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An Electrochemical Method for the

Determination of Phosphate in Natural Water

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ABSTRACT

AN ELECTROCHEMICAL METHOD FOR THE DETERMINATION OF
PHOSPHATE IN NATURAL WATER

The objective of this project was to develop a method for
the determination of phosphate in natural water which
would be an improvement over the presently accepted
spectrophotometric technique in terms of detection limit
and freedom from interference. Cathodic stripping chrono-
potentiometry was found to be an analytically sensitive
method for phosphate analysis.

The technique is based upon the reversible oxidation of a
metallic indicator electrode to an insoluble phosphate
salt film. When copper is used as the indicator electrode,
the detection limit is 10 ppb. Control of the pH at 6.0
and removal of oxygen from the solution eliminates anti-
cipated interferences in natural water samples. The
major drawback of the method is that under the electroly-
sis conditions employed, salt of mixed stoichiometry is
deposited which subsequently results in two separate
stripping steps.

When mercury is the indicator electrode, the system
approaches true Nernstian behavior, so a detection limit
considerably below 10 ppb is anticipated. However, an
observed interference of chloride ion has, to the present,
limited application of the electrode to solutions con-
taining phosphate in excess of 50 ppb.

ACKNOWLEDGEMENT

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NOTATION

symbol	quantity
E	potential
V	volts
t	time
s	seconds
μA	microamperes
mv	millivolts
τ	chronopotentiometric transition time
t_{el}	anodic electrolysis time
t_D	delay time at zero current between anodic and cathodic cycles
i_c	cathodic current density
i_a	anodic current density
SCE	saturated calomel electrode
F	formal concentration (gram formula weights per liter), which is independent of equilibrium state
M	molar concentration (moles per liter of a particular ionic species at equilibrium)
b	spectrophotometric cell width
λ	wavelength

The Axes in the figures are labelled in quantity calculus terms. Examples: E/V is to be read "potential in volts" and t/s is "time in seconds".

1. INTRODUCTION

Electrochemical methods have been extensively employed for the determination of trace quantities of metal ions in aqueous systems. The most commonly used of these methods are d.c. polarography, pulse polarography, linear sweep voltammetry, and anodic stripping voltammetry by which about 35 metals can be determined. The detection limits of these methods are 10^{-5}, 10^{-7}, 10^{-6} and 10^{-11}M, respectively.

A comparable method for the determination of non-metal anions, cathodic stripping voltammetry (CSV), has been reported, but few applications of the method have appeared. In a recent review, Brainina compiled a list of anions which have been determined by CSV along with their detection limits. The list included only the following nonmetals: Chloride (5 x 10^{-6}M), bromide (1 x 10^{-6}M), iodide (5 x 10^{-8}M), sulfide (5 x 10^{-8}M), sulfate (5 x 10^{-8}M), and certain organic anions[1]. Sulfate was determined only after prior reduction to sulfide. In addition, several workers have reported anodic polarograms for phosphate at a mercury electrode[2,3]. The polarographic waves which result from the oxidation of mercury to an insoluble phosphate salt were not useful for analytical purposes, but their presence indicates that CSV may be applicable to phosphate analysis.

The goal of the present research was to develop an electrochemical method for the determination of phosphate. Particular emphasis was placed on the development of a method which: would be suitable for studies of natural water systems, would have a detection limit lower than the presently accepted spectrophotometric technique, and would be routinely applicable. The techniques initially considered in this study were stripping analysis, d.c. polarography, and linear sweep voltammetry. Preliminary experiments eliminated the latter two from consideration as trace analytical methods for phosphate.

2. THEORY

The fundamental problem in developing an electro-chemical method for the determination of phosphate is that the ion cannot be oxidized or reduced in the accessible potential region of present solvent and electrode systems. Thus, only three possible approaches are available: (1) potentiometry at an ion selective electrode; (2) galva-nometry or voltammetry based upon reversible oxidation of a metal electrode to an insoluble phosphate salt; and (3) polarography or voltammetry of an electrochemically active complex of phosphate. The former was not investigated in this project because of the failure of previous workers to develop such an electrode suitable for natural water systems[4]. Polarographic theory is extensively discussed elsewhere[5]; therefore, only the theory of the second approach will be described here.

The second approach is based upon the thermodynamic prediction that a metal can more readily be oxidized to an insoluble salt of its cation than to the free, soluble cation. The difference in oxidation potential depends on the solubility product of the salt, stoichiometry of the salt, and the concentration of the anion. Thus, it is theoretically possible to apply a potential to such an electrode at which the oxidation occurs quantitatively by the route

$$M - ne^- + \frac{n}{p} (X^{-p}) \rightleftharpoons MX_{n/p} \qquad 2-1)$$
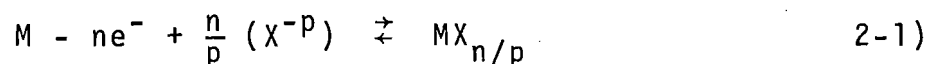
where M is the metal; X, the anion; n, the charge of the cation; and p, the charge of the anion. Since the potential of salt formation is a function of the anion concentration, the potential approaches the oxidation potential of the metal to the free cation at low X^{-p} concentration. Hence, both Reactions 2-1 and 2-2 occur in the analytically significant case of low anion concentration

$$M - ne^- \rightleftharpoons M^{+n} \qquad\qquad 2-2)$$

A second factor which generally precludes selection of conditions by which the electrode can be quantitatively oxidized by Reaction 2-1 is that considerable overvoltages are typically associated with the nucleation and growth of anodic films[6]. Voltages of 10 to 1000 mV positive of the equilibrium potential are usually required to initiate and sustain film growth. The latter is particularly important for analytical work since relatively thick films are needed to obtain easily measurable transition times upon stripping. Factors which contribute to the growth over-voltage are the energy required to transfer metal ions through the film and the energy required to move active sites to the surface of the metal.

The class of films of interest in this project are the porous, noncontinuous films which are formed when the metal cation initially enters the solution adjacent to the metal and is subsequently precipitated onto the surface.

A possible problem is that a portion of the precipitate will not adhere to the electrode. Stirring must be limited to minimize the loss of precipitate. In addition, the total quantity of film must be kept below the point at which the salt physically dislodges.

The traditionally used technique for anion analysis based upon film formation is cathodic stripping voltammetry (CSV). In this experiment, a potential is selected at which Reaction 2-1 occurs. At a given time the potential is applied which initiates the pre-electrolysis portion of the experiment. The solution is stirred to maintain a constant flux of X^{-p} to the electrode. During this forward electrolysis the quantity of film deposited is a function of time and X^{-p} concentration. After a measured time, the electrode potential is scanned toward negative values. If the film formation is reversible, at some potential a cathodic current resulting from the reduction corresponding to the reverse of Reaction 2-1 will occur. A continuous scan will produce a current peak since the current must drop to zero when the film is totally reduced to the metal and free anion. The current peak is proportional to the following: X^{-p} concentration, electrode area, scan rate, and forward electrolysis time; it also depends upon the rate of stirring during the deposition. If all the parameters are controlled, a linear plot of peak current vs. X^{-p} can be obtained in

theory. The linearity of the working curve is not altered by competition from Reaction 2-2 as long as the electrode potential remains constant during the deposition.

Selectivity of the method is achieved by the fact that if the electrode reactions are totally reversible (that is, if the rate of electron transfer is sufficiently rapid in both directions to permit the insoluble salt/metal couples to remain at equilibrium as the potential is varied), the reduction potentials of any two insoluble salts deposited during the pre-electrolysis will differ in proportion to the logarithm of the ratio of their solubility products; the more insoluble salt will be stripped at the more negative potential. Unfortunately, deviation from totally reversible behavior generally occurs because of the complicated nature of the nucleation of the film, surface dipole effects, and structural and stoichiometric differences between the portion of the film in contact with the solution and that in contact with the metal substrate[6]. In addition, electrode passivation can cause deviation from ideal electrode behavior. Electrode passivation occurs when the deposited film insulates the electrode and, therefore, halts or slows further reaction at a given potential. Passivation is not common when the film contains an ion in common with the substrate.

A variation of cathodic stripping voltammetry which we have developed utilizes constant current deposition and

stripping. The technique can be called cathodic stripping chronopotentiometry (CSC). When constant current deposition is employed, the quantity of material deposited will depend upon the fraction of the oxidation occurring by Reaction 2-1. This fraction, in turn, depends upon the concentration of X^{-p}, the applied current per unit area of the electrode, and the efficiency of stirring (that is, the flux of X^{-p} to the electrode). The quantity deposited during the forward electrolysis at a given anodic current is the fraction multiplied by the electrolysis time.

The stripping is performed using a sufficiently low cathodic current to assure that the reverse of Reaction 2-1 occurs with 100 percent efficiency. The time required to remove the film is the analytical parameter of interest. During the stripping the electrode potential is nearly constant and corresponds to the stripping potential observed in the voltammetric method. Removal of the film is followed by a potential transition toward more negative values since the electrode must seek a process which can support the applied current (generally this process is the reduction of hydrogen ions in aqueous, acid solution). The transition time, τ, is the increment between current reversal and the potential transition. τ depends upon the quantity of film, the value of n in Reaction 2-1, and the cathodic current per unit electrode area.

An important point in the constant current method is

that to be analytically applicable, deposition must occur
with less than 100 percent current efficiency. This point
can be illustrated by considering the case where the
concentration, current density, and stirring rate were
adjusted to obtain 100 percent deposition efficiency. The
equivalents of salt deposited, Z, would be $\frac{i_a t_{el}}{F}$, where F
is the Faraday; i_a, the anodic current in μA; and t_{el}, the
forward electrolysis time in seconds. The stripping time,
τ, observed upon current reversal is ZF/i_c or $i_a t_{el}/i_c$.
Therefore, under conditions of 100 percent deposition
efficiency, τ is not a function of concentration. Hence,
it is necessary to define the applied current density for
each order-of-magnitude concentration of X^{-p} to be able to
maintain the condition of the fraction of Reaction 2-1
being a function of concentration. As a result of this
effect, the working curves (τ vs. X^{-p} concentration) are
non-linear except over narrow concentration ranges.

The constant current method does possess certain
advantages, however. Dissolution of the electrode through
Reaction 2-2 is minimized since the quantity of electric-
ity passed per unit time is less (and the fraction of
oxidation by Reaction 2-1 is greater) than with controlled
potential deposition. This is not an important factor
when a hanging mercury drop electrode is employed since it
is simple to use a new electrode for each experiment; but
with a solid electrode, the dissolution precludes a con-

stant surface area from experiment to experiment, and would necessitate frequent replacement of the electrode.

A second advantage is that the readout baseline is better defined by CSC than CSV. As seen by comparing Figures 1A and 1B, the small difference between the deposition and stripping potentials results in poor definition of the CSV baseline but is not a problem in the constant current method.

Another related method employs controlled potential deposition with stripping performed at constant current, Cathodic Stripping Chronopotentiometry with Controlled Potential Deposition. This technique possesses the major advantage of CSV that the amount of film deposited per unit time is greater than with CSC but retains the well-defined baseline of CSC. A qualitative sample readout is shown in Figure 1C. A stringent instrumental requirement of this method is a switching circuit which converts the controlled potential to the constant current mode without applying a current or voltage spike to the electrode or allowing the electrode to drift at open circuit during the switching transient. Such a circuit is discussed in the next section.

