

Electrochemical and Kinetic Studies Of  
Iron III And Fulvic Acid 'Redox Equilibria'

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ABSTRACT

ELECTROCHEMICAL AND KINETIC STUDIES OF  
IRON(II) AND FULVIC ACID "REDOX EQUILIBRIA"

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Fulvic acid extracted from a Prince Edward podzol soil was prepared and purified using 0.5N sodium hydroxide extraction and cation exchange demetallation.

A detailed qualitative investigation of iron(II) redox interaction with fulvic acid has been carried out using several polarographic techniques (dc and differential pulse polarography and cyclic voltammetry) at several pH levels at 25°C using a carbon electrode. This investigation was carried out in order to answer the fundamental question of the usefulness of equilibrium methods in the theory of metal fulvate redox interaction.

Fe undergoes redox chemistry of a rational sort on complexing with fulvic acid (FA), but it does not behave in a simple reversible fashion in part, because of adsorption.

Following these results we studied kinetics of the release of iron from fulvic acid as a function of "initial" oxidation state of the Fe added. The data show according to the systems studied two and three kinetically distinguishable components for the release of Fe from FA. In comparing systems studied, data for Fe(II)/Fe(III)-FA system revealed three components, one of which reacts quite rapidly, faster than kinetics of initial Fe(III) present in comparison to two components for the Fe(II)-FA system. Thus, the system Fe-FA in presence of O<sub>2</sub> does not appear to have reached a redox equilibrium.

## RESUMÉ

L'acide fulvique obtenue à partir d'un podzol de l'Ile du Prince Edouard fut extraite à l'aide d'une solution d'hydrate de soude 0,5N, et purifiée par une résine cationique.

Nous avons entrepris une étude qualitative détaillée de la réaction d'oxydoréduction entre Fe(III) et l'acide fulvique à l'aide de diverses techniques polarographiques (polarographie à tension continue, à impulsion différentielle, et voltamétrie cyclique), sous différents pH à 25°C, à l'aide d'une électrode de carbone. Le but de cette étude était de répondre à la question fondamentale de l'utilité des méthodes d'équilibre dans la théorie de la réaction d'oxydoréduction des fulvates métalliques.

En se complexant avec l'acide fulvique (FA), le fer doit logiquement se soumettre aux lois de l'oxydoréduction. Mais il ne se comporte pas tout à fait comme dans une simple réaction réversible, étant donné un phénomène d'adsorption.

Suite à ces observations, nous avons donc étudié la cinétique de la libération du fer de l'acide fulvique comme une fonction de l'état d'oxydation "initial" du fer ajouté. Selon le système étudié, les données montrent deux et trois composants cinétiquement distincts pour la libération du fer de FA. En comparant les systèmes étudiés, les données obtenues révèlent, pour le système Fe(II)/Fe(III)-FA, trois composants dont l'un réagit très rapidement, plus rapidement que la cinétique du Fe(III) initialement présent; et deux composants pour le système Fe(III)-FA. Ainsi, le système Fe-FA, en présence de O<sub>2</sub>, ne paraît pas atteindre un équilibre d'oxydoréduction.

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## I. INTRODUCTION

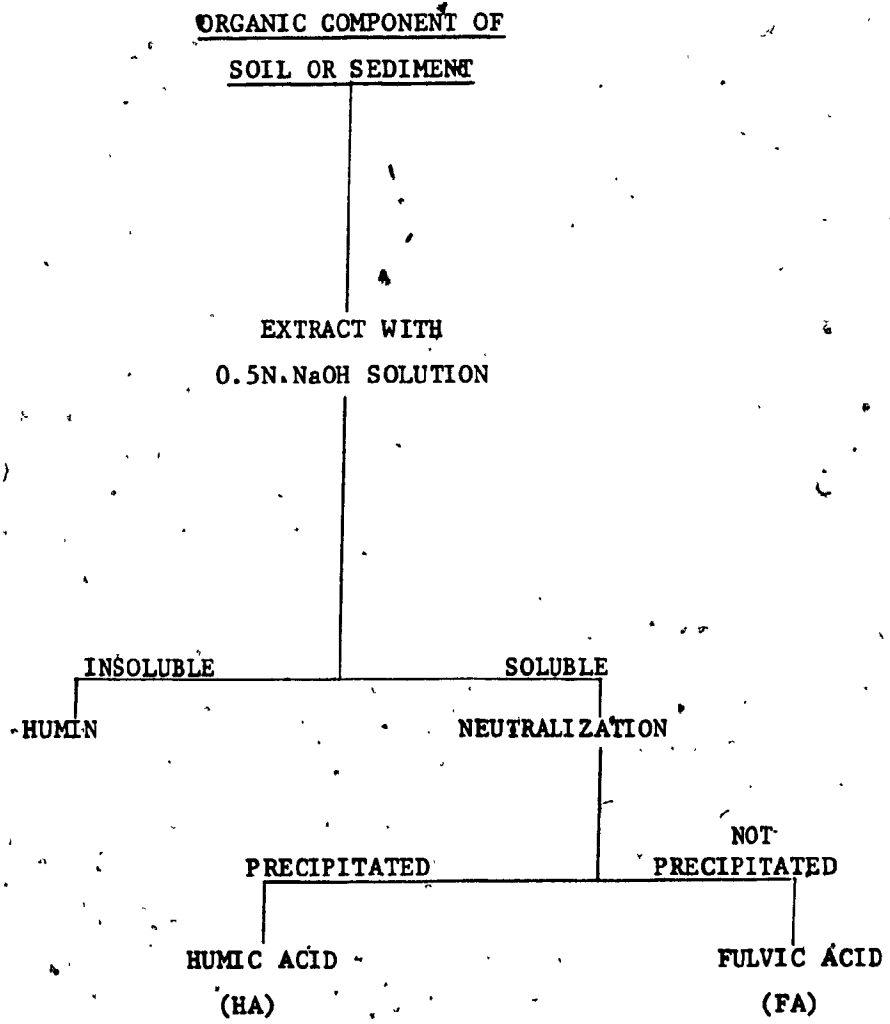
### A. Background

In recent years much attention has been given to the study of the complexation of heavy metals to Humic substances (1,2,3) including the soluble fulvic acid fraction. The studies of soil organic matter fulvic acids are of interest because of (i) a possible role in altering the geochemical mobility of metal ions (4,5,6), (ii) the effect on biological availability or toxicity of complexed versus uncomplexed metal ions (7,8) and (iii) its effect on water treatment processes for removal of metal ions (9).

Humic substances are a broad class of naturally occurring compounds which result from modification of plant derived organic matter by chemical and microbial action in soil or in our aquatic environment (1,2). These diagenetic compounds are categorized as "geopolymers".

Fractions of soil organic matter are known as humic acid, fulvic acid and humin, and are distinguished as represented in figure (1).

FRACTIONATIONS OF SOIL ORGANIC MATTER



Background (Cont'd)

Based on their solubility in alkali and acid, humic substances are partitioned into three main fractions:

- i) Humic acid HA which is soluble in dilute alkali but is precipitated by acidification of the alkaline extract.
- ii) Fulvic acid, which is that humic fraction which remains in solution when the alkaline extract is acidified, that is, it is soluble in both dilute alkali and dilute acid.
- iii) Humin which is that soil organic fraction that cannot be extracted from the soil or sediment by dilute base and acid.

It becomes apparent from the analytical data published in the literature (6) that structurally these three humic fractions are similar. They differ mainly in molecular weight, and also to some degree in ultimate analysis and functional group content.

This thesis extends work on a well characterized FA which was introduced by Schnitzer (6), who established by chemical degradation followed by separation and identification procedures, that humic substances have a variety of single ring aromatic phenol carboxylates which suggest the molecules have high degree of aromaticity and cannot be structurally homogeneous.

Thus it seems reasonable to consider our fulvic acid a mixture. Based on Schnitzer's reports (6,13), one plausible component of such a mixture could be represented by figure 1B.

Fulvic acid functional groups which can be protonated and deprotonated in the pH range (3-9) common to natural waters include carboxylates and phenols. These enable the molecule to behave as a polyelectrolyte (8,9), which is significant to binding and mobilization of metal ions, nutrient ions and pesticides in soils and in fresh water. With these acidic functional groups, our material could aggregate by H-bonding. In fact, Schnitzer and Khan (13), have suggested a structure for fulvic acid shown in figure 2. Perhaps a mixture of components like the one in figure 1B aggregated as in figure 2, comes closest to characterizing fulvic acid.

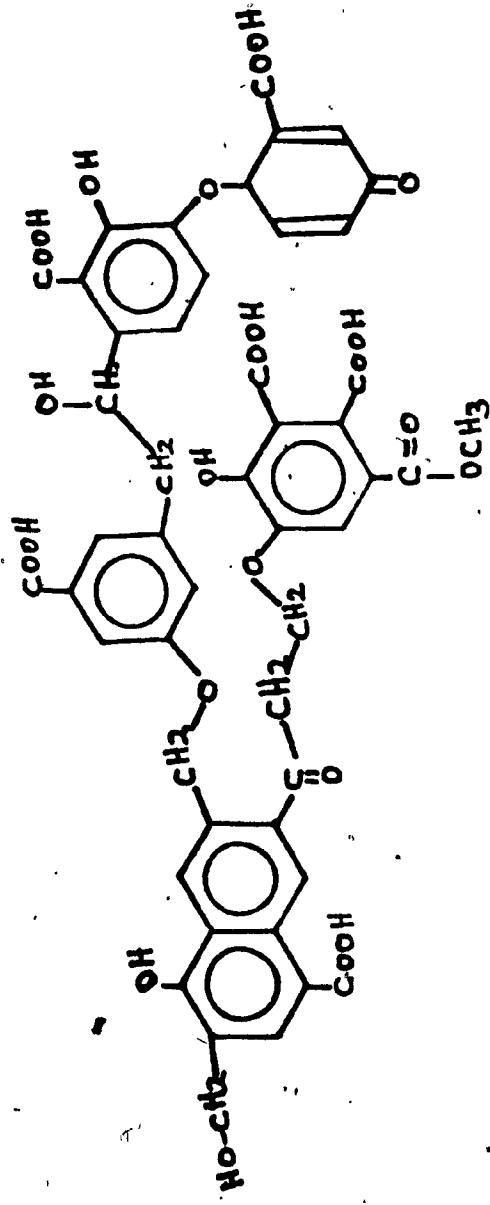


Figure 1B. A speculative sketch of a plausible component of fulvic acid mixture.

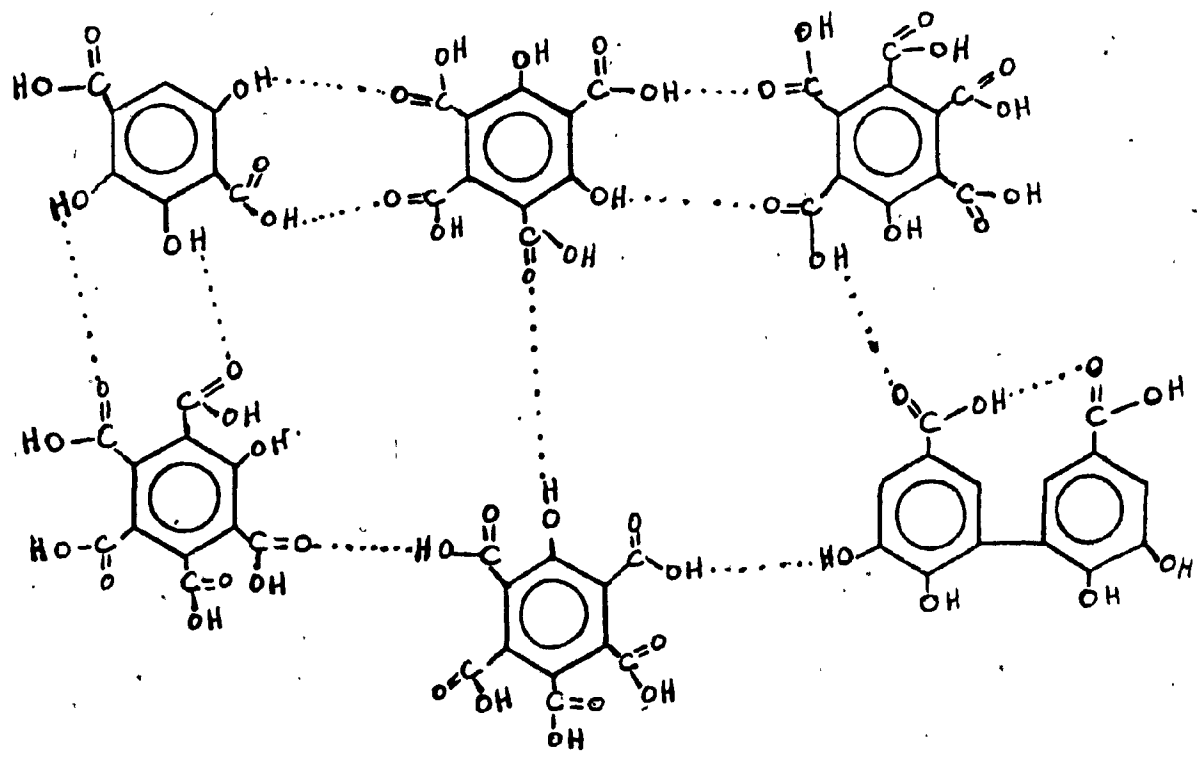


Figure 2. Structure of fulvic acid proposed by Schnitzer and Khan.

## B. Function Group Analysis

Schnitzer and Gamble (6) reported the functional group analysis for fulvic acid on a per gram basis, shown in Table 1, from several methods used to identify oxygen containing functional groups (10,51). These include total acidity, carboxyl group content, carboxyl group content, hydroxyl group content, both total acidity phenolic and quinone and methoxyl group contents.

Recently high field NMR evidence has improved understanding of the structure of humic substances and made it clear that carbohydrates and alkali residues had been somewhat underestimated in degradation studies. A careful NMR study of material, the "contech" FA distributed by contech, ETC Ottawa and prepared in our group has been carried out by Gamble et al (21).

The functional group analysis is very close to that given by Schnitzer (51). It is shown in Table 1 along with Schnitzer values which are used in this thesis for calculations.

Fulvic acid has three types of functional groups that should influence the metal fulvic acid complexes. (i) Phenolic OH groups. (ii) Type I carboxyl groups, which are probably ortho to the phenolic groups and (iii) less acidic Type II carboxyl groups, which are meta to the phenolic groups or on non-OH bearing rings. There are also two types of reactions between the metal ions and the fulvic acid molecule.



TABLE 1

OXYGEN-CONTAINING FUNCTIONAL GROUPS IN HUMIC SUBSTANCES (meq/gm)

<u>Type of Material</u>	<u>Phenolic OH</u>	<u>Alcoholic OH</u>	<u>Ketonic C=O</u>	<u>CO<sub>2</sub>H</u>	<u>Quinonoid C=O</u>	<u>Methoxyl</u>
HA	3.3	1.9	1.2	4.4	1.0	0.3
Humic	2.2		3.1	3.1	2.0	0.4
FA	3.9	4.0	1.4	8.1	0.6	0.4
FA NMR	3.3			7.7		

I. Outer Sphere electrostatic binding of ions by a polyanion without displacement of water from the ion.

II. Inner Sphere chelation probably at bidentate sites having a salicylic acid type structure or dicarboxylate sites similar to O-phthalic (12). Schnitzer (6) reported a number average aggregate weight of 951 for our fulvic acid, but recent studies by Wilson and Weber (11) alter assumptions (with respect to small ions) in the calculation and lower this value to approximately 600. This sort of uncertainty results in our choice to characterize fulvic acid in terms of its function, which encompasses interaction with protons and metal ions, rather than structure.

