

DEVELOPMENT OF A THIN LAYER
ELECTROCHEMICAL CELL FOR ANODIC STRIPPING
VOLTAMMETRY

by
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Submitted to the Faculty of the Oregon Graduate Center in
partial fulfillment of the requirements for the degree of
Master of Science.

Oregon Graduate Center
August 1972

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ABSTRACT

This thesis is the development of a method for detection and quantitative determination of trace levels (10^{-12} moles in a 1 ml sample or 0.02 ppb Pb) of metal ions in complexing and noncomplexing media. The method used was anodic stripping voltammetry using a thin mercury layer (10^{-7} moles/cm²) plated on a graphite electrode. But, instead of using a large volume cell, as has been common, a cell was used that had a very thin (10^{-3} cm) layer of solution in contact with the indicator electrode. The solution in the thin layer was forced through the cell by a syringe drive.

The purpose of this work was three fold: (a) the development of the thin layer cell and the mathematics that describe it, (b) the application of the cell to the detection of trace metals, and (c) the study of the strength of complexes of metal ions formed with ligands such as may be found in natural waters.

INTRODUCTION

Anodic stripping is an electrochemical technique which involves plating metal ions out of a solution at some sufficiently negative potential for a period of time, and then the potential is swept positive. As the potential at which a metal atom can be oxidized and become an ion is reached the metal leaves the electrode and enters the solution. If one is recording the current versus the potential in some manner, this point shows up as a peak in the current. Each metal has a characteristic potential at which it is oxidized, so that by measuring the position and the area of the current peak one can identify the metal and the quantity. Also, from the shape of the peak and the shift of the peak from the reference potential a number of factors about reactions in the solution and on the electrode can be inferred. (1)

The advantage of anodic stripping techniques is that the deposition step allows the concentration of extremely dilute metal ions into a small volume giving a major increase in sensitivity. In principle there is no lower limit on the sensitivity but experimental factors and the patience of the experimenter have placed the lower limit at about 10^{-12} moles (0.02 ppb Pb) of metal ions in a 10 ml sample with a deposition time of 20-30 minutes (2). My work has reduced both the plating time and the amount of sample necessary. With my system it takes 5 minutes and 1 ml of sample to obtain a measurement and 10^{-12} moles (0.02 ppb Pb.) of metal ion in 1 ml of sample can be detected. I have thus achieved an approximately 60 fold increase in sensitivity (i.e. sample volume - analysis time) over previous work.

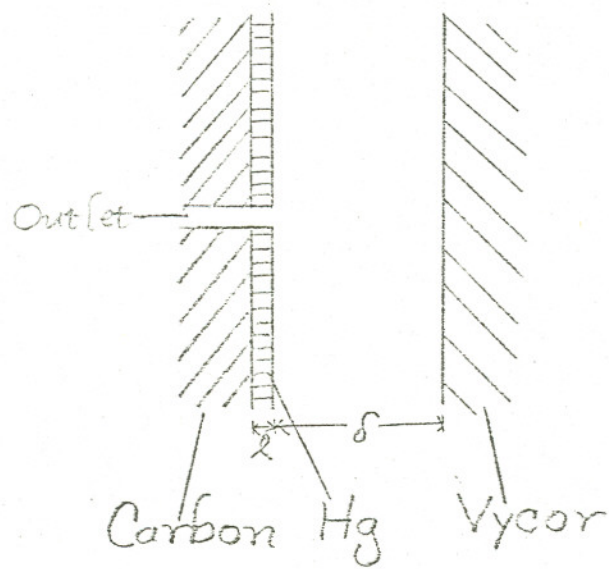
This was done by use of a thin solution-layer cell. A thin solution layer cell is an electrochemical cell that has a very thin (a few thousandth's of a cm) separation between the test electrode and the counter electrode (or

the porous Vycor salt bridge that isolates the counter electrode from the solution being studied) (Fig. 1). There has been a moderate amount of work done using thin layer cells for kinetic studies (9, 10, 11) but very little work done using thin layer cells as analytic tools. The reason is that there is room for only a few microliters of solution in a thin layer cell, so the sensitivity available was very poor. I was able to overcome this problem by building a syringe drive that forced solution through the cell slowly (1 ml in 300 sec.). This allowed the test electrode to deposit enough material to give clean, high resolution stripping curves at higher sensitivities than have been obtained before.

The disadvantage of a cell with large volume in anodic stripped voltammetry is that no matter how vigorously one stirs the solution in it there is still an undisturbed layer on the surface of the test electrode which limits the maximum rate at which metal ions can diffuse to the surface and be deposited. In a thin layer cell this diffusion limitation is reduced by making the total thickness of the cell of the same magnitude as that of the diffusion layer. One then has a situation where, if one forces solution through the cell, the rate of deposition of metal ions is not as limited by diffusion because the diffusion layer is forced to be very thin and it is constantly being replenished with fresh solution. Thus the thin layer cell gives better results than a large volume cell with impossibly high stirring rates (3) (i. e. stirring well enough to reduce the diffusion layer to a negligible value).

In order to make maximum use of a thin layer cell the test electrode must have certain characteristics. For the work I was doing these were basically (1) low background due to hydrogen evolution and other side reactions, (2) good peak resolution, (3) good collection efficiency, (4) minimum contamination of experimental results by components of the test

figure 1



Model of thin layer Cell

electrode, and (5) good reproducibility. The composite mercury-graphite electrode, which is a very thin (10^{-7} moles/cm²) layer of mercury electrodeposited on a graphite (arc carbon in this case) rod (4, 7, 8, 12), has all these properties. Its only disadvantage is that it is quite sensitive to mechanical wear, but, with careful handling, this can be avoided. I found work done by Roe and Toni on amalgamated nickel electrodes (6) helpful in elucidating the mathematical complexities of the model of the composite mercury-graphite electrode.

THEORETICAL

The theoretical section is divided into four parts, the first dealing with the collection efficiency of the thin layer cell, the second developing the equation describing the anodic stripping curves obtained by stripping into a thin solution layer cell in the absence of a complexing agent, the third section developing the equations describing the same stripping into a large excess of complexing agent, and the fourth section describing stripping into a low level of complexing agent.

Part I. Collection Efficiency

The collection efficiency of the thin solution layer cell is the ratio of the amount of metal collected on the test electrode, $[M(Hg)]$, to the total amount of metal ions that pass through the cell, $[M]$. Since the process is first order we know that

$$\frac{[M(Hg)]}{[M]} = 1 - \exp\left(-\frac{\tau}{\tau_D}\right) \quad (1)$$

where τ_D is the time necessary for an ion to diffuse to the electrode, and τ is the residence time of a metal ion in the cell. The diffusion time can be estimated from the random walk equation:

$$\tau_D = \frac{\delta^2}{D} \quad (2)$$

where D is the diffusion coefficient for the ion in question, and δ is the thickness of the cell (Fig. 1). If one takes $\delta = 2.5 \times 10^{-3}$ cm and $D = 10^{-5}$ cm²/sec, 3×10^{-6} cm²/sec, or 10^{-6} cm²/sec (these values correspond to fast, medium, and slow ions respectively) one obtains diffusion times of 0.6 sec, 2.1 sec, and 6.3 sec respectively.

The residence time is equal to the volume of the thin layer cell divided by the flow rate. Since my test electrode is circular with a hole in the middle the residence time is

$$\tau = \frac{\pi \delta (r_1^2 - r_2^2)}{J} \quad (3)$$

where r_1 is the radius of the electrode, r_2 is the radius of the hole, J is the flow rate, and δ is the thickness of the cell. From my experimental work these numbers are: $r_1 = .350$ cm, $r_2 = .058$ cm, $\delta = 2.5 \times 10^{-3}$ cm and $J = 3.4 \times 10^{-3}$ cm³/sec. So $\tau = 2.8$ sec. Thus, for the three diffusion times calculated the collection efficiency would be 99%, 73%, and 37% respectively.

It is clear that the above numbers are rather crude approximations. The major reason is that, because the solution is being pumped in all around the edge of the electrode but goes out only through a small hole, the velocity of the solution in the cell varies with its radial distance. This invalidates the random walk assumption of diffusion to a great extent. Also this derivation does not make any allowance for nonideality of the cell and the electrode. But it does give a fairly reasonable estimate of what to expect.

Part II. Derivation of an Equation Describing the Anodic Stripping Curve of a Metal Ion out of a Mercury Film Electrode into a Thin Solution Layer Cell Filled with Noncomplexing Media.

