopotentiometry one must know the thickness of the layer of solution that falls away with the drop, and the thickness of the diffusion layer at the time the drop falls. The latter may be estimated by substituting experimental values of C , i , and τ into equation (4) and solving for x , the distance at which $C_{(x,\tau)} = 95\%$ or 99% of the bulk concentration.

Actual numerical data are not available which would indicate the thickness of the solution layer carried away by the drop, although that information should be available from hydrodynamic calculations. In the absence of such information, it is difficult to assess the magnitude of the depletion effect in chronopotentiometry. The simplest approach would be empirical, that is, to observe chronopotentiograms run on the first and on successive drops to see if differences are evident. The experimental results of such observations are included in Chapter IV.

The Electrical Double Layer

Application of the Sand equation assumes that the total applied current is going toward the faradaic process under study. In actuality, this is never the case. A portion of the applied current is consumed in background processes, such as charging the electrical double layer, the adsorption or desorption of charged species on the electrode surface, and the formation and reduction of oxide films on the electrode surface. In DME work, oxide films are not likely to occur and this factor can be ignored. Double-layer charging and adsorption-desorption phenomena, however, can consume a significant portion of the applied current.

The electrical double layer results from the accumulation of ions of a particular charge along the interface between the metal electrode and the solution due to the potential difference across the interface. The quantity of charge associated with this layer of ions changes with the potential of the electrode, and the electrical double layer behaves much like a capacitor. But while the capacitance, or the quantity of charge associated with a given change in potential, is constant over a wide range of potential for a passive electrical capacitor, the capacitance of the electrical double layer varies with potential. For this reason, correcting for the current consumed by double-layer charging is a difficult task. At high current densities, when the transition time is very short, or for low concentrations of electroactive substance, the rate of change of potential is rapid, even during the transition period when the E vs. t curve is relatively flat. This means that, at the short transition times used in DME chronopotentiometry, charging of the double layer consumes a significant portion of the total applied current. Elec-

trolysis of adsorbed species can also consume significant portions of the applied current. The experimentally measured τ will be greater than expected and the value of the chronopotentiometric constant, $i\tau^{\frac{1}{2}}/C$, will be too large.

One may represent the total current, i , in terms of the component currents

$$i = i_f + i_{dl} + i_{ads} \quad (12)$$

where the subscript f indicates the current going to the faradaic process of interest; dl , the double-layer charging current; and ads , the faradaic current going to the oxidation or reduction of adsorbed species. Each of these component currents can be expressed in terms of its causative process:

$$i = \frac{nFaD^{\frac{1}{2}}\pi^{\frac{1}{2}}C}{2\tau^{\frac{1}{2}}} + \frac{C_{dl}\Delta E}{\tau} \pm \frac{nFa\Gamma}{\tau} \quad (13)$$

The first term is the Sand equation describing the faradaic process of interest, the second term describes the charging of the double layer where C_{dl} is the average differential double-layer capacitance, and the third term, the electrolysis of adsorbed species where Γ is the fractional coverage of the electrode surface by the adsorbed species.

Bard⁴ was the first to propose representing the fractional currents in this manner. Using the chronopotentiometric constant $A = \frac{nFaD^{\frac{1}{2}}\pi^{\frac{1}{2}}}{2}$ and the constant $B = C_{dl}\Delta E + nFa\Gamma$ and rearranging, equation (13) takes the form

$$i\tau = AC\tau^{\frac{1}{2}} + B \quad (14)$$

A plot of $i\tau$ vs. $C\tau^{\frac{1}{2}}$ for a series of chronopotentiograms of a given electroactive substance varying either C or i or both should give a straight line with slope A , the true chronopotentiometric constant, and intercept B , the number of coulombs associated with the double-layer charging and adsorption processes.

The value of B need be determined only once for a particular electroactive substance if the same supporting electrolyte and electrode area are used in subsequent experiments. Once B is known, it may be applied in various ways to correct chronopotentiometric data. Corrected individual chronopotentiometric constants can be calculated by subtracting B from $i\tau$ and dividing the result by $C\tau^{\frac{1}{2}}$. If the total applied current remains constant over a series of experiments, one can plot τ vs. $C\tau^{\frac{1}{2}}$, determine the residual τ , τ_{res} , from the intercept, and correct individual transition times by subtracting $\tau_{\text{res}}/\tau^{\frac{1}{2}}$ from the experimentally determined $\tau^{\frac{1}{2}}$. The resulting value is the $\tau^{\frac{1}{2}}$ which would have been measured in the absence of double-layer and adsorption effects. τ_{res} may be evaluated more directly by running a chronopotentiogram (preferentially a derivative chronopotentiogram) on the background electrolyte and measuring the time required to charge the double layer in the absence of the electroactive substance of interest. The true faradaic current, i_f , can be determined by subtracting B/τ , the non-faradaic current, from the total current. The chronopotentiometric constant can then be calculated in terms of $i_f\tau^{\frac{1}{2}}/C$. These corrections are summarized in Table 1.

Table 1. Summary of Bard-type Corrections

Measured Parameter	Correction Applied	True Chronopotentiometric Constant
$\tau^{\frac{1}{2}}$	$\tau^{\frac{1}{2}} - \frac{\tau_{\text{res}}}{\tau^{\frac{1}{2}}} = \tau_{\text{corr}}^{\frac{1}{2}}$	$\frac{i\tau_{\text{corr}}^{\frac{1}{2}}}{C} = A$
i	$i - \frac{B}{\tau} = i_f$	$\frac{i_f \tau^{\frac{1}{2}}}{C} = A$
$\frac{i\tau^{\frac{1}{2}}}{C}$	$\frac{i\tau - B}{C\tau^{\frac{1}{2}}} = A$	A

Another approach to the double layer problem is to use instrumental compensation. Shultz et al.¹¹ described an arrangement of matched cells; one cell contains background electrolyte and the other background electrolyte and the electroactive substance. The potential across the first cell is maintained by a potentiostat at the output potential of the galvanostat which supplies current to the second cell, thereby keeping the potentials across the two cells equal at all times. The current used for background processes by the first cell is electronically added to the galvanostat input so that the current passing through the second cell is the sum of the applied current and the current necessary for background processes. While this type of arrangement performs adequately in compensating for background processes, it is difficult to set up on a practical

basis because of the improbability of matching two cells exactly, especially DME cells where one must have identical capillary characteristics and perfectly synchronized drop detachment.

The instrumental method of double layer compensation used in the present work is based on the fact that the rate of double-layer charging is a function of the rate of potential change. For the initial and final steeply rising portions of the chronopotentiogram, almost all the applied current goes toward charging the double layer. On the relatively flat transition plateau, where E changes much more slowly, the rate of double-layer charging is less. That means that the double-layer charging is a function of dE/dt . The latter can be obtained by electronically differentiating the E vs. t signal. A portion of the dE/dt output is converted to a current which is added to the applied current by positive feedback. For the initial and final large values of dE/dt the feedback current is great, but during the transition when dE/dt is much less, the feedback current is proportionately smaller. The fixed proportion of the differentiator output which is used is based on the double-layer capacitance in the potential range of the transition. Therefore, it will be different for different electroactive species, supporting electrolytes, and electrodes. A simple empirical method to optimize double-layer compensation is to run a series of Bard-plots on a given solution, varying the amount of feedback used for each series. When the line in a plot of $i\tau$ vs. $C\tau^{\frac{1}{2}}$ is linear and passes through the origin, the amount of feedback used exactly compensates for the double-layer charging. No additional Bard-type corrections need be made to the data collected for that electroactive species so long as the supporting electrolyte and electrode area remain

unchanged.

Derivative Method for Measuring Transition Time

A typical "good" reversible chronopotentiogram is presented in Figure 1a. If the electrode reaction is irreversible, a curve as in Figure 1b is obtained. In the presence of severe double-layer charging, the experimental curve may be distorted to look like that in Figure 1c. These curves serve to illustrate the fact that the measurement of transition times, especially the very short ones of DME chronopotentiometry, is not a straightforward process. The rising initial and final portions of the curve may not be vertical, parallel to each other, or even linear.

Russell and Peterson compared various methods of graphical analysis; all require extrapolations along the sharply rising initial and final portions of the chronopotentiogram. The transition time is measured as the distance between these extrapolated lines, but the actual points between which the measurement is made are arbitrarily chosen to achieve the best fit between experimental data and theory.

In derivative chronopotentiometry one does away with this arbitrary choice for measuring τ . The rate of potential change with respect to time, dE/dt , is recorded as a function of time. During the transition, dE/dt reaches a minimum which is quantitatively related to the transition time. Peters and Burden³ have worked out the relationships based on the Nernst-type equation for chronopotentiometry.

$$E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{t^{\frac{1}{2}}}{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}} \quad (15)$$