All the described techniques are best performed in the three electrode mode. In this mode, the reference electrode is electronically isolated from the current path through the cell, and an auxiliary (counter) electrode is
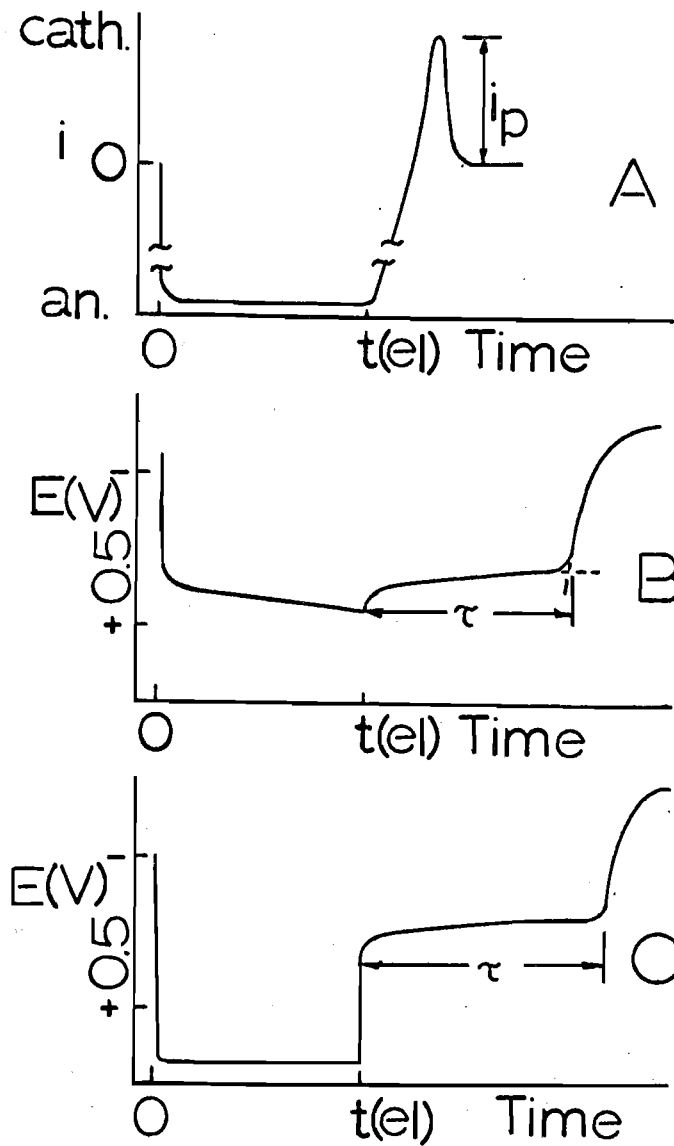
Figure 1. Typical Readout Displays in Film Stripping
         Analysis.

         A. Constant potential deposition and
             potential scan stripping.

         B. Constant current deposition and stripping.

         C. Constant potential deposition and constant
             current stripping.

employed to complete the current path from the indicator electrode.

The electrochemical methods employed in this study require the use of a supporting electrolyte (a salt, which is not oxidized or reduced in the potential range of interest, added to the solution to carry the current across the cell). In this work 0.1M KNO_3 was generally the supporting electrolyte.

3. EXPERIMENTAL

The instrumentation used in this study consisted of (1) a general purpose operational amplifier instrument capable of operating as a potentiostat or galvanostat; (2) Wavetek Model 114 Function Generator; (3) Tektronix 564B Oscilloscope; (4) Hewlett-Packard 7101B Recorder; (5) Beckman Century SS pH Meter; and (6) Beckman DK-1A Spectrophotometer. Philbrick-Nexus P25AU Operational Amplifiers and a PR-300 Power Supply were used in the general purpose instrument.

The basic circuits for the potentiostat and galvanostat are of conventional design. The switching circuit is similar to one which we have previously described[7]. A detailed circuit is shown in Figure 2. The mode selector switch, S1, must be a shorting type 3-pole-2 position switch. An equivalent relay (or gang of relays) can be used if faster switching is desired. The use of relays minimizes the possibility of drift during the switching time, however, such drift was not a problem when a mechanical switch was employed. The function switch, S2, must also be a shorting type.

The current selecting resistors provide a wide range of anodic and cathodic values, but when they are employed, current reversal is mechanical. This procedure is acceptable for the analytical procedures outlined, but when the instrument was used in fundamental investigations
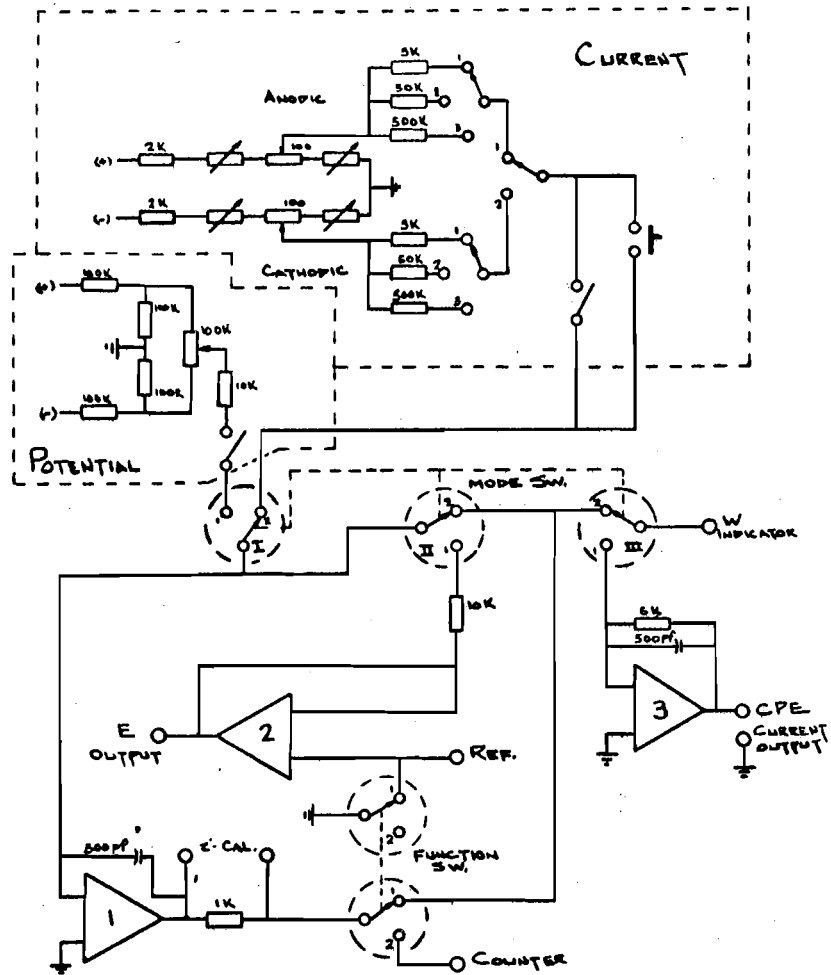
Figure 2.   General Purpose Operational Amplifier
Potentiostat and Galvanostat.

of the electrode mechanisms, the square wave generator
coupled to Amplifier 1 through a series resistor at the
auxiliary input was used to provide the current.

Amplifier 3 was used to monitor the electrolysis
current in the controlled potential mode. As drawn, the
output is 5 mV per μA. Other current sensitivities are
available by changing the 5 K feedback resistor. The 10
pf capacitor across the amplifier was inserted to elimi-
nate high frequency oscillation. A similar stabilizing
capacitor appears across Amplifier 1.

Either a hanging mercury drop electrode (HMDE),
dropping mercury electrode (DME), or copper wire electrode
served as the indicator. The DME was of conventional
design[8]. The HMDE was either the platinum contact type
described by Shain[9] or a Beckman Mercury Drop Electrode
Assembly, which yielded identical results. The copper
electrode was prepared by heat sealing 22 gauge electro-
lytic grade copper wire into 6 mm o.d. soft glass tubing
using the procedure described by Wheeler[10]. The wire was
trimmed to yield approximately 1 cm sq. surfaces. When
needed, the exact surface area was measured using chrono-
potentiometry of a standard ferricyanide solution and
fitting the resulting transition time to the Sand
Equation[5].

The reference electrodes were either Coleman fiber
junction saturated calomel electrodes (SCE) or platinum

quasi-reference electrodes (a platinum wire sealed into glass, electrolytically oxidized, and then placed in contact with the supporting electrolyte). The latter were employed when exact potentials were less important than the ability to exclude chloride from the solution. In either case, the reference was isolated from the cell by a Luggin capillary salt bridge. Unless otherwise stated, potentials are reported vs. the SCE. The counter electrode was a platinum wire heat-sealed into soft glass tubing.

The cells employed were of three types. For most studies the cell was constructed from a 30 ml Buchner funnel with a coarse glass frit (Kimble No. 28400). The solutions were deaerated by passing a stream of nitrogen gas, which was pre-saturated with water, through the frit. Through use of a three-way stopcock, a vacuum could be pulled on the frit to remove the solution at the end of the experiment and to flush the cell. In the off-position, the back-pressure is sufficient to prevent leakage of the solution during the experiment. The nitrogen stream was diverted over the top of the solution during the experiments. A tapered Teflon lid held the counter, indicator, and reference electrodes and the nitrogen inlet. It was tapped to allow venting of the gas through a single port. Magnetic stirring was used to provide convection. The low cost of this cell enables several to be used in rotation at each experimental station.

The cells were cleaned by rinsing with 50 percent HNO_3, soaking in 10 percent HNO_3 overnight, and leaching in doubly distilled water changed daily for several days. They were oven-dried prior to use.

The second type of cell was a 200 ml electrolysis beaker which was reduced to a 50 ml volume on a glass-blowing lathe. A tapered Teflon lid identical to that described above, except for inclusion of a gas dispersion tube for deaeration, was employed. The cell was somewhat easier to clean than the above type because the frit is not an integral component.

The third type of cell was a Metrohm Polarographic Cell (Brinkmann Instruments). This unit is similar to the second type but requires longer deaeration times because a capillary tube is used instead of a frit. As a result of elimination of the frit, the cell is easier to clean for the trace level experiments.

The chemicals used were Reagent Grade. The KNO_3 and salts used in the preparation of the buffers were twice recrystallized from doubly distilled water.

The solution preparation was as follows:

Standard Solutions:

KH_2PO_4 was weighed into a beaker, or a small volume of a standard previously prepared by weight was transferred to a beaker by pipet. Sufficient KNO_3 was added to give a concentration of 0.1M upon final dilution. The

salts were dissolved and diluted nearly to volume with
doubly distilled water. Dilute KOH or HNO_3 was added to
adjust the pH. Alternatively, concentrated buffer of the
desired pH was added. The solution was quantitatively
transferred to a volumetric flask and diluted to volume.
The final pH was verified. Solutions below $5 \times 10^{-5} M$
were not stored longer than a few hours since they
proved to be unstable.

Natural Samples:

Grab samples of lake water were obtained 2 feet
below the surface. 200 ml Pyrex Milk Dilution Bottles
were used as sampling containers. 2 ml of chloroform
and 2.0 gm of KNO_3 were added to the water immediately.
100 ml of the solution was transferred to a beaker and
the pH adjusted as above. The final solution was then
diluted to 200 ml. Pond samples were obtained in an
identical manner except that the water was filtered,
when necessary, through Millipore Fiberglass pre-filters
to remove algae.