Two basic assumptions must be made prior to the derivation. These are that (a) diffusion in the mercury layer can be ignored and (b) diffusion in the solution layer can be ignored. The first of these holds to a very good approximation because the mercury layer on the graphite electrode is about 5×10^{-6} cm thick. The second can be made to hold by carefully limiting the operating conditions. Ideally an anodic stripping peak should have a base width of about 100 mv. Estimating that in order to achieve peaks that are undisturbed by diffusion effects (this is seen by a broadening and rounding of the peak) the time the sweep takes to pass through this peak should be about ten times the diffusion time of the metal ion in question, one can get some idea of sweep rates that are useable. Using cadmium, as an example, which has a diffusion coefficient of 8.3×10^{-6} cm²/sec the diffusion time across the cell is 0.75 sec. Thus at a sweep rate of 10 mv/sec one would expect virtually no distortion, at a sweep rate of 50 mv/sec one would expect a small amount of distortion, and at 100 mv/sec one would expect a fair amount of broadening of the peak. It should be noted, however, that though the peak is broader and more rounded it still contains the same area, and thus the peak broadening from high sweep rates does not effect the quantitative measurement of the amount of material present. It may, however, result in a loss of resolution.

On the basis of the model (Fig. 1) the flux out of the mercury as a function of time is developed. The definition of the terms to be used are:

$$\begin{aligned} [M^0] &= \text{the initial solution concentration of metal ions} \\ [M(\text{Hg})^0] &= \text{the initial concentration of metal in the mercury film} \end{aligned}$$

$[M]$ = the solution concentration of metal ions at any time t
 $[M(Hg)]$ = the concentration of metal in the mercury film at any time t

$\phi = \frac{nF}{RT}$ where n = number of electrons transferred for each metal ion

F = Faraday constant = 96,487 coulombs

R = Gas constant = 8.314×10^{-7} erg/deg mole

T = Temperature

v = sweep rate

l = thickness of mercury layer

δ = thickness of solution layer

E_i = initial potential

E_t = potential at time t

E_p = potential of peak

E^{f_0} = formal potential of metal ion corrected for ionic strength

i = current

i_p = peak current

Under these conditions the Nernst equation gives

$$\frac{[M^0]}{[M(Hg)^0]} = \exp \phi (E_i - E^{f_0}) \quad (4)$$

The boundary conditions are

$$\frac{[M]}{[M(Hg)]} = \frac{[M^0]}{[M(Hg)^0]} \exp \phi vt \quad (5)$$

$$l[M(\text{Hg})^0] + \delta[M^0] = l[M(\text{Hg})] + \delta[M]$$

or

$$\frac{l d[M(\text{Hg})]}{dt} = -\delta \frac{d[M]}{dt} \quad (6)$$

The initial potential, E_i , is taken as the potential at which the current is zero. Time is also referenced to the same point because the sweep rate, v , is linear with time. Thus the potential at any time is given by $E_t = E_i + vt$. $[M(\text{Hg})]$ is a function only of time and is assumed uniform throughout the mercury layer.

Taking the partial derivative of eq. (5) with respect to time gives

$$\frac{d[M]}{dt} = \frac{[M^0]}{[M(\text{Hg})^0]} \exp \phi v t \left[\frac{d[M(\text{Hg})]}{dt} + [M(\text{Hg})] \phi v \right] \quad (7)$$

which relates the change in the solution concentration of the metal ion with time to the initial concentrations of metal ions in the two layers of the cell and the change in the potential since that time. Substituting eq. (7) into eq. (6) one obtains:

$$\frac{d[M(\text{Hg})]}{dt} = \frac{\frac{\delta[M]}{l[M(\text{Hg})^0]} \phi v \exp \phi v t}{1 + \frac{\delta[M^0]}{l[M(\text{Hg})^0]} \exp \phi v t} \quad (8)$$

Separating variables and integrating gives:

$$\frac{[M(\text{Hg})]}{[M(\text{Hg})^0]} = \frac{\frac{l}{\delta} + \frac{[M^0]}{[M(\text{Hg})^0]}}{\frac{l}{\delta} + \frac{[M^0]}{[M(\text{Hg})^0]} \exp \phi v t} \quad (9)$$

which is the fraction of the metal left in the mercury layer at any time.

For convenience define

$$\psi = \frac{[M(Hg)]}{[M(Hg)^0]}$$

$$y = \phi vt$$

Now, to obtain an expression for the flux out of the mercury with respect to time eq. (9) must be differentiated with respect to y giving:

$$\frac{d\psi}{dy} = \frac{\left(\frac{l}{\delta} + \frac{[M^0]}{[M(Hg)^0]}\right) \left(\frac{[M^0]}{[M(Hg)^0]} \exp \phi vt\right)}{\left(\frac{l}{\delta} + \frac{[M^0]}{[M(Hg)^0]} \exp \phi vt\right)^2} \quad (10)$$

where $\frac{[M^0]}{[M(Hg)^0]} \ll \frac{l}{\delta}$

which is the requisite equation describing the anodic stripping curves out of thin mercury films in thin layer cells.

Several other useful equations can be developed from eq. (10). The current in anodic stripping for the thin layer cell model being studied is

$$i = nF[M(Hg)^0] \phi v \frac{d\psi}{dy} \quad (11)$$

Substituting eq. (10) into eq. (11) one obtains

$$i = nF[M(Hg)^0] \phi v \left[\frac{\frac{l}{\delta} \exp \phi (E_t - E^0)}{\left(\frac{l}{\delta} + \exp \phi (E_t - E^0)\right)^2} \right] \quad (12)$$

Taking the derivative of eq. (12) with respect to time, setting it equal to zero, and then substituting the result back into eq. (12) gives the equation for the peak current which is

$$i_p = \frac{nF[M(\text{Hg})^0] \phi \nu}{4} \quad (13)$$

Also of interest is the potential at i_p . This is obtained by taking the value of y at i_p and substituting eq. (4) into it giving:

$$E_p = E'^0 + \frac{2.303}{\phi} \log \frac{l}{\delta} \quad (14)$$

Thus the peak current is directly proportional to $[M(\text{Hg})^0]$ and to the scan rate. The peak potential is independent of scan rate but does depend on known cell dimensions. In Fig. 2 graphs of three numerical solutions of eq. (10) are given. The conditions are $[M(\text{Hg})^0] = 10^{-9}$ moles, $l = 2.5 \times 10^{-5}$ cm, $\delta = 2.5 \times 10^{-13}$ cm $n = 2$ and respectively $\nu = 10$ mv/sec, 50 mv/sec, and 100 mv/sec. As can be seen from the graph the peaks are quite sharp. In practice there is excellent separation between the lead and cadmium peaks (see picture 1) and they are both quite sharp.

Part III. Relationship of Peak Potential Displacement in Presence of Excess Complexing Agent.

The equilibrium constant of a metal-ligand system is

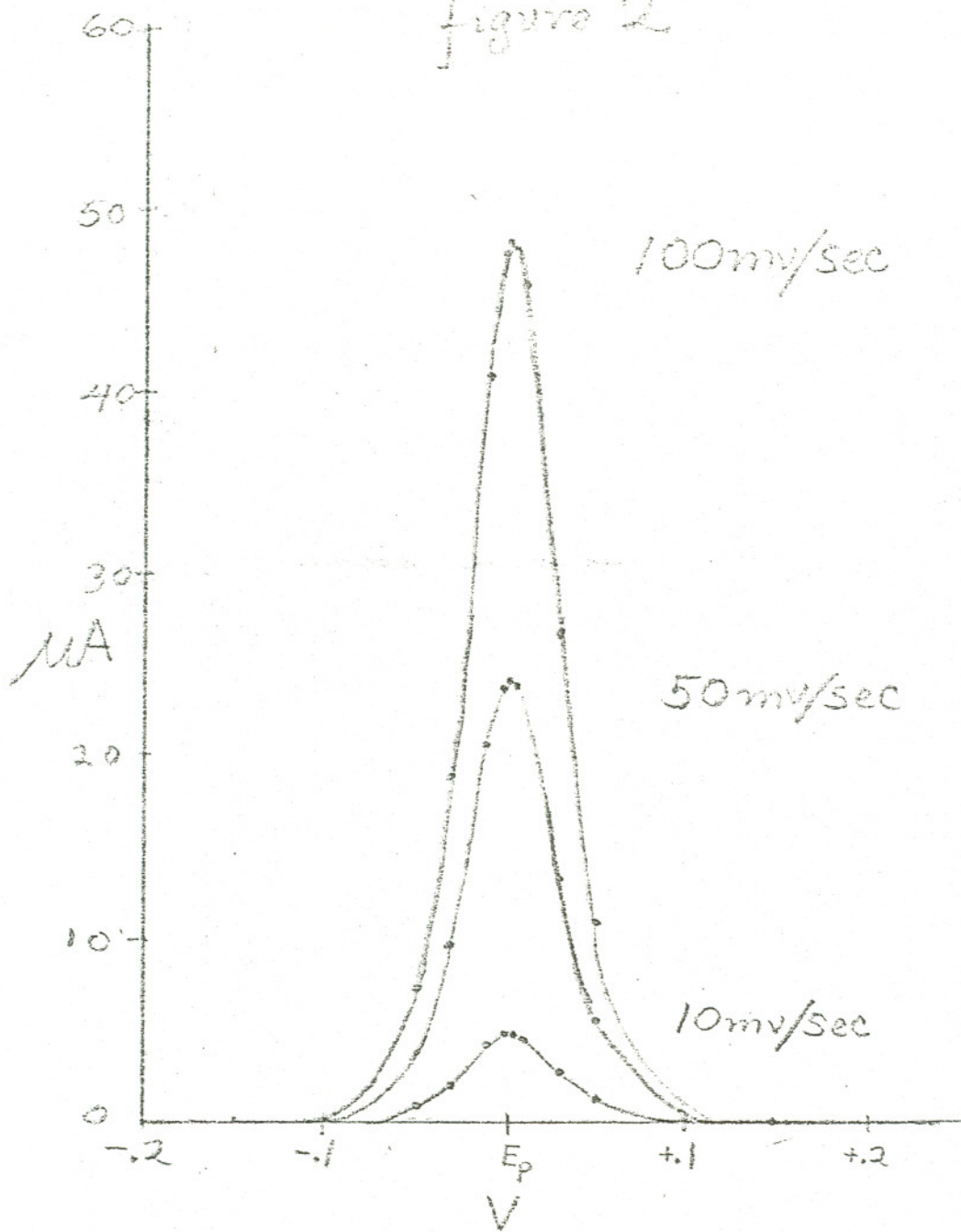
$$K = \frac{[ML_m]}{[M][L]^m} \quad (15)$$