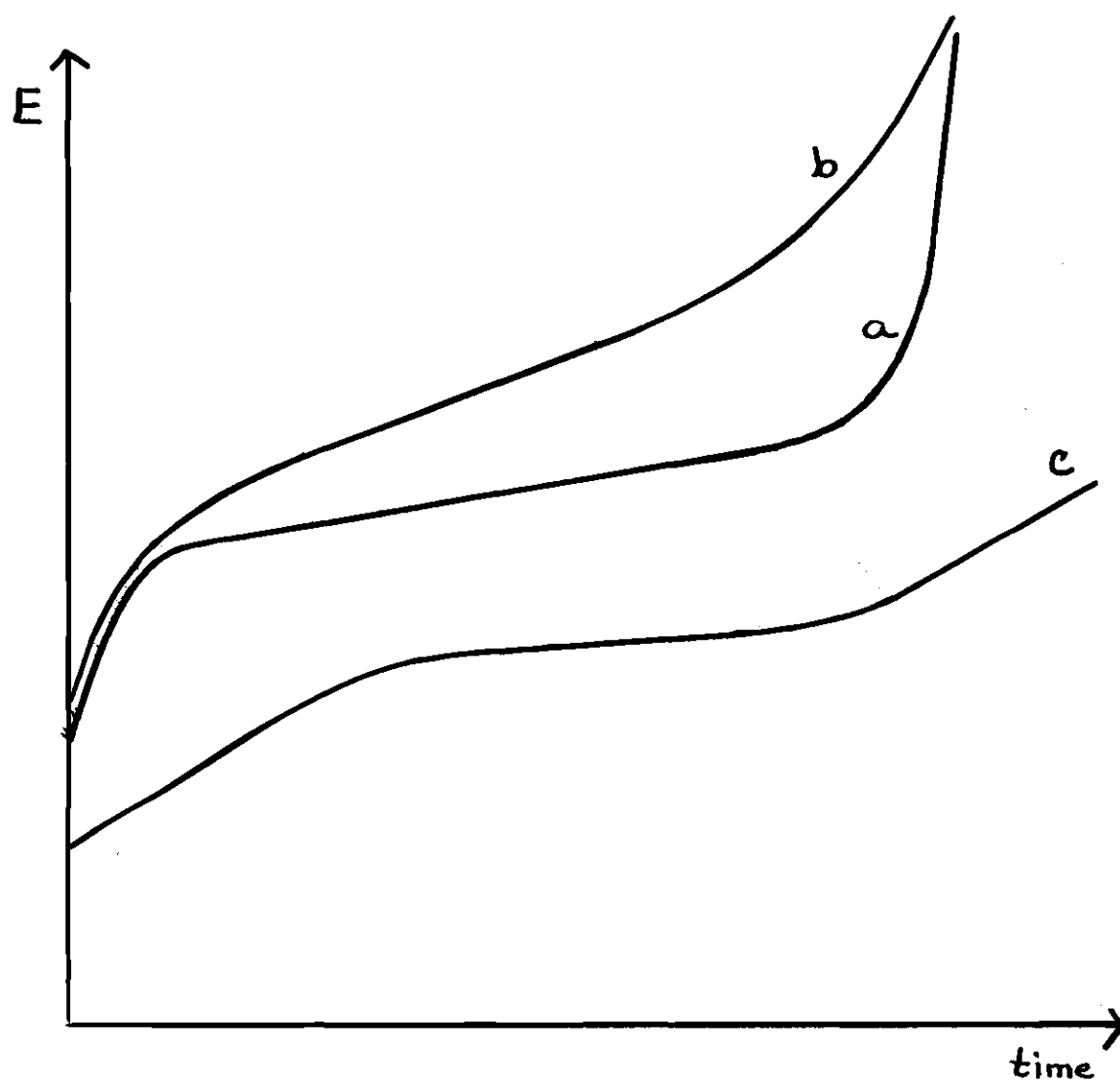


Figure 1. Typical Chronopotentiograms

- a) reversible reaction
- b) irreversible reaction
- c) distorted by double-layer charging

By taking the second derivative of this expression, it can be shown that $(dE/dt)_{\min}$ occurs at $t = 4/9\tau$ for a reversible reaction. From the same equations it can also be shown that, for a reversible reaction,

$$(dE/dt)_{\min} = - \frac{27}{8} \frac{RT}{nF\tau} \quad (16)$$

Combining constants for an $n = 2$ reaction at 25°C and rearranging, this reduces to the simple relationship

$$\tau = - \frac{.04332}{(dE/dt)_{\min}} \quad (17)$$

where τ is in seconds and dE/dt is in volts/second. In Figure 2 a derivative chronopotentiogram is compared to a conventional one for the same reversible reaction. The value for $(dE/dt)_{\min}$ can be read easily and with good accuracy, and τ can be calculated readily by Equation 17.

For an irreversible case, the expression analogous to Equation 16 is

$$(dE/dt)_{\min} = - \frac{2RT}{\alpha n_a F\tau} \quad (18)$$

where α is the transfer coefficient and n_a is the number of electrons transferred in the rate limiting step. If τ can be obtained by conventional means, then $(dE/dt)_{\min}$ can be used to evaluate α .

In addition to the advantages already mentioned, derivative chronopotentiometry minimizes the problem of double-layer charging. (dE/dt) is minimum at the time when the rate of potential change is the least. Con-

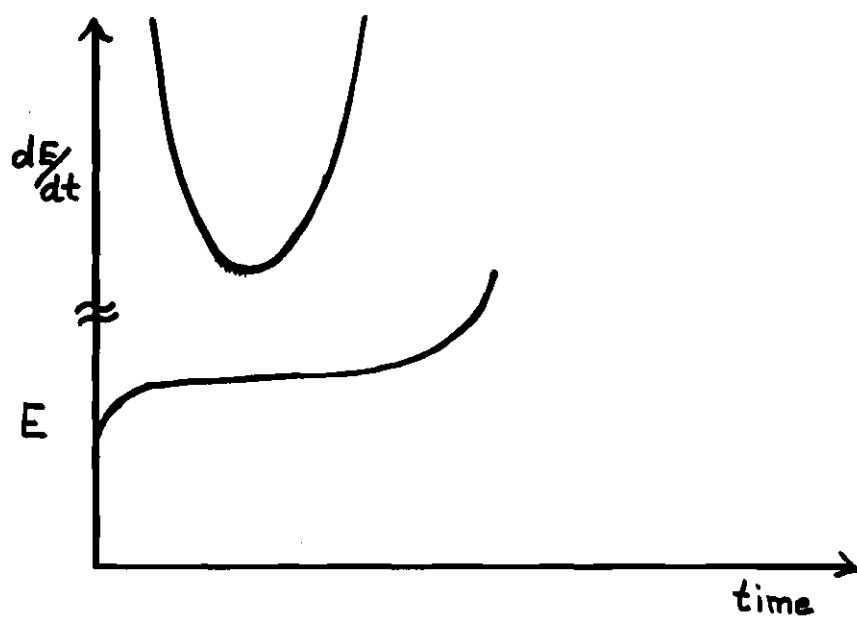


Figure 2. Conventional and Derivative Chronopotentiograms for the Same Reaction

sequently, the effect of the double-layer charging is minimized at this point and the transition times measured by the derivative technique are not as enhanced by double-layer charging as are those measured conventionally.

Multicomponent Systems

Chronopotentiometry of solutions containing two or more electroactive substances which undergo consecutive electrode reactions suffers the inherent disadvantage that the faradaic current for the second and subsequent components is reduced by the amount of the residual diffusion current from the more easily electrolysed components. This has the effect of increasing the transition times for the subsequent components. Chronopotentiograms for cadmium alone and for the same amount of cadmium in the presence of an equimolar concentration of lead are compared in Figure 3.

Previous attempts to correct the transition time of the later component were based on theoretical concentration-transition time relationships derived by Delahay and Mamantov¹³ for two consecutive processes and which were extended to multicomponent systems by Reilly et al.¹⁴ Sturrock, Gibson, and Anstine⁶ derived the complex theoretical potential-time relationships for multicomponent chronopotentiometry that required the assistance of a digital computer, but the equations are sufficiently complex for the evaluation of certain terms. It is possible to evaluate τ for second and third components by using a computer prepared tabulation of "a," a parameter which is dependent on $(dE/dt)_{\min}$ for the component in question, and the sum of the transition times for the preceding waves.

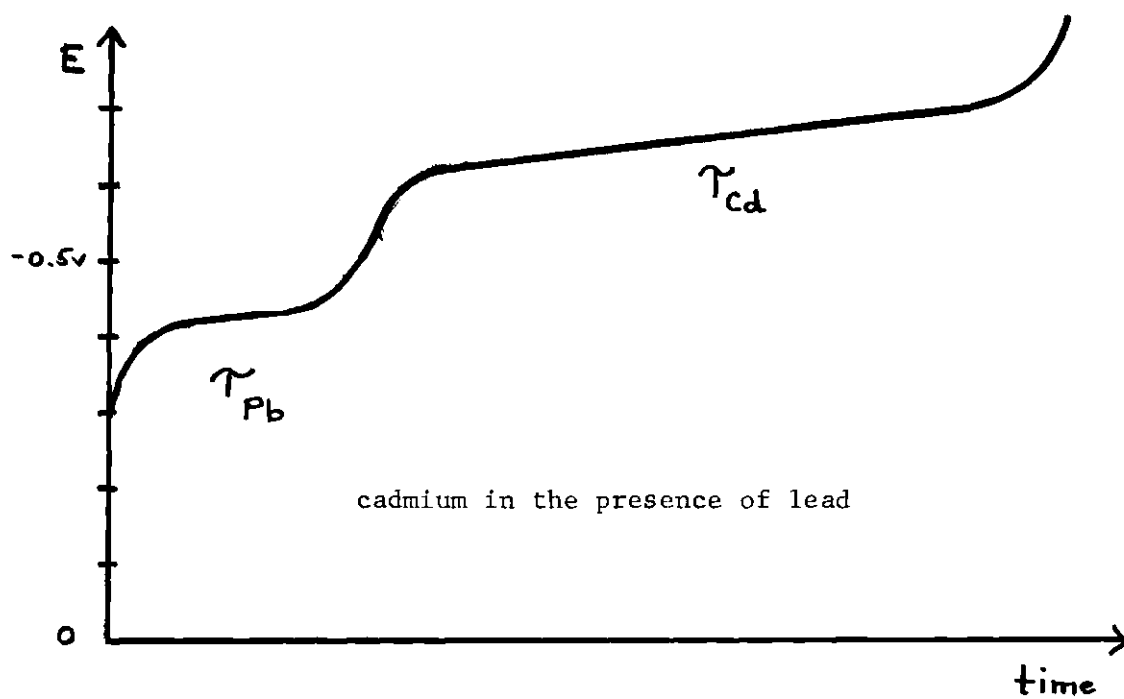
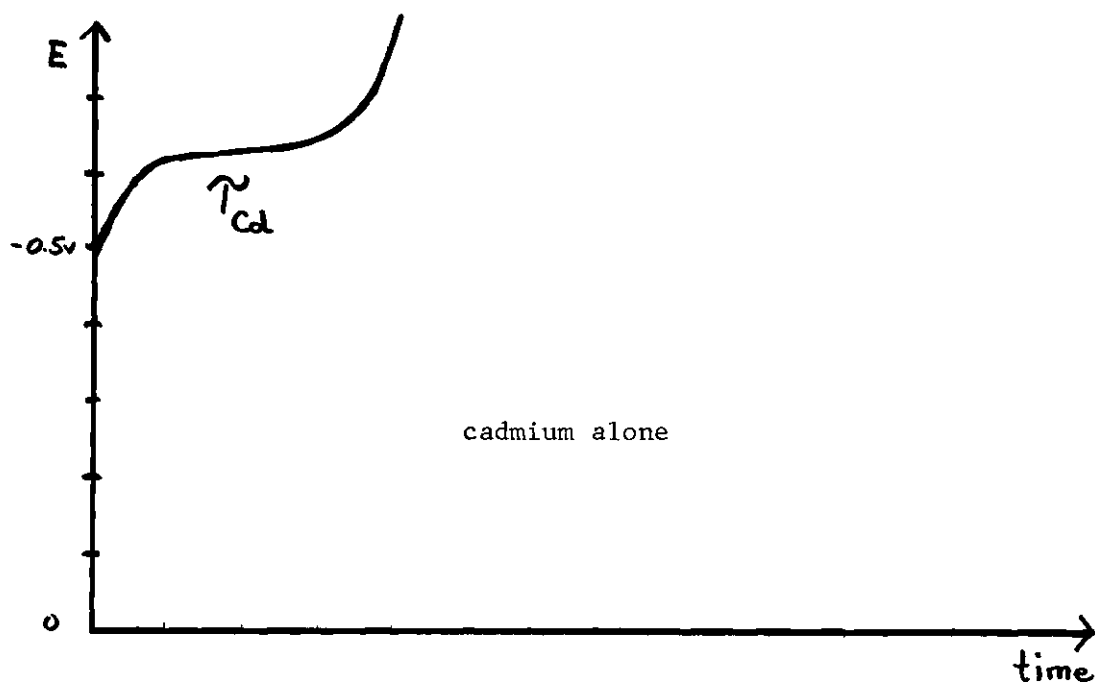


Figure 3. Change in a Chronopotentiogram of Cadmium Caused by Presence of Equimolar Concentration of Lead

The same authors proposed a standard addition type analysis to determine the concentration of the component in question since "a" is essentially independent of dilution. This type of analysis cannot be applied to very dilute solutions or to transition times much shorter than three milliseconds because it is impossible to apply a Bard-type separation of faradaic and capacitative currents to correct for double-layer charging.