4. CATHODIC STRIPPING CHRONOPOTENTIOMETRIC DETERMINATION OF PHOSPHATE AT A COPPER ELECTRODE.
A. INVESTIGATION OF THE ELECTRODE MECHANISM.

The development of an analytical method based upon film stripping proceeds through five stages: (1) obtaining evidence for reversible film formation, (2) optimizing conditions for the formation and subsequent stripping of the film, (3) interpreting any departures from theoretical behavior, (4) testing the analytical relationship, and (5) testing the method on natural samples.

That a copper electrode can be electrochemically oxidized to an insoluble phosphate salt is visually evident. Upon application of 0.4v. vs. SCE to copper in a de-aerated 0.1M KNO_3 solution containing .01 F PO_4^{-3} at pH 6.0, blue crystals are observed at the electrode surface. Under identical conditions in the absence of PO_4^{-3} no film is seen. In the former case, if the electrode is polarized longer than a few seconds, crystal formation occurs throughout the solution. Apparently sufficient cupric ion is generated to exceed the solubility product of copper phosphate in bulk solution as well as in the layer of solution adjacent to the electrode surface; however, the bulk precipitate may consist, in part, of surface film which is mechanically dislodged from the electrode. The latter event would preclude

subsequent electrochemical reduction of the film.

To prevent such loss of the film experimental conditions must be adjusted to eliminate excessive build-up. Electrolysis times must be short when the phosphate concentration is high, and constant current deposition should be employed rather than controlled potential electrolysis.

Reversibility of the oxidative film formation was demonstrated by cyclic chronopotentiometry. Figure 3 contains cyclic chronopotentiograms obtained under three sets of conditions: (A) a stirred 0.1M KNO_3 solution, (B) unstirred 0.1M KNO_3, and (C) a stirred mixture of 0.01F PO_4^{-3} in 0.1M KNO_3; all solutions were adjusted to pH 6.0 with dilute HNO_3 and KOH.

With conditions A and B, the oxidation half-cycle is expected to produce soluble Cu(II). Since the current is constant, the equivalents of the ion produced are directly proportional to t_{el}. When the solution is unstirred, diffusion is the only means of transport of the ions away from the electrode; a plot of concentration of Cu(II) vs. the distance from the electrode has the shape of the mathematical function $1 - \frac{2}{\pi} \int_0^x e^{-\lambda^2} d\lambda$, the error function complement (higher at the electrode surface and decaying to zero away from the electrode). Upon current reversal, Cu(II) will be reduced to Cu(0) at the electrode surface, so that in the vicinity of the electrode the concen-

tration will decrease. Ultimately, the concentration will approach zero at the electrode surface and at some point a distance x from the electrode. A maximum will appear at an intermediate distance, x. At x, the probability that a given ion will diffuse toward the electrode is equal to the probability that it will diffuse further away. In either case, it would eventually be reduced since at infinite time x will traverse the entire cell, but during the time of the experiment a portion of Cu(II) does not return to the electrode surface. Hence, the equivalents reduced is less than the equivalents oxidized. A solution of Fick's Second Law of Diffusion predicts that if $i_a = i_c$, $\tau = t_{el}/3$, where τ, the transition time is the time required to lower the surface concentration of Cu(II) to a value which can no longer support the constant cathodic current, which results in the electrode potential's slewing toward a more negative value at which another cathodic process can occur. Figure 3B illustrates that the above prediction is followed in unstirred 0.1M KNO_3.

When the solution is stirred throughout the experiment, a build-up of Cu(II) at the electrode surface cannot occur in a simple salt solution; therefore, Figure 3A does not show a reverse transition. With a faster time base, a very short τ may be observed due to reduction of Cu(II) in the thin layer of solution adjacent
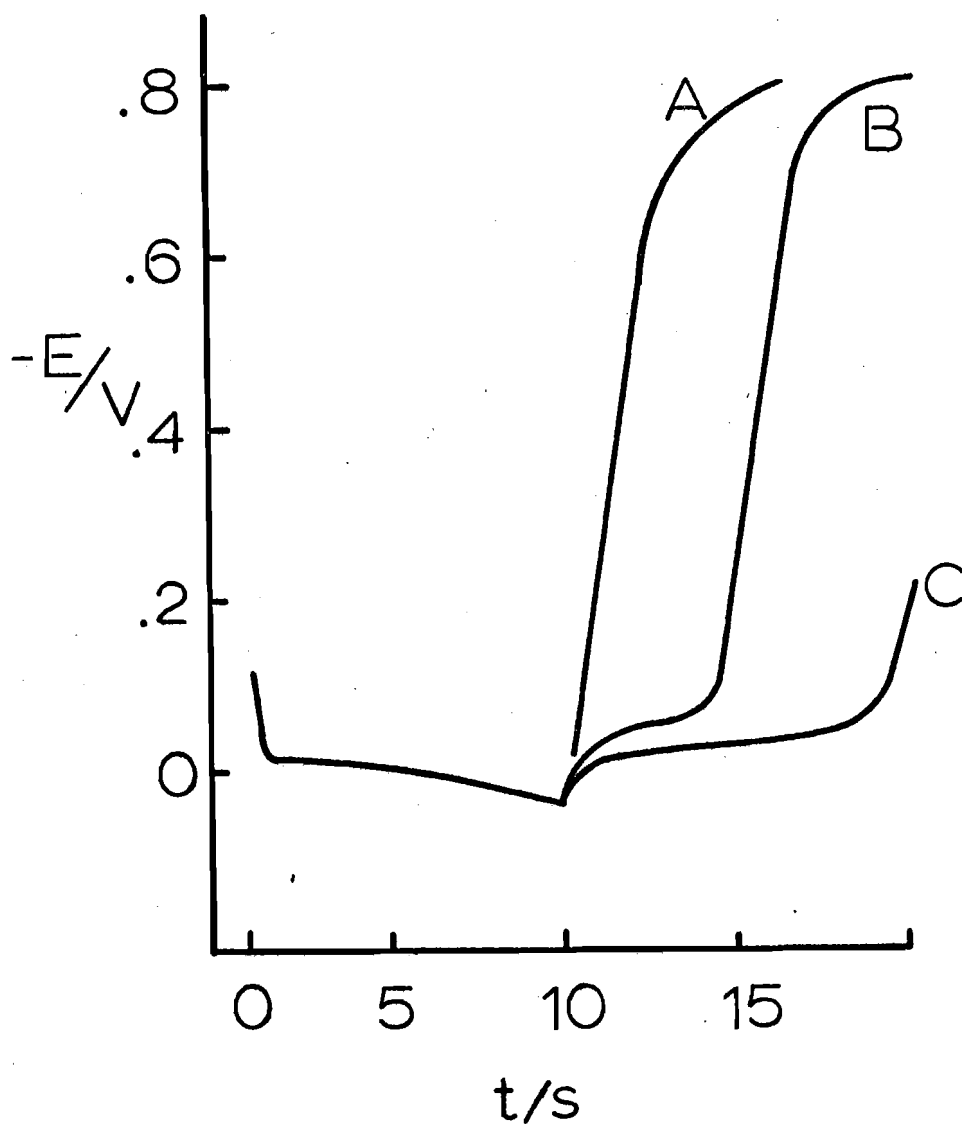
Figure 3. Cyclic Chronopotentiometry of a Copper
Electrode in Phosphate Medium.

A. stirred 0.1M KNO_3

B. unstirred 0.1M KNO_3

C. stirred 0.01F PO_4^{-3} in 0.1M KNO_3

$i_a = i_c = 50$ μA cm^{-2}, pH = 6:0

to the electrode which is not disturbed by stirring (the Diffusion Layer).

If the oxidation of the electrode results in an insoluble film, loss of Cu(II) by diffusion will not occur. If the film formation is reversible, a change in current polarity should result in the electrode establishing a potential at which the film is reduced until the process is complete. If $i_a = i_c$, the stripping time should be identical to t_{el} in both stirred and unstirred solution. Figure 3C is consistent with this prediction. The experimental current efficiency, $\dfrac{100\ i_c\tau}{i_a t_{el}}$, is 80 percent rather than the 100 percent predicted for the case of reversible film formation. This departure from theory is discussed later.

The use of pH 6.0 in the previous experiments was the result of a study of current efficiency vs. pH for the copper electrode. The results are summarized in Table 1. That 6.0 is the optimum pH indicates that the monobasic and/or dibasic phosphate ions are incorporated in the salt film since they are the predominant phosphate anions at that acidity.

Optimizing conditions for film formation and stripping also required the determination of appropriate anodic and cathodic current densities and forward electrolysis times. As discussed previously, the anodic current density must be sufficiently high to obtain less

TABLE 1

Effect of pH on the Current Efficiency of Cyclic Chrono-
potentiometry of a Copper Electrode in Phosphate Medium

i_a $\mu A\ cm^{-2}$	i_c $\mu A\ cm^{-2}$	$F_{PO_4^{-3}}$	pH	$\dfrac{100\ i_c\tau}{i_a t_{el}}$
50	50	0.01	3	10
50	50	0.01	4	35
50	50	0.01	5	50
50	50	0.01	6	85
50	50	0.01	7	75

than 100 percent current efficiency since the analytical
method requires that the deposition efficiency (the ratio
of Reaction 2-1 to the total amount of oxidation) be a
function of concentration. Table 2 summarizes the effect
of the current densities on the stripping time. It
should be noted that current efficiency is not used as
the analytical function in Table 2 because of the above
mentioned experimental design to prevent 100 percent
efficiency.

At the higher PO_4^{-3} concentrations, the results are
straightforward; high anodic currents with low cathodic
currents increase the stripping time. However, it should
be noted that when the stripping current density is low,
the current efficiency is only about half the value when
equal anodic and cathodic currents are employed which

TABLE 2

Effect on Anodic and Cathodic Current
Densities on the Film Stripping Efficiency.

i_a, μAcm^{-2}	i_c, μAcm^{-2}	t_{el}, min	τ, min	$F_{PO_4}^{-3}$
50	2	1.0	11.2	0.01
50	5	1.0	6.7	0.01
50	10	1.0	2.3	0.01
50	20	1.0	1.2	0.01
50	50	1.0	.85	0.01
500	50	0.25	.55	0.01
50	50	15	.02	2×10^{-5}
500	50	15	.42	1×10^{-5}

indicates that a competing chemical process is occurring.
In dilute solution, a high anodic current is apparently
necessary to produce a significant quantity of film.
This may reflect a need for a larger flux of Cu(II) to
accomplish the necessary supersaturation to produce
nucleation in the solution layer adjacent to the electrode
when the PO_4^{-3} concentration is low.

The necessary large anodic currents for film for-
mation at low PO_4^{-3} concentration result in an important
problem in the stripping cycle: two cathodic transitions
appear rather than the single step shown in Figure 3C. A
typical result is represented in Figure 4. The anodic
and cathodic current densities were 500 and 50 $\mu A\ cm^{-2}$,
respectively, and the analyte was 0.01F PO_4^{-3} at pH 6.0

in 0.1M KNO_3.