For the metal being stripped into a noncomplexing medium the potential is

$$E^{\text{non}} = E^0 + \frac{RT}{nF} \ln \frac{[M]}{[M(\text{Hg})]} \quad (16)$$

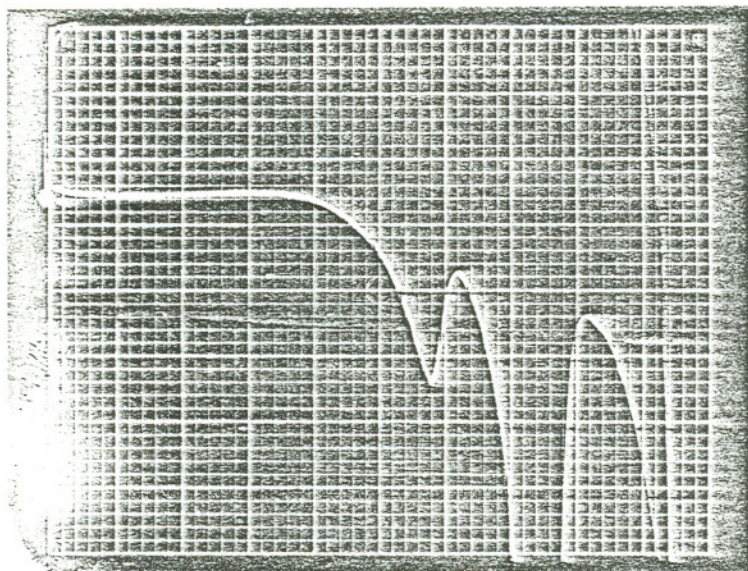
For the metal being stripped into a complexing medium eq. (15) and eq. (16) combine to give

figure 2



Theoretical Anodic
Stripping Curves

Piccolo!



0.1 V/div

$5 \mu\text{A/div}$

Cd Pb Hg

Sample Stripping curve

$$E^{com} = E^o + \frac{RT}{nF} \ln \frac{[ML_m]}{K[M(Hg)][L]^m} \quad (17)$$

Subtracting eq. (17) from eq. (16) an expression for ΔE is obtained

$$\Delta E = \frac{RT}{nF} \ln \frac{K[M][L]^m}{[ML_m]} \quad (18)$$

But at E_p $[M] = [ML_m]$ so

$$\Delta E_p = \frac{RT}{nF} \ln K [L]^m \quad (19)$$

A value for m may be obtained by plotting $\frac{\Delta E_p nF}{RT}$ against $\ln[L]$. The slope of the line produced equals m . K may then be calculated by using eq. (19) in the form:

$$K = \frac{\exp\left(\frac{nF}{RT} \Delta E_p\right)}{[L]^m} \quad (20)$$

One can also obtain the ΔG of formation for the metal-ligand couple from:

$$\Delta G = -RT \ln K \quad (21)$$

Since there is a large excess of L in the solution that the metal is stripped into, there will be a single peak observed in the anodic stripping corresponding to the oxidation of the metal to form the complex. Since the concentration of the metal is the limiting reagent, the mathematics describing the peak form are identical with those derived in Part II. The only difference between the two cases is that the peak will be at a different potential, the change being described by eq. (19).

Part IV. The Effect of Low Levels of Complexing Agent on the Stripping Peaks Obtained by Anodic Stripping out of a Thin Mercury Layer into a Thin Solution Layer.

Symbolically this case is $1[M(\text{Hg})] > \delta m[L]$, that is the amount of metal being oxidized out of the mercury is greater than the amount of complexing agent available.

This case is handled in a similar manner to the noncomplexed case except that the limiting reagent is now the L not the M. Since mL 's are consumed by each M complexed, the concentration shows up raised to the m power in equilibrium expressions.

Terms to be used:

- $[ML_m^0]$ = initial concentration of metal-ligand complex
 $[ML_m]$ = concentration of metal-ligand complex at any time t
 $[L^0]$ = initial concentration of ligand
 $[L]$ = concentration of ligand at any time t
 E_C^{10} = formal potential of the complex metal ion electrode

all other symbols as in Part II.

The Nernst equation is then

$$\frac{[ML_m^0]}{[L^0]^m} = \exp \phi (E_i - E_C^{10}) \quad (22)$$

The boundary conditions are:

$$\frac{[ML_m]}{[L]^m} = \frac{[ML_m^0]}{[L^0]^m} \exp \phi vt \quad (23)$$

$$\frac{\ell d[ML_m]}{dt} = -\delta [L]^m \frac{d[L]}{dt} \quad (24)$$

Taking the partial derivative with respect to time of eq. (23) gives:

$$\frac{d[ML_m]}{dt} = \frac{[ML_m^0]}{[L^0]} \exp \phi v t \left(m [L]^{m-1} \frac{d[L]}{dt} + [L]^m \phi v \right) \quad (25)$$

which relates the time rate of change of the concentration of ML_m to the initial concentrations of ML_m and L and the change in the potential since that time. Substituting eq. (25) into eq. (24) one obtains:

$$\frac{d[L]}{dt} = \frac{-\frac{\ell}{m\delta} \frac{[L][ML_m^0]}{[L^0]} \phi v \exp \phi v t}{1 + \frac{\ell [ML_m^0]}{\delta [L^0]} \exp \phi v t} \quad (26)$$

Separating variables and integrating yields:

$$\frac{[L]}{[L^0]} = \left[\frac{\frac{\delta}{\ell} + \frac{[ML_m^0]}{[L^0]}}{\frac{\delta}{\ell} + \frac{[ML_m^0]}{[L^0]} \exp \phi v t} \right] \exp(m)t \quad (27)$$

Defining, for convenience,

$$\psi = \frac{[L]}{[L^0]}$$

$$y = \phi v t$$

one can obtain an expression for the rate of change of the concentration of L with respect to the sweep rate. Differentiating eq. (27) with respect to y which gives:

$$\frac{d\psi}{dy} = \frac{\left(\frac{\delta}{\ell} + \frac{[ML_m^0]}{[L^0]} \right) \left(\frac{[ML_m^0]}{[L^0]} \exp \phi v t \right)}{\left(\frac{\delta}{\ell} + \frac{[ML_m^0]}{[L^0]} \exp \phi v t \right)^2} \exp(m)t \quad (28)$$

where $\frac{[ML_m^0]}{[L^0]} \ll \frac{\delta}{l}$

From the above equation several other useful equations can be derived, in particular the current, i , the peak current, i_p , and the peak potential, E_p . The first is obtained by combining the equation for the current:

$$i = nF \frac{dC_r}{dt} \quad (29)$$

where C_r is the concentration of the reduced species, with eq. (22) and eq. (28) giving:

$$i = nF \delta [L^0] \phi v \left[\frac{\frac{\delta}{l} \exp \phi (E_T - E_c'^0)}{(\frac{\delta}{l} + \exp \phi (E_T - E_c'^0))^2} \right] \exp(m) \quad (30)$$

The value of i_p is obtained by differentiating eq. (30) with respect to time, setting the result equal to zero, and substituting what is left back into eq. (30) yielding:

$$i_p = \frac{nF \delta [L^0] \phi v}{4} \exp(m) \quad (31)$$

The value of E_p is obtained as a byproduct of the calculation of eq. (31), and is:

$$E_p = E_c'^0 + \frac{1}{\phi} \ln \frac{l}{\delta} \quad (32)$$

Intuitively it is clear that if the $\delta m [L] < l [M(Hg)^0]$ one gets double peaks. The more negative corresponds to the metal being complexed as it is oxidized, and the less negative corresponds to the metal oxidizing into the solvent after the ligand supply has been exhausted. This would seem to make the calculation of peak voltages and currents more difficult. To a good approximation it does not. Why this is so is best shown graphically,

(Fig. 3). The K in all cases is taken to be 10^8 , $[M] = 10^{-6}$ M, and $m = 1$. All other necessary data is by each graph. As can be seen from these idealized curves, which ignore the change of ligand concentration with potential, as the concentration of the ligand decreases the peak shift diminishes, and, when the concentration of the ligand becomes comparable to that of the metal ion, double peaks do show up. But it can also be seen that as long as the complexed species is present in significant amounts (10% of the metal ions or more) the peaks are quite distinct and can be considered independent. Granted that in the valley between the peaks this does not hold but, since only the peak potentials, peak current, and total area under both peaks are of interest analytically, this does not effect the measurements.