Bowman and Bard⁷ were able to decrease the effect of a preceding wave by imposing a constant potential between the two waves for a measured time before applying the constant current for the chronopotentiometry of the second component. The current during the potential step is dependent on the diffusion of the first component and obeys the Cottrell equation

$$i_d = \frac{n_1 F A D_1^{1/2} C_1}{\pi^{1/2} t^{1/2}} \quad (19)$$

Current during the potential step decreases as a function of the square root of time. The current is allowed to decay for a time T_c ; then the cell is switched from potentiostat to galvanostat and a constant current, i , is applied. Then

$$i\tau^{1/2} = i\tau_2^{1/2} + i\tau_1^{1/2}X \quad (20)$$

where τ without subscript is the measured transition time for the second component and τ_1 and τ_2 are the true transition times for the first and second components and $X = 2/\pi \tan^{-1} T_c/\tau$. Potential step-current step

chronopotentiograms are run and X calculated for varying ratios of T_c/τ . Then $i\tau_2^{\frac{1}{2}}$ is obtained from the intercept of a plot of $i\tau^{\frac{1}{2}}$ vs. X . Thus a series of chronopotentiograms is required to determine a single value of T_2 .

Extension of the potential step technique was undertaken in the present work. If the prebias potential is applied for a long enough time, the diffusion current of the first component decays to a small and nearly constant value. If the chronopotentiometric current is applied at any time within the flat portion of the i vs. t curve, the diffusion current can be considered to be constant over the short (1-50 msec) time span of the chronopotentiometric wave. The constant diffusion current, i_d , can be subtracted from the applied current to give the current going toward the faradaic process for the second component.

$$i - i_d = i_f \quad (21)$$

The value of i_f is used with the observed transition time to calculate the $i\tau^{\frac{1}{2}}/C$ ratio for the second component. The chronopotentiometric constant is stated in terms of a corrected current, rather than a corrected transition time.

There are various methods, based on the Cottrell equation (Eq. 18), for obtaining a value for i_d . Ilkovic treated the problem of diffusion to an expanding sphere such as a DME by substituting into the Cottrell equation a term which expresses the area of the electrode as a function of the increasing volume of the sphere, that is, as a function of the mercury flow rate and the drop time,

$$i_d (\text{av}) = 607 \text{ nm}^2 / 3D^{\frac{1}{2}} t_d^{\frac{1}{6}} C \quad (22)$$

where m is the flow rate of mercury in mg/sec, t_d is the drop time in sec, i_d is expressed in microamperes, and C is in nmoles/cm².

In order to get an instantaneous rather than an average current, one must use the actual time in the drop life and introduce a factor of $\sqrt{7/3}$ to account for the growth of the drop into the depleted layer of solution.¹⁵ The resulting equation describes the current-time behavior at potentials at which the current is diffusion limited.

$$i_d = 708.2 \text{ nm}^{\frac{2}{3}} D^{\frac{1}{2}} t_d^{\frac{1}{6}} C \quad (23)$$

The disadvantage of calculating instantaneous currents by the modified Ilkovic equation lies in the inaccuracies introduced by the use of so many measured parameters.

To reduce the number of experimentally measured parameters involved, a new expression was derived in the course of this work combining the Cottrell and Sand equations. The concentration of electroactive substance in the bulk solution was expressed in terms of the Sand equation, then this expression was substituted for C in the Cottrell equation along with the previously mentioned factor $\sqrt{7/3}$ to account for the expansion of the drop.

$$i_d = \sqrt{\frac{7}{3}} \frac{nFAD^{\frac{1}{2}}}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} \left[\frac{2i\tau^{\frac{1}{2}}}{nFAD^{\frac{1}{2}} \pi^{\frac{1}{2}}} \right] \quad (24)$$

This expression simplifies to

$$i_d = \frac{2}{\pi} \sqrt{\frac{7}{3t}} (i\tau^{\frac{1}{2}}) \quad (25)$$

where t is the delay time (the length of time that the growing drop is subject to the prebias before the chronopotentiometric current is applied) and i and τ are obtained from a chronopotentiogram of the first component without prebias at time t in the drop life. Essentially, i_d for a single component is calculated from a single chronopotentiogram of that component.

In the course of this investigation, a simpler method was discovered to determine diffusion currents. A prebias potential beyond the first wave is maintained for time t , then sufficient current is applied from a continuously variable, calibrated source so that the prebias potential is just maintained. Under such conditions, the applied current is exactly equal to the diffusion current of the first species. If the applied current is less than the diffusion current, the concentration of electroactive species will increase at the electrode surface and the potential will change in accord with the Nernst equation. Likewise, too large an applied current will deplete the electroactive substance at the electrode surface faster than it can be supplied by diffusion, and the potential will move in the opposite direction. The diffusion current measured in this way is subtracted from the total current to obtain i_f . A simpler method is to use an uncalibrated, variable current source adjusted to supply just the current necessary to equal the diffusion current and maintain the prebias potential. Then this current can be electronically added to the applied current so that nominally all the applied current is available for the second faradaic process. In a multicomponent situation where

one is trying to measure a transition for a wave on top of several others, this method is superior to the use of the Sand-Cottrell calculation which can be applied only with difficulty to multicomponent systems. It is also superior to the application of the Ilkovic equation which involves summing the diffusion currents for each of the preceding waves. In the new instrumental method, the total residual diffusion controlled current is measured without regard to the number or magnitude of its components.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

The Chronopotentiometer

The instrument used in this work is a multipurpose galvanostat employing a unique combination of digital logic and analog circuits. It was designed and fabricated locally to be used for single sweep, reverse sweep, and cyclic chronopotentiometry and as a signal generator for a variety of symmetric and unsymmetric triangular voltage waveforms.

The instrument incorporates separate anodic and cathodic current sources and can function as a potentiostat to maintain a constant prebias potential. Logic circuits control the selection of input signal as well as the voltage amplitude and center of the current sweep. The logic circuits also control a drop detaching solenoid and are used to synchronize the application of the current sweep with a desired drop size. There are outputs for both conventional (E vs. t) and derivative (dE/dt vs. t) chronopotentiometry. The differentiator can also accept an external signal such as might result from rapid sweep polarography using the galvanostat as the source for the triangular voltage wave. The instrument is suitable for use with both two and three electrode cells. In this work, three electrode cells were used exclusively to minimize problems from iR drop across the cell.

In the course of this work, several additions were made to the instrument, including an uncalibrated current source for diffusion current

compensation, and a positive feedback circuit using the dE/dt output to produce a compensation current for double-layer charging.

Theory of Operation

A functional block diagram of the instrument is given in Figure 4.

Galvanostat

The heart of the instrument is the galvanostat with an Analog Devices 142 A operational amplifier used as the control amplifier. The cell is in the primary feedback loop of the galvanostat. In response to a current input, a current of equal magnitude but opposite sign is forced through the feedback loop in order to maintain a zero total current at the summing point of the amplifier. The working electrode of the cell is connected to the summing point and is held a virtual ground. Instead of the cell, a 10 μ f or 0.1 μ f capacitor can be switched into the feedback circuit. In this case, the galvanostat functions as a current integrator and its output voltage is a repetitive triangular wave if the current inputs are switched alternately from anodic to cathodic. This triangular waveform can be used for a variety of purposes other than chronopotentiometry.

Potentiostat

When the prebias switch is on, a second feedback loop consisting of a voltage follower and a resistor is connected between the reference electrode and the control amplifier input. This prebias feedback loop has greater influence on the galvanostat and forces the output voltage to be equal and opposite to the voltage input from the prebias control. Thus the galvanostat functions as a potentiostat.