There are many variables that can affect the strength of association between fulvic acid and metal ions. Some reflect real variations, some experimental difficulty, see Table 2. Complexation effects may be explained by considering  $H^+$  competing with the metal ions for anionic binding sites on the fulvic acid and  $OH^-$  competing with fulvic acid for the cationic metal ion. As the pH increases the fulvic acid molecule becomes more available for complexation and the metal ion becomes less available. However, at an intermediate pH complexation is most favored between the metal ions and the fulvic acid. The possible variation in configuration is presented in figure 2B. The complexation properties of fulvic acid vary from sample to sample, though similarities are substantial (13,11). Fulvic acid derived from soil (SFA) has largely the same metal complexing properties as fulvic acid extracted from fresh water (WFA). The present study employs soil fulvic acid, because it is less difficult to extract than water fulvic acid and a large well characterized sample is possible.

TABLE 2

FACTORS THAT INFLUENCE APPARENT FULVIC ACID -  
METAL ION COMPLEXATION

THE SOURCE OF FULVIC ACID

THE METHOD OF ISOLATION

THE CONCENTRATION OF FULVIC ACID

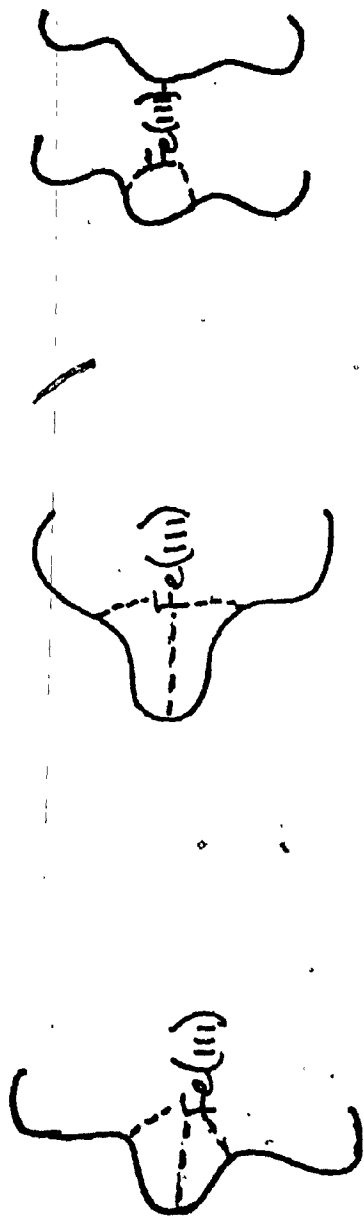
THE IONIC STRENGTH

TEMPERATURE

pH (AFFECTS BOTH FULVIC ACID AND METAL IONS)

THE METHOD OF ANALYSIS FOR COMPLEXES

THE METHOD OF DATA MANIPULATION AND STABILITY CONSTANT CALCULATION



(a)

(b)

(c)

Figure 2B. Possible configurations of FA-metal complexes:  
 (a) and (b) FA-metal complexes with different degree of flexibility,  
 (c) FA-metal bridging.

Techniques avoiding separation are employed in this study, to distinguish between free and complexed metal ions in situ and to measure their labilities. Buffle and Greter (3) used several polarographic techniques to study the factors that influence the kinetic aspects of fulvic acid complexing with lead at pH6. They found a reversible wave and obtained evidence that the fulvic acid complex adsorbed on the electrode.

In a more detailed study Wilson et al (10) investigated metal binding of fulvic acid by Anodic Stripping Voltammetry and differential pulse polarography. From the data obtained for the measurements of the concentration of Aquo ions in the presence of fulvic acid conditional stability constants were estimated. The measurements were in agreement with those of other researchers (3,5,11) and also indicative of fulvic acid adsorption on the electrode.

Langford et al (17) in kinetic studies, filtration experiments and light scattering found that the presence of fulvic acid caused an increase in particle size in a precipitating hydrous ferric oxide solution at pH6. As well, the organic material actually increased the speed with which iron reacted with ferrozine to form a light absorbing complex with iron (11) in comparison to corresponding iron hydrous oxides.

In another kinetic study (19) at least two components were found for the fulvic acid complex at pH4. A fast component which is probably monomeric Fe(III) species and a slow component which is at least polymeric and probably colloidal.

Szilgyi (18) reported that Fe(III) ions in humic acid solutions are partially reduced to ferrous ions and that they are fixed by the cation exchange action on the humic acids. He found that Fe(III) is reduced by the humic material between pH1 and pH5 and that the reduction varies at pH3 according to the quantity of ferric ion used. Similarly, Skogerboe and Wilson (14) have reported reducing properties of fulvic acids with respect to iron and have suggested that redox equilibrium is established in samples aged for a few hours.

### C. Purpose and Scope of the Present Investigation

Since Gamble's work on acidometric titration (6) a theory of cation complexation equilibrium titration of fulvic acid has been available (6,21). This theory will be reviewed below. The emphasis on the role of FA in nature has been directed to metal complexation which can be treated by the methods of Gamble and in fact, Gamble's approach is necessary to be able to consider correctly competition among bound species especially metal ions. But, work such as Skoegerboe and Wilson (14) shows that FA's are similarly implicated via redox chemistry. In fact, a field study by Khan (20) seems to show that the redox properties of FA dominate metal ion mobilization by organic materials in a stream. In order to deal with this, we might seek an analog of the Gamble's approach for redox equilibria if reactions do, in fact occur sufficiently rapidly to allow equilibration on the time scale of experimental titration. Skoegerboe and Wilson (14) have suggested this approach should have good prospects. The main purpose of this study is to explore the reversibility of redox equilibria.

It seemed to us that the implication of the study by Wong, Langford and Underdown (17) was that electron transfer reactions involving Fe(II)/Fe(III) and FA would not equilibrate rapidly. This implication is contrary to the suggestion of Skoegerboe and Wilson (14), thus, the precursor to a development of a detailed theory for redox behaviour of FA's intended to parallel Gamble's theory of complexation is evaluation of the kinetic features of electron transfers. It is necessary to know what limits will be imposed on the use of electrodes to monitor "titrations".

The methods we adopted for this study include Voltammetry because of its favourable characteristics for studies at low concentrations and the techniques of kinetic spectrometry developed earlier in this group (17,32).

Among voltammetric methods studied we used differential pulse polarography because of the high sensitivity available and cyclic voltammetry because of its power to unravel coupled chemical electrochemical processes. The kinetic analyses are complimentary to the experiments of Wong (34). The point here was to explicitly examine the effect of an initial mixing of iron oxidation states. The first reagent is ferrozine which is a reagent for Fe(II).

The choice of ferrozine was made because it is an Fe(II) specific colorimetric reagent and it has been used earlier (19,34,35) for kinetic studies to differentiate hydroxy-iron(III) polymer from iron(II) in which two components were observed. Ferrozine offers optimum sensitivity and stability, it is inexpensive, and is highly water soluble this being ideally suited for directly determining Fe(II) in water.

Hopefully the results obtained by these methods would shed light on the mechanism of the redox reaction and aid in determining the number and types of Fe(III) binding sites on the fulvic acid molecule and their relative reducing "power" and "rate". In particular, earlier studies have shown that 100% of Fe bound by FA could be recovered by either an Fe(II) or an Fe(III) colorimetric reagent. This suggests FA can accept or supply electrons as necessary, when reactions are "forced" by a reagent favouring one or the other Fe oxidation state. Our questions are the two difficult ones: (1) What is the best description of the oxidation



state of Fe bound to fulvic acid, and (2) What is the rate of electron transfer equilibrations.

In a study by Visser (25) redox potentials of humic acids from a tropical Sphagnum peat deposit were obtained with a platinum and hydrogen gas electrode upon titration with potassium and Ferric-cyanide. The redox potentials ranged from 0.38 to 0.32 V and depended on the depth at which the humic acids were recovered.

In another study, Senesi (26) found two types of Fe(III) sites on the humic and fulvic acid molecules. Their EPR studies gave information on site symmetries and on the resistance of Fe(III) to reduction at two types of sites. They suggested the following:

- I. Fe(III) is strongly bound and is protected by octahedral or tetrahedral coordination. In this form iron exhibits considerable resistance to complexation by known sequestering agents and to reduction.
- II. Fe(III) is absorbed on external surfaces of organic matter, it is weakly bound and is easily complexed or reduced.

In this case the resistance to reduction is a masking phenomenon which may simply imply non lability (24).

## II. THEORETICAL

### A. Formulism of the Binding Equilibrium Function

In 1970 Gamble and Schnitzer (6), formulated a theory of acid-base titration (21), they gave a suitable formulism for analysis of binding of an ion by a mixture (6). It is of importance to develop this theory in modest detail to indicate the goals that would be set for an equilibrium theory of redox reactions of FA. Also we need to see the form of a theory which can treat FA binding equilibria although we will not need the details for the present study. The case chosen is the binding of Cu(II) to chelating sites in the mixture as studied by Gamble, Underdown and Langford (12).

The mixture under analysis is assumed to provide bidentate sites for binding metal in four ways. 1. Monodeprotonated "Salicylic" type sites, 2. Orthodicarboxylate type sites. 3. Sites with two carboxylates on the same polymer molecule but not on the same ring and 4. Carboxylate groups from two hydrodynamically distinct ligands. The latter case can produce special type of "chelate" site if the organic parts can interact.

When these four contributing types are considered, one can write for the mixture.



$$\bar{K} = \frac{M_c M_H}{M_{SH} M_m} \quad (2)$$

Where M = a molal concentration

And the subscripts are:

c = the complex

m = free metal ion

The parameter defined is:

$\bar{K}$  = the equilibrium function and is defined by a Mass action expression applied to the mixture of chelating sites. It must be remembered that  $\bar{K}$  is not an equilibrium constant. In fact, a number of workers have shown experimentally that  $\bar{K}$  is anything but constant.

If one recognizes that the bar over the  $K$  in the (2) above equation reflects the averaging over components of the mixture, then the expression for any (ith) component of the mixture can be given by:

$$K_i = \frac{M_{Cl} M_H}{M_{Si} M_m} \quad (3)$$

The above expression is related to thermodynamic and/or conditional equilibrium constants since it deals with individual components of the mixture.

The material balances are expressed as:

$$M_c = \sum_i M_{Cl} \quad (4)$$

$$M_{SH} = \sum_i M_{SiH} \quad (5)$$

When the above equations are combined with equation (2) (which is the experimentally accessible expression) one can derive the expression given the form:

$$\bar{K} = \frac{\sum_i K_i M_{SiH}}{\sum_i M_{SiH}} \quad (6)$$

The above equations define  $\bar{K}$ . This means that the experimental function is a weighted average over constants for the components of the mixture.

Now, since fulvic acid is a polyelectrolyte it is useful to factor the  $K_i$  values for components into intrinsic ( $K_i^0$ ) and electrostatic ( $\Delta G_i^{el}$ ) terms as in the following equation:

$$K_i = K_i^0 e^{-(\Delta G_i^{el}/RT)} \quad (7)$$

Transforming the variable in equation (6) into mole fraction units, then  $\bar{K}$  can be given the form:

$$\bar{K} = \frac{1}{X_{SH}} \sum_i K_i^0 e^{-(\Delta G_i^{el}/RT)} (\Delta X_{SH})_i \quad (8)$$

When  $X_{SH}$  = the mole fraction of ligand sites in a monodeprotonated form.

Considering the above equation leads to the idea that  $\bar{K}$  may not be only an average, but indeed very well approximated by a continuous function of  $X_{SH}$  for three reasons: (a) the coefficient  $1/X_{SH}$  (b) the relatively large number of individual  $K_i$  values suggested by Schnitzer's analysis are constituents for which separate titration equivalence points cannot be identified, and (c) the weakly continuous increase in electrostatic effects as a charge accumulates on the polymer molecule during titration.

It is postulated that  $\bar{K} = \bar{K}(X_{SH})$ .

The final theoretical equation is thus given by:

$$\bar{K} = \frac{1}{X_{SH}} \int X_{SH} K dX_{SH} \quad (9)$$

Notice that  $\bar{K}$  is directly accessible from experiment but is not a constant in any sense!  $K$  is the quantity related to the thermodynamic or conditional equilibrium constants and Gibbs free energies and is a differential quantity in this model.

One could easily imagine a similar theory where  $\bar{K}$  is replaced by  $\bar{E}$  and  $K_i$  by  $E_i^0$ , then the analysis would follow the Nernst equation. This

will be useful if redox equilibration is sufficiently rapid.

### B. Polarographic Analysis Method

For the redox analysis of the reduction of Fe(III) by fulvic acid the derivation of the expression for a polarographic wave obtained by differential pulse polarography and cyclic Voltammetry is employed.

According to theory of polarography, when the applied potential at the electrode surface becomes more negative than the equilibrium potential of the solution to be analysed, a reaction occurs at the electrode and takes the form:



Where

O = Species Oxidized in solution

R = Species Reduced at the electrode

n = number of electrons involved in the reaction

The concentration of O at the electrode  $C_o$  ( $x = 0$ ) becomes less than the initial concentration in the bulk solution  $C_o^0$  and the current  $i$  is controlled by the rate of Diffusion of O to the electrode. Thus the "Rate" of diffusion =  $D_o \frac{\Delta C_o}{\Delta X}$

Where

$D_o$  = Diffusion coefficient,  $\text{cm}^2/\text{sec.}$

$\Delta C_o = C_o^0 - C_o(x = 0)$ ,  $\text{mol}/\text{cm}^3$ .

$\Delta x$  = Distance from the electrode to a point  $x$  in solution where O equal  $C_o^0$ , cm.

If  $C_0$  ( $x = 0$ ) is equal approximately to zero (i.e. the potential strongly favours reduction), the Ilkovic equation for the diffusion limiting current may be derived (32).

$$i_d = 607 n m^{2/3} D_0^{1/2} t^{1/6}$$

Thus the average current is merely six-sevenths of the maximum current.

$n$  = number of electrons involved in the reduction

$m$  = the rate of mercury flow from the DME capillary  
(in mg/sec)

$D_0$  = diffusion coefficient of reducible species  
(in cm<sup>2</sup>/sec)

$t$  = time necessary for the formation of one drop of mercury (in sec)

$C_0$  = concentration of reducible substance (in mol/cm<sup>3</sup>)

a. The Polarographic Wave

The above equation is based on the assumption that  $C_o(x=0)$  is negligible (practically = 0) before drop dislodgement. In the event  $C_o(x=0)$  is not equal to zero the Ilkovic equation becomes,

$$\bar{i} = 607 n m^{2/3} D_o^{1/2} \tau^{1/6} \{C_o - C_o(x=0)\} \quad (25^\circ\text{C}) \quad (2)$$

$$\text{or } \bar{i} = \bar{i}_d - 607 n m^{2/3} D_o^{1/2} \tau^{1/6} C_o(x=0) \quad (3)$$

Considering the reaction  $O + ne \rightleftharpoons R$  if we define  $C_R$  as  $[R]$  at electrode surface,

$$C_o - C_o(x=0) = C_R(x=0)$$

Therefore,

$$\bar{i} = 607 n m^{2/3} D_R^{1/2} \tau^{1/6} C_R(x=0) \quad (4)$$

From equation (3) and (4)

$$\frac{C_o}{C_R}(x=0) = \frac{D_R^{1/2}}{D_o^{1/2}} \frac{\bar{i}_d - \bar{i}}{\bar{i}} \quad (5)$$

Applying the Nernst relationship, for the case where electrode reaction is rapid,

$$\begin{aligned} E_{O/R} &= E_{O/R}^o + \frac{0.059}{n} \log \frac{D_R^{1/2}}{D_o^{1/2}} \frac{\bar{i}_d - \bar{i}}{\bar{i}} \\ &= E_{1/2 O/R} + \frac{0.059}{n} \log \frac{\bar{i}_d - \bar{i}}{\bar{i}} \quad (25^\circ\text{C}) \end{aligned} \quad (6)$$

Where

$$E_{1/2 O/R} = E_{O/R}^o + \frac{0.059}{n} \log \frac{D_R^{1/2}}{D_o^{1/2}}$$

$E_{1/2}$  is called the half wave potential and is used to characterize the polarographic wave. If electron transfer is slow the above equation will not characterize the wave. In such case the wave will be more

"extended". The observed  $E_{1/2}$  for reduction will be more cathodic.

b. Differential Pulse Polarography (DPP)

The differential pulse polarographic technique originally developed as an off shoot of square wave polarography, consists of superimposing a fixed height potential pulse at a regular interval on a slowly stepped potential as associated with dc polarography. The pulse is repeated for each drop and is synchronized with the period of maximum growth of the mercury drop, as shown in figure 3a where a Hg drop electrode is used.