There are three reasonable explanations for the appearance of two stripping transitions: (1) the first few monolayers of deposited salt may have electrochemical properties different from the remainder of the film; (2) the film may consist of copper phosphate salts of two stoichiometries; and (3) the film may contain salt of a single stoichiometry but of different crystal structures.

The appearance of two transitions only at higher deposition current densities can be explained in two ways. The total quantity of film is much greater at higher currents. In addition, the potential of the indicator electrode is significantly more positive at higher anodic currents, so processes with higher overvoltages can occur.

The possibility that the two stripping transitions result from the above-listed thickness effect was examined by studying the effect of forward electrolysis time on τ_1 and τ_2 as defined in Figure 4. t_{el} was varied from 0.1 seconds to 30 minutes at anodic current densities of 10 to 500 μA cm^{-2}. The stripping current was generally 50 μA cm^{-2}. Plots of τ_1 and τ_2 vs. t_{el} are shown in Figure 5, and the behavior of the function τ_1/τ_2 with t_{el} is illustrated in Figure 6.

In Figure 5, it can be seen that qualitatively the two transitions vary in the same manner with t_{el}. After an initial increase with t_{el}, the quantity of film deposited becomes essentially constant.
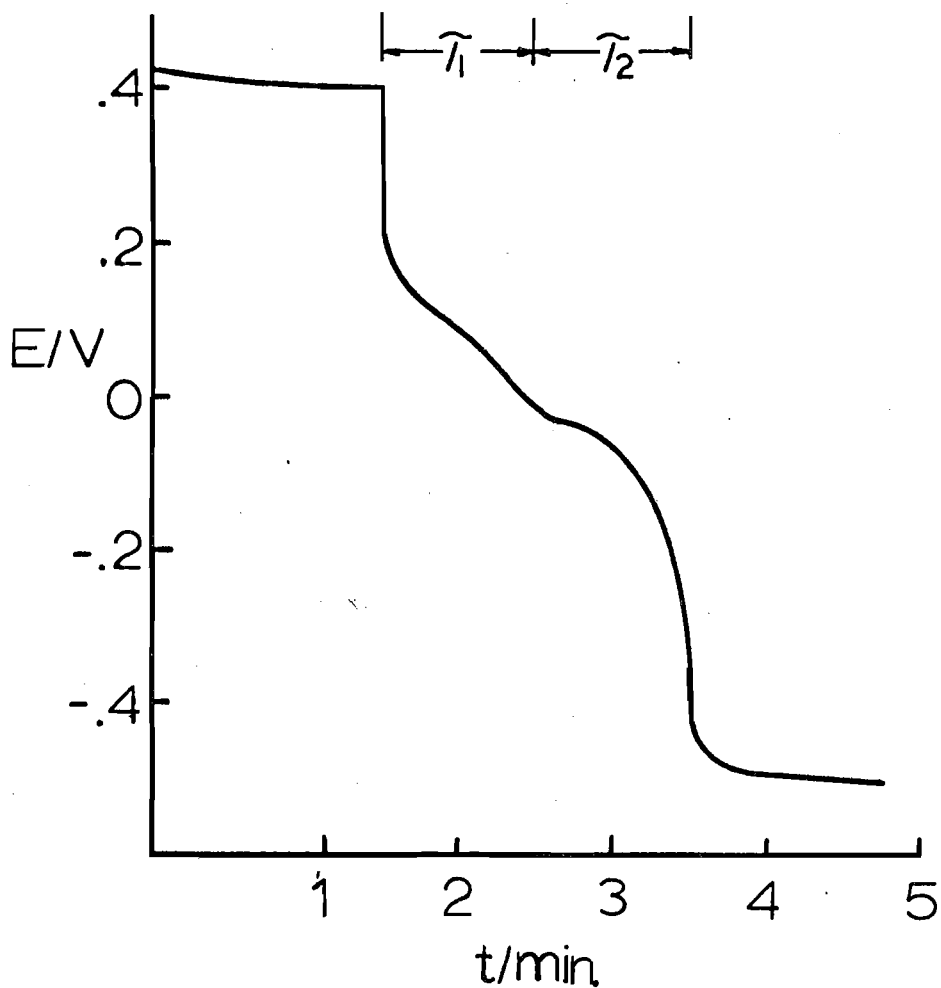
Figure 4. Cyclic Chronopotentiometry of a Copper Electrode in Phosphate Medium at High Anodic Current Density.

Solution: $0.01F$ PO_4^{-3} in $0.1M$ KNO_3 at pH 6.0.

i_a, 500 μA cm^{-2}; i_c, 50 μA cm^{-2}.

These facts have important analytical consequences. Since, the initial increase is non-linear, the working curves constructed for this technique must be at the exact electrolysis times employed in the analysis; the slopes cannot simply be corrected for electrolysis time differences. In addition, that the film build-up reaches a limiting value demonstrates that the analytical readout, τ, cannot be indefinitely increased by lengthening the forward electrolysis time. Fortunately, this limiting value is sufficiently high to yield easily measurable transition times upon stripping and, therefore, does not restrict the development of the analytical method.

A better comparison of the behavior of τ_1 and τ_2 with t_{el} can be made by examining Figure 6. The film formation process which results in τ_1 upon stripping predominates at short deposition times. At times greater than 1 minute, the two processes occur at approximately the same rate.

Of the above-listed three explanations for the two-stripping transitions, the interpretation of Figure 6 argues against the mixed crystal alternative. In such a case, a finite rate of recrystallization would be expected which would result in a trend in τ_1/τ_2 with t_{el} without an inflection point.

Further evidence against the mixed crystal alternative was obtained by a delay time experiment. Here,
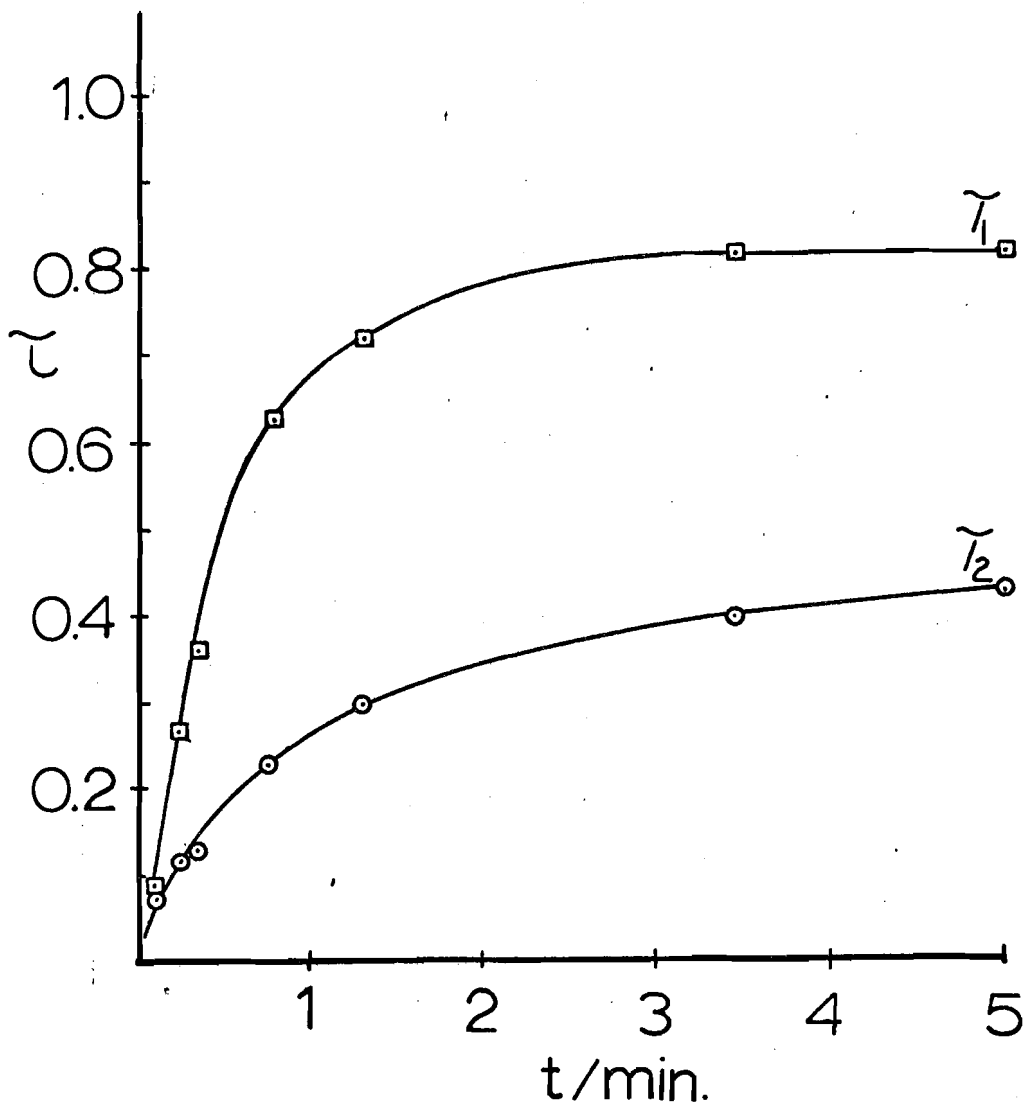
Figure 5. Effect of Anodic Pre-electrolysis Time on the Stripping Transition Times of the Copper Phosphate Film.

τ_1, first stripping transition

τ_2, second stripping transition

i_a, 500 μA cm^{-2}; i_c, 50 μA cm^{-2}
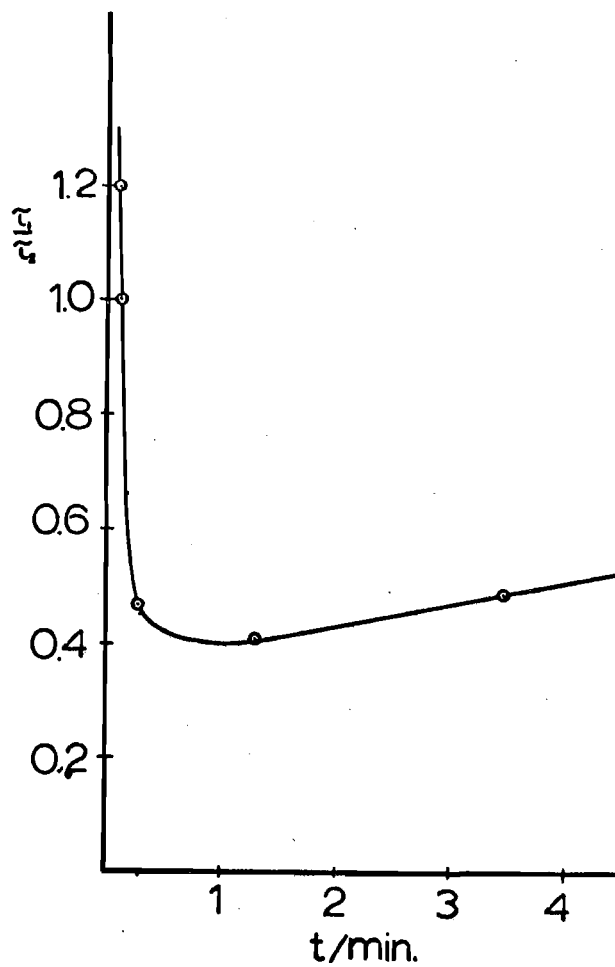
pH, 6.0; C_{PO_4}-3, 0.01F.