EXPERIMENTAL

This section is divided into two parts. Part I is a description of equipment and procedures necessary for setup and maintenance of the system. Part II describes the actual experiments done and their results. In both sections I shall first list the most successful techniques and results and then list less successful trials or failures and their causes.

Part I.

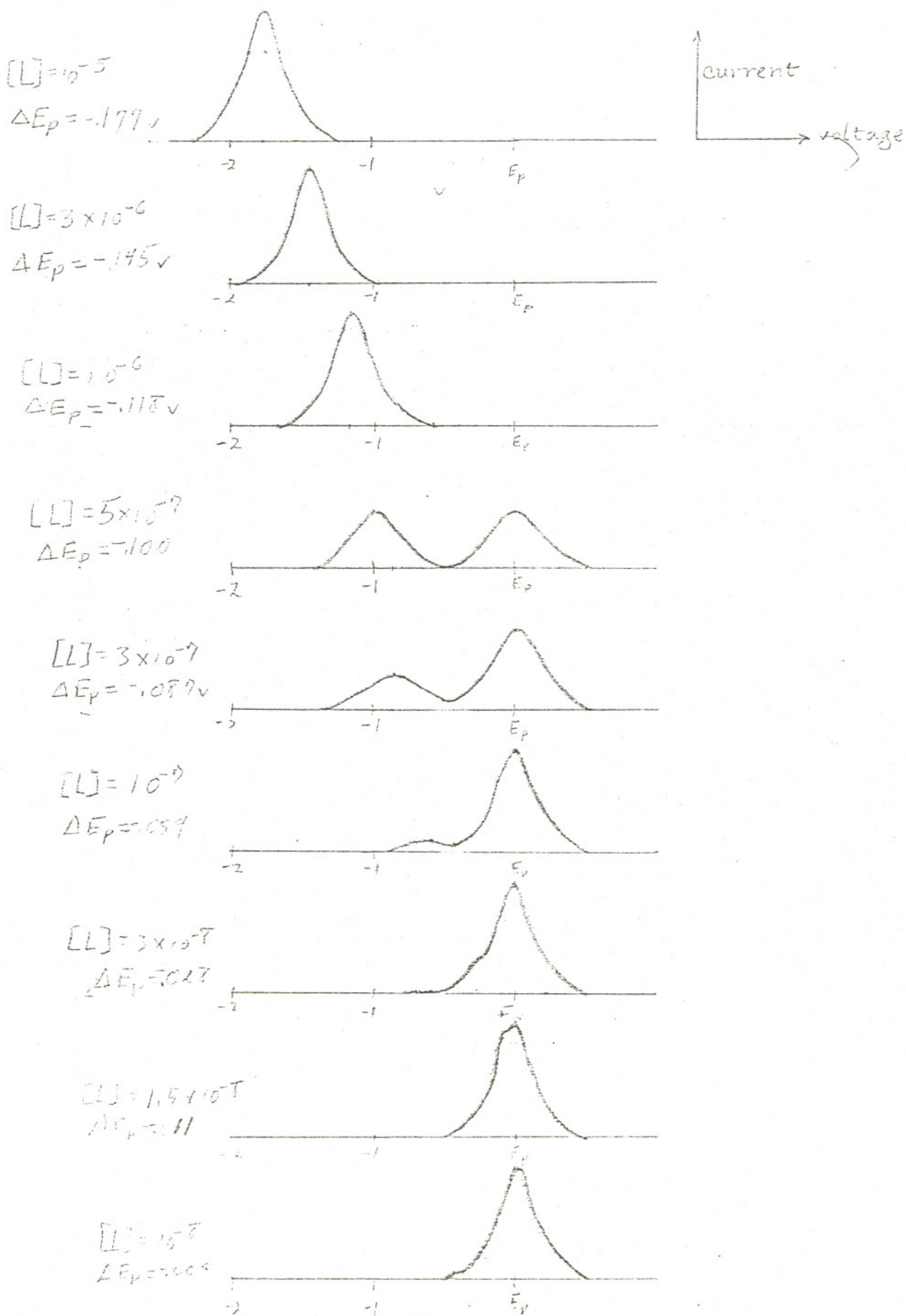
A. Preparation of the Electrode

The mercury film carbon electrode was developed by W. Matson and D. Roe (4, 7, 8). I used W. Matson's Ph.D. Thesis (8) as the basis for the construction of my electrode.

Preparation of the electrode began by machining a piece of arc carbon rod to the dimensions needed. The electrode was then put in

figures

Amount of ligand vs. peak shift



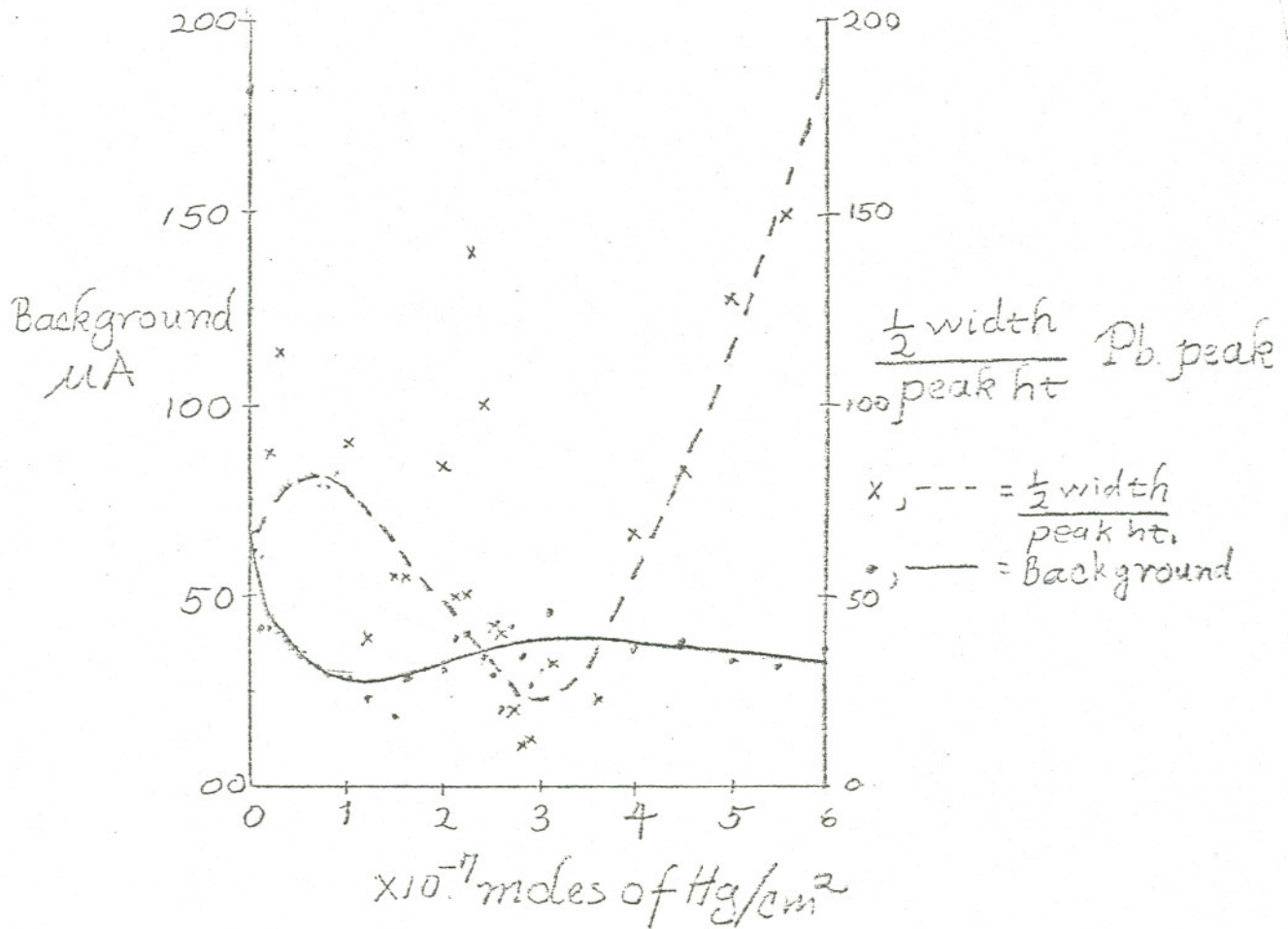
liquid microtome specimen mounting wax and the pressure reduced by use of a mechanical vacuum pump. When the electrode stopped bubbling the pressure was allowed to return to atmospheric and the electrode allowed to sit in the hot wax for a few minutes. The pressure was then reduced again and the cycle repeated. After three or four of these cycles the electrode was thoroughly impregnated with wax. Care was taken to be sure there was a heavy layer of wax (.0025 - .005 cm) on the outside of the electrode. This was achieved by alternately dipping the electrode in the hot wax and dipping it in cold water until the desired thickness of wax was achieved.