The dpp instrumentation then samples the current flowing into the working electrode twice during each operating interval by use of electronic switching and crystal timing. The first current sample taken just before the application of the potential pulse would be equivalent to that obtained in the normal d.c. polarography. Immediately after the sample taking process, a sudden pulse of potential, usually between 5 and 100 mv is applied to the electrode. The application of this sudden change in potential produces a concurrent change in the current flow. First, additional current must flow to change the double layer capacitance of the electrode to the new applied potential. Simultaneously an additional current may flow if the applied potential has changed to a potential where the equilibrium between O and R is shifted.

The pulse potential is maintained for a period of time long enough to allow the capacitance current to decay to a low value. During this time the faradaic current also decays somewhat but still does not reach the diffusion-controlled level. At the end of this period, a current sample is taken again. The difference between these two current samples (developed by applying the two signals stored in the memories to a differ-



ential amplifier) is then amplified and presented to the output of the system. This difference current-curve, which is proportional to the concentration of  $O$ , has the appearance of a peak rather than the usual polarographic step as shown in Figure 3b.

The dpp technique has many advantages over the conventional dc method. The most significant is that the influence of the capacitance current is minimized by the pulsing and sampling process, providing for peak relationships which improve resolution and for a considerable lowering of the detection limit for the concentration of  $O$ .

c. Rapid-Sweep Voltammetry

In conventional voltammetry the potential is changing in a slow linear ramp over a relatively long period of time, so that, in the intervals during which the current is measured, the potential can be considered stationary. In single and cyclic voltammetry techniques, the  $i$ - $E$  relationship is obtained by the use of a rapid potential sweep. The sweep rate is usually of such a magnitude that the full range of potential (range of interest) can be covered within the lifetime of one Hg drop when the dme is used. As such, the dme can be considered as a stationary hanging mercury drop electrode (HMDE). In general, these techniques utilize stationary electrodes (e.g., HMDE or solid electrodes).

When discussing voltammetry with continuously variable (rapid-sweep) potential, a distinction should be made between the  $i$ - $E$  relations obtained in single-sweep, multi-sweep and cyclic-sweep approaches.

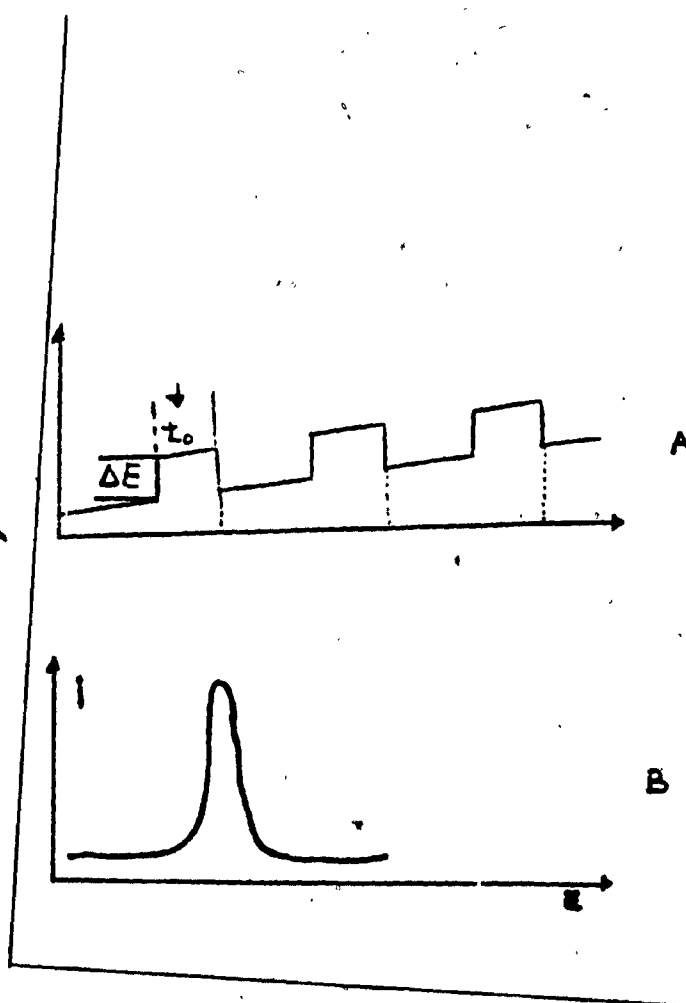


Figure 3. A. Potential Program for several drops in DPP  
B. Current-Potential curve obtained

d. Single-Sweep Voltammetry

The method derives its name from the fact that each drop (dme) during its life receives only one impulse of polarization potential, usually a ramp. The production of very rapid voltage sweeps necessitates the use of electronic impulse generators which permit good linearity and variation of the sweep frequency within wide limits. For example, a frequency of 50Hz with an amplitude of 2 volts corresponds to a sweep rate of 100 volts/second. The saw-toothed voltage must also have exact linearity, besides being as constant as possible in duration and amplitude.

Whereas in ordinary polarography the diffusion current is independent of the speed of the voltage sweep, in rapid-sweep polarography the peak current is influenced by the rate of voltage sweep, as will be shown later. In addition, the choice of timing at which the impulse is applied to the dme is of utmost importance. In order to obtain good reproducible results, the impulse and drop-time must be exactly synchronized. This is achieved electrically by applying the potential with regular controlled intervals (delays) as shown in Figure 4a.

Minimization of charging current is obtained by applying the potential pulse towards the end of the drop life. This consideration is not of interest when stationary electrodes are used, as in the present case.

If one considers the reduction of an analyte in an unstirred solution containing an excess of background electrolyte, so that linear diffusion is maintained, and the Nernst relation is assumed to be applicable to the electrode process the following analysis applies. The sweep voltage can be represented by:

$$E = E_1 - Vt \quad (7)$$

Where

$E_i$  = initial potential (volts)

$V$  = rate of potential sweep (volts/sec.)

$t$  = electrolysis interval (sec.).

No reduced substance is assumed to exist at  $t = 0$ ; hence, with the exception of the variable potential  $Vt$ , conditions are identical to those for conventional polarography.

The diffusion problem for rapid-sweep polarography was first solved and translated into a current potential relationship independently by Randle and Sevcik (27,28). The  $i$ - $E$  curve exhibits a maximum or peak, and the peak current is given by:

$$i_p = Kn^{3/2} A D_o^{1/2} C_b V^{1/2} \quad (8)$$

Where

$i_p$  = peak current (amperes)

$A$  = electrode surface area ( $\text{cm}^2$ )

$K$  = Randle-Sevcik constant

$C_b$  = concentration of analyte (moles).

It should be noted that the peak current ( $i_p$ ) is directly proportional to the concentration and the sweep rate.

The  $i$ - $E$  curves obtained from single-sweep polarography are commonly called peak polarograms, and the technique became known as peak voltammetry. This is due to the nature of the electrode process. In this technique, the full process occurs within the lifetime of a single mercury drop or at a stationary electrode. Consequently, as the potential sweep passes the peak potential ( $E_p$ ), the electrode process results in a depletion

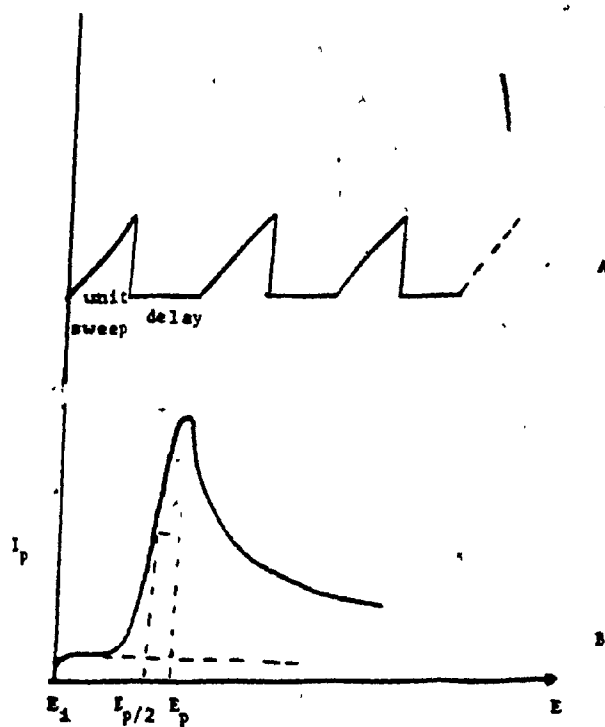


Figure 4. A. Potential Program applied with regular controlled intervals in RSP

B. Current-Potential curve obtained

of depolarizer (analyte) in the vicinity of the electrode so that the system displays a current drop, as can be seen in Figure 4b.

The single-sweep polarogram may be characterized by the peak potential ( $E_p$ ) or the half peak potential ( $E_{p/2}$ ). The latter is defined as the potential at which  $i = i_{p/2}$ . The relationships between charge transfer and peak height, location, and shape and their correlation to the polarographic half-wave potential, were derived by Chivot, Devynick et al (29) as follows:

For reversible processes at 25°C,

$$E_p = E_{1/2} - \frac{0.029}{n}V \quad (9)$$

$$E_{p/2} = E_{1/2} + \frac{0.028}{n}V \quad (10)$$

$$E_p - E_{p/2} = -\frac{0.057}{n}V \quad (11)$$

$$\text{or } |E_p - E_{p/2}| = \frac{0.057}{n}V \quad (12)$$

It can be seen from Equation (12) that the peak polarogram of a reversible system is sharp, spanning a voltage range of roughly 0.12 volts for a one electron transfer system. The peak potential in a reduction process is 0.029/n volts more cathodic than the corresponding  $E_{1/2}$ , and the half peak potential is 0.028/n volts more anodic. In practice, the peak for a reversible process at a stationary electrode is fairly broad and extends over a range of several millivolts. Hence, it is sometimes convenient to use the half peak potential (Equation (10)) as a reference point (30), although this has no direct kinetic or thermodynamic significance. In addition, it has been shown that the polarographic  $E_{1/2}$  can be estimated from a reversible stationary electrode polarogram, based on

the fact that it can be found at a point 85.17% up the cathodic slope (28).

The equations for totally irreversible systems are much more involved, and no simple relationship exists between  $E_p$  and  $E_{1/2}$ . One has to consider the rate of electron transfer and its relationship to the rate of potential sweep, etc. For simple quasi irreversible cases, it has been shown (31,32) that one obtains:

$$E_{p/2} - E_p = \frac{0.048}{\alpha n} V \quad (13)$$

where;  $\alpha$  = charge transfer coefficient (rate). It can be seen that as  $\alpha$  decreases the peak polarogram becomes more spread out and rounded at the maximum.

Finally, the Randle-Sevcik constant,  $K$  in Equation (8) has been shown to be a function of the experimental parameters, i.e., electrode type and shape, cell structure and the nature of analyte and supporting electrolyte. Consequently,  $K$  has a range from  $2 \times 10^5$  to  $3 \times 10^5$  coulombs/(volt)<sup>1/2</sup>.

#### e. Cyclic Voltammetry

In cyclic voltammetry, the potential decreases at the same rate as it increases and results in a triangular wave as shown in Figure 5a. Two polarograms are thus produced, one representing reduction and the other oxidation, with both occurring during one unit sweep or cycle. Each polarogram is, of course, the same as would be obtained from single-sweep voltammetry. However, the height and position of the anodic (oxidation) peak of the polarogram will depend on the switching potential,  $E_{sw}$ , being applied, as shown in Figure 5b.

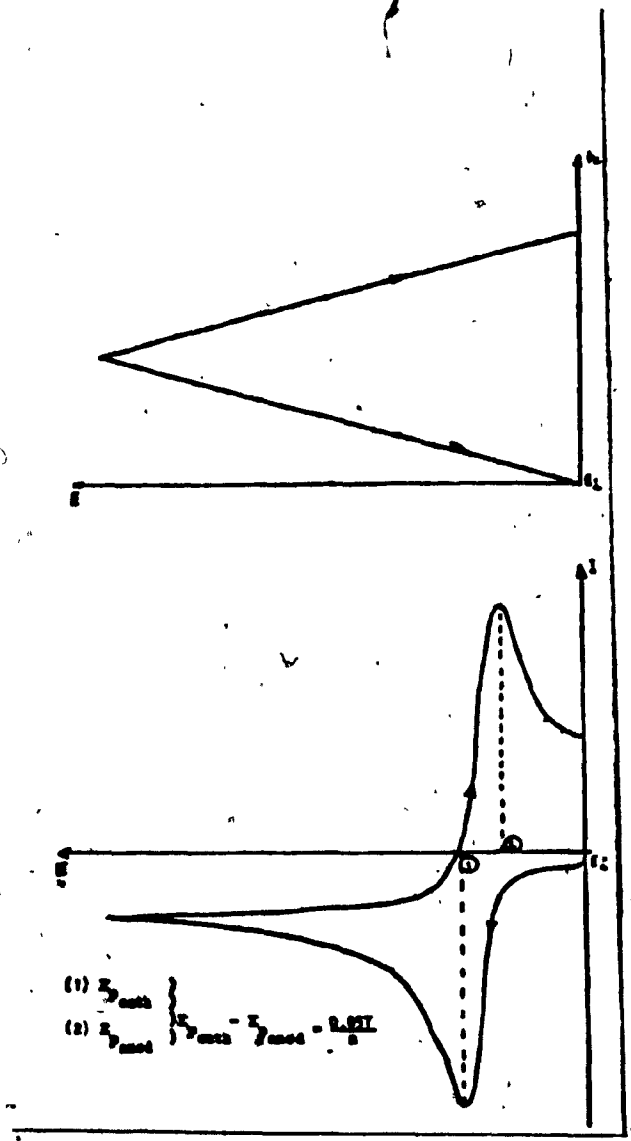


Figure 5. A. Potential Program resulting in a Triangular wave in CV  
 B. Current-Potential curve obtained



Cyclic voltammetry is not commonly used for analytical purposes due to the cost factor and the availability of more sensitive techniques. However, due to the nature of the technique, CV can be employed as an excellent tool for the study of electron reactions, kinetics and mechanisms of complex reactions. Within its working range of analyte concentration, CV also can be applied for qualitative and quantitative analysis with results somewhat better than D.C. polarography.

In CV there are definite correlations between the separation of peaks ( $\Delta E_p$ ), peak height ratios and the general polarogram shape to the nature of the electrode reaction and chemical processes. For example, Equation (9) shows that  $E_p$  for reduction is  $0.029/n$  volts more cathodic than  $E_{1/2}$ . Correspondingly,  $E_p$  for the oxidation of the same species will be  $0.029/n$  volts more anodic than  $E_{1/2}$ . Hence, the potential increment between the peaks for a reversible system will be (26,27).

$$E_{p(o)} - E_{p(r)} = 2(0.029/n) = 0.058/n \text{ volts} \quad (14)$$

Consequently, peak separation becomes a function of the reversibility of the reaction, and a  $n\Delta E_p$  of equal to or less than 60mV indicates a highly reversible reaction.