Figure 6. Effect of Pre-electrolysis Time on the
Stripping Transition Time Ratio of the
Copper Phosphate Film.

Conditions same as Figure 5.

the basic cyclic chronopotentiometry experiment was modi-
fied to include a time, t_D, where i = 0 between the anodic
and cathodic half-cycles. Typical data is recorded in
Table 3.

TABLE 3

Effect of Delay Time on the Stripping
Transition Times of Copper Phosphate.

i_a,μA	i_c,μA	t_{el},sec	t_D,sec	τ_1,sec	τ_2,sec
500	50	15	0	21.6	11.3
500	50	15	3.8	18.7	10.8
500	50	15	15	12.7	10.8
500	50	15	45	4.2	11.7
500	50	15	90	2.0	11.3
500	50	15	120	0.0	11.3
500	50	15	180	0.0	9.4
500	50	15	360	0.0	6.1

C_{PO_4}-3, 0.01F; electrode area, 1.0 cm^2; pH 6.0.

At total film lifetimes (t_{el} + t_D) of 15 to 135
seconds prior to cathodization, the second transition time
is independent of the lifetime. Thus, the species in-
volved in the second reduction does not chemically exchange
with other species in the film; therefore, mixed crystal
structure, which would probably show exchange, is not a
likely cause of the two observed transitions.

The first transition time shown in Table 3 exhibits

a regular decrease with delay time. Either the film is being chemically corroded at open circuit, the film slowly dissolves at open circuit, or the current offset of the operational amplifiers is sufficient to reduce the film. The latter is only 0.2 μA which was independently demonstrated to be insufficient to cause the stripping on the time scale employed. Chemical corrosion is considered unlikely because the solution is free of both reducing agents and anions of insoluble copper salts other than phosphate. Hence, chemical dissolution is the apparent cause. That the dissolution is selective toward the τ_1 species is reasonable since the electrode potential is sufficiently positive to provide anodic protection of the τ_2 dissolution.

Two additional experiments were performed to clarify the nature of the two stripping transitions. Cyclic chronopotentiometry on a short time scale was performed under the solution conditions of Table 3. The results are shown in Figure 7.

From Figures 7C and 7D it can be observed that the ratio τ_1/τ_2 approaches zero at short t_{el}. This behavior demonstrates that the plot in Figure 6 would show a maximum near time zero. Further, at the shorter electrolysis times, the electrode potential is less positive. Apparently the species responsible for τ_2 is deposited at a lower overpotential.
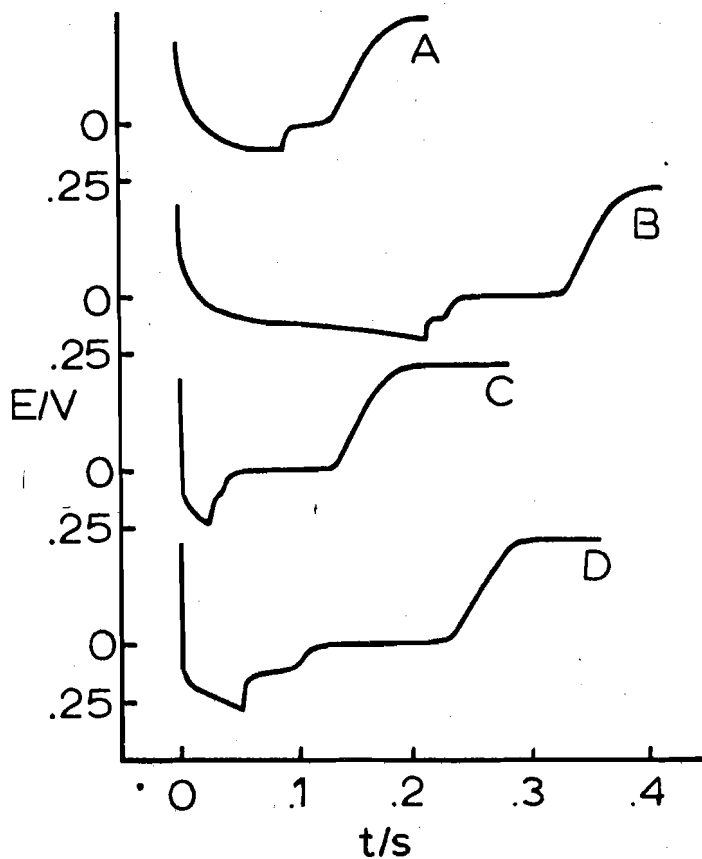
Figure 7.   High Frequency Cyclic Chronopotentiometry of
            a Copper Electrode in Phosphate Medium.

A. i_a, 50 μA cm^{-2}; i_c, 50 μA cm^{-2}; t_{el}, .09 sec.

B. i_a, 50 μA cm^{-2}; i_c, 50 μA cm^{-2}, t_{el}, .21 sec.

C. i_a, 500 μA cm^{-2}; i_c, 50 μA cm^{-2}; t_{el},
     .025 sec.

D. i_a, 500 μA cm^{-2}; i_c, 50 μA cm^{-2}; t_{el},
     .050 sec. pH, 6.0; C_{PO_4} -3, 0.01F.

The latter point is confirmed by the data in Figures 7A and 7B which was obtained with a lower anodic current. When t_{el} is less than 0.1 second, the copper electrode remains less positive than .12 v vs. SCE, and only a single stripping transition corresponding to τ_2 is observed. At longer t_{el} the positive potential excursion increases, and two stripping transitions are again observed. These results when considered with the fact that both τ_1 and τ_2 increase with t_{el} in Figure 5 preclude electrochemical differences between the first monolayer and the bulk film as the cause of the two transitions.

Positive evidence that τ_1 and τ_2 correspond to salts of different stoichiometry was obtained by repeating the study summarized in Table 3 and Figure 7 at other acid-ities. In more acid solution, such as pH 4.0, the ratio $H_2PO_4^-/HPO_4^{-2}$ is 100 times the ratio at pH 6.0; hence the monobasic phosphate salt would be favored in the acid solution. In pH 5.0 solution, a second transition appears but is small compared to the first.

B. PROCEDURE AND APPLICATION.

Based upon the characterization of the mechanism of
the reversible oxidation of the copper electrode in phos-
phate media in Section 4, the following analytical pro-
cedure for the determination of phosphate in water was
devised.

The copper electrode to be used is first chemically
cleaned in a mixture of sulfuric, nitric, and hydro-
chloric acids. The procedure is summarized by Wheeler[10].
The solution to be analyzed is deaerated while the
instrument is held in the Standby mode (Position 1 on the
function switch in Figure 2). After 5 to 10 minutes the
nitrogen stream is diverted over the top of the solution
and the instrument is switched to "cell" (position 1,
mode switch, Figure 2). About -1.2 v vs. SCE is applied
to the copper indicator electrode for 2 minutes. This
procedure is repeated prior to each experiment in order
to electrochemically clean and condition the copper
electrode surface. The instrument is switched to the
galvanostat mode (position 2) at zero current. Stirring
is commenced by a mechanical magnetic stirrer. An
anodic current is applied for a time t_{el} after which a
cathodic current is employed. The potential-time curve
is monitored. The transition time is measured from the
time of current reversal to a time corresponding to
removal of the phosphate film. The latter is somewhat

empirical (see Delahay[11], Chapter 8).

Typical working curves are shown in Figures 8 and 9. For comparison, a working curve was constructed using the spectrophotometric molybdenum blue technique (Figure 10). Figure 8 was obtained at the lowest phosphate concentration range which was studied. The detection limit from the working curve is 20 ppb, which approximates that of the molybdenum blue method of Murphy and Riley[12]. If the pre-electrolysis time was extended to 20 minutes, 10 ppb phosphate could be detected, but the data is too scattered to be analytically significant.

Figure 9 is a working curve over several orders of magnitude. A positive deviation from linearity is seen as the concentration is increased. The behavior is expected since the process becomes more efficient at high concentrations as explained earlier in Section 2. These results also show the need for definition of electrolysis conditions at each concentration level. Table 4 contains optimum parameters for several concentration levels.

When the above parameters are employed, the method is typically reproducible to 3 percent over the entire concentration range. A sample set of results is shown in Table 5. The standard deviation of the 8 trials is 1.2 seconds.