The end that was to be used as the test electrode was then polished to a dull matte finish. If the electrode was polished to a high gloss finish it had a very short useful life span, and if the surface still showed obvious scratches the background current level of the electrode was very high.

The electrode was then put in a solution containing a mercury salt. I found that a solution of 10^{-3} M Hg (NO₃)₂ in 1 M NaNO₃ worked well because it allowed the mercury that had been deposited on the electrode to be stripped off cleanly so that the rate of deposition could be established. The optimum amount of mercury seemed to be between 1 and 5×10^{-7} moles/cm². Less than 1×10^{-7} moles/cm² gave high background current levels and more than 5×10^{-7} moles/cm² gave peak broadening of the metals being stripped and reduced the useful life of the electrode (Fig. 4).

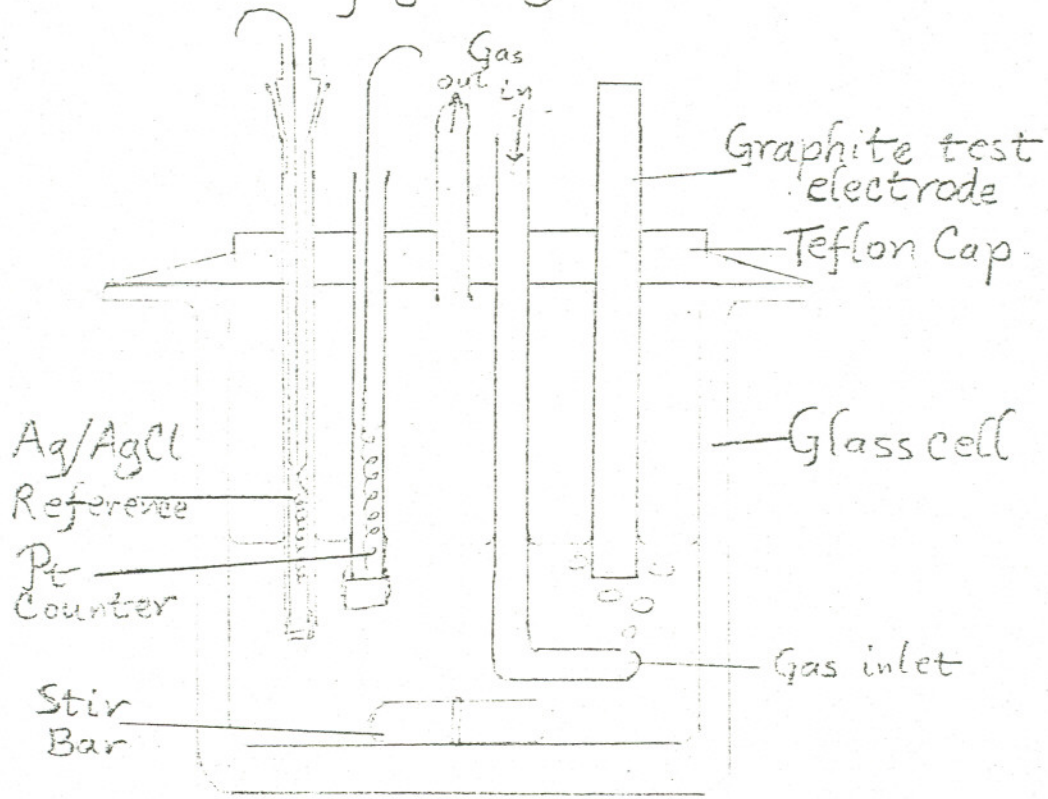
Electrode life has several variables. In the thin layer cell (Fig. 6) an electrode was good for six to eight hours of use and deteriorated if left unused for more than a couple days. In the large volume cell (Fig. 5) the electrode was good for about 40 hours of work and deteriorated after a couple weeks if unused. All these times are for storage in NaCl solutions.

figure 4



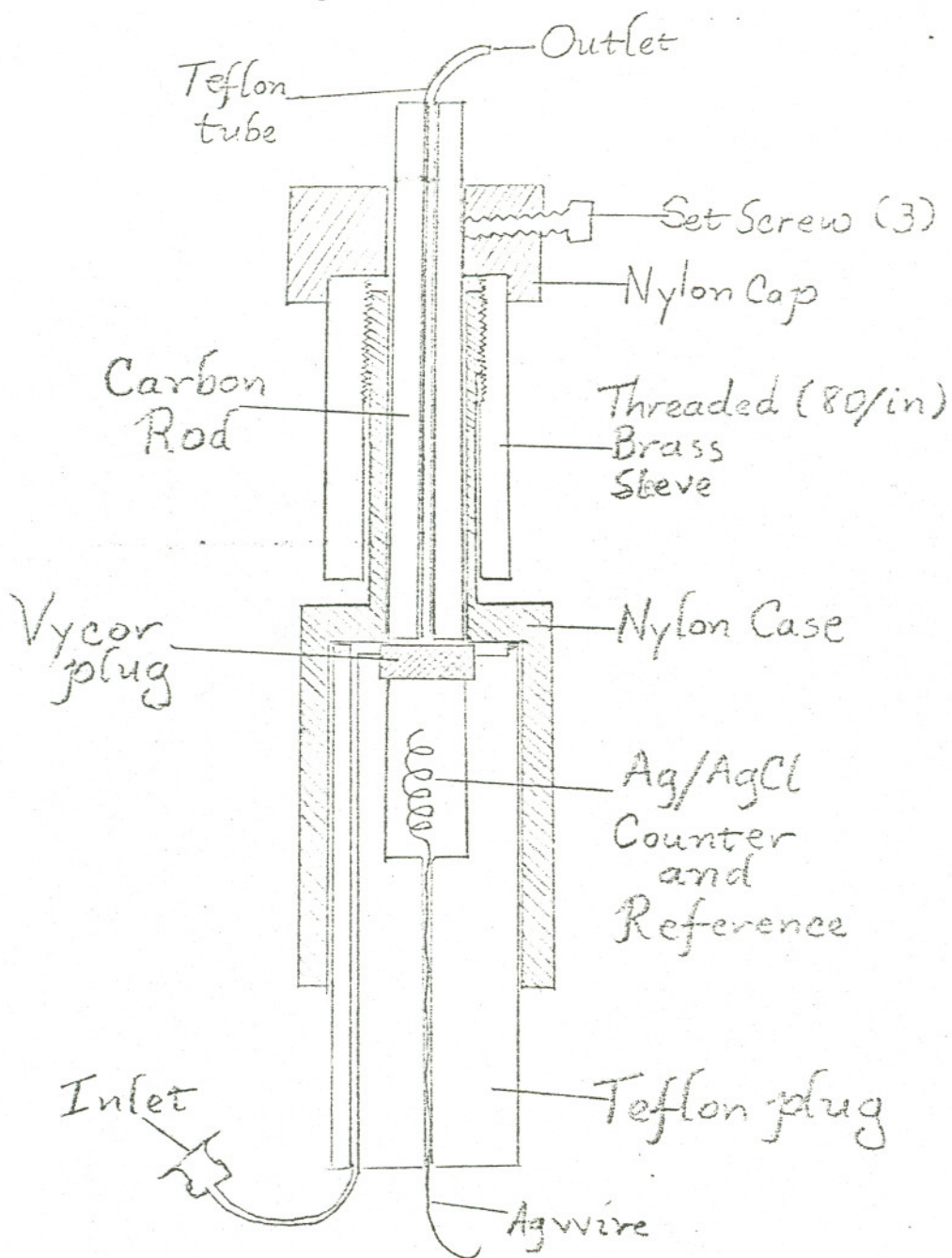
Optimization of mercury layer

figure 5



Large Cell

figure 6



Thin Layer Cell

Storage in NaNO_3 solutions reduces the lifetime, and if the electrode became dry it was necessary to renew the mercury layer.