Finally, in a manner similar to that for single sweep work, a distinction should be made between the first two or three cycles and continuing cycles. In the absence of a coupled chemical reaction, continuing cycles merely alter gradually the concentration profile near the electrode surface. The anodic and cathodic peaks change slightly in shape and decrease in size until a steady-state condition is achieved.

f. Electrode Systems

In the analytical cell of a modern voltammetric system the potential and its corresponding current are controlled and monitored by the use of a three electrode system. These are the working electrode, the reference electrode and the auxiliary electrode as hereafter described.

g. Working Electrodes

In voltammetry, the term "working electrode" (WE) is reserved for that electrode at which the primary polarographic reaction occurs (i.e., the electrode at which the species of interest is either oxidized or reduced). However, strictly speaking, any electrode may be called a working electrode whenever a net current flows through the cell.

A number of working electrodes have been employed, and these may be classified as follows:

- a. Dropping mercury electrodes (dme)
- b. Stationary electrodes
  1. quiet solutions
  2. stirred solutions
  3. flowing electrolyte
- c. Rotating electrodes
- d. Vibrating electrode systems.

Working electrodes can also be classified according to the electrode material. These are often selected on the basis of price, of durability, and, most importantly, from the viewpoint of their effect on the overall product yield, purity and effective working potential range. Common WE materials are mercury electrodes (dme or HMDE), platinum, gold, carbon, graphite and thin-layer mercury electrodes.

The size and shape of the working electrode are also of considerable importance, since they govern the nature of the mass transfer action and other parameters of the electrochemical process. The carbon electrode is used in this study because it is effective at anodic potentials.

#### h. Reference electrodes

The potential within the analytical cell (i.e., the potential of the WE) is measured with respect to a reference electrode. This latter involves a half-cell having a known and stable potential. The most frequently used reference electrode (REF.) is the standard calomel electrode. For certain purposes the silver-silver chloride (Ag/AgCl) system is useful. Mercury-mercurous sulfate and lead amalgam-lead sulfate systems have been used.

All the reference half cells used in polarography/voltammetry can be coupled to any type of WE. There are no specific types peculiar to stationary or solid electrodes. The potential of the chosen reference electrode is standardized by measurement against a standard hydrogen electrode or a fixed potential system.

In general, unless another system is specifically required, the standard calomel (SCE) system is used, since much of the polarographic half-wave potentials ( $E_{1/2}$ ) in the literature are reported versus SCE.

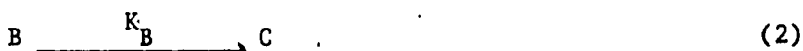
#### i. Auxiliary electrodes

In experiments where the ohmic potential drop in solution ( $iR_s$ ) may be high, a three electrode system is employed. The current is passed between the working electrode and an auxiliary electrode. The auxiliary

electrode can be any electrode desired, since its electrochemical properties will not affect the behaviour of the electrode of interest, it is usually chosen to be an electrode that will not produce substances by electrolysis that will reach the working-electrode surface and cause interfering reactions. This electrode is placed in a compartment separated from the working electrode.

### C. Kinetic Analysis Method

In this study, the kinetic method of iron analysis introduced by Langford and Khan (19) was employed to study the speciation of iron. For the present studies, the graphical treatment of multi-component kinetics<sup>\*\*</sup> described in texts such as Frost and Pearson (33) proved adequate. In the kinetic method, a reagent system is added to the sample which favours conversion of the target element (iron) into a common product which is readily detectable (the ferrozine complex). The original species A and B are distinguished by the rate constants for their conversion to the common product according to equations 1 and 2.



Clearly for this simple description to work, reactions must be pseudo First Order. This is insured by adding a large excess of ferrozine and buffering the reagents solutions. The differential rate expression for a system like this is as follows:

$$\frac{dC}{dt} = A_0 (1 - e^{-K_A t}) + B_0 (1 - e^{-K_B t}) + \dots + x \quad (3)$$

The .... allows for possible additional components and x is a time independent term which may represent either component which reacts too fast for the kinetic method in use or a blank absorbance.  $A_0$  and  $B_0$  are initial concentrations at  $t = 0$  and therefore, the quantitative analysis parameters of the original sample containing A and B. An integral expression for the common product C, is given at any time t, by the rate expression:

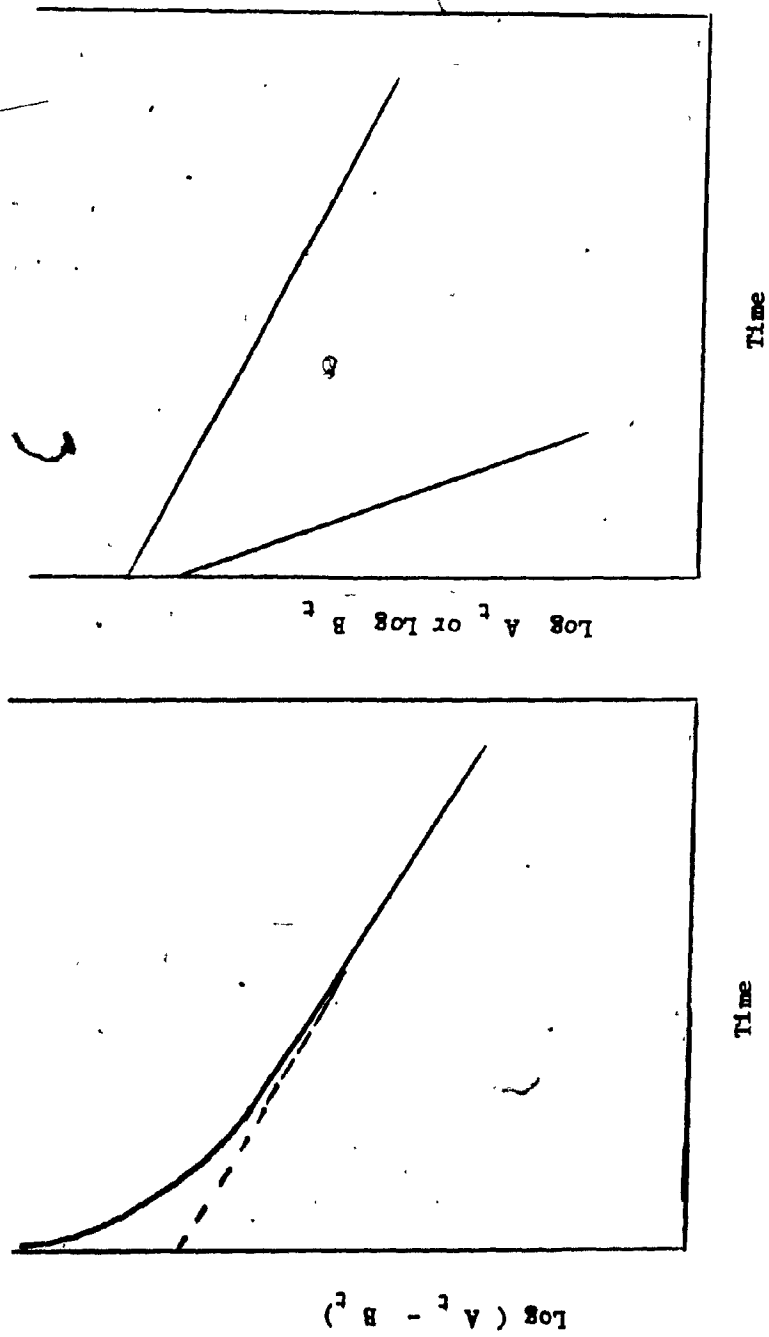


Figure 6. (a) Rate data obtained for the mixture.  
(b) Rate data obtained for each component separated.

$$C_{\infty} - C_t = A_t + B_t = A_0 e^{-K_A t} + B_0 e^{-K_B t} \quad (3)$$

In the case where the rate of reaction of A is larger than that of B, the term  $A_0 e^{-K_A t}$  becomes very small compared to  $B_0 e^{-K_B t}$  at any time after A has reacted essentially to completion, and can be considered negligible.

Taking the Logarithm of both sides of equation (3) gives:

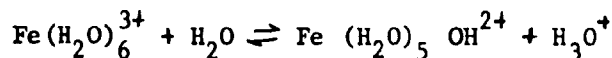
$$\ln (A_t + B_t) = \ln (C_{\infty} - C_t) = -K_B t \ln B_0 \quad (4)$$

The plot of  $\ln (C_{\infty} - C_t)$  vs time  $t$ , yields a straight line with a slope of  $-K_B$  and an intercept (at  $t = 0$ ) equal to  $\ln B_0$  Figure 6.

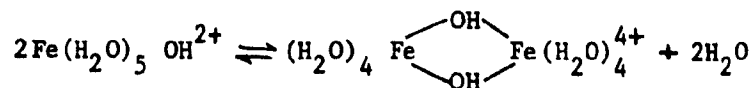
The value of  $A_0$  thus, may be obtained by subtracting  $B_0$  from the total initial concentration  $C_{\infty}$ . The first rate constant  $K_A$ , can be determined by extrapolation of the slower component back to  $t = 0$  Figure 6a and subtracting the absorbance effect of B to separate the two components as seen in Figure 6b.

#### D. Iron(III) Hydrolysis and Complex Formation

In aqueous solutions pH 3 ferric iron is present mainly as an hydroxo species. Metal ions particularly those having charges  $3^+$  and higher are readily deprotonated in aqueous solutions by the following type of process.



The hydroxy group  $\text{OH}^-$  that bonds to the metal ion can function as a bridging group joining two or more metal ions together.



When the process is allowed to continue colloidal hydroxo polymers are formed which finally precipitates. This process is the general process by which hydrated iron(III) or ferric hydroxide  $\text{Fe}(\text{OH})_3$  precipitates from solutions containing iron(III). At pH values below precipitation, the polymers are poly hydroxo cations, which can be represented as  $[\text{Fe}(\text{OH})_2^+]_n$ . As the pH increases these become neutral but the colloids are stabilized against aggregations mainly by positive charge.

Iron(III) forms very stable complexes with polyphenol ligands and phenol carboxylates. The range of pH for complex formation depends on the acidity of the hydroxyl groups. Ligands with strong electron withdrawing groups form complexes at lower pH than those without.

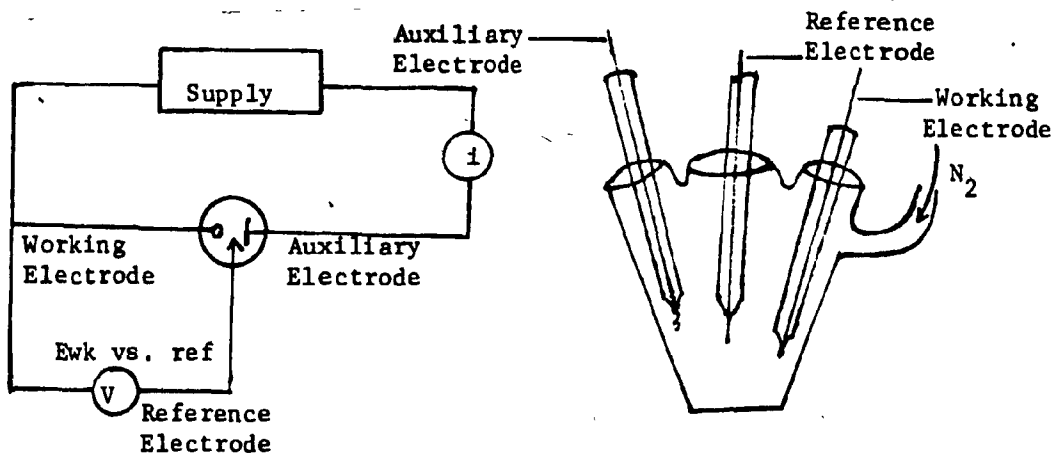


### III. EXPERIMENTAL

#### Electrochemical Experiments

##### A. Apparatus

The polarograms dc and dpp were obtained with a PAR Polarogram Analyzer Model 364 and were recorded on a Fisher 2000 X.Y. recorder. The polarographic cell can be described as consisting of three types of electrodes, a calomel reference, a carbon graphite working and a platinum wire auxiliary electrode. The design of the cell is shown in Figure 7a.



Three-electrode Cell

And Polarographic Cell

The cyclic Voltammograms were obtained with a VA - Scanner E612 Metrohm; a Polarecord E506 Metrohm and were recorded with a Hewlett Packard Mosely Division X.Y. recorder. Dissolved oxygen was removed with nitrogen gas ( $N_2$ ) prior to analysis. All measurements were made at  $25^\circ C$ . And all pH measurements were made on an Orion Model digital pH meter with B.J.C. electrode that was regularly calibrated against pH4 and pH7 buffer.

**B. Reagents**

All reagents used in this investigation were obtained from the sources listed below in the grades specified and used without further purification.

<u>Chemical</u>	<u>Source</u>
A.R. Grade iron wire Fe(III).	A.C.S. Anachem Limited.
Reagent Hydroquinone.	A.C.S. American Chemical Limited.
Reagent Sulfosalicylic Acid (SSA).	Certified Eastman Organic Chemicals.
Reagent Potassium Chloride (KCl).	Certified Fisher - Scientific Company.
Reagent Ferrozine.	Certified Diagnostic - Chemical Limited.
Reagent Sodium Hydroxide (NaOH).	Certified A.C.S. Fisher Scientific Company.
Dowex-50 Cation Exchange-Resin.	Certified A.C.S. - American Chemical Limited.
Analytical Hydroxylamine-Hydro- chloride Acid.	A.C.S. Mallinckrodt Chemical Works.
Reagent Perchloric Acid.	Certified American Chemical Limited.
Reagent Ferrous Ammonium-Sulphate.	A.C.S. Anachemia.

### C. Preparation and Purification of Fulvic Acid

The preparation of fulvic acids by researchers at Agriculture Canada following procedures introduced by Schnitzer has yielded reproducible samples. However, as the procedure has evolved, it has not been fully documented. The author spent some weeks at Agriculture Canada to establish a standard procedure based on earlier work which is documented here.

This fulvic acid was extracted from a Bh horizon podzol soil from Armadale Prince Edward Island, Canada. The soil has been collected regularly in the same location by an officer of the Charlottetown station of Agriculture Canada. 2 kg of the air dried soil was extracted with 20 liters of 0.5M NaOH solution in a polypropylene jug while displacing air with high purity N<sub>2</sub> gas. The extract was allowed to stand overnight in a cold (5°C) dark room with occasional shaking. The insoluble portion was removed by settling and centrifugation for 30 minutes at 2000 rpm.

Experience has shown that most of the silicate minerals in this particular soil are separated at this step. We note that this is a favourable special case since clay colloids are often difficult to remove from humic substances. The alkaline extract required several weeks of preparation for purification and trace metal analysis. It was repeatedly resaturated with nitrogen gas and stored in the cold dark room.

The experimental apparatus design for the purification method is shown schematically in Figure 7B. Two glass columns were used, connected with tygon tubing from the alkaline extract reservoir. The "roughing" column (A) and the "finishing" column (B) were both filled with Dowex 50W; 20 - 50 Mesh size cation-exchange resin. The fulvic salt extracted was

passed through each column, the roughing first, then the finishing, while simultaneously bubbling nitrogen gas to the eluate.

The flow rate for the system was kept at approximately one drop per second. When the pH of the effluent in the column rose above 7, the column was regenerated with 1.0M hydrochloric acid solution followed by rinsing with redistilled water. The effluent was monitored by a flame test for sodium ions ( $\text{Na}^+$ ) and by silver nitrate ( $\text{AgNO}_3$ ) test for chloride ions ( $\text{Cl}^-$ ) until a negative result was obtained.

The number of passes (through the finishing column) necessary for purification of this fulvic acid was determined by graphite furnace Atomic-Absorption Spectrophotometry. The critical metal monitored was iron. The number of passes is two to three to reduce Fe below  $10^{-2}$  moles/g of FA. Reported in Table (3) are the level of trace metals determined.

The fulvic acid solution obtained at the end of the purification methods was freeze-dried in a cabinet type lyophilizer. The freeze-dried fulvic acid powder was stored in a tightly stoppered container in a dark room at room temperature.