The regular trend in τ is a result of a gradual increase in effective area of a given electrode with
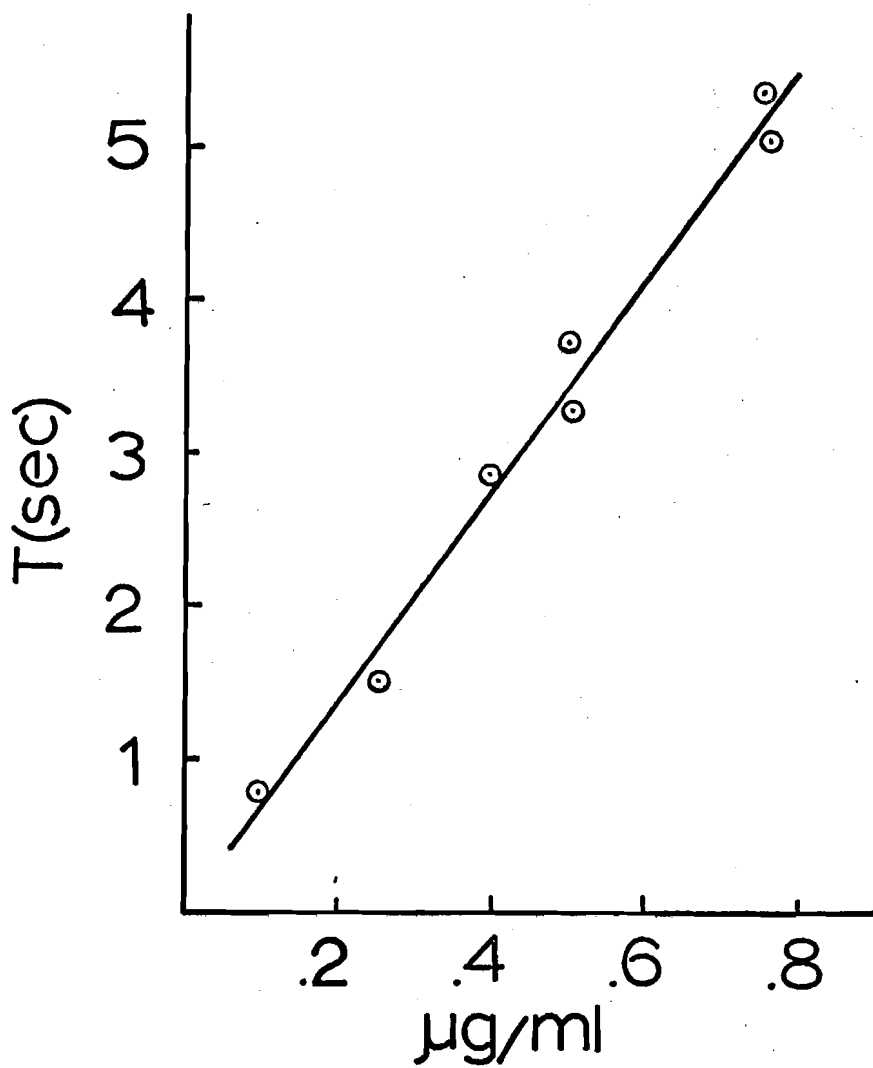
Figure 8. Phosphate Working Curve at the sub-ppm Level
for Stripping Analysis with a Copper Electrode.
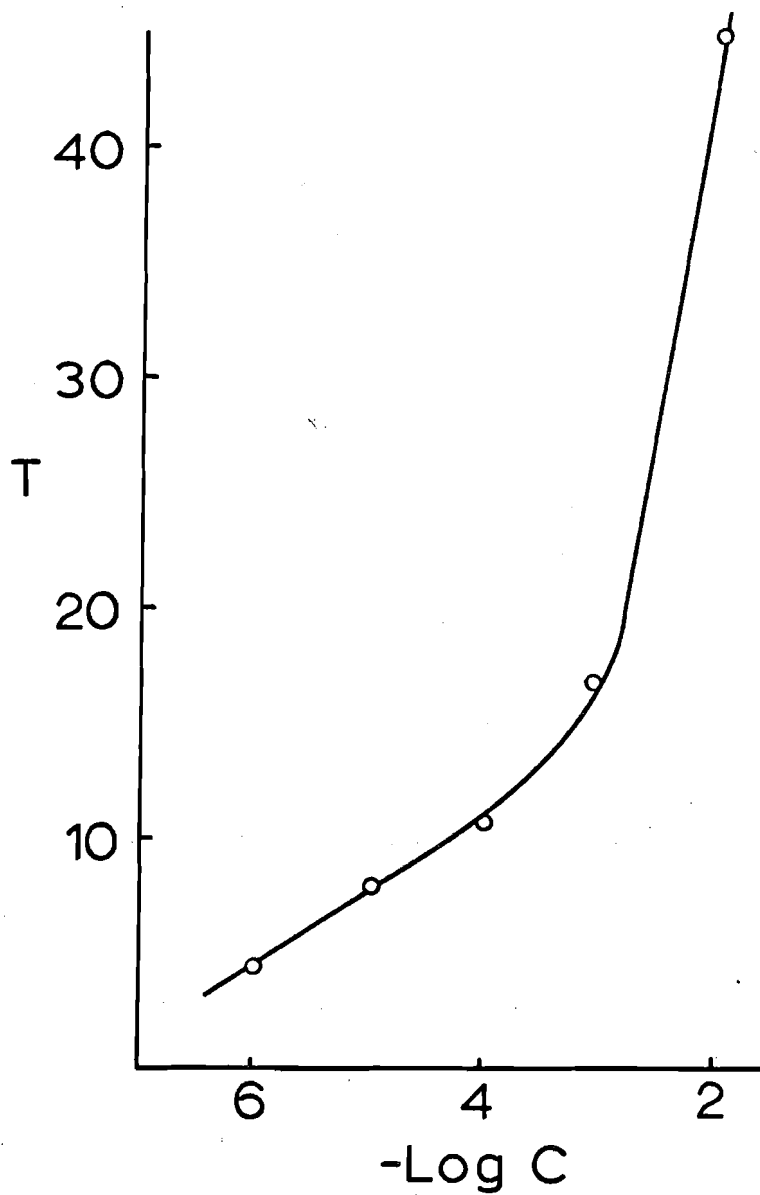
i_a, 500 µA cm^{-2}; i_c, 5 µA cm^{-2}; t_{el}, 10
minutes.

Figure 9. Wide Range Phosphate Working Curve for
Stripping Analysis at a Copper Electrode.

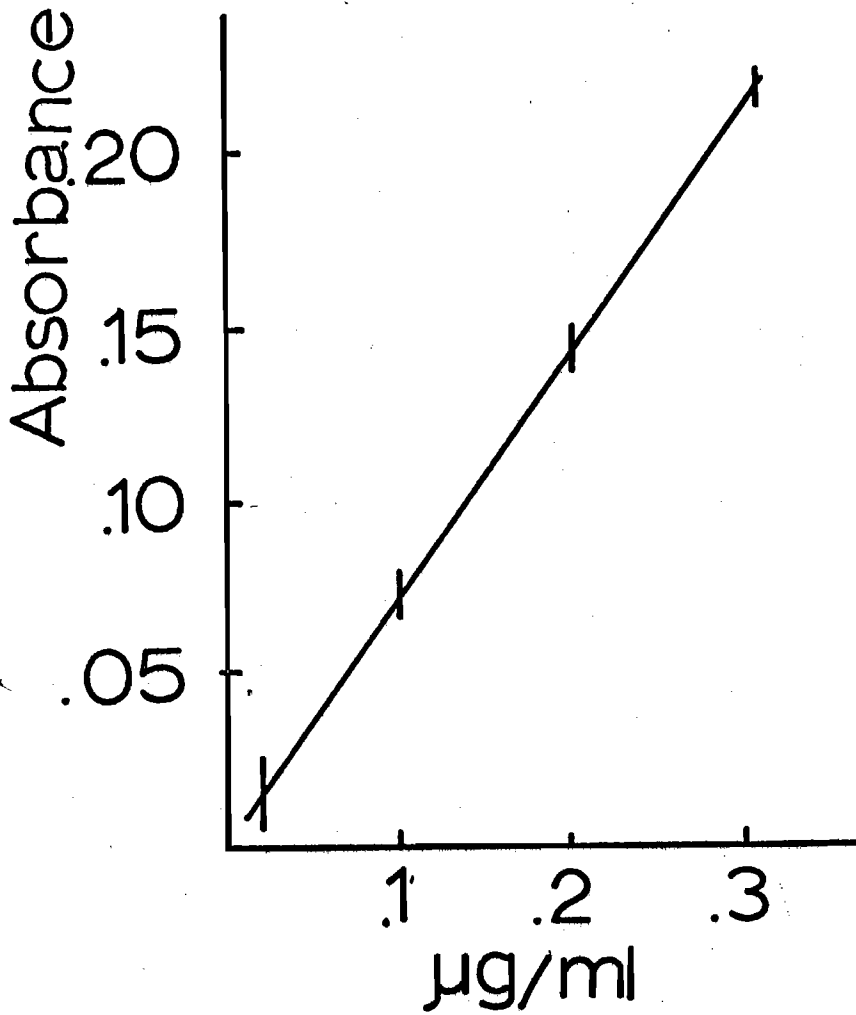i_a, 500 μA cm^{-2}; i_c, 50 μA cm^{-2}, t_{el}, 5
minutes.

Figure 10. Phosphate Working Curve at the ppb Level for the Molybdenum Blue Spectrophotometric Method.

b, 1.0 cm; λ, 882 nm.

TABLE 4

Electrolysis Parameters for the Determination of
Phosphate by Cathodic Stripping Chronopotentiometry

$C_{PO_4}-3$, ppm	i_a, μA cm^{-2}	i_c, μA cm^{-2}	t_{el}, min.
0.02-1.0	500	5	10
1.0-10	500	10	5
10-100	500	25	5
100-1000	500	50	2

TABLE 5

Reproducibility of the Cathodic Stripping
Chronopotentiometric Method at the Copper Electrode

trial	τ, sec	trial	τ, sec
1	39	5	41
2	39	6	41
3	40	7	42
4	41	8	42

$C_{PO_4}-3$, $1.0 \times 10^{-3}F$; i_a, 500 μA cm^{-2}; ic, 50 μA cm^{-2};
t_{el}, 45 sec.

continuous use. The electrode is initially smooth, but
the deposition-stripping cycles cause a general roughening
of the surface which increases the area. Such behavior
is probably the limiting factor in the reproducibility of
any non-potentiometric application of solid electrodes

which are partially corroded or oxidized in use.

The reproducibility can be enhanced by using the Standard Addition Method (see Reference 13, Chapter 8) rather than the working curve technique since the error is then given by the reproducibility of consecutive trials in Table 5. The assumption that the readout is directly proportional to concentration is valid if the concentration after the addition of the standard is within an order of magnitude of the concentration of the unknown alone (see Figure 8, for example).

Four general classes of interferences in cathodic stripping analysis have previously been discussed. Of these, three appeared in our limited study.

The formation of copper hydroxide occurs in basic solution and causes an increased stripping blank. The use of acidic solution is a convenient means of eliminating the problem.

In air-saturated solution, oxygen is present in sufficiently high concentration to control the electrode potential in the region of phosphate film stripping. Oxygen is easily removed by the described nitrogen purge.

Finally, agents which form strong complexes with copper interfere by solubilizing the phosphate film. While these materials are generally in low concentration in natural water, the interference limits the choice of buffers which could be employed to control the pH. For example, in citrate buffer phosphate film formation was

not observed at the copper electrode.

While no other interferences were found, the use of the Standard Addition Method is recommended as a check on the quantitative results. In fact, the method is generally recommended when studying natural samples.

To compare the electrochemical method to the generally accepted spectrophotometric technique, several natural samples have been analyzed. A typical set of results is compiled in Table 6. Grab samples obtained from Lake-on-the-Campus, Southern Illinois University, Carbondale, Illinois, were used in the reported comparison.

TABLE 6

Comparison of the Electrochemical to the Spectrophotometric
Method for Phosphate Determination in Natural Water

Sample	ppb PO_4^{-3} Spectrophotometry[12]	ppb PO_4^{-3} Cathodic Stripping
1	51	29
2	82	140
3	72	48
4	57	86
5	30	30

The methods are in good agreement; however, both techniques showed considerable data scatter.

The major cause of scatter in the electrochemical method is that the ratio of the analytical signal to the

blank is very low. For example, in Sample 3 the blank transition time was 12 seconds while the analytical transition time was only 16 seconds. In addition, error is involved in measuring the length of the second transition because the process does not occur as a well-defined potential as seen on the sample stripping chronopotentiogram in Figure 11. The use of the low stripping current density and the quasi-reversibility of the reduction are responsible for the drawn out nature of the curve in comparison to Figure 4.