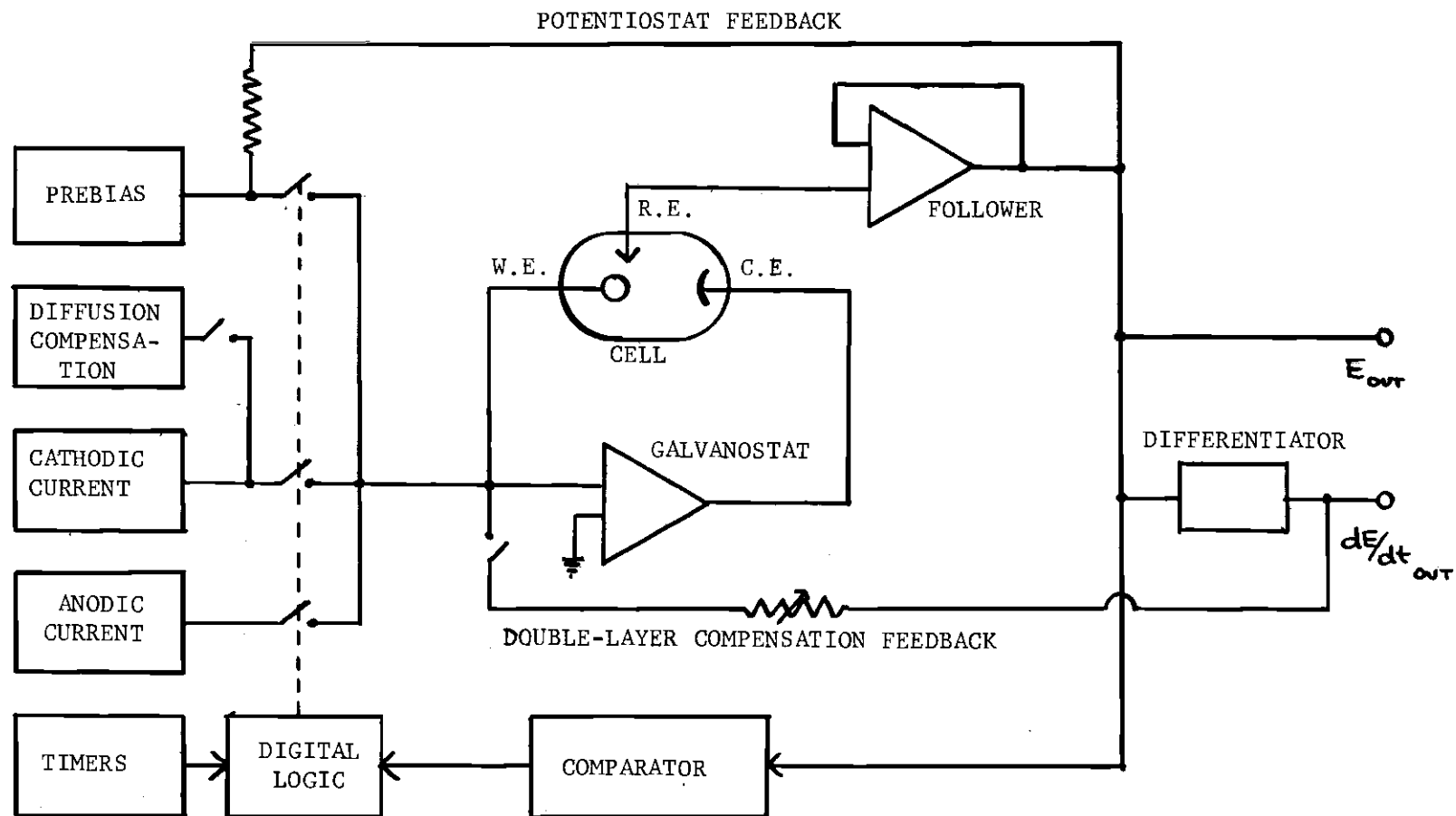


Figure 4. Diagram of Chronopotentiometer

Follower

In order to measure the cell voltage without the effect of iR drop, it is necessary that no current flow through the reference electrode. An Analog Devices 142 A operational amplifier functions as a high impedance, unity gain, non-inverting voltage follower, isolating the reference electrode from any current drawn on the E output. An input selection switch allows the follower to monitor either the reference or counter electrode so that the cell may function in either two or three electrode configuration.

Current Sources

Three enhancement mode MOSFETs are used to switch the galvanostat input. These are controlled by the digital control logic and select anodic, cathodic, or prebias inputs to the galvanostat. The anodic and cathodic current sources are derived from ten-turn potentiometers connected to the ± 15 v power source. Unity gain, non-inverting amplifiers isolate the potentiometers from the current load to maintain linear calibrated input currents. Range switches are used to select the appropriate resistor to provide input currents of 1-11 μ a, 10-110 μ a, and 0.1 - 1.1 ma. The prebias source is also a ten-turn potentiometer isolated by a follower and is calibrated to provide prebias potentials of 0 to ± 2 v.

Control Logic and Timing

The various functions of this instrument are controlled by digital logic which is in turn controlled by a comparator and timers. The cycle timer uses a differential amplifier to compare a selected voltage to the voltage across a 200 μ f capacitor which is charged at a constant rate. Increasing the selected voltage increases the time it takes for the volt-

ages to become equal and to produce an output signal. The delay timer, of similar design, starts its cycle at the same time as the cycle timer, but is generally set to produce its output signal at a time less than the cycle time. The cycle timer controls the drop detacher; the delay timer output signal triggers the digital logic which controls the application of an excitation to the cell, and the trigger signal for the oscilloscope.

A comparator is used as an interface between the analog and digital circuits. It compares the centering and amplitude voltages to the cell voltage and produces a signal to the digital logic to change the input signal. Pulses and dc levels are used to control the bistable flip flops, monostable vibrators, and gates of the digital logic.

Differentiator

The analog differentiator consists of a medium speed operational amplifier with input capacitors and feedback resistors selected by a four deck switch to give values of dE/dt ranging in 15 steps from 1 to 10,000 v/sec for each volt output. For stability, small input resistors and feedback capacitors are used to increase the rise time and decrease the noise level of the output.

Diffusion Current Compensator

The current for diffusion compensation is derived from the -15 v power supply through a ten-turn potentiometer and a fixed resistor to provide an uncalibrated cathodic current in the range of 0-50 μA . Manual switching is arranged so that diffusion compensation current alone may be applied to the cell, or so that it may be added to the calibrated cathodic current selected by the main panel current control, or added to a combination of main cathodic and positive feedback currents.

Double-layer Charging Compensator

The current for double-layer charging compensation is derived from the 10 v/sec per volt output range of the differentiator. This voltage is converted to a current for positive feedback by applying it across a fixed resistor (51 k Ω) and a one-turn potentiometer (0-250 k Ω). It may be selected in combination with the main cathodic current or in combination with that current and the diffusion compensation current.

In order to preserve stability in the galvanostat circuit, it was necessary to increase the rise time of this particular differentiator setting by using a larger input resistor. Without this precaution, serious oscillation may result. Because the double-layer compensation is based on a single differentiator speed, the useful range of transition time which can be evaluated with good accuracy is severely limited. One is not able to base the choice of differentiator output range on the magnitude of the dE/dt to be measured, but by changing the display amplification of the oscilloscope, one has some latitude in the size of the dE/dt (hence the magnitude of τ) that can be measured. Noise considerations impose an upper limit of about 30 msec for τ , and the increased rise time of the differentiator imposes a lower limit of about 5 msec. It would be far better to use two separate differentiator circuits, one set for optimal performance as a source of double-layer compensation, and the other with the necessary speed and flexibility to provide dE/dt output for display purposes.

Solenoid Drop Detacher

A solenoid drop detacher is operated by the discharge of a 20 μ f capacitor which has been charged to 170 v. The discharge of the capacitor

is triggered by the cycle timer. As the capacitor discharges, it momentarily activates the solenoid causing a plunger to move forward to strike the capillary and to dislodge the mercury drop. The plunger is returned to the starting position by a soft spring.

The design of a detacher which will dislodge a drop without causing significant oscillation of the capillary is difficult. If the capillary oscillates from the impact of the solenoid plunger, the growing mercury drop vibrates and the diffusion layer around the drop is disturbed. The drop detacher designed in the course of this work is illustrated in Figure 5. It depends on the rapid damping of oscillations by elastic restraints with different time constant. The solenoid is held in position by a jig which also holds the capillary. The distance between the plunger in its relaxed position and the capillary must be finely adjusted so that the stroke applied to the capillary is sufficiently short to reproducibly detach the drop without appreciably moving the capillary. The capillary is held in a semicircular groove in the jig by an elastic band or metal spring with sufficient tension to return the capillary to its original position but not so strong that it prevents sufficient motion to dislodge the drop. The back side of the groove is covered with a section of rubber tubing which serves to damp recoil motion when the capillary reseats itself, with a different elastic time constant than the spring. A small segment of tubing may be fitted onto the capillary to serve the same purpose.

Other Equipment

The E vs. t and dE/dt vs. t outputs of the chronopotentiometer are displayed on a Tektronix type 564B storage oscilloscope with a type 2A63

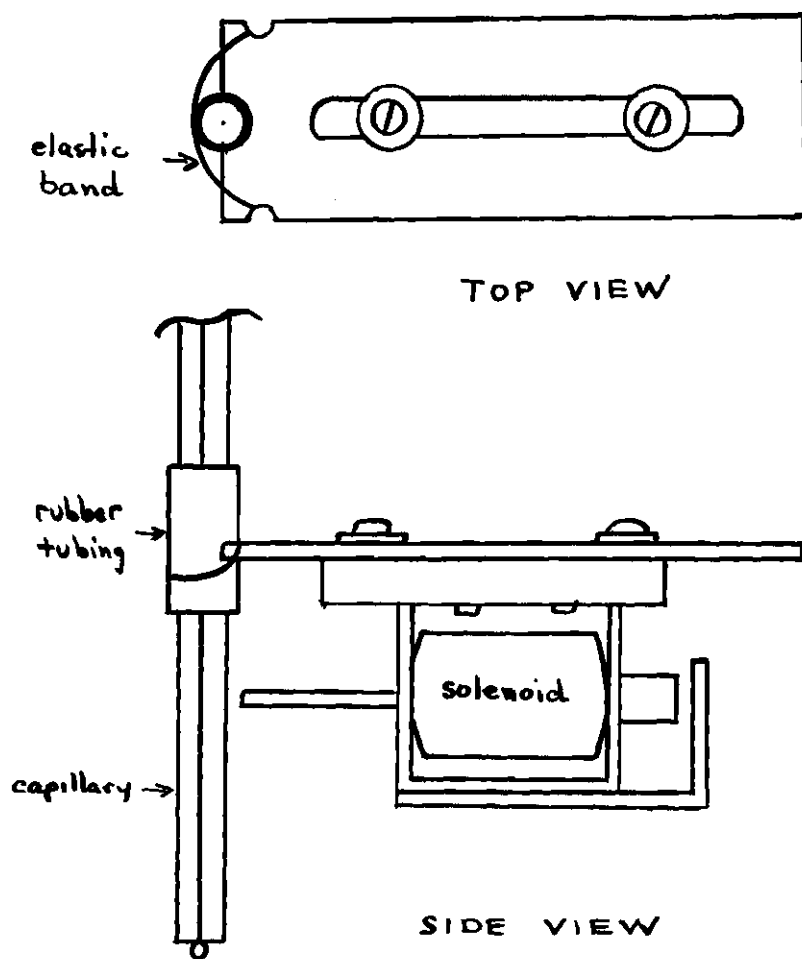


Figure 5. Solenoid Drop Detacher

differential amplifier and a type 3B4 time base unit. Photographs of the traces were taken with a Tektronix C-27 oscilloscope camera using Polaroid type 107 film.