The carbon, hydrogen and nitrogen contents of the sample were analysed by Guelph Chemical Laboratories, Limited. The values for this batch are tabulated below with those of the first batch.

Sample	<u>Percentage of C.N. and H.</u>		
	Carbon	Nitrogen	Hydrogen
Current, FAB	49.52	0.58	4.6
Agriculture's, FA1	49.50	0.80	4.50



TABLE 3  
METAL CONTENT OF FULVIC ACID BATCH FAB  
BY ATOMIC ABSORPTION

<u>ELEMENT</u>	<u>CONCENTRATION m mole/g</u>
Fe	$3.0 \times 10^{-3}$
Cu	$< 10^{-3}$
Na	$1.1 \times 10^{-4}$
K	$5.7 \times 10^{-4}$
Al	$5.3 \times 10^{-3}$
Mg	$1.8 \times 10^{-4}$
Ca	$1.1 \times 10^{-4}$
Mn	$< 10^{-3}$
Si	$< 10^{-3}$

Gamble (21) in a study with statistical averaging of several titrations with sodium hydroxide NaOH determined, that fulvic acid batch FA1 had equivalence points at 4.98 and 7.74 m mol (g FA)<sup>-1</sup>. These equivalence points determined by titration with 0.5N sodium hydroxide NaOH were reproducible in the present fulvic acid batch FA8 within 2%.

#### D. Preparation of Stock Solution

The preparation of stock solutions used in these experiments was as follows:

All solutions were prepared from analytical grade chemicals and redistilled deionized water.

Fulvic acid solutions were prepared by dissolving 100 mg of the dried powder in 100 ml redistilled deionized water. This corresponds to an acid group concentration of 7.7  $\mu$  moles/g

Standard iron(III) solutions were prepared from A.R. grade iron wire that was cleaned and dissolved in concentrated nitric acid added dropwise and warmed until the wire was thoroughly dissolved, then diluted to make 1000 ppm solution. This solution was stored in a polyethylene bottle.

Iron(II) solutions had to be freshly prepared prior to each experiment by dissolving known amount of A.R. reagent ferrous ammonium sulfate  $\text{Fe SO}_4(\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  and diluting to required volume.

Ferrozine (monosodium salt of (3-(2-pyridyl)-5, 6-bis(4-phenylsulfonic acid)-1, 2, 4-triazine)  $\text{C}_{20}\text{H}_{13}\text{N}_4 (\text{SO}_3)_2\text{Na}$ ) solutions were prepared by dissolving required amount of powder and diluting to required volume just prior to each experiment.

The supporting electrolyte solutions were 0.100 M potassium chloride (KCl) prepared by dissolving A.R. grade potassium chloride in redistilled deionized water and diluting.

Sulfosalicylic acid (SSA) solutions were prepared by dissolving known amount of recrystallized Eastman (SSA) and diluting to required volume.

The buffers used were prepared from standard ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and hydrochloric acid (HCl) prepared from the concentrated reagents.

Sodium hydroxide solutions used for extraction and cleaning the columns were prepared from A.R. grade sodium hydroxide pellets dissolved in required amount of water to make 0.5 and 0.1 molar. The acid solutions used for regeneration were diluted to 1M from concentrated reagent grade HCl. Portions of all standard solutions were diluted as required just prior to use.

#### E. Preparation of Complex

Fulvic acid metal complexes were prepared for analysis as follows:

The iron(III) concentration in all solutions was at  $6.87 \times 10^{-4} \text{M}$ , prepared by diluting  $3.48 \pm 0.01$  ml of stock solution in 100 ml of redistilled water. To obtain the nominal complexation ratios 2:1 and 1:1 of the Fe-FA complexes, 1.0 and 2.0 ml of fulvic acid stock solution (1 gr/l as above) was mixed with the iron prior to final dilution to 100 ml. The pH of this solution was adjusted as required. On the functional group analysis assumption that fulvic acid has 3.3 meq phenolics which are available for iron binding. Per gram a 10 times dilution of FA stock gives  $3.3 \times 10^{-4} \text{ meq L}^{-1}$  of phenol carboxylates.



#### IV. ELECTROCHEMICAL ANALYSIS OF Fe(III)-FA COMPLEXES

A first approach to the problem is electrochemistry. We can show that a metal like Fe undergoes redox chemistry at a carbon electrode of a rationalizable sort on complexing with fulvic acid (FA), but it will be seen that it does not behave in a simple reversible fashion. At least in part, this is because of adsorption of FA at the electrode.

All experiments were carried out in much the same manner. The typical sample solutions were prepared as follows:

To the PAR cell was added 10 ml of 0.100 M KCl supporting electrolyte and acidic standard iron(III) solution, the pH of this solution was adjusted as required, dissolved oxygen was removed by passing nitrogen gas and the solution was scanned at 50 mV sec<sup>-1</sup>. Three successive replications of polarograms were recorded by the three polarographic methods used, direct current, differential pulse polarography and cyclic voltammetry, abbreviated DC, DPP and CV, from here on.

##### A. Fe(III)-FA Analysis

In order to study the complexation of iron(III) by fulvic acid a sample solution of  $1.1 \times 10^{-4}$  M FA, and the supporting electrolyte 0.100 M KCl were placed into the polarographic cell, the pH of the solution was adjusted and dissolved oxygen removed. Then the solution was scanned anodically and polarograms were recorded in triplicate to be used as reference. Then iron(III)  $6.87 \times 10^{-4}$  M was added to the cell solution, again

the pH was adjusted, dissolved oxygen removed by degassing for 5 minutes and the solution was scanned anodically at 50 mV/sec scan rate and sensitivities of 50; 100; and 200  $\mu$ A, polarograms were recorded for each determination. The pH dependence of fulvic acid redox process was evaluated using these runs.

#### Results and Discussion:

pH dependence of polarographic measurements on Fe(III)-FA complexes were attempted by both dc and dpp. Interpretable results were obtained only by the latter method. Results of dc runs showing the low resolution appear in Figure 9. An analysis of the peak potentials  $E_p$  and peak current  $I_p$  was made for the various pH values investigated.

The results for the pH dependence measurements of Fe(III)-FA complex by dpp are given in Table 4. For the pH range investigated, it is interesting to note that the peak potentials decreased (shifted cathodically) with increasing pH.

Observe that the peak current also decreases as the pH increases. This decrease in peak current  $I_p$  arises as the polymers become less diffusive (45). However there is some irregularity in the trend of the peak potential. It is shown in Figure 8, that the shift in the wave affects the base line quite prominently and the precise location of peaks suffers in consequence.

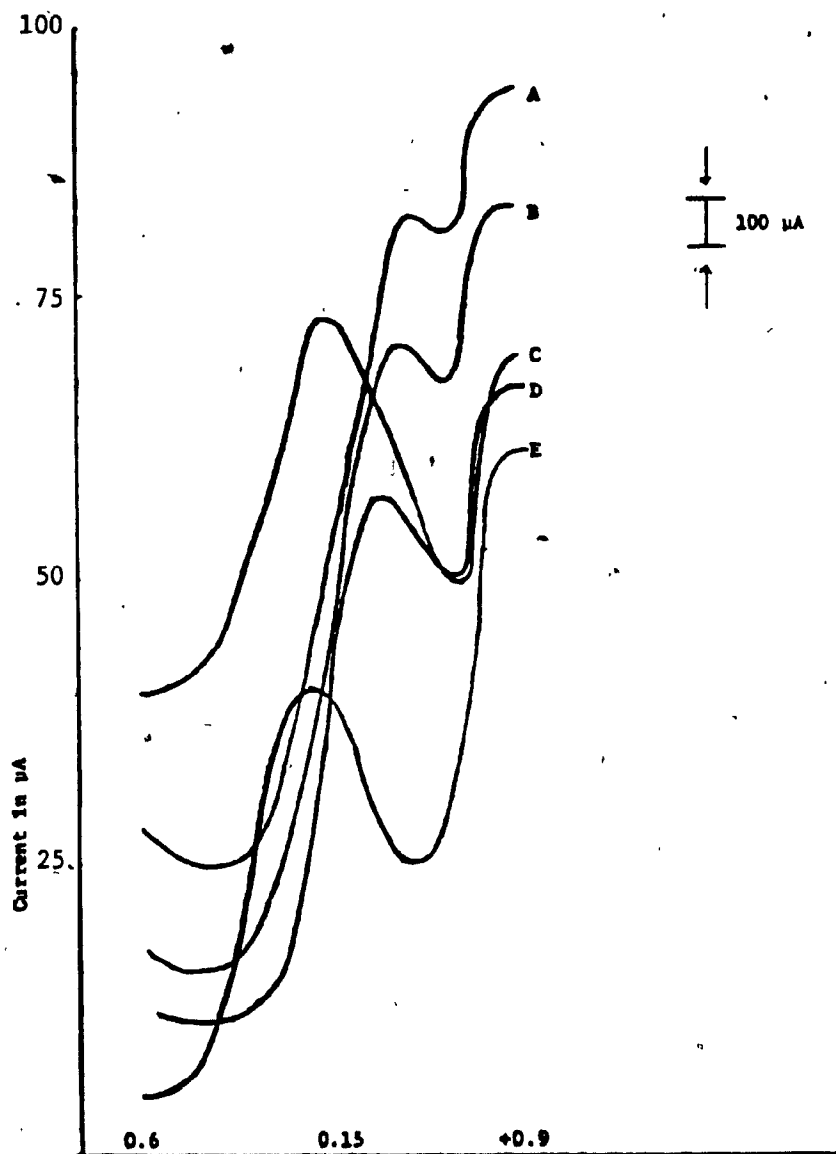


Figure 8. pH Dependence of Fe(III)-FA complexes by Dpp.

Curves are displaced on the current axis for clarity. All baselines are at the same level. A = pH 2.5; B = pH 4.0; C = pH 5.0; D = pH 6.0 and E = pH 8.0. Scan rate  $50 \text{ mV s}^{-1}$ , sensitivity  $100 \mu\text{A}$ .

TABLE 4

pH DEPENDENCE OF Fe(III)-FA COMPLEXES BY DPP

<u>pH</u>	<u>Ep V</u>	<u>Ip <math>\mu</math>A</u>
2.5	0.48	41.96
4.0	0.43	41.56
5.0	0.39	33.72
6.0	0.19	23.52
8.0	0.10	27.10

Current Potential Curves of FA and Fe-FA by DC

Fast Sweep Polarography

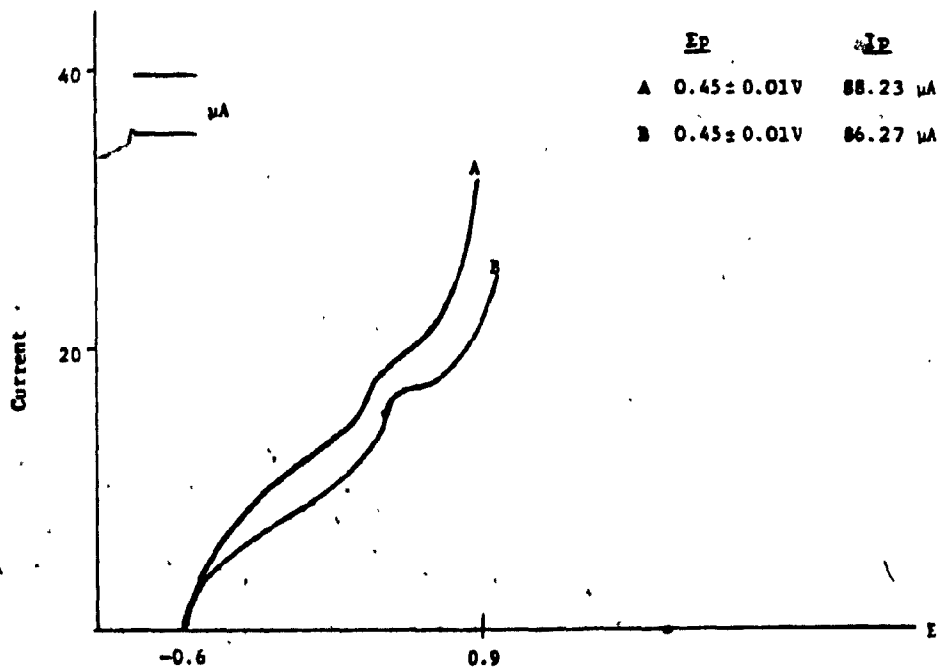


Figure 9. DC Polarograms of (A) FA; (B) Fe-FA at pH 2.5

Iron(III) =  $1.87 \times 10^{-4}$  M FA =  $1.12 \times 10^{-4}$  M.

Scan rate  $50 \text{ mVs}^{-1}$  scanning anodically from -0.6

One other observation needs to be mentioned, there is a large capacitive current observed for the polarograms recorded in Figure 9 for both FA and the Fe(III)-FA complex by the dc fast sweep polarography at pH 2.5. This may in part be associated with adsorption.

B. The Role of Adsorption of FA onto Carbon Electrode

In order to investigate interference from FA adsorption in electrode reactions of Fe(III)-FA complexes, solutions were prepared as in section IV A, pH adjustments were made and the solutions were purged with nitrogen. Then two methods referred to as "A" and "B" were employed. "A"'s method involves removal of the working electrode from solution to be scanned (during preparation and degassing period and replacing it a moment prior to scanning) in order to avoid slow adsorption processes. "B"'s method involves having the working electrode in solution during degassing period. Polarograms were recorded in triplicate.

Results and Discussion:

One problem that can interfere with our effort to evaluate the degree of reversibility of electron transfer reactions of Fe-FA complexes using electrochemistry is the problem of adsorption. The carbon electrode is necessary for studies in the anodic region of interest, but it has a large area and well known tendencies to adsorb organic solutes from water. The role of "slow" and "non-rapidly reversible" adsorption was evaluated by the fairly simple tactic method "A" and "B".

Current potential curves were recorded in the Dpp mode using two methods "A" and "B". Concentrations of FA varied over the range 0.010; 0.019; 0.029 and 0.076 gm. of FA. Polarograms obtained are shown in Figure 10. At low fulvic acid concentration a single peak was observed with both methods employed, as fulvic acid concentration increases a second peak appears at more cathodic potentials, this is with A's method. However, with B's method the peak shifted slightly cathodically, there is no evidence of a second peak.

The two peaks observed in "A"'s method suggest possibility of resolving distinct oxidizable species in iron-fulvate solutions. Clearly, if the electrode is allowed to "equilibrate" with fulvic acid solution an adsorbed layer is formed which masks part of the behaviour. That this interpretation is largely correct is easily established. Notice that the original behaviour in type A experiments can be restored to electrodes after performing type B experiment by simply cleaning the electrode surface.

Data on  $E_p$  (peak potentials) from experiments "A" and "B" (without and with) equilibration of the electrode with solution during deaeration are presented in Table 5, along with approximate  $I_p$  (peak current) values.

In the case of type A experiments, the peak near +0.25V remains essentially constant from 0 to maximum FA concentrations. This peak is assigned to the hydrous oxide of Fe(III). It is also seen at low FA concentrations in method B experiments. Examination of pH potential diagrams for Fe in Garrels and Christ (50) indicates a value near -0.25V vs (SCE) is consistent for an  $Fe^{2+}$  hydrous  $Fe_2O_3$  equilibrium at pH = 6.