When an electrode deteriorated to the point of uselessness it was easily regenerated. It was wiped on a paper towel or Kimwipe to remove the old mercury, the end repolished, placed in a mercury solution, and replated.

Two other methods for insulating the sides of the electrode were tried and found less effective. The first was, after waxing, to shrink a piece of shrinkfit tubing over the electrode to provide better insulation. This method worked quite well for the large volume cell but could not be used in the thin layer cell since the unpredictable shrinkage of the tubing would not fit the close tolerances of the smaller cell. The second procedure was to use Teflon shrink tubing instead of the polyethylene shrinkfit. This would shrink uniformly but, since the wax would not wet the Teflon, voids were left under it which defeated the whole purpose of the tubing.

B. Cell Design

There were two basically different cell designs used in the experiments. The first was a fairly standard beaker type of cell with the electrodes hanging in the solution (Fig. 5.). The second was a thin layer cell (Fig. 6), similar in principle to other thin layer cells which have micrometer movements connected to one electrode, but of quite different design.

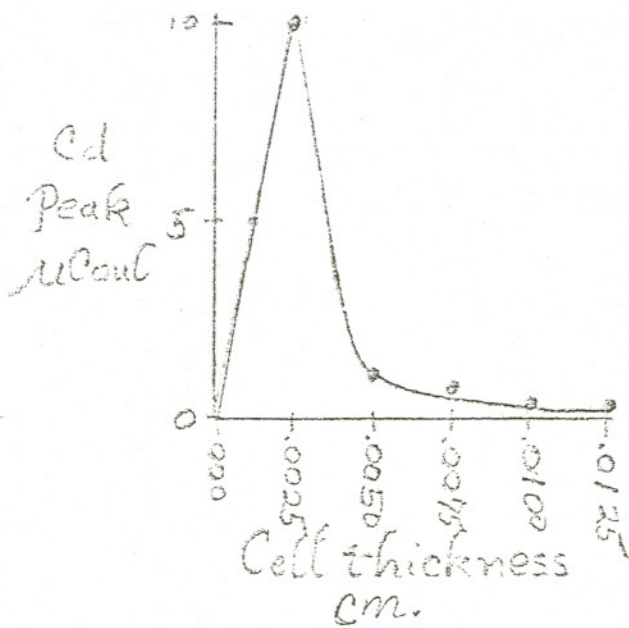
As can be seen from Fig. 5 the large cell was a conventional three electrode cell using the carbon rod with mercury film plated on its end

as the test electrode; a platinum coil in 1M NaCl, isolated from the cell by a porous Vycor plug, as the counter electrode; and a silver-silver chloride reference electrode, also isolated via a porous Vycor plug. Nitrogen was bubbled through the solution to reduce the oxygen partial pressure and a Teflon coated magnetic stir bar was used to stir the solution. 10-15 ml. of solution were used in the cell and maximum sensitivity was about 10^{-7} moles per liter of metal ion with a plating time of 10 to 20 min.

The thin layer cell (Fig. 6) was the result of a great deal of trial and error. Exacting dimensional tolerances were necessary. In its final form it consisted of a carbon rod with a hole down the middle and a thin film of mercury on one end forming the test electrode. A silver/silver chloride electrode acted both as a counter and a reference electrode. The latter was isolated from the solution being studied by a porous Vycor plug. The gap between the Vycor plug and the test electrode was varied between .0013 and .0125 (Fig. 7) cm with .0025 cm being found about optimum. At .0025 cm the efficiency of the cell was between 10% and 20%; the cell had a sensitivity of about 10^{-10} moles of metal ion per liter. The flow rates through the cell were varied between 160 sec/ml and 500 sec/ml by varying the voltage of the motor of the syringe drive (described in next section). 300 sec/ml (see Fig. 8) was found to be the optimum balance between efficiency of the cell and the analysis time.

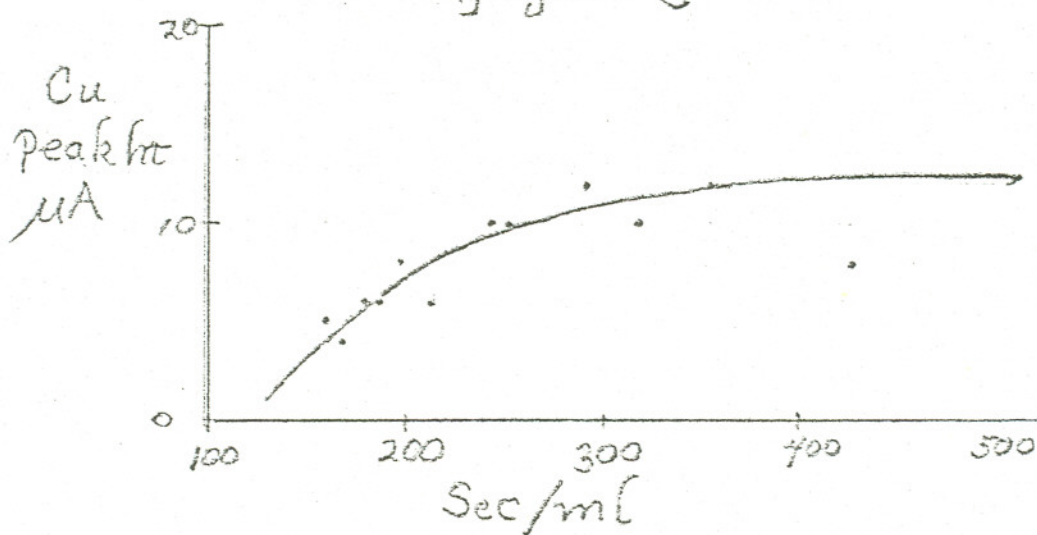
Flow both directions through the cell was tried. The setup, as diagrammed, with the inlet through the plug containing the counter electrode and outflow through the center of the electrode, was found to give the best results. The slight trough in the Teflon plug around the Vycor disc was found to be critical to the establishment of uniform flow rates. Operation without it gave very poor results. Originally the carbon rod was machined

figure 7



Optimization of
cell thickness

figure 8



Optimization of flow rate

to fit the nylon case very closely, allowing for only a minimal coating of wax. This was found to be unwise because the wax was easily abraded away on insertion so that the solution could contact the sides of the carbon rod. The result was a high background level which obscured the stripping peaks. This was overcome by machining the electrode .005 cm to .01 cm too small and then alternately dipping the previously wax impregnated electrode in wax and then chilling it in water until the requisite thickness was built up. This wax layer had the added advantage of giving a tighter seal between the electrode and the case which reduced leakage out of the cell. A similar problem with exposed carbon was encountered in the internal hole of the carbon rod. This was defeated by drilling the center hole big enough to accept a small Teflon tube. This was slid through the center hole to within half a millimeter or so of the test electrode end, and sealed in with wax. The best way of getting a smooth seal between the carbon and the end of the tube and keeping the tube from being blocked by the wax was found to be to blow air through the tube after waxing while the wax was still hot.

The outside of the nylon case at the end that held the test electrode was machined about .005 cm larger than the i.d. of the brass sleeve. The threads on the brass sleeve were then used to cut the threads on the nylon. The brass sleeve was threaded 80 threads per inch to make it easy to differentiate between various thicknesses of the thin solution layer between the electrodes. Originally the entire threaded sleeve-electrode holder assembly was a single piece of brass but it was found that occasionally the solution leaked down the outside of the carbon electrode and wet the brass which was in turn in electrical contact with the test electrode through the set screws. This turned the entire unit into a large electrode which increased the background tremendously. The substitution of the nylon cap and the heavier waxing of the test electrode defeated this. Glass was originally used for the case but it proved too fragile.

C. Syringe Drive

The syringe drive (see Fig. 9) was made using a 30 rpm D.C. motor obtained from Edwards Scientific Supply. It was rated at 3V but ran quite well between 1.2 and 6V. The drive was designed to take a 10 ml syringe and had a spacer rod to allow it to accept a 2 ml syringe. The latter proved to be the most useful. A standard variable D.C. power supply was used to run the drive.