All experiments were run with three electrode cells. A dropping mercury electrode of conventional design fitted with the drop detacher described previously was used as the working electrode. The counter electrode was a heavy gauge platinum foil, about one centimeter square sealed in glass at one corner so that both flat surfaces were exposed to the solution. The reference electrode was a Fisher saturated calomel electrode of the porous plug type.

The solutions were outgassed by dry nitrogen dispersed through a sintered glass bubbler. The nitrogen stream was first passed over heated copper to remove any residual oxygen. Bubbling was also used for mixing when solutions were added to the cell during the course of an experiment.

The cell itself was a 100 ml Berzelius beaker fitted with a rubber stopper drilled to accommodate the three electrodes and the bubbler, with an extra hole for addition of solutions by pipette or burette. The hole for the DME had to be large enough so that the capillary tube did not touch the stopper. Otherwise, contact would interfere with drop detachment.

CHAPTER IV

EXPERIMENTAL VERIFICATION OF APPLIED CORRECTIONS

The validity of the various corrections proposed in Chapter III was tested on lead-cadmium solutions using potassium nitrate as the supporting electrolyte. The transition for the reduction of lead occurs at approximately -0.4 v vs. SCE. The reduction wave for cadmium occurs at a potential about 0.2 v more negative. Both metals are reduced reversibly, and neither species is known to be adsorbed on a mercury electrode.

Calculation and Measurement of Diffusion Currents

Diffusion controlled currents for lead were determined at a prebias of -0.52 v by the three methods outlined in the previous chapter: direct measurement, Sand-Cottrell calculation, and Ilkovic calculation.

To 50 ml of 1 F KNO_3 supporting electrolyte were added 2 ml portions of 2×10^{-2} F $\text{Pb}(\text{NO}_3)_2$. The solution was deaerated after each addition and allowed to become quiet. The delay time for switching from prebias to controlled current modes was 2.625 sec into the drop life. The diffusion current was measured by adjusting the calibrated main cathodic current control to exactly maintain the prebias voltage for a period of 50 msec, thus giving a horizontal trace on the oscilloscope. The magnitude of the applied current was read directly from the dial of the current control potentiometer.

To obtain data required for the Sand-Cottrell calculation, derivative chronopotentiograms were run on the above solutions with the prebias switched off. Values of $(dE/dt)_{\min}$ for the lead wave were converted to transition times. Using delay time, t , equal to 2.625 sec, and combining numerical terms, the modified Sand-Cottrell equation (Eq. 25) reduces to

$$i_d(\text{in } \mu\text{A}) = 0.600 (i\tau^{\frac{1}{2}}) \quad (26)$$

Experimental values of i and τ were used to calculate i_d for solutions with different lead concentrations.

The Ilkovic calculation was based on the following experimentally measured parameters:

$D^{\frac{1}{2}} = 0.00290 \text{ cm/sec}^{\frac{1}{2}}$	(calculated from the Sand equation using experimental values of i , τ , a , and C)
$t = 2.625 \text{ sec}$	(delay time measured from oscilloscope trace of E vs. t from drop detachment to application of constant current)
$m = 2.393 \text{ mg/sec}$	(from weighing the mercury which flowed from the capillary in 298 sec)
$C = (\text{variable})$ mmoles/l	(calculated from known amounts of Pb added to the supporting electrolyte solution)

Combining numerical terms, the modified Ilkovic equation (Eq. 23) reduces to:

$$i_d(\text{in } \mu\text{A}) = 8.63 C$$

The values of i_d obtained for lead solutions over a concentration range from $7.69 \times 10^{-4} \text{ F}$ to $4.38 \times 10^{-3} \text{ F}$ are summarized in Table 2 and are presented graphically in Figure 6. Diffusion current is a linear function of concentration of the diffusing species. Values for diffusion currents calculated by the Sand-Cottrell and the Ilkovic equations agree extremely well. The diffusion currents obtained by direct measurement were consistently higher by about six percent.

The Ilkovic and Sand-Cottrell equations both ignore the effects of spherical diffusion and depletion on successive drops. At times late in the drop life these effects tend to cancel each other. For normal polarographic applications ignoring these effects does not introduce appreciable discrepancies between experimentally measured diffusion currents and those calculated by the Ilkovic equation (16). During the application of the prebias, the situation at the electrode is exactly the same as in polarography and one would expect the Ilkovic equation to be applicable. The validity of this new approach to calculating diffusion currents is confirmed by the fact that the Sand-Cottrell equation yields the same results as does the Ilkovic equation.

The value of $D^{\frac{1}{2}}$ used in the Ilkovic calculation was obtained from chronopotentiometry. It occurs as part of the numerator of the chronopotentiometric constant as it is usually expressed. If, instead, the value of $D^{\frac{1}{2}}$ calculated from the polarographic diffusion current constant (17) is used, the i_d 's calculated by the Ilkovic equation correspond closely to the directly measured i_d 's. This is consistent with the observations in this laboratory over a number of years that the chronopotentiometric constants obtained from DME data are low by about seven percent

Table 2. Lead Diffusion Currents

Conc. Pb (mmoles/l)	Diffusion Current (μ A)			
	Direct Measurement	Sand-Cottrell Calculation	Ilkovic Calculation	
			Chronopotentiometric $D^{\frac{1}{2}}$	Polarographic $D^{\frac{1}{2}}$
0.77	7.3	6.72	6.63	6.91
1.48	13.6	12.8	12.8	13.3
2.14	19.6	18.6	18.5	19.3
2.76	25.2	23.8	23.8	24.8
3.33	30.3	28.6	28.7	30.0
3.87	35.4	33.4	33.4	34.8
4.38	40.1	37.5	37.8	39.4

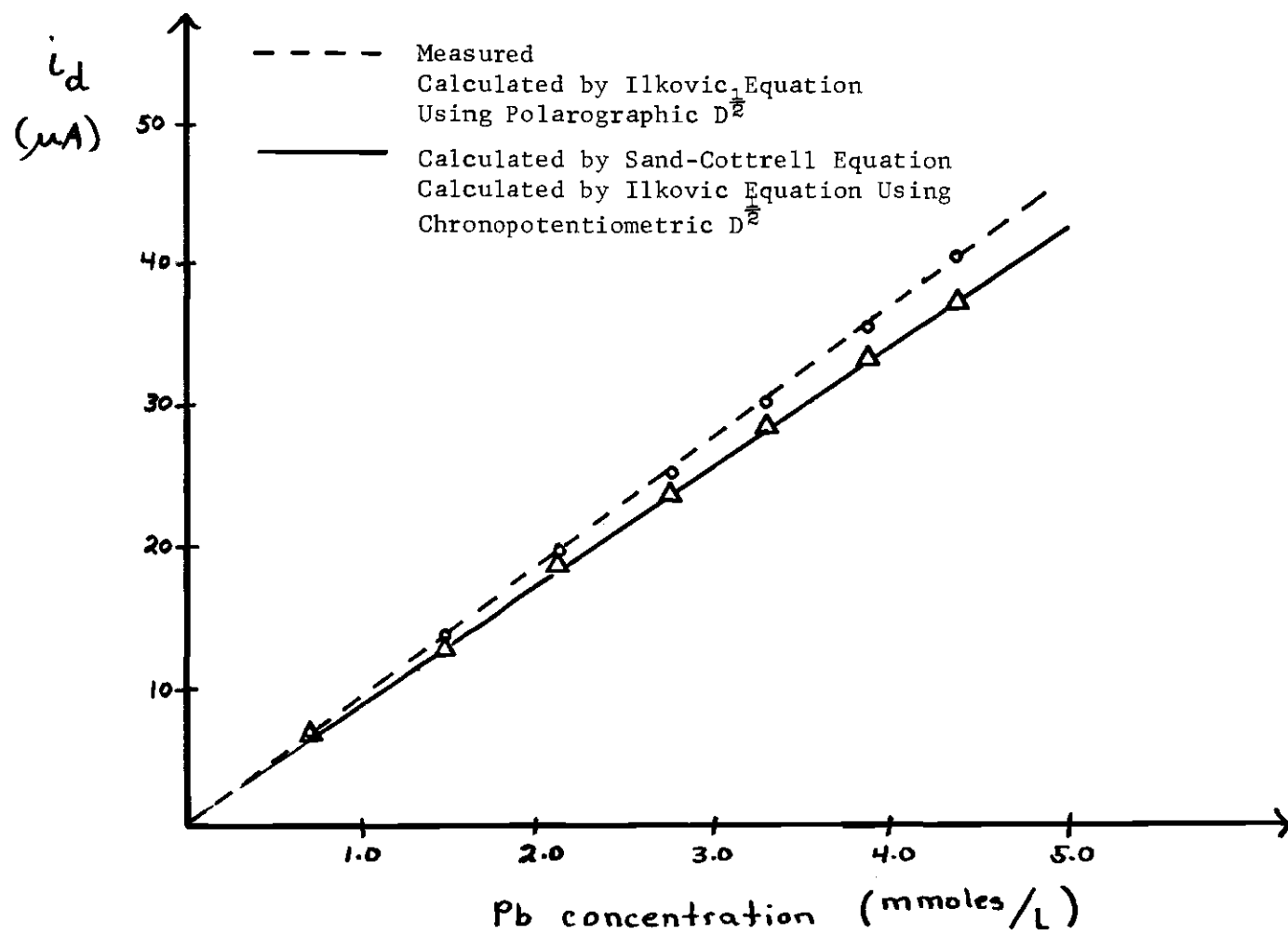


Figure 6. Lead Diffusion Currents

compared to the constants calculated from data obtained with solid electrodes.

Contributions to the apparent diffusion current from charging the double layer of the increasing drop are insignificant. For a drop area change of one percent ($\Delta a = 0.0003 \text{ cm}^2$) and a typical double-layer capacitance of $20 \text{ } \mu\text{f}/\text{cm}^2$, charging the double layer requires approximately $0.006 \text{ } \mu\text{coul}/\text{v}$. The point of zero charge for a 1.0 F KNO_3 solution was determined by drop-time curves to be in the vicinity of -0.4 to -0.5 v . At a prebias of -0.52 v over a time of 50 msec , the required current would be

$$i = \frac{C_{dl} \Delta V}{\Delta t} = \frac{0.006 \text{ } \mu\text{coul} \times 0.1 \text{ v}}{0.05 \text{ sec}} = 0.012 \text{ } \mu\text{A}$$

This is insignificant compared to the magnitude of the diffusion currents reported in Table 2.