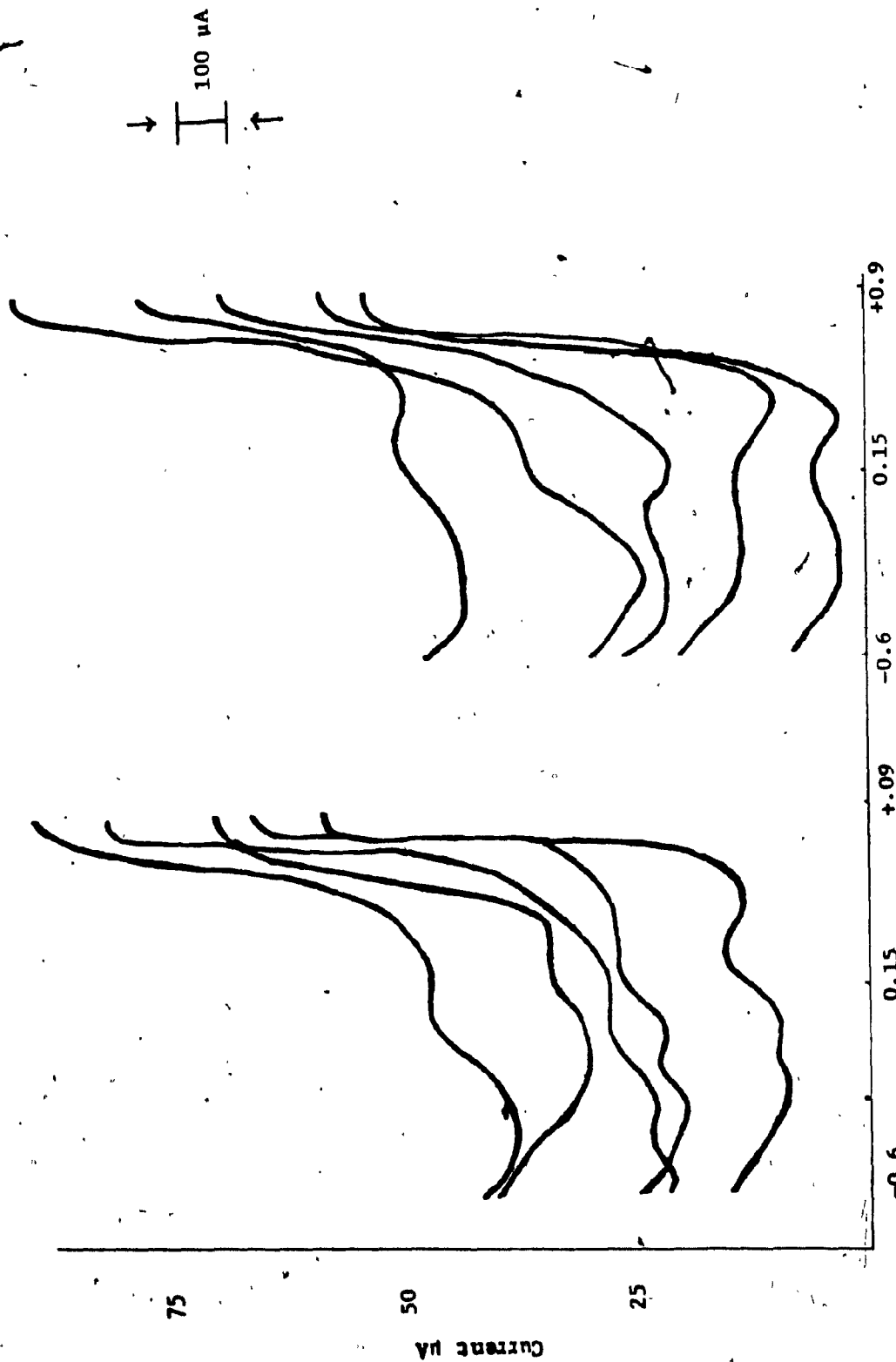


Figure 10. Effect of FA  $1.1 \times 10^{-4} M$  when added to  $Fe(III) 1.87 \times 10^{-4} M$  during the electrode process.

Scan rate  $50 mVs^{-1}$ . A. Degassing with W.E. removed from solution. B. Degassing with

W.E. present in solution. Baselines are displaced for clear visibility of each curve.



TABLE 5

TITRATION OF Fe(III) WITH FA AT pH6.0 STUDIED BY DPP

<u>FA ml</u>	<u>Method A<sup>a</sup></u>		<u>Method B<sup>a</sup></u>	
	<u>Ep V</u>	<u>Ip <math>\mu</math>A</u>	<u>Ep V</u>	<u>Ip <math>\mu</math>A</u>
0.00	-, 0.22	-, 5.09	-, 0.20	7.06
1.00	-, 0.25	-, 2.35	-, 0.25	3.92
2.00	-0.17, 0.24	1.56, 2.74	0.21, -	1.96
3.00	-0.18, 0.24	1.20, 2.35	0.17, -	0.78
8.00	-0.16, 0.24	1.17, 2.70	0.21, -	1.18

a. In method A, the carbon electrode was not immersed in the solution until deaeration was complete. In method B, the electrode was in the solution throughout.

This leaves the attractive possibility that the peak which grows in method "A" runs at higher FA concentrations is associated with an iron-fulvate colloidal complex which does not equilibrate with "free" (hydrous oxide) iron species on the time scale of the polarographic experiments. The question is only what is, in fact, electroactive? An iron in a fulvate complex or the fulvate itself. The absence of a permanent peak at  $-0.17V$  in the absence of Fe supports the former. This would of course, imply a significant stabilization of Fe(III) over Fe(II) in the fulvate complexes compared to hydrous oxides. (That is the fulvic acid (FA) bound Fe is more readily oxidizable). This seems consistent with Wong's (34) results which imply extensive reaction of iron(III) oxide colloids with FA.

The decreases in  $i_p$  can be consistently interpreted with the model suggested. The main factor is decreasing diffusion coefficients of electroactive species as colloidal particle size grows.

### C. Cyclic Voltammetric Analysis

In an attempt to verify the results suggested by fast sweep Dc and Dpp, we employed cyclic voltammetric methods referred to as CV. Studies utilized solutions prepared as in earlier experiments IV A, the reference electrode used is Ag/AgCl electrode, sweep rate 3V/min.

Data from peak potential measurements  $E_p$  for Fe(III) and Fe(III)-FA complexes as a function of pH are presented in Table 6. Curves are reproduced in Figure 11 and Figure 12.

One can see that at pH 2.5 shown in Figure 11, the shapes of the cyclic voltammetric curves in both cases are in agreement with diagnostic criteria

TABLE 6

pH Dependence of Fe(III)-FA Complexesby Cyclic Voltammetric Methods

<u>Complex</u>	<u>pH</u>	<u>Anodic Ep</u>	<u>Cathodic Ep</u>	<u>Ep/2</u>
Fe(III)	2.5	0.65	0.54	0.61
Fe(III)-FA	2.5	0.66	0.56	0.62
"	4.0	0.42'	0.76'	0.36
		0.76"	0.56"	
"	6.0	0.48'	0.78'	0.39
		0.73"	0.63"	
"	8.0	0.48'	0.75'	0.40
		0.77"	0.67"	

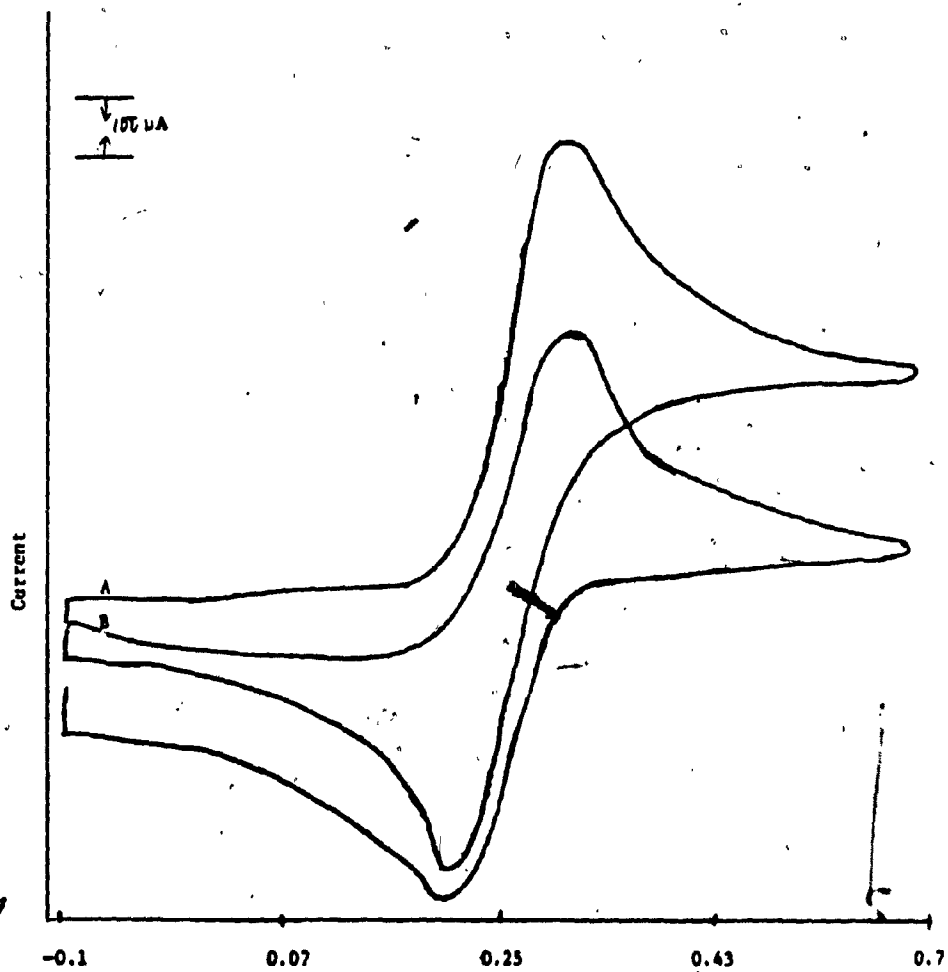


Figure 11. Cyclic voltammetric curves of Fe(III) Fe(III)-FA complex at  
pH = 2.5; Fe(III) =  $1.07 \times 10^{-4}$  M; FA =  $1.1 \times 10^{-4}$  M.  
A = Fe(III)-FA; B = Fe(III)

proposed by Nicholson and Shain (32) for rapid charge transfer process for the Fe(III)-Fe(II) system which behaves almost reversibly. The anodic wave is proportional to oxidized Fe(II) concentration and the cathodic wave is proportional to reduced Fe(II) concentration. Addition of FA has little effect on the shape of the curve. This is consistent with binding parameters for this pH range as reported by Langford and Khan (19) and Wong (34), which show that Fe(II) is not bound unto species containing FA under concentration conditions like those of the present experiments. In fact, their kinetic experiments suggest free Fe is essentially "monomeric" forms at pH 2.5.

Turning to FA solutions at higher pH small reversible waves are observed in Figure 12, at quite anodic potentials which might be due to "monomers", but they are small enough signals to leave one uncertain as to the interpretations.

The evident peak associated with FA complexation is the relatively irreversible peak which is associated with a well defined oxidation wave in the anodic scan, but a much smaller reduction wave in the cathodic direction, apparently the oxidation product undergoes a slow subsequent chemical reaction. Since FA contains quinone functional groups, hydroquinone conversions may account for this effect (65). But the potential for such a reaction is 0.5V (18) for the model compound. As Figure 13 shows the potential parameters are not related clearly to either of the two obtained by Dpp.

In theory there exists a relationship between  $E_p$ ,  $E_{p/2}$  and the conventional  $E_{1/2}$  of polarography at 25°C for the reversible case as shown in Section B.d. equation 9, 10 and 11. However, in the present case this

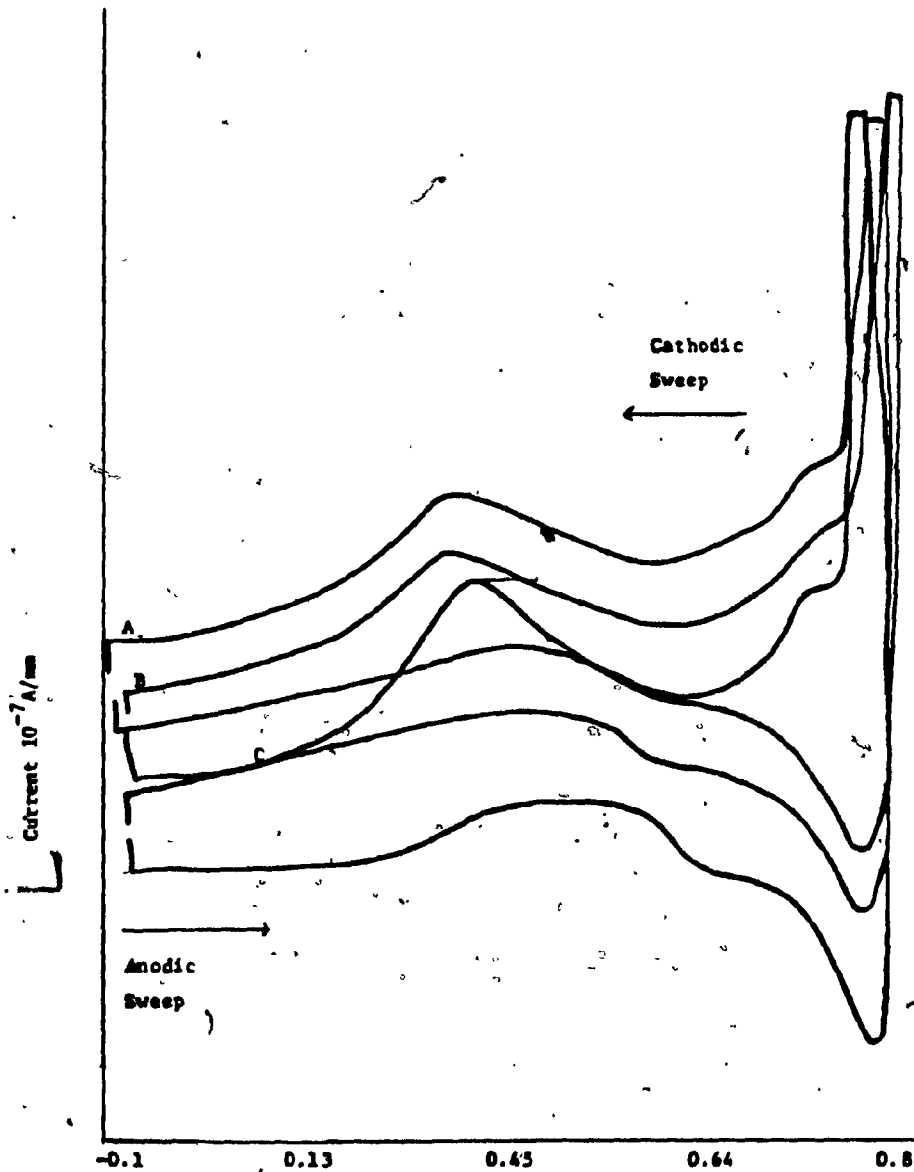


Figure 12. Cyclic voltammograms of Fe(III)-FA complexes at various pH's  
 A = 4.0; B = 6.0; C = 8.0.  $\text{Fe(III)} = 1.87 \times 10^{-4} \text{ M}$   $\text{FA} = 1.1 \times 10^{-4} \text{ M}$ .  
 Curves are cut at the top and are displaced on the current axis  
 for clarity and convenience.