D. Electrical Equipment

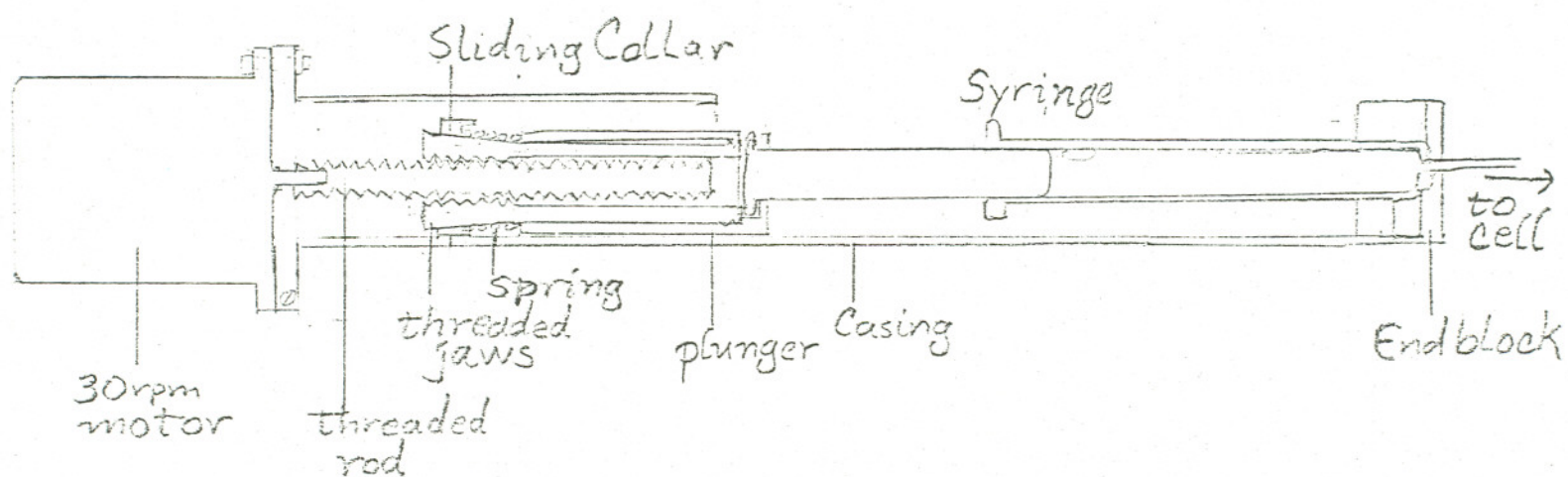
Two sets of equipment were used in the course of this experimental work. The first set was an operational amplifier potentiostat that D. Roe had built which used an EAI 1131 graphical recorder. Part way through the research it became clear that the unit was too cumbersome and that the graphical recorder was not a particularly useful way for me to take data, so I switched to using a Tektronix 564B storage oscilloscope with a 310 readout amplifier and a 205 polarographic time base, both plug-ins products of Chemtrix, Inc. The occasional hard copies that I needed were made with a Tektronix C-12 oscilloscope camera with a Polaroid back, using ASA 3000 high contrast black and white film.

Part II. Experimental

A. Determination of Plating Efficiency of Thin Layer Cell.

The preparation of the mercury film electrode was done in various ways. The most successful technique was to put the wax coating on the test electrode, polish it, and then put it in the thin layer cell. The spacing desired was then set and enough mercury salt solution was pumped

figure 9



Syringe drive

through with the syringe drive to plate about 2.5×10^{-7} moles/cm² on the electrode surface (see Part I-A). The other technique that was tried was plating the electrode with mercury in the large volume cell and then transferring it into the small cell. This worked fairly well and was used in the initial development period of the thin layer cell, but gave too high a background and was not reproducible enough for accurate analytic use.

Estimates of the collection efficiency of the cell were given in Part I of the Theoretical Section. Experimental collection efficiencies were determined directly by the following procedure. First the electrode was plated with mercury by pumping 2 ml of 10^{-3} M $\text{Hg}(\text{NO}_3)_2$ in 1M NaNO_3 through the cell with an applied potential of -0.8V. The background current was checked to ensure that the cell was operative. Then 1 ml of 10^{-6} M $\text{Cd}(\text{NO}_3)_2$ in 0.1M NaNO_3 was pumped through the cell with an applied potential of -1.0V and the anodic stripping current was recorded. From the area of the recorded current peak of cadmium, the number of moles of deposited metal ions was calculated; the ratio of this number to the number of moles in the solutions (10^{-9} moles) was the collection efficiency. Typical values were in the range of 10 to 20%. A check was then made as to the actual amount of mercury deposited in the first step of the procedure. If necessary, more mercury solution was admitted to the cell to obtain the optimum thickness of mercury for peak resolution. Although in principle the mercury could have been determined by anodic stripping, the currents were generally too large (over 5 mA) for the current amplifier.

B. Determination of Thin Layer Cell Sensitivity

The determination of the thin layer cell sensitivity was done with increasingly dilute solutions of cadmium. At first I tried to use copper and then lead for these measurements, but I found that it was impossible to reduce the background level of either of them below about 10^{-7} M. Copper

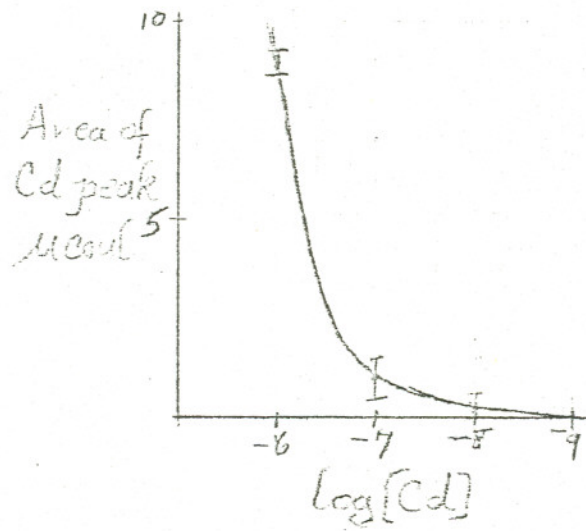
had the added problem of having its E_p in the range that the toe of the mercury peak begins to show up, which increases the background tremendously, and buries the Cu peak if it is at low level. I am sure that if one could get the background level low enough the sensitivity of Pb and Cu would be as good as that for Cd.

As can be seen from the graph (Fig. 10), if one takes $\pm 5\%$ as the acceptable margin of error, 1ml of 10^{-7} M Cd (10^{-11} moles allowing for the efficiency) is the limit of analytic applicability, and 10^{-12} moles of Cd is the limit of detectability above the background level. If the background level of about 15 micro amps could be reduced, these limits would go down accordingly.

C. Confirmation of the Theoretical Model Derived in Part II of the Theoretical Section

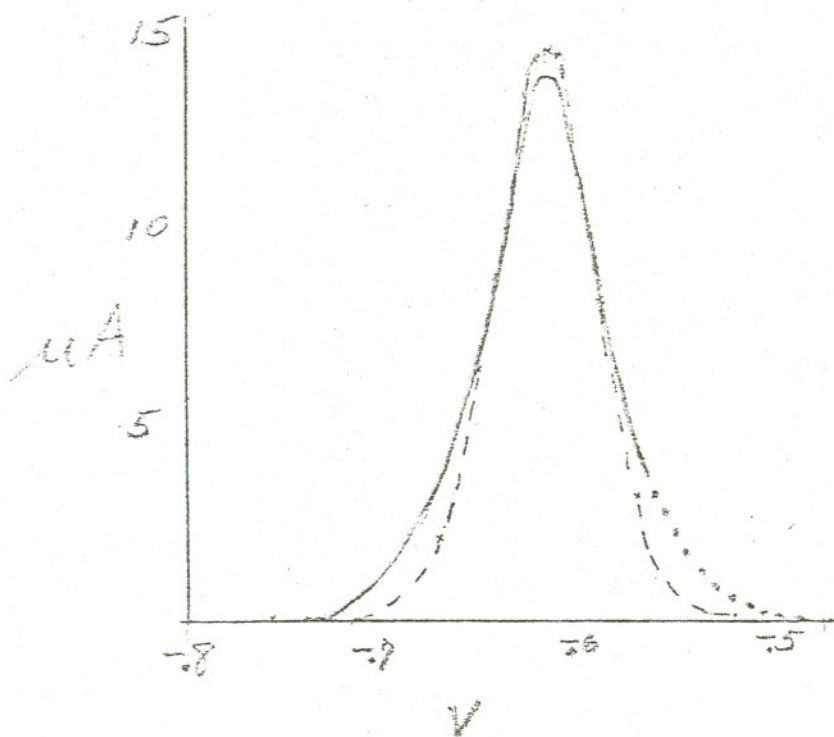
In order to confirm the theoretical model, the conditions of the model were conformed to as closely as possible. The thickness of the mercury layer was about 2.5×10^{-6} cm, the thickness of the solution layer was 2.5×10^{-3} cm, cadmium was used so that $n = 2$, and, remembering that the efficiency of the cell was about 17%, 6 mls of 10^{-6} M Cd solution was run through. The sweep rate was 50 mv/sec. The resulting curve (picture 1) is plotted in Fig. 11 against the theoretical curve for the same sweep rate, with the same volume. As can be seen the experimental peak is slightly broader and lower than the theoretical peak, which is to be expected from the sweep rate. Other runs were tried at slower sweep rates, but none of them corresponded to the theoretical curve as well as this one. At slower sweep rates other effects, such as radial diffusion out of the thin layer, begin to show up.