Depletion Effects

A semi-quantitative evaluation of the magnitude of the depletion effect can be gained by examining the changes in successive chronopotentiograms of an electroactive substance as the depleted layer resulting from a prebias is replenished by continued diffusion after the prebias is switched off.

A cadmium solution ($1.1 \times 10^{-3} \text{ F}$ in 1.0 F KNO_3) was subjected to a prebias of -0.76 v until a steady state diffusion current ($10 \text{ } \mu\text{A}$) was observed at the usual delay time. Then the prebias was switched off manually to coincide as closely as possible to drop detachment. Derivative and conventional chronopotentiograms were run on the next four drops of

mercury (see Figure 7). The thickness of the depleted layer resulting from the chronopotentiograms is small compared to the depleted layer created by the prebias. Between chronopotentiometric sweeps, continued diffusion of cadmium lessens the concentration gradient and the thickness of the depleted layer. Part of the depleted solution is carried away by each mercury drop.

With an applied current of 100 μA and an electrode area of 0.0290 cm^2 , $\tau^{\frac{1}{2}}$ values were 0.128, 0.145, 0.152, and 0.153 $\text{sec}^{\frac{1}{2}}$. The increase in $\tau^{\frac{1}{2}}$ of approximately 20 percent from the first to the fourth drop indicates a corresponding increase in the apparent concentration of cadmium at the electrode surface. Stated in another way, application of a prebias to a DME electrode results in a residual concentration polarization such that the concentration of electroactive species seen by the newly formed drop may be as much as 20 percent less than the true bulk concentration. For this reason, the diffusion currents presented in Table 2 were all obtained after a steady state of depletion was reached. The same steady state conditions were used in subsequent work.

No depletion effect was observed on any chronopotentiograms run normally, that is, without a prebias beyond the reduction potential for that substance. Chronopotentiograms on the first and subsequent drops were identical for single component systems. For multicomponent systems, with a prebias set between the reduction potentials of the different components, chronopotentiograms of the first few drops were not identical. Discrepancies between first and subsequent drops can be explained by considering the variation of current required to set up the diffusion layer for the more active component. As the current required to set up the

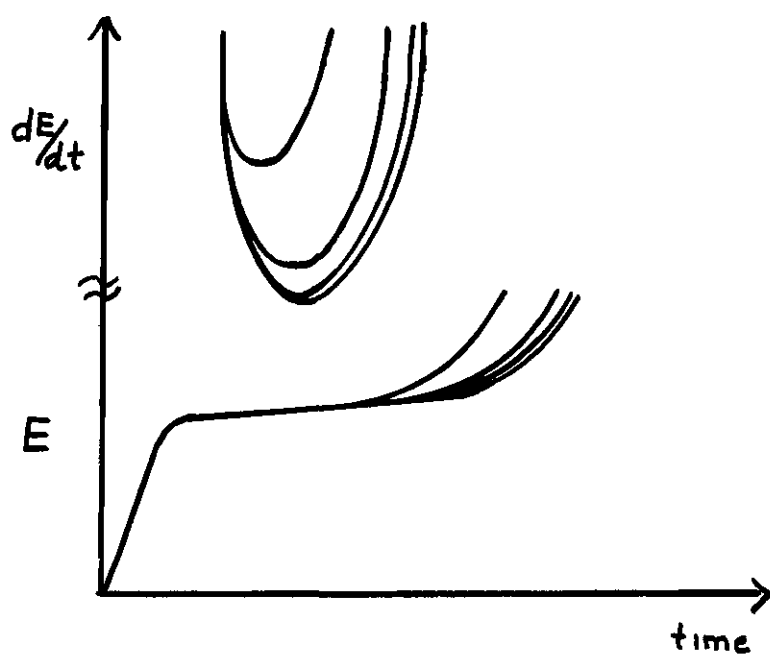


Figure 7. Effect of Depletion--Chronopotentiograms of Cadmium on Successive Drops of Mercury After Switching Off a -0.76 V Prebias

diffusion layer decreases, the fraction of the total current which is used for the chronopotentiometric process increases. Once a steady state is reached in the diffusion of the more active component, the chronopotentiograms of the less active component will superimpose so that successive traces on a storage oscilloscope appear as one trace.

Correction for Double-layer Charging

The number of microcoulombs required to charge the double layer during the cadmium transition was evaluated graphically from the $i\tau$ intercept of Bard-type plots of $i\tau$ vs. $C\tau^{\frac{1}{2}}$. For cadmium in 1 $\underline{\text{F}}$ KNO_3 with an electrode area of 0.0290 cm^2 , the amount of electricity associated with the double-layer charging is 0.032 to 0.035 μcoul . This means that during a one msec transition, the current required to charge the double layer is about 30 μA . For a dilute ($< 10^{-3}$ $\underline{\text{F}}$) solution of electroactive species, double-layer charging may consume 50 percent or more of the applied current. Relationships between i , τ , and C are meaningless unless appropriate corrections are made. Uncorrected and Bard-corrected values of $i\tau^{\frac{1}{2}}/aC$ are included in Table 3 for a range of cadmium concentrations from 3.6×10^{-6} $\underline{\text{F}}$ to 4.29×10^{-3} $\underline{\text{F}}$.

Instrumental compensation was employed for these same solutions. The variable resistor used to convert the dE/dt signal to a positive feedback current was not calibrated and the setting of this feedback resistor was recorded in scale units, the sole purpose of which was to allow re-setting to the same value. Double-layer compensation for cadmium was optimized on a solution 1.1×10^{-4} $\underline{\text{F}}$ in cadmium and 1.0 $\underline{\text{F}}$ in KNO_3 such that a plot of $i\tau$ vs. $C\tau^{\frac{1}{2}}$ passed through the origin. Current was varied in random steps from 13 to 40 μA ; corresponding values of τ ranged from

Table 3. Chronopotentiometric Constants for Cadmium
in the Presence of 2×10^{-3} F Lead

Conc. Cd (moles/l)	Uncompensated Data					Instrumentally Compensated Data				
	Uncorrected			Bard-corrected		Uncorrected			Bard-corrected	
			$\frac{i\tau^{\frac{1}{2}}}{aC}$					$\frac{i\tau^{\frac{1}{2}}}{aC}$		
	i (μ A)	τ (msec)		i_f (μ A)	$\frac{i_f\tau^{\frac{1}{2}}}{aC}$	i (μ A)	τ (msec)		i_f (μ A)	$\frac{i_f\tau^{\frac{1}{2}}}{aC}$
4.29×10^{-3}	400	19.7	451.2	398.5	449.5	400	19.7	451.2		
3.15×10^{-3}	300	19.7	460.9	298.5	458.4	300	19.7	460.9		
1.37×10^{-3}	150	15.5	469.8	148.1	463.6	150	14.9	461.5		
7.4×10^{-4}	100	10.2	470.8	97.1	457.0	100	9.62	457.4		
5.83×10^{-4}	50	25.5	472.3	48.7	460.3	50	24.1	458.9		
3.62×10^{-4}	50	10.31	483.9	46.9	454.0	50	9.02	452.6		
1.89×10^{-4}	20	18.1	490.4	18.2	447.1	25	9.84	452.7		
1.42×10^{-4}	30	5.70	550.2	24.4	447.3	25	5.55	452.6		
9.09×10^{-5}	30	3.38	662.3	20.5	453.5	15	6.37	454.3		
6.25×10^{-5}	20	4.25	719.4	12.5	448.7	10	6.99	461.3		
3.22×10^{-5}	10	6.66	874.5	5.19	454.7	10	1.86	462.4		
1.66×10^{-5}	20	2.28	1982.4	4.43	439.1	2.0	12.74	469.1		
1.07×10^{-5}	30	1.35	3549.4	3.70	438.2	2.0	8.02	577.5	1.55	448.0
7.4×10^{-6}	20	1.99	4158.0	2.16	449.2	1.0	15.47	579.8	0.77	466.1
3.8×10^{-6}	20	1.92	7970.1	1.56	621.0	1.0	7.73	798.4	0.54	426.3

NOTE: i = applied current; $a = .0290 \text{ cm}^2$; $i_f = i - \frac{B}{\tau}$; B for uncompensated data = .035 μcoul ; B for compensated data = .0036 μcoul .

Units for $\frac{i\tau^{\frac{1}{2}}}{aC}$ in $\frac{\mu\text{A-sec}^{\frac{1}{2}}}{\text{cm}^2\text{-mmole}}$.

37.7 to 3.97 msec.

It was not possible to optimize the double-layer compensation for cadmium in an ammonia-ammonia buffer of pH 10. The cadmium-ammonia complex reduces at a more negative potential than does the uncomplexed cadmium. The magnitude of the double-layer capacitance at this potential is less and the use of positive feedback resulted in oscillation in the control amplifier circuit. Increasing the speed of the differentiator increased the amplitude of the oscillations. Decreasing the differentiator speed damped the oscillations, but not quickly enough for the dE/dt output to be useful for measuring transition times. This illustrates the need for separate differentiator circuits for feedback and for dE/dt output to the oscilloscope.

Consistency of the Chronopotentiometric Constant for Cadmium in the Presence of Lead

A series of solutions which were 3.8×10^{-6} F to 4.3×10^{-3} F in cadmium and 2.0×10^{-3} F in lead was prepared by adding portions of solutions which were 1.0×10^{-3} F or 1.0×10^{-4} F in cadmium and also 2.0×10^{-3} F in lead and 1.0 F in KNO_3 to a solution which was 2.0×10^{-3} F in lead and 1.0 F in KNO_3 . Thus the concentration of lead and supporting electrolyte was held constant while the concentration of cadmium was increased. A series of chronopotentiograms was run on these solutions using a prebias of -0.52 v and instrumental compensation for the lead diffusion current. The diffusion current was checked after each addition and was found to be invariant. No attempt was made to measure the transition times for cadmium without a prebias above the lead wave since the

τ 's thus measured are so greatly enhanced that they are useless for direct analytical applications. The chronopotentiograms were run with and without instrumental double-layer compensation.

Three sets of chronopotentiometric constants were calculated: from the uncompensated and uncorrected data; from uncompensated data corrected according to Bard; and from data compensated instrumentally. The results are shown in Table 3. Consistency was achieved for cadmium concentrations as low as 1.66×10^{-6} F both by Bard corrections and by instrumental compensation. For Cd solutions on the order of 10^{-6} F, Bard-corrected results were more consistent than were the instrumentally compensated results. The results from the latter were improved by applying Bard corrections. $i\tau$ vs. $C\tau^{\frac{1}{2}}$ plots of the compensated data showed a residual double-layer effect of about 0.0036 μcoul . This is one-tenth the double-layer effect in the uncompensated data and becomes insignificant at concentrations of 10^{-5} F and higher, but it consumes a significant portion of the very low currents used for lower concentrations.