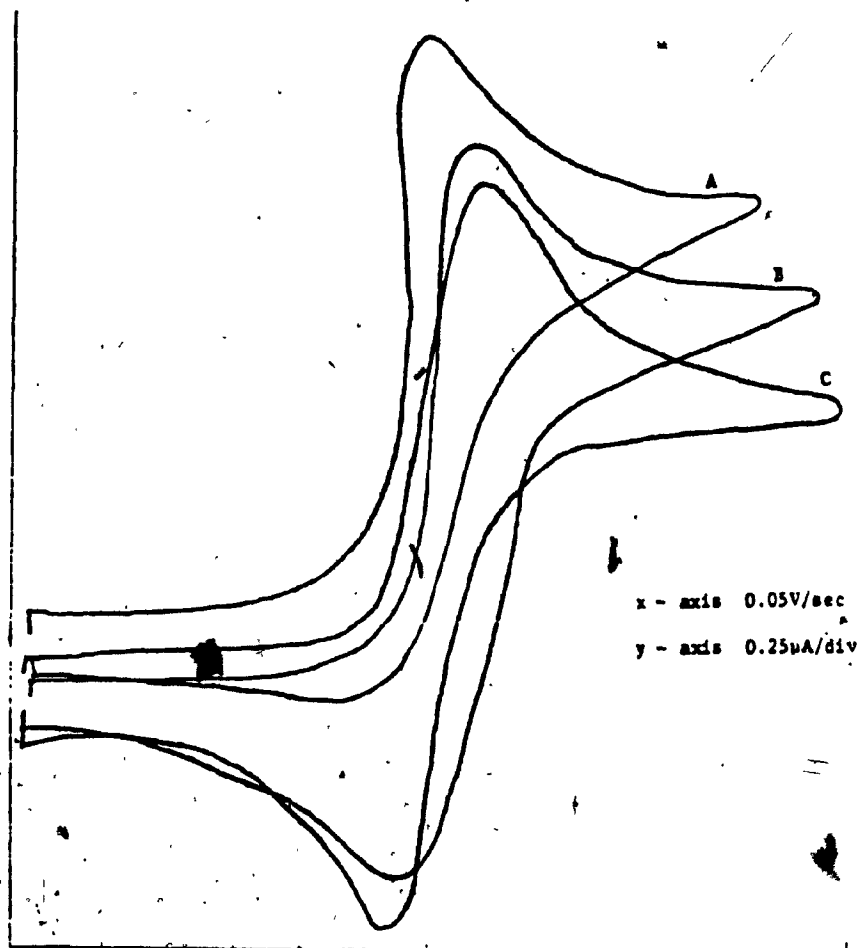


Figure 12B. Cyclic Voltammograms of Fe(III)-FA Complexes as a Function of Scan Rates at pH 2.5.

A Sweep Rate = 0.03V/sec, B = 0.05V/sec, C = 0.1V/sec

relationship does not exist between  $E_p$ ,  $E_{p/2}$  and  $E_{1/2}$ . This is because we are dealing with an irreversible case where

$$E_{p/2} - E_p = \frac{0.048}{\alpha n a} V$$

This expression involves both heterogeneous rate constant for charge transfer and transfer coefficient identifying other parameters, especially voltage, and sweep rate.

We must compare the two experiments with respect to sweep rates since the CV experiment does clearly show that the reaction is not fully reversible. If the peak potential sweep rate relation is examined to connect 0.03V/sec in CV to 0.05V/s in Dpp. We find that if the scan rate is medium as in Dpp the system behaves reversibly. When the scan rate is low as in CV the system becomes irreversible. This behaviour agrees with the criteria proposed by Shain (32) for reversible electrode processes followed by an irreversible chemical reaction and is shown in Figure 12B.

If we assume the above argument for consistency of Dpp and CV is sound; we can look at the pH trend in Figure 13 in terms of iron chemistry. The slope from pH = 2 to pH = 6 is +0.01V, compared to the slope of -0.05V in the  $E_h$  - pH diagram in Garrels and Christ. It appears that the hydrous oxides of Fe are involved.

From the data obtained in this experiment we believe that fulvic acid is cathodically oxidized in the solution by Fe(III). Then the Fe(II) formed is reoxidized by the electrode at an applied potential.



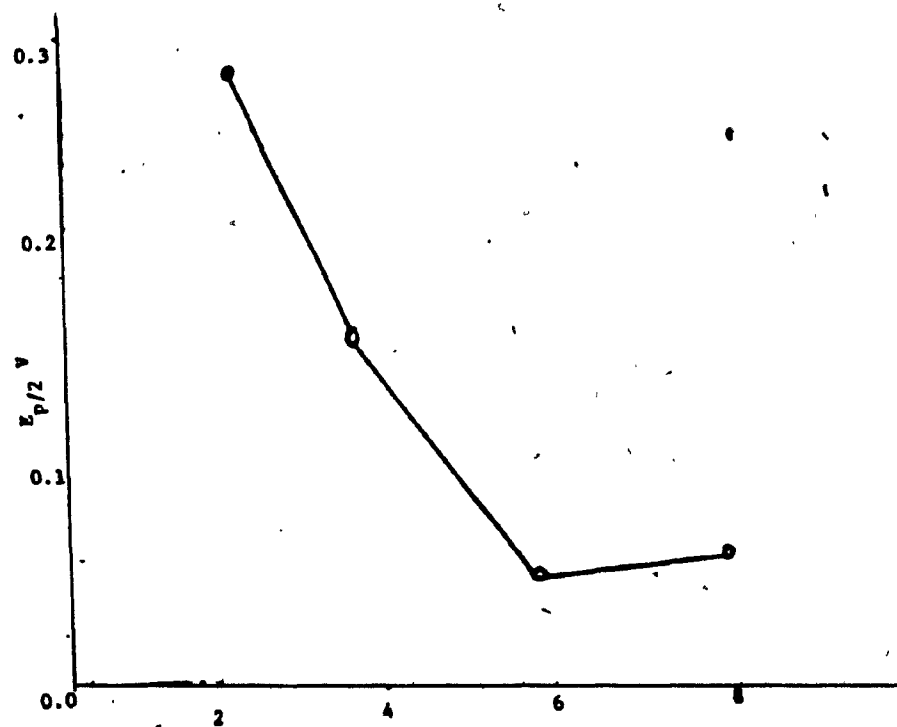


Figure 13. Plot of  $E_{p/2}$  as a function of pH.

V. SPECTROPHOTOMETRIC METHOD FOR FOLLOWING  
Fe COMPLEX DECOMPOSITION KINETICS

A. Ferrozine Chemistry

Two of the earliest and best known colorimetric reagents for the determination of iron were prepared and characterized during the early 19th century, they are 1. 10-phenanthroline and 2. 2-bipyridine, following that many related types of compounds were synthesized and investigated (15,16,22).

One such compound is ferrozine (23) shown in Figure 14A, this compound is a monosodium salt of 3-(2-pyridyl)-5,6-bis(4-phenyl-sulfonate)-1,2,4-Triazine and is known to react with divalent iron to form stable ferrous complex species which is soluble in water. It is supplied by Diagnostic Chemicals, Limited, Charlottetown, Prince Edward Island.

This ferrous complex exhibits a sharp single peak in its visible absorption spectrum (wave-length of maximum absorbance at 562 nm; molar absorptivity, 27900). The structure of this complex is shown in Figure 14B. It is similar to tris (2,2-bipyridine) iron(II), with three planar bidentate ligands coordinated to the ferrous ion, each of these ligands is bound to the iron to form a five membered ring with two nitrogen atoms. The nitrogen atoms form a nearly octahedral configuration about the central metal ion. The sulfonate groups improve the water solubility of the complex. The absorption band is assigned as a metal triligand charge transfer process (24).

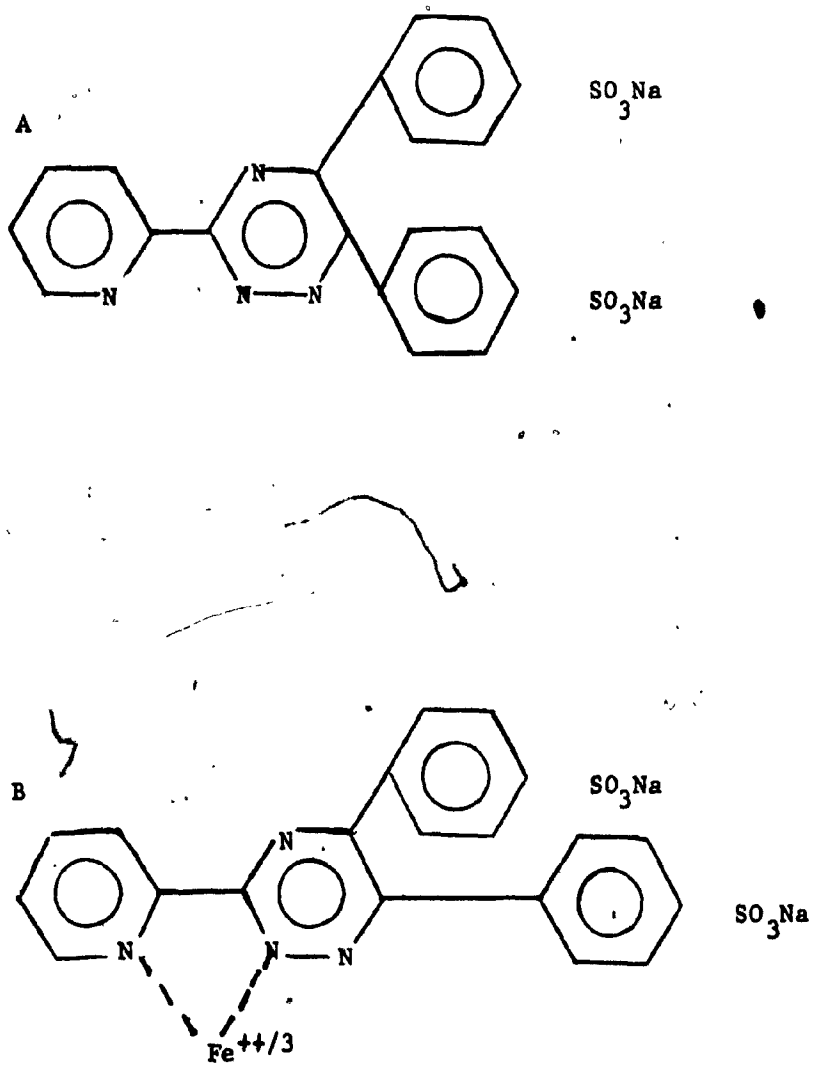


Figure 14. (A) Structure of Ferrozine  
(B) Hindrance-free chelation of Triazine

### B. Analysis of Fe(II)/Fe(III) Mixture by Ferrozine

In these experiments, it is desired to study Fe speciation in both Fe(II) and Fe(III) oxidation states. Although Wong (34) has shown that Fe(III) complexes of FA react with ferrozine by exploiting the FA as a reducing agent, this complicates interpretations. To avoid this, the reagent system in these experiments includes a reducing agent, hydroxylamine hydrochloride. The Kinetics are as follows:

Assuming the rate of reaction of a mixed solution as in the present case to be

$$\text{rate} = K [\text{Fe}] [\text{L}]^a [\text{Re}]^b$$

Where

Fe = an iron species

L = Ferrozine

Re = hydroxylamine hydrochloride

and the approximate values of a and b are equal to 1 and 0 respectively (34), it presumes that Kinetics are approximately first order in ligand and zero order in hydroxylamine hydrochloride concentrations. Thus the rate is given the form:

$$\begin{aligned} \text{rate} &= K [\text{Fe}] [\text{L}]^1 [\text{Re}]^0 \\ &= K_{\text{obs}} [\text{Fe}] \end{aligned}$$

Where

$$K_{\text{obs}} = K [\text{L}]$$

$$K = \frac{K_{\text{obs}}}{[\text{L}]}$$

A half life,  $t_{1/2} = \frac{0.693}{K}$ , for pseudo first order reaction.

C. Kinetics

a. Fe(II)/Fe(III) System

In order to confirm the ability of ferrozine to differentiate Fe(III) from Fe(II) and to test Kinetic differentiation of species of iron originating in each oxidation state, the following simple experiment was performed.

A solution of Fe(III)/Fe(II) in equilibrium was prepared from a fresh  $2.5 \times 10^{-5} \text{ M FeSO}_4(\text{NH}_4)_2\text{SO}_6 \cdot \text{H}_2\text{O}$  acid solution mixed with  $2.5 \times 10^{-5} \text{ M Fe(III)}$  stock solution. The pH of the solution was carefully adjusted to pH = 6.0. The Fe(II) to Fe(III) ratio is 1:1.

The solution was aged for 48 hours to attain "equilibrium" with respect to hydrolytic polymerization. Then it was mixed with an equal volume of  $3.0 \times 10^{-3} \text{ M ferrozine}$  and  $6.0 \times 10^{-3} \text{ M NH}_2\text{OH} \cdot \text{HCl}$  in  $1.0 \times 10^{-2} \text{ M HClO}_4$  in a volumetric flask. Approximately 4cc of this solution was pipetted into the spectrophotometer cell and absorbance readings were monitored periodically at wavelength of 562 nm for approximately 185 hours.

Fe(III):Fe(II) Ratio 1:1

Concentration	Rate Constant
A : $2.26 \times 10^{-5} \text{ M}$	$K_A = 1.6 \times 10^{-1} \text{ sec}^{-1}$
B : $1.30 \times 10^{-5} \text{ M}$	$K_B = 3.7 \times 10^{-3} \text{ sec}^{-1}$
x : $1.44 \times 10^{-5} \text{ M}$	
Mass Balance	
$2.26 \times 10^{-5}$	
$1.30 \times 10^{-5}$	71.2%
<u><math>1.44 \times 10^{-5}</math></u>	28.8%
$5.0 \times 10^{-5}$	

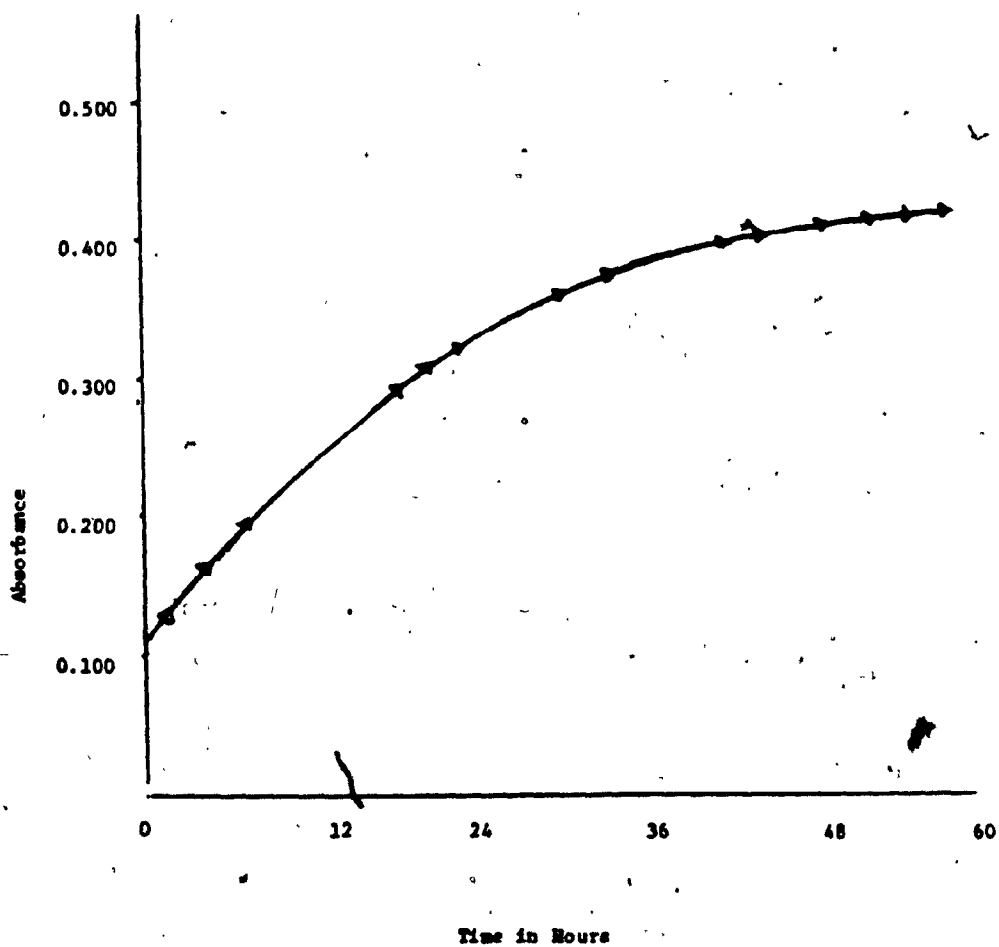


Figure 15. Plot of Absorbance vs Time for the mixture Fe(III)/Fe(II)  
 $2.5 \times 10^{-5} M$ ,  $NH_2OH \cdot HCl$   $6.0 \times 10^{-3} M$   $HClO_4$ ,  $1.0 \times 10^{-2} M$  Ferrozine  
 $3.0 \times 10^{-3} M$