Two sources of error were present in the spectrophotometric method. A slight turbidity of the samples remained after pretreatment. The resulting light scattering is undoubtedly the major cause of the observed data scatter. In addition, the natural samples were somewhat colored; the blank absorbances were on the order of 0.020 in a 1.0 cm cell at 882 nm. If the coloration were due to a phosphate species or any other species reacting with the molybdenum blue reagent, a simple subtraction of the blank from the absorbance of the molybdenum blue complex would not be accurate. Even a slight change in the blank would be significant because the analytical absorbances were on the order of 0.030.
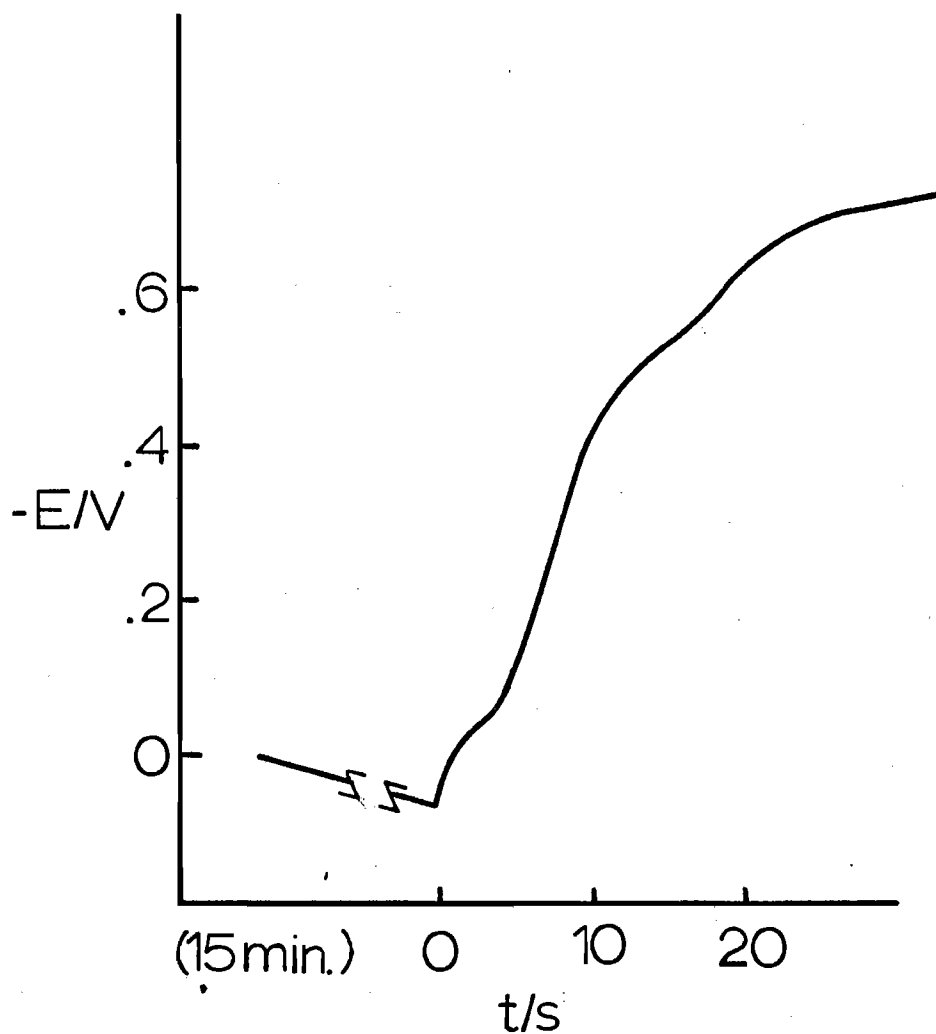
Figure 11. Cathodic Stripping Chronopotentiogram of a Natural Sample.

i_a, 500 μA cm^{-2}; i_c, 5 μA cm^{-2}; pH 6.0.

5. CATHODIC STRIPPING ANALYSIS AT A MERCURY ELECTRODE.

The formation of insoluble mercurous phosphate upon the electrochemical oxidation of a mercury electrode in phosphate medium was previously demonstrated by Lingane[2]. However, no previous attempt has been made to utilize the film formation as the basis of a stripping analysis method.

The mercury electrode has several advantages over copper. The electrode area when used in hanging drop configuration is highly reproducible; a new drop can routinely be used for each experimental trial; the behavior of mercury in all common electrolytes is well-known, while the copper electrode has not been characterized; and the surface area of the liquid electrode will not significantly vary during a given experiment because roughening of the mercury does not occur.

The major disadvantage of mercury is that sulfate and the halides will form insoluble mercurous salts upon oxidation of the electrode and may, therefore, interfere with the determination of phosphate. For this reason, copper had been selected for our initial study.

The reversible formation of a mercurous phosphate film on the electrode was demonstrated by cyclic chronopotentiometry in stirred solution. Typical results are shown in Figure 12. The transition is better defined and the current efficiency is higher than in the
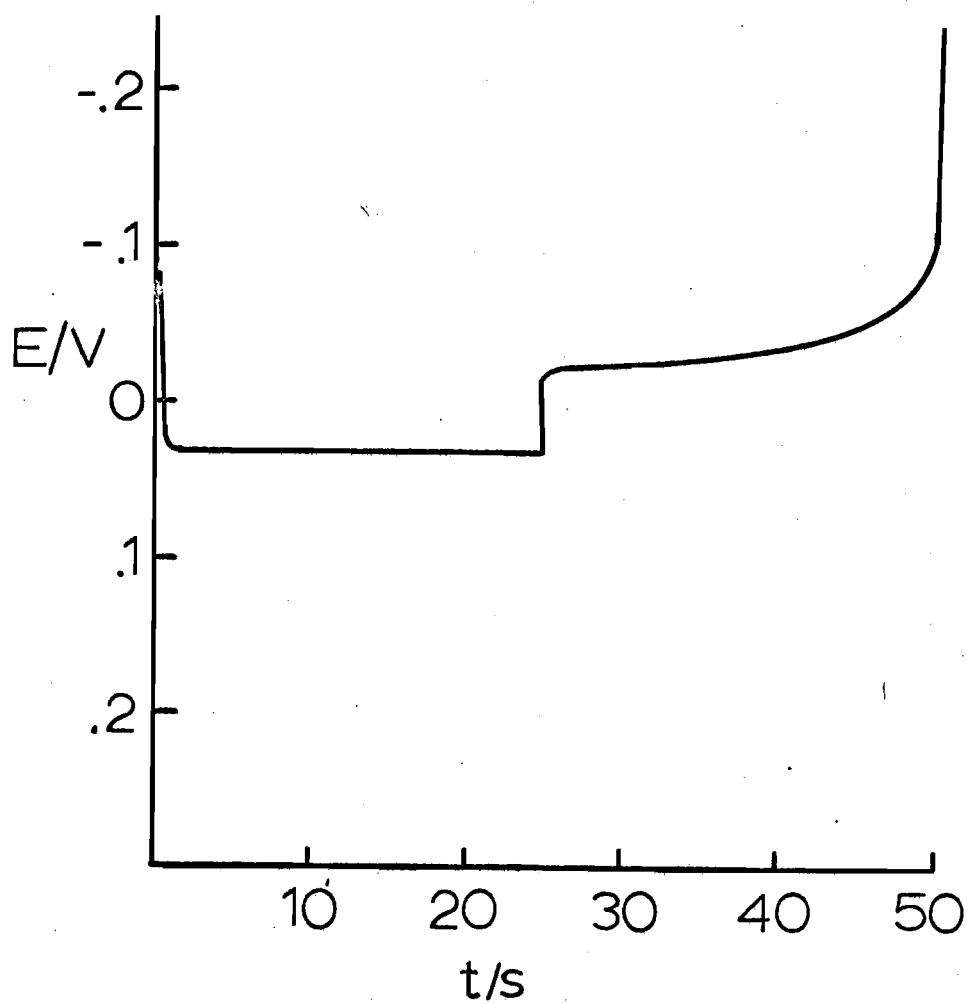
Figure 12. Cyclic Chronopotentiometry of a Mercury
            Electrode in pH 4.0 Phosphate Medium.

comparable experiments performed with the copper electrode.

That the electrode potential varies only a few mv during the film reduction indicates the electrode process approaches true Nernstian behavior; therefore, it may be possible to determine phosphate at the mercury electrode in mixtures with halides and sulfate since for a Nernstian system in very dilute solution the stripping potentials for the components of the film will depend upon their solubility products. However, in the specific case of chloride, the stripping of mercurous chloride and of mercurous phosphate occur at nearly identical potentials. Figure 13 contains a cathodic stripping chronopotentiogram of a mixture of chloride and phosphate. The small difference in stripping potentials makes accurate measurement of the transition time difficult. An analytical method in which the mercury is employed will apparently have to include a means of removing or masking the chloride ion. Because of the interference, a platinum quasi-reference electrode was used rather than an SCE for studies with the mercury electrode.

Whereas the optimum pH for determining phosphate at the copper electrode was found to be 6.0, a study of current efficiency vs. pH demonstrates that 3.0 to 4.0 is the optimum range with a mercury electrode. The results are shown in Table 7. Apparently monobasic phosphate ion is primarily involved in the film formation reaction.
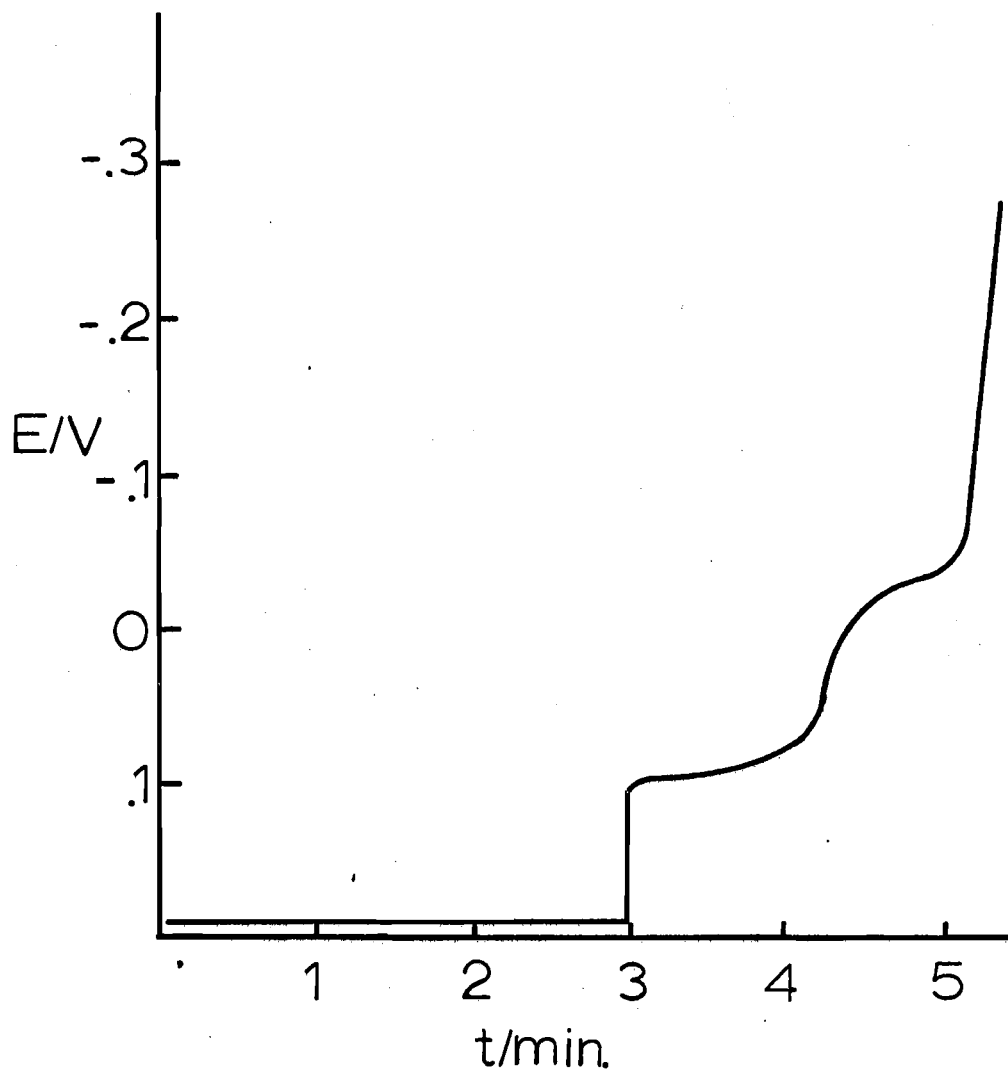
Figure 13. Cathodic Stripping Chronopotentiometry of Chloride and Phosphate Mixtures at a Mercury Electrode.

pH 4.0; C_{PO_4}-3, 1 x 10^{-3}F; C_{Cl}-, 5 x 10^{-4}M; i_a, 10 μA; i_c, 10 μA.