The lowest current setting available on the instrument used was one μA . For a 3.8×10^{-6} F cadmium solution using double-layer compensation, this lowest current yielded a τ of 7.73 msec, too near the lower limit imposed by the speed of the differentiator for an attempt to analyze more dilute solutions. There is reason to believe that with a lower applied current and a more sophisticated double-layer compensator, this concentration limit can be extended to the lower 10^{-6} range and perhaps beyond.

It should be emphasized that in these experiments the amount of lead present was 0.5 to 500 times the amount of the cadmium. Consistency

of $i\tau^{\frac{1}{2}}/aC$ was attained despite the presence of large amounts of lead, an interference which would render impossible the detection of cadmium by a.-c. polarography.

CHAPTER V

APPLICATION TO ANALYSIS

The concentration of an electroactive substance can be determined by chronopotentiometry by substituting experimental values for the other parameters into the Sand equation and solving for C . The value obtained, however, is subject to considerable error owing to the large number of variables used. Standard addition and titration methods offer a better approach. A series of chronopotentiograms is used to obtain data for the analytical curves.

Constancy of the $\frac{i\tau^{\frac{1}{2}}}{C}$ ratio is a necessity if chronopotentiometry is to be used for standard addition or titrametric determinations. Either instrumental compensation or arithmetic corrections can be used to assure the constancy of $\frac{i\tau^{\frac{1}{2}}}{C}$ over the range of concentration to be spanned during the titration or standard addition. Generally, instrumental compensation will yield values for τ that can be used directly in plotting an analytical curve. Arithmetical corrections require that many more calculations be performed before the data can be applied, but they do make it possible to operate under conditions that are not amenable to instrumental compensation (see Chapter IV).

Standard Addition Determinations

For a standard addition determination it is essential that a plot of $i\tau^{\frac{1}{2}}$ vs. C (which is equivalent to a Bard-type plot of $i\tau$ vs. $C\tau^{\frac{1}{2}}$)

intercept the C-axis at the point $C=0$. If double-layer effects are not eliminated by compensation or corrections, the $i\tau^{\frac{1}{2}}$ vs. C line may be displaced upward, giving a negative C-intercept and indicating the presence of the substance when there is none.

When the electroactive substance of interest is present initially, a plot of $i\tau^{\frac{1}{2}}$ versus the amount of that substance added will give a negative C-intercept. The magnitude of the displacement along the C-axis represents the amount of the substance originally present.

If the solution which is being determined contains two or more electroactive species, these species can be determined independently in the same solution. Cadmium is determined in the presence of lead by using the prebias and diffusion current compensation techniques discussed in Chapters III and IV. As aliquots of a standard cadmium solution are added to the test solution, the concentration (not the amount) of lead present is decreased. Thus the lead diffusion current changes after each Cd addition, and the diffusion current must be checked and the compensation readjusted.

When a sufficient number of additions (3 to 5) has been made and data obtained for the cadmium standard addition curve, the prebias is lowered to a potential below the lead wave and aliquots of a standard lead solution are added, yielding data for the lead determination. A solution of several electroactive substances can be analyzed by this means as long as the reduction potentials for the substances are separated sufficiently for a prebias to be imposed between the waves.

It is important that the substance which is reduced at a more

negative potential be determined first. The additional amount of that substance which remains in the solution as a result of the standard additions acts as supporting electrolyte and does not interfere when the more easily reduced species is determined. If, on the other hand, the more easily reduced species is determined first, the additional amount present in the test solution interferes in the determination of the less easily reduced species. The more of the former present, the more difficult it becomes to compensate for it.

Volume changes during the course of a standard addition determination cause curvature in a plot of $i\tau^{\frac{1}{2}}$ versus amount added. In order to create a perfectly linear plot, it is necessary to correct for dilution. This is done by multiplying $i\tau^{\frac{1}{2}}$ by the factor $\left(\frac{\text{total volume}}{\text{initial volume}}\right)$. If very small portions of a highly concentrated standard solution are added, for instance by microburette, the volume of the test solution may not change appreciably and volume changes can be ignored.

Another precaution is worthy of note. To achieve the best precision, the amount of electroactive substance added in each increment should be of the same order of magnitude as the total amount of that substance initially present. Addition of considerably larger amounts greatly compresses the concentration axis and reduces the precision by which small amounts may be determined. If, on the other hand, the increments are much smaller than the amount to be determined, extrapolation over a long distance adds to the uncertainty of the result.

An example of a two component standard addition determination is presented in Figure 8a. Cadmium in the amount of 0.2 μmoles was determined

in the presence of 100 μ moles of lead.

Extension of the Standard Addition Technique to a Zn-Cd-Pb System

All attempts to determine zinc in the presence of cadmium and lead gave results which were low by as much as 50 percent. Holding i constant, plots of $\tau^{\frac{1}{2}} - (\tau_{\text{res}}/\tau^{\frac{1}{2}})$ versus amount of zinc added exhibited varying degrees of curvature (bent away from the concentration axis), making extrapolation difficult. Attempts to determine zinc alone in potassium nitrate supporting electrolyte gave similar results, suggesting a problem related to the zinc rather than to the presence of other electroactive components.

Bard plots for zinc solutions showed negative $i\tau$ intercepts. This indicates that some other process besides double-layer charging contributes significant interference. Adsorption processes cause increases in the positive $i\tau$ intercept and appear as double-layer effects. Desorption of a positively charged electroactive substance, on the other hand, creates a current opposed to the applied current and results in a negative $i\tau$ intercept if the magnitude of the desorption effect is greater than that from double-layer charging.

To confirm the desorption hypothesis, drop time curves were run on zinc-potassium nitrate solutions. A curve for 3.5×10^{-3} \underline{F} zinc in 0.1 \underline{F} potassium nitrate is presented in Figure 8b. Adsorption is indicated at potentials from -0.6 v to -0.9 v. The reduction wave for zinc occurs at -1.0 v.

Studies by Christie and Osteryoung (18) have shown that adsorption of zinc occurs in potassium thiocyanate supporting electrolyte and that varying the prebias potential has a significant effect on the magnitude

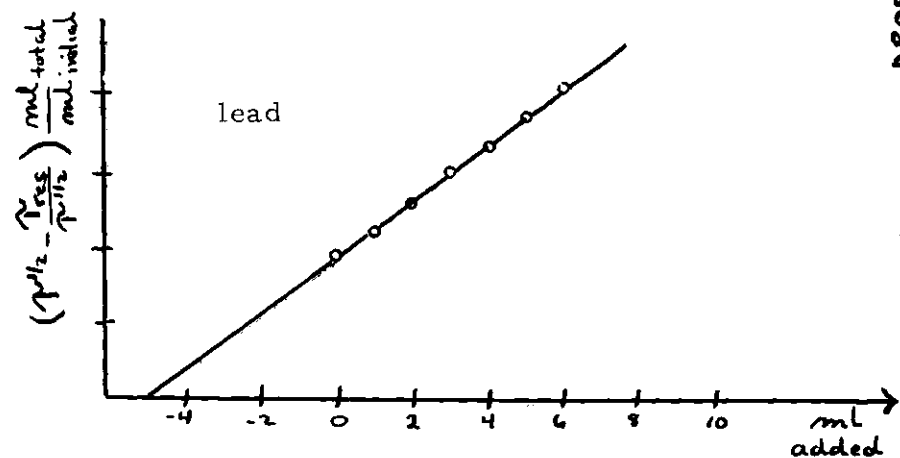
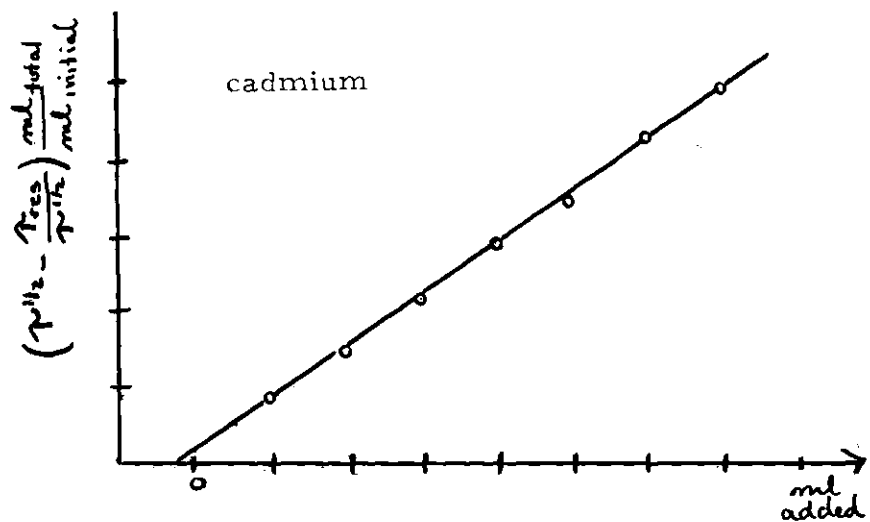


Figure 8a. Standard Addition Curves for Determination of Lead and Cadmium in an Admixture

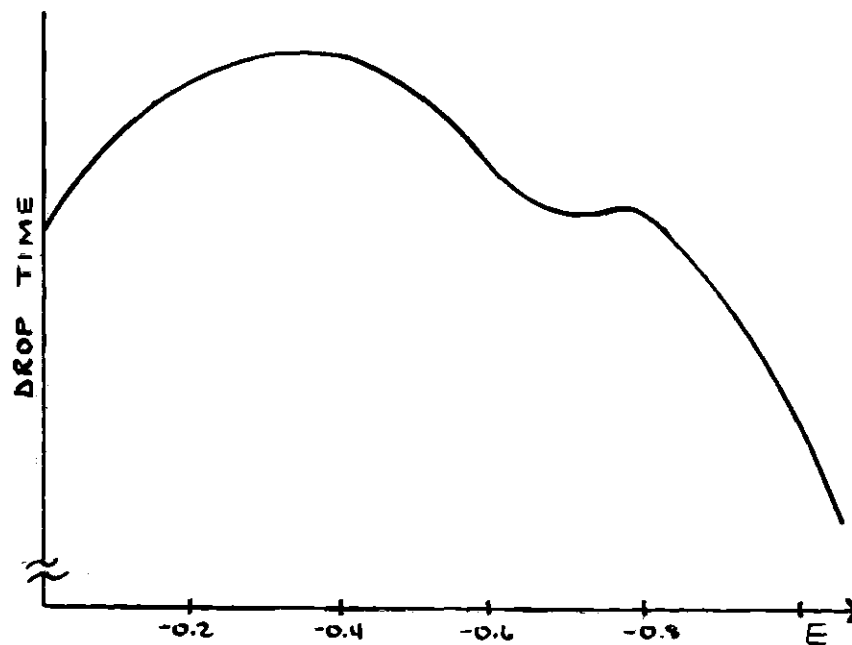


Figure 8b. Drop-time Curve for $3.5 \times 10^{-3} \text{ F}$ Zinc in 0.1 F Potassium Nitrate

desorption as the potential moves toward a range in which adsorption does not occur. In potassium thiocyanate solutions, the desorption of Zn does not occur when prebias potentials are greater than -0.9 v. In the present work it would appear that a similar desorption occurs and continues to cause difficulties even with prebias potentials greater than -0.9 v. No attempt was made to investigate the cause for the adsorption-desorption phenomenon. It might be due to the zinc itself or be caused by impurities in the system.