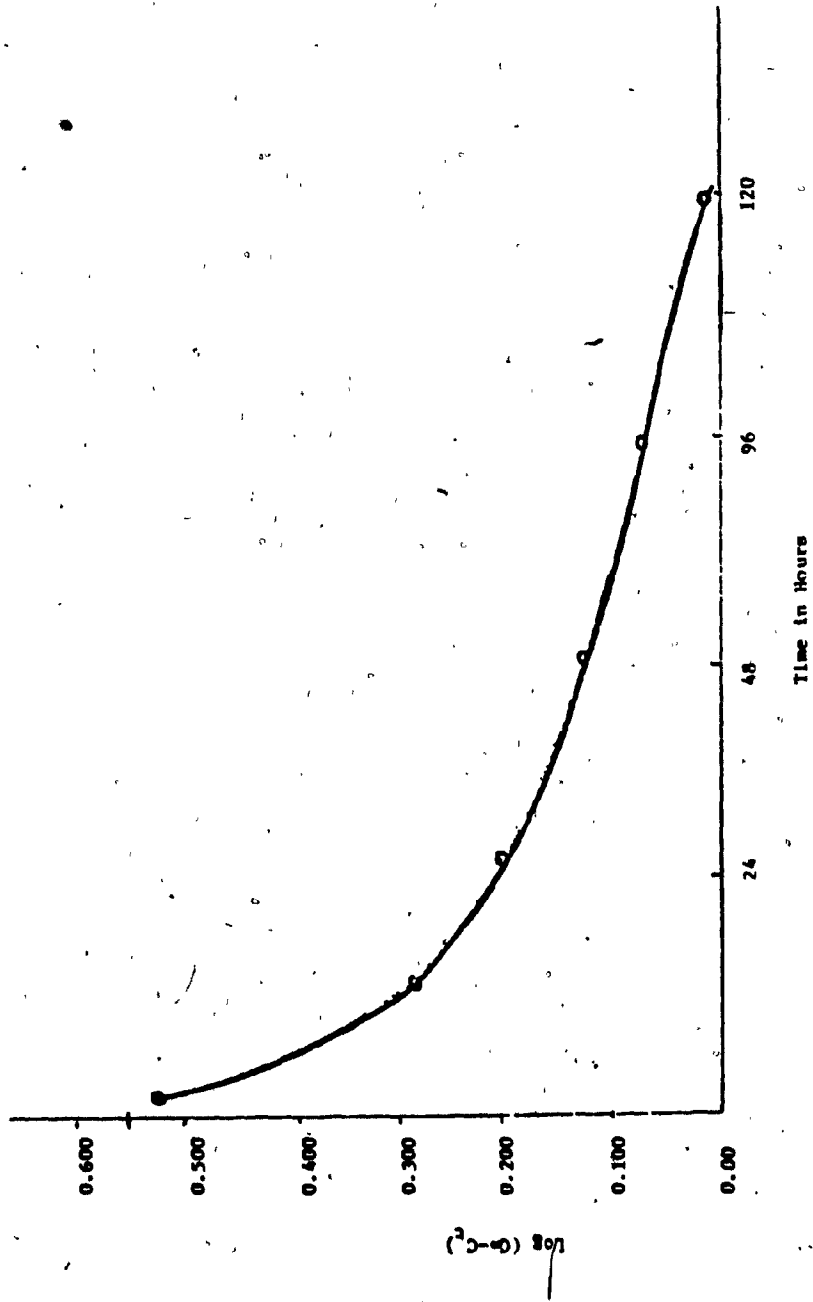


Figure 16. A plot of  $\ln(O-C)$  vs Time for the mixture  $\text{Fe(III)/Fe(II)} 2.5 \times 10^{-5} \text{M}$ ,  $\text{NH}_4\text{OH.HCl}$   $6.0 \times 10^{-1} \text{M}$ ,  $\text{HClO}_4$   $1.0 \times 10^{-2} \text{M}$  with Ferrozine  $3.0 \times 10^{-3} \text{M}$ .

b. Fe(III)-FA System

A solution was prepared by adding Fe(III)  $5.0 \times 10^{-5}$  M to FA  $1.67 \times 10^{-5}$  M. After ageing with the indication of differentiation, the Kinetic method was applied to solutions containing FA. This solution was mixed with a solution of equal volumes of ferrozine  $3.0 \times 10^{-3}$  M;  $\text{NH}_2\text{OH.HCl}$   $6.0 \times 10^{-3}$  M in  $\text{HClO}_4$   $1.0 \times 10^{-2}$  M in a volumetric flask. The remainder of the procedure was carried out as in the above Fe(II)/Fe(III) system.

Fe(III)-FA Ratio 1:1

Concentration

Rate Constant

A :  $3.447 \times 10^{-5}$  M

$K_A = 7.4 \times 10^{-2} \text{sec}^{-1}$

B :  $1.55 \times 10^{-5}$  M

$K_B = 3.2 \times 10^{-3} \text{sec}^{-1}$

Mass Balance

$3.447 \times 10^{-5}$

$1.55 \times 10^{-5}$

$4.99 \times 10^{-5}$  99.8±1%

c. Fe(III):Fe(II):FA System

A solution of Fe(II)/Fe(III) in equal volumes was prepared from a fresh  $2.5 \times 10^{-5}$  M  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  acid solution mixed with  $2.5 \times 10^{-5}$  M Fe(III) stock solution. This solution was added to FA  $1.67 \times 10^{-5}$  M and aged for 48 hours. Then it was mixed with an equal volume of  $3.0 \times 10^{-3}$  M ferrozine and  $6.0 \times 10^{-3}$  M  $\text{NH}_2\text{OH.HCl}$  in  $1.0 \times 10^{-2}$  M  $\text{HClO}_4$  in a volumetric flask, followed by the same treatment as in a and b.



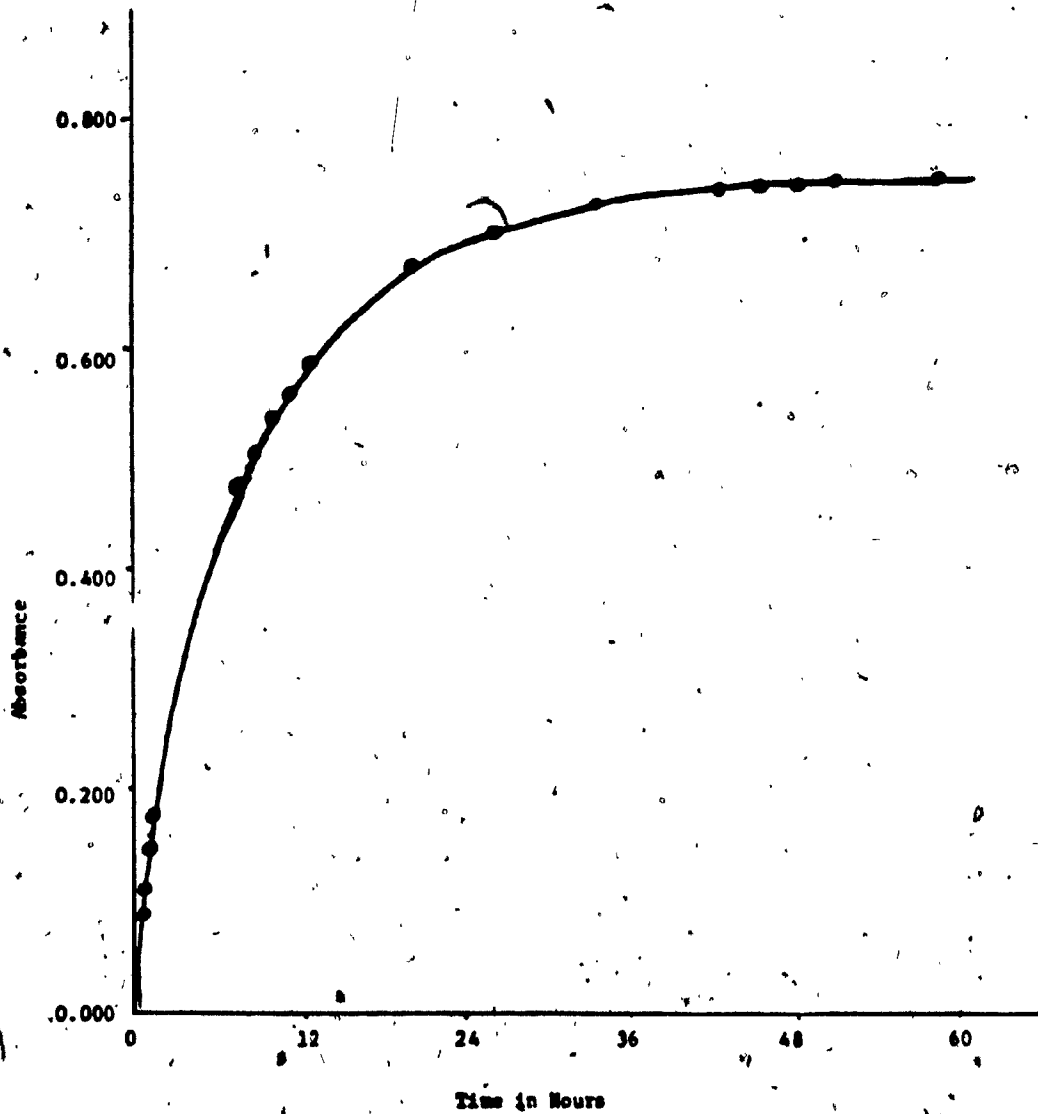


Figure 17. A plot of Absorbance vs Time for the mixture Fe(III)  
 $5.0 \times 10^{-3} M$ , FA  $1.67 \times 10^{-3} M$ , Ferrozine  $3.0 \times 10^{-3} M$ ,  $NaClO_4$   
 $1.0 \times 10^{-2} M$  and  $NH_4OH \cdot HCl$   $6.0 \times 10^{-3} M$ .

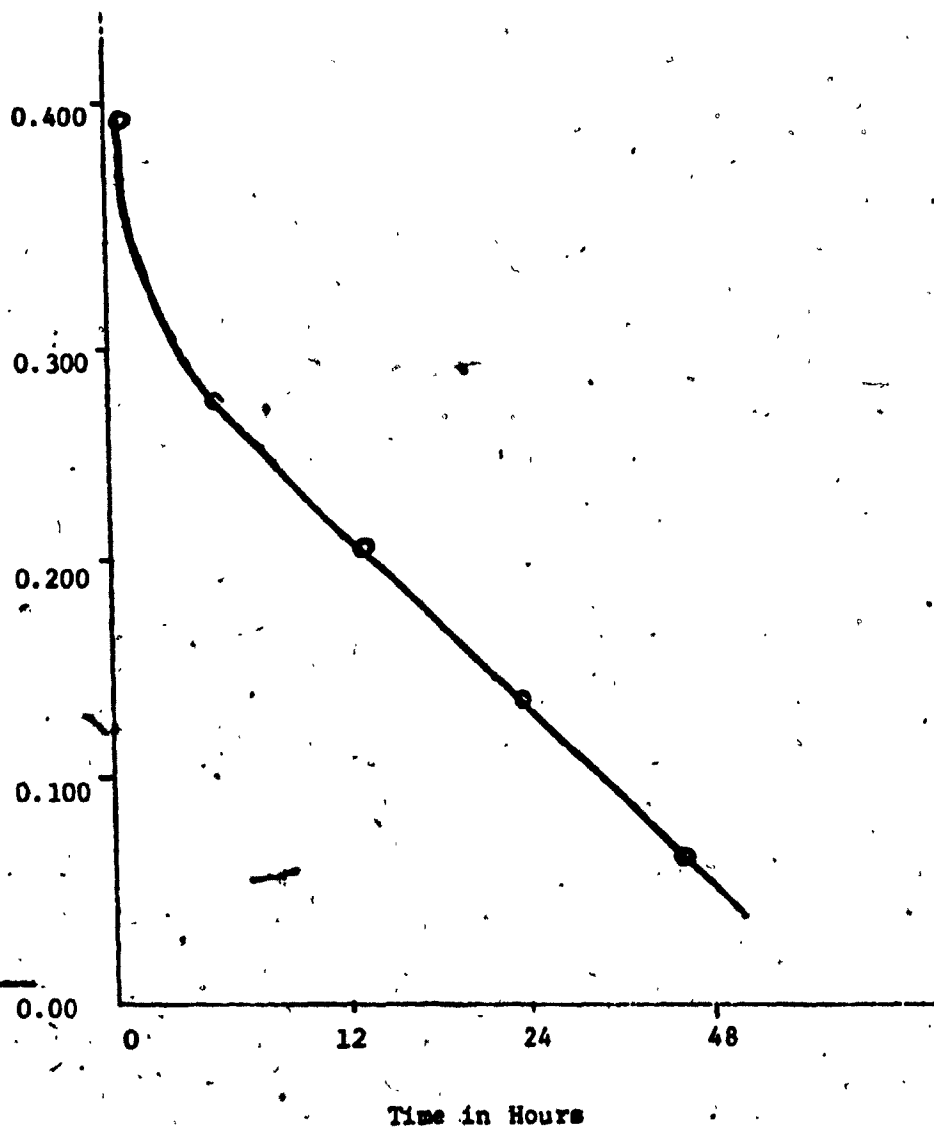


Figure 18. A plot of  $\ln(C_0 - C_t)$  vs.  $t$ , for the mixture  
Fe(III)  $5.0 \times 10^{-5} M$ , FA  $1.6 \times 10^{-5} M$ , Ferrozine  
 $3.0 \times 10^{-3} M$   $HClO_4$   $1.0 \times 10^{-2} M$  and  $NH_2OH.HCl$   
 $6.0 \times 10^{-3} M$ .

Fe(III)-Fe(II)-FA Ratio 1:1:2

Concentration	Rate Constant
A : $1.136 \times 10^{-5} \text{ M}$	$K_A = 2.9 \times 10^{-1} \text{ sec}^{-1}$
B : $2.35 \times 10^{-5} \text{ M}$	$K_B = 2.1 \times 10^{-3} \text{ sec}^{-1}$
x : $1.51 \times 10^{-5} \text{ M}$	
Mass Balance	
$1.136 \times 10^{-5} \text{ M}$	
$2.35 \times 10^{-5}$	69.7%
<u><math>1.51 \times 10^{-5}</math></u>	30.28%
$4.996 \times 10^{-5}$	

### Results and Discussion:

Kinetic data obtained for the three systems studied a. Fe(II)/Fe(III), b. Fe(III)-FA and c. Fe(II)-Fe(III)-FA are presented. The first sample studied Fe(II)/Fe(III) revealed three distinct components for the product absorbance as a function of time Figure 15. Observe at  $t = 0$  a very large component which reacts quite rapidly (too fast to measure). This component corresponds to the time independent term in equation 3. II. C. An intriguing possibility is that this fast reacting species is Fe(II) which is generally labile and reacts with most complexing agents on the stopped flow time scale.

The linear Kinetic plot shown in Figure 16 yields two slowly reacting components with respect to the time scale of minutes. They react with rate constants  $1.6 \times 10^{-1} \text{ sec}^{-1}$  and  $3.7 \times 10^{-3} \text{ sec}^{-1}$ . These values are similar to those reported by Sommers et al (36) and Langford et al (37), thus it seems reasonable to conclude, these slowly reacting components comprises of iron oxide particles.