TABLE 7

Effect of pH on the Current
Efficiency of Cyclic Chronopotentiometry
at a Mercury Electrode in Phosphate Medium

$F_{PO_4}^{-3}$	t_{el}	pH	current efficiency, %
.01	100	2.0	2.0
.01	100	3.0	89
.01	40	3.0	90
.01	20	3.0	86
.01	100	4.0	83
.01	20	4.0	80
.01	100	5.0	56
.01	20	5.0	50

As seen in Figure 12, the stripping of mercurous phosphate occurs in a single step rather than with the two transitions observed in the case of the copper salt. Under all experimental conditions the single transition was observed as long as the total phosphate was on the order of 10 ppm or greater. Hence, it is concluded that the film contains salt of a single stoichiometry.

In solutions containing less than 10 ppm phosphate, two transitions occur as shown in Figure 14. The second transition decreased when recrystallized KNO_3 was used as the supporting electrolyte, so it is apparently the result of an impurity rather than an electrode phenomenon involving phosphate. The presence of the impurity presently is the limiting factor in our efforts to

develop a stripping method with the mercury electrode.

At phosphate concentrations sufficiently high to make the impurity negligible, good working curves have been obtained. A typical example is shown in Figure 15. The ratio of the analytical signal to the blank is significantly higher than in the case of the copper electrode. When a convenient method for removing or masking the interfering ions is developed, it is apparent that cathodic stripping at the mercury electrode will have a significantly lower detection limit than either cathodic stripping at the copper electrode or the spectrophotometric method.
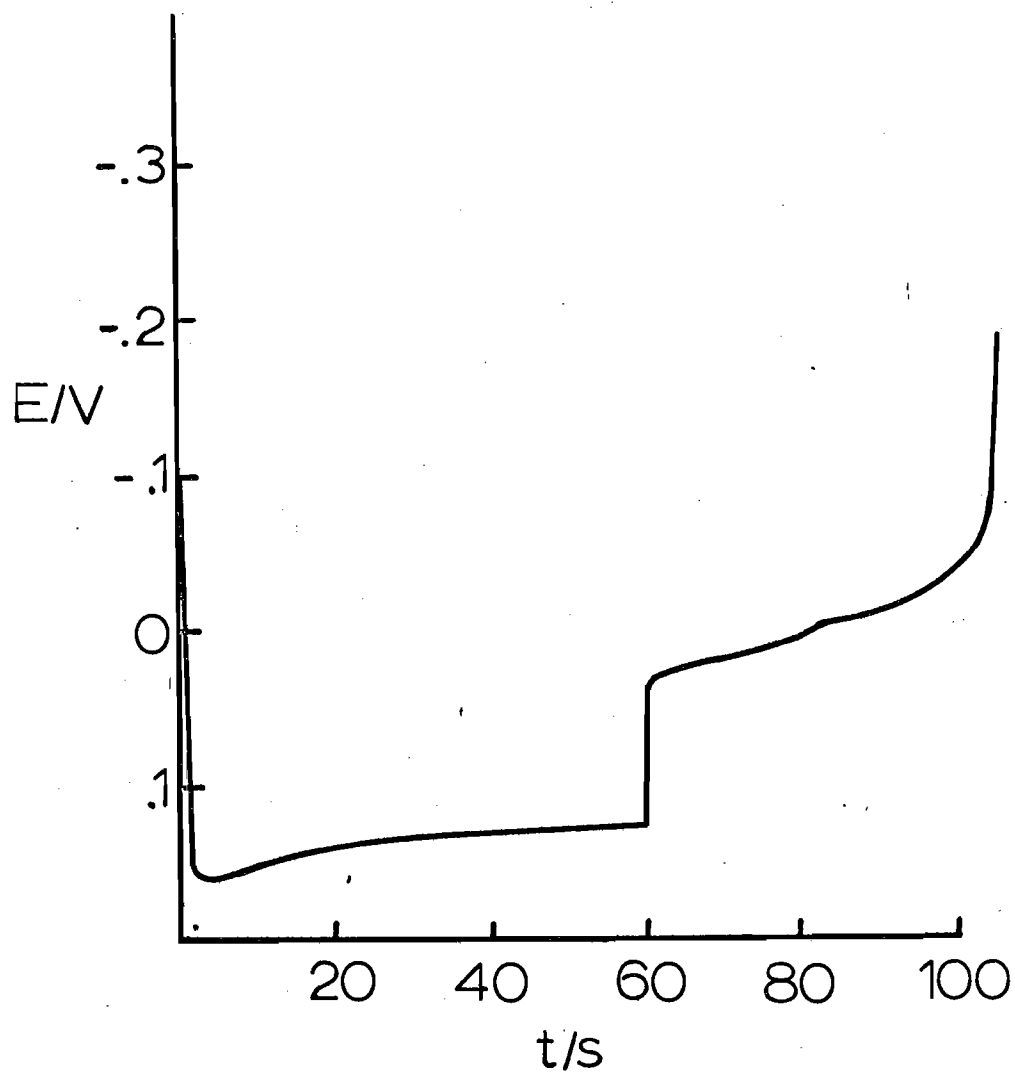
Figure 14. Cathodic Stripping Chronopotentiometry of
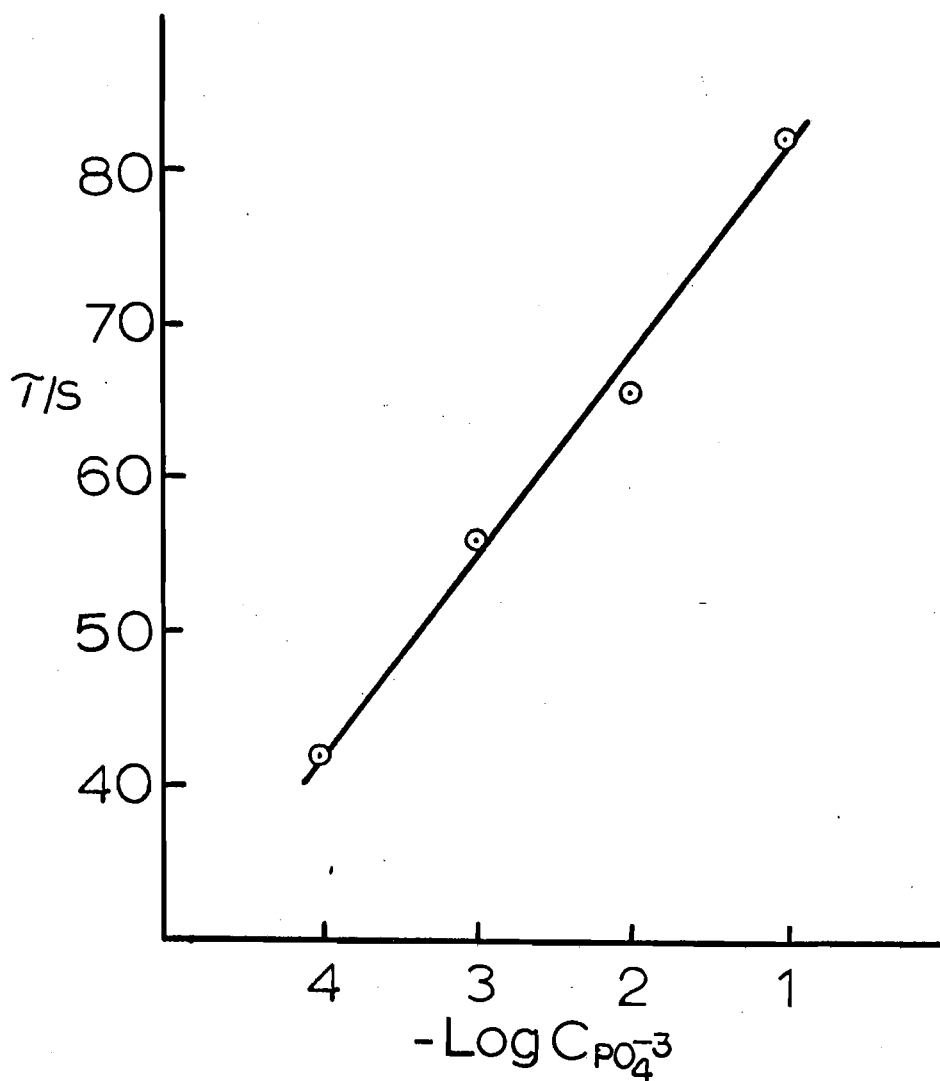5 ppm Phosphate in 0.1M KNO_3 at a Mercury
Electrode.

Figure 15. Cathodic Stripping Chronopotentiometry
Working Curve for Phosphate at a Mercury
Electrode.

pH = 4.0; i_a, 10 µA; i_c, 10 µA; t_{el}, 100 sec.

6. CONCLUSION

Cathodic Stripping Chronopotentiometry has been found to be analytically comparable to the spectrophotometric method for the determination of phosphate in natural water samples. Both methods have detection limits on the order of 10 ppb, and while the spectrophotometric method has greater reproducibility when laboratory standards are determined, the data scatter and average results observed on natural samples are nearly identical.

When copper indicator electrodes are used in Cathodic Stripping Chronopotentiometry, linear working curves are obtained over an order-of-magnitude concentration range. Over wider ranges the plots are non-linear. Common species in natural samples do not interfere with the determinations if the pH is maintained at 6.0 and the solutions are deaerated prior to initiation of the experiment.

The detection limit is established by a combination of electron transfer kinetic efforts and the solubility of the salt film when copper electrodes are used. Because the rate of the electrochemical reduction of copper phosphate is slow, low cathodic current densities do not produce a well-defined stripping transition. Hence, the analytical signal cannot be reliably differentiated from the background signal at phosphate concentrations below 10 ppb.

A second cause of data scatter is a result of the
finite solubility of copper phosphate salt. To initiate
nucleation of the film, it is necessary to exceed the
solubility product of copper phosphate in the diffusion
layer of the electrode. Hence, when the phosphate
concentration is low, the anodic current must be in-
creased to yield a high flux of copper ions. Such
currents irreversibly alter the surface area of the copper
electrodes and, therefore, limit the reproducibility. 0.5
mA cm^{-2} anodic current is the maximum value which can be
reliably used. At this level ±3 percent precision can be
obtained.

The method is further complicated by the formation
of copper phosphate of mixed stoichiometry when high
anodic currents are employed. Two distinct stripping
transitions occur which increase the potential range over
which the stripping proceeds. The resulting 500 mv
stripping range increases the number of possible inter-
fering ions.

The use of mercury electrodes in Cathodic Stripping
Chronopotentiometry results in an increase in sensitivity
in the determination of phosphate. In addition, linear
working curves are obtained over 3 orders of magnitude.
However, chloride ion interferes when present at the
same, or greater, concentration as phosphate. This inter-
ference presently establishes the detection limit at
about .1 ppm.

Whereas the electrochemical method developed in the
present study is not a significant improvement over
present techniques, it does have considerable promise.
Further research on Cathodic Stripping Chronopotentiometry
will undoubtedly produce an improved detection limit for
phosphate and comparable methods for other anions. In
contrast, because of the extensive studies already per-
formed with the molybdenum blue method for phosphate,
further improvement of that system is not anticipated.

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