figure 10



Sensitivity

figure 11



— = Experimental curve
--- = Theoretical curve

Comparison of calculated
curve to actual Cd^{II}
stripping curve

D. Complexing of Metal Ions

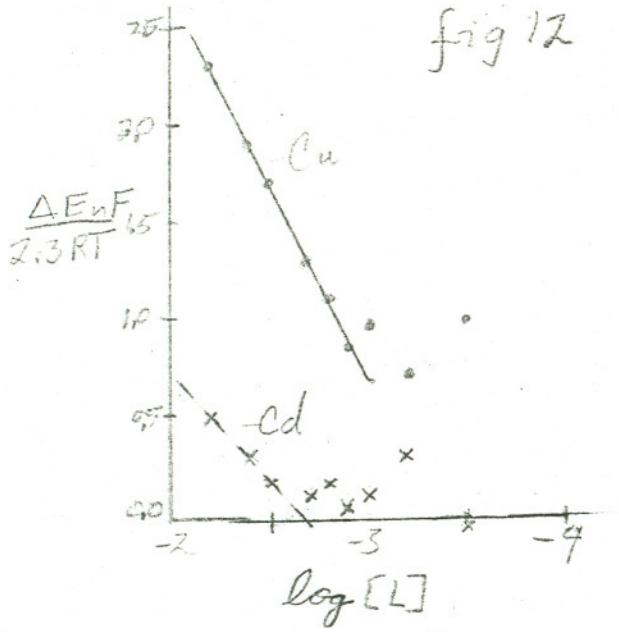
Part III of the theoretical section develops the equations necessary for the determination of the equilibrium constant, the number of complex molecules associated with each ion, and the ΔG of the reaction from the ΔE_p . The purpose of this section is to summarize the ΔE_p of some metal-ligand systems and compare the results to the values available in the literature (5).

The ligands used were chosen with the thought in mind that one of the projected uses of the thin layer cell was the study of complexing of metal ions in ground waters. It should be noted that the effects observed are independent of cell configuration.

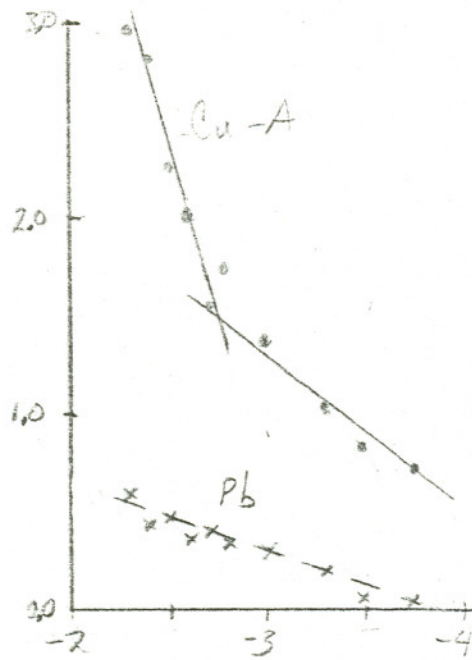
From the literature (13,14,15) it is evident that the complexing agents in natural waters were mostly organic acids formed from decomposing plant and animal material and that the K_{eq} of the metal complexes were in the $10^5 - 10^{15}$ region. Thus glycine, histidine, and tryptophan were chosen because they have K_{eq} in the correct ranges and are amino acids.

The results of the experiments are graphed in figures 12-16. Each graph plots $\frac{\Delta E_p nF}{2.3 RT}$ vs. $\log [L]$. The resulting slopes give m which, combined with equation 20, gives a value for K_{eq} . These results are tabulated in Table I. The results for Cu and Cd in histidine and tryptophan are quite good, the variation between the calculated and the tabulated is probably due to differences in the mediums used for measurements. The second copper curve (Cu-B) in tryptophan does not correspond to any value that I could find. I would guess, since the measurements were taken in a solution containing Cl^- , that it represents a mixed ligand situation. The results for Pb in histidine are not good, being two orders of magnitude off. I am not

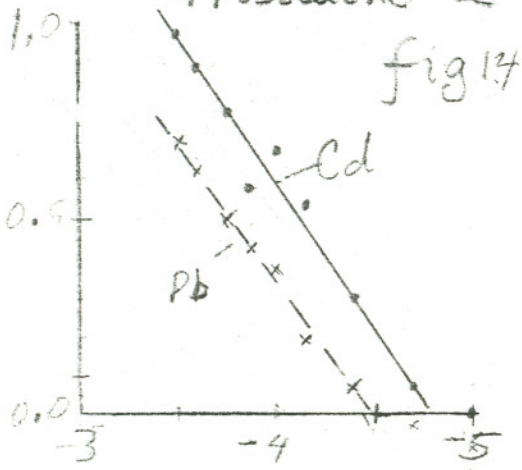
Histidine-1
fig 12



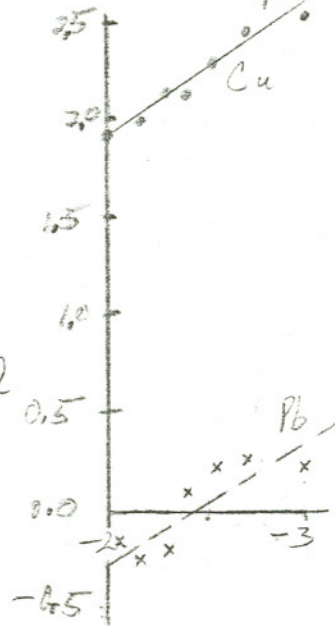
Tryptophan-1
fig 13



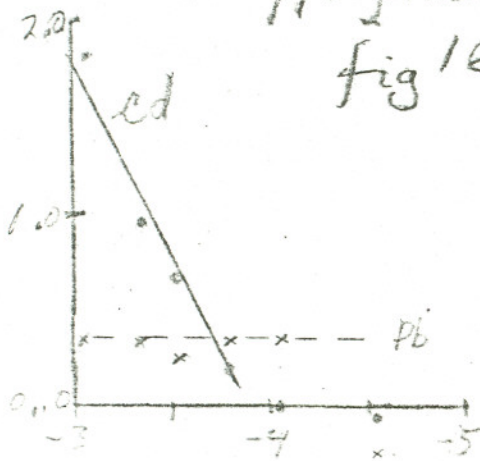
Histidine-2
fig 14



Glycine
fig 15



Tryptophan-2
fig 16



Peak Shifts with
Complexing

Table I. Complexing of Metal Ions

Metal	Ligand	Experimental m	Experimental K _{eq}	K _{eq} -Tab (5)	ΔG Reaction Kcal
Cu	His	2.03-2.11	5.8×10^8 (a)	1.7×10^8 (b)	-11.9
	Try A	3.23-4.3	1.4×10^{14} (a)	8.32×10^{14} (c)	-19.3
	Try B	1.33-1.58	3.4×10^4 (a)	not tab	- 6.2
Cd	His	.72- .83	3.0×10^4 (a)	1.3×10^4 (b)	- 6.1
	His	1.10-1.08	3.0×10^4 (a)	1.3×10^4 (b)	- 6.1
	Try	1.77-2.16	3.5×10^8 (a)	1.2×10^8 (b)	-11.6
Pb	His	.65- .77	1.6×10^4 (a)	6.9×10^6 (d)	- 5.7
	Try	.35- 45	8.0×10^2 (a)	not tab	- 4.0
	Try	0	0	not tab	0

a. 10^{-1} M NaCl

b. 10^{-2} M

c. .3 M

d. .15M KNO₃

sure why, but the difference between .15M KNO_3 and .1M NaCl may have a fair amount to do with it. There are no tabulated values for Pb tryptophan complexes available so I have no comparison for my K_{eq} . Intuitively I would guess that it is quite far off because the other two metal complexes with tryptophan were several orders of magnitude larger than their histidine complexes. The Pb histidine complex equilibrium constant is 6.9×10^6 tabulated or 1.6×10^4 from my own work.

The behavior of the metal glycine complexes is peculiar. The slope of the Cu line is between -.54 and -.87 and the slope of the Pb line is between -.36 and -.93. After reviewing my experimental procedures I am convinced that the measurements recorded are not artifacts, but real. But the results are clearly abnormal. I would guess that I am observing some process other than simple complexing. Both Cu(I) and Pb(II) are not simple ions in Cl^- solutions; PbCl_2 is rather insoluble, and both Pb and Cu complex with Cl^- and glycine, giving the possibility of mixed ligand situations. Since glycine is the weakest complexing agent studied, this second possibility may also explain why this kind of behavior was only observed in this series of experiments.

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