It was not possible to use instrumental double-layer compensation with zinc. Overcompensation always resulted. This is consistent with the hypothesis that desorption more than compensated for double-layer effects.

Bard corrections were applied in the previously mentioned attempts to determine zinc by using a corrected $\tau^{\frac{1}{2}}$, that is, $\tau^{\frac{1}{2}} - (\tau_{\text{res}}/\tau^{\frac{1}{2}})$. τ_{res} was obtained from the supporting electrolyte solution. Obviously this method resulted in corrections being applied in the wrong direction when zinc was present in the solution. This caused increased curvature in the plot of $i\tau^{\frac{1}{2}}$ versus amount of zinc added. Plots using $\tau^{\frac{1}{2}}$ without corrections were more nearly linear, but the intercepts still indicated less zinc than was actually present. This of course corresponds to the negative $i\tau$ intercept (or positive concentration-axis intercept) for the Bard plots of zinc in potassium nitrate. The complications made the determination of zinc by chronopotentiometry difficult if not impossible.

Titration Using Chronopotentiometric End Point Detection

Cadmium can be titrated with EGTA ([ethylenebis(oxyethylenenitrilo)]

tetraacetic acid) in the presence of copper if an ammonia-ammonium buffer of pH 10 is used. The ammonia strongly complexes the copper and masks it for reaction with EGTA. The $\text{Cd}(\text{NH}_3)_4^{2+}$ complex is weaker and does react with the EGTA. End point detection is difficult, however, because copper interferes with metallo-chromic indicators such as Eriochrome Black-T which is routinely used for the EGTA titration of cadmium.

As EGTA consumes cadmium during the course of the titration, chronopotentiometry can be used to measure the decreasing cadmium concentration. A plot of $i\tau^{\frac{1}{2}}$ versus ml EGTA added makes a good titration curve. Except in the region of the end point where an insufficient shift in equilibrium causes curvature, the initial and final portions of the titration curve are linear and can be extrapolated to intersect at the equivalence point.

As the concentration of cadmium decreases, double-layer effects become prominent. Bard corrections work well to deal with these effects. The τ measured by derivative means which occurs beyond the equivalence point is τ_{res} , the apparent transition time due to double-layer charging. It is constant at points well beyond the equivalence point where the concentration of cadmium not complexed by EGTA is essentially zero. If $\tau^{\frac{1}{2}} - (\tau_{\text{res}}/\tau^{\frac{1}{2}})$ is plotted versus ml EGTA added, the portion of the titration curve beyond the equivalence point coincides with the x-axis. Thus the point where the extrapolated initial portion of the titration curve intersects the x-axis is taken as the end point.

If volume changes during the titration are significant, volume corrections must be applied, just as they are in the case of standard addition

determinations. Chronopotentiometric end point determination lends itself to the use of concentrated titrant which can be added in small volume, eliminating the need for volume corrections. In titrations with visual end point detection, a concentrated titrant can cause one to overshoot the end point with a single drop of titrant. With chronopotentiometric end point detection, the region around the end point cannot be used because of the curvature existing in that portion of the titration curve. In the vicinity of the end point, titrant can be added in larger increments, so long as several points are obtained in the linear regions before and beyond the end point.

An EGTA solution was standardized against a standard cadmium solution using Eriochrome Black-T and an ammonia-ammonium nitrate buffer of pH 10. A series of identical solutions was made as follows: 1.00 ml standard Cd solution ($2 \mu\text{moles Cd}$) was added to 5 ml buffer, 10 ml 1.0 F KNO_3 , and sufficient water to make 50 ml total. The concentration of Cd in these test solutions was $4.00 \times 10^{-5} \text{ F}$. The EGTA titrant was determined to be exactly $1.00 \times 10^{-3} \text{ F}$ ($1 \mu\text{mole/ml}$).

The same titration was performed using chronopotentiometry. The chronopotentiometric titration curve is presented in Figure 9a. For this determination, electrode area = 0.02899 cm^2 , current = $30 \mu\text{A}$, and pre-bias = -0.66 v . The cadmium-ammonia complex is reduced around -0.8 v .

The same procedure was repeated on a new test solution, identical to the preceding one except for the presence of $50 \mu\text{moles copper}$. Diffusion current compensation was used to eliminate interference from the Cu. The titration curve is presented in Figure 9b.

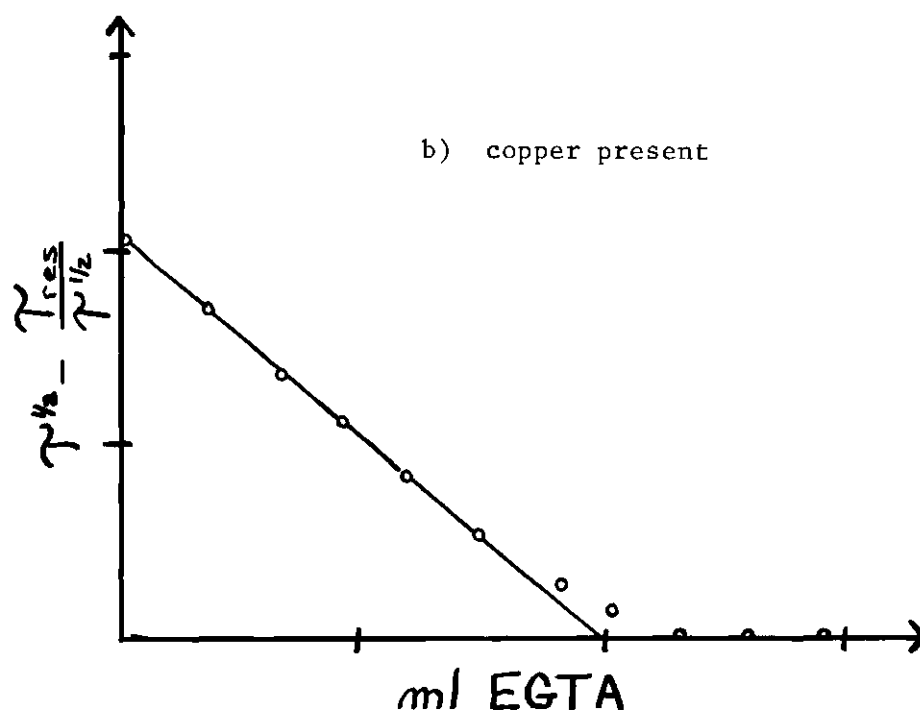
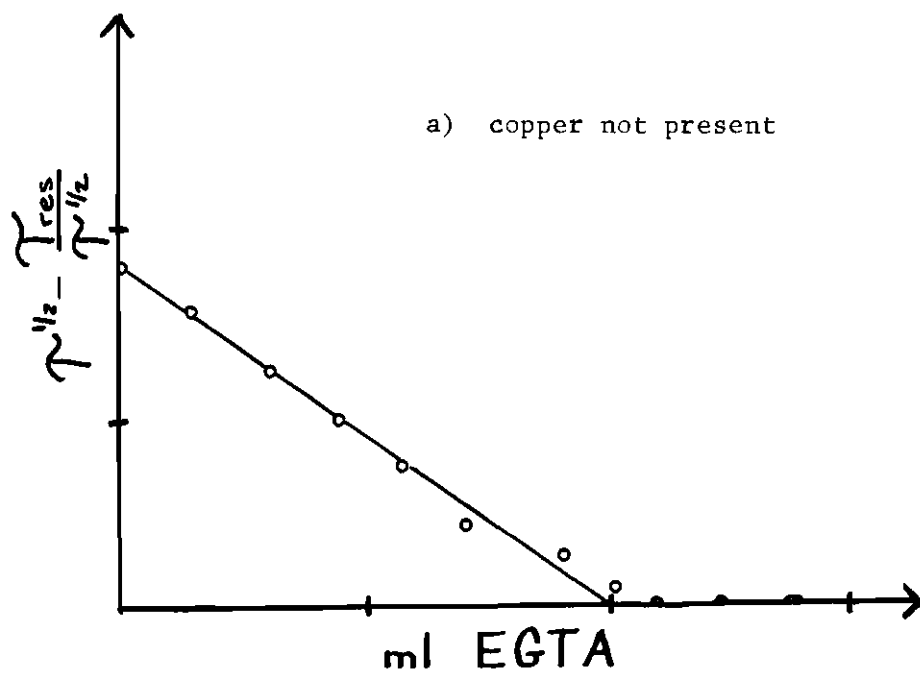


Figure 9. Titration Curves for Determination of Cadmium

The results of the two cadmium titrations using chronopotentiometric end point detection are identical to the result of the series of titrations using Eriochrome Black-T, and demonstrate the feasibility of titrating multicomponent mixtures using chronopotentiometry.

Choosing Between Standard Addition and Titration Methods

Cadmium in the presence of copper could also have been determined by standard addition methods. The important criterion for choosing between the two methods should be the initial concentration of the species to be determined. DME chronopotentiometry is best used when the concentration of the electroactive material is in the range 10^{-5} to 10^{-3} F.

If the initial concentration of the substance to be determined is near the upper end of the range, a titration procedure which decreases the amount of the substance present is to be preferred. If the initial concentration is low, however, then standard additions which increase the concentration of the species are more feasible. The magnitude of the initial concentration can be estimated very easily from trial chronopotentiograms (which require only a few seconds apiece) and the appropriate analytical method chosen from this information.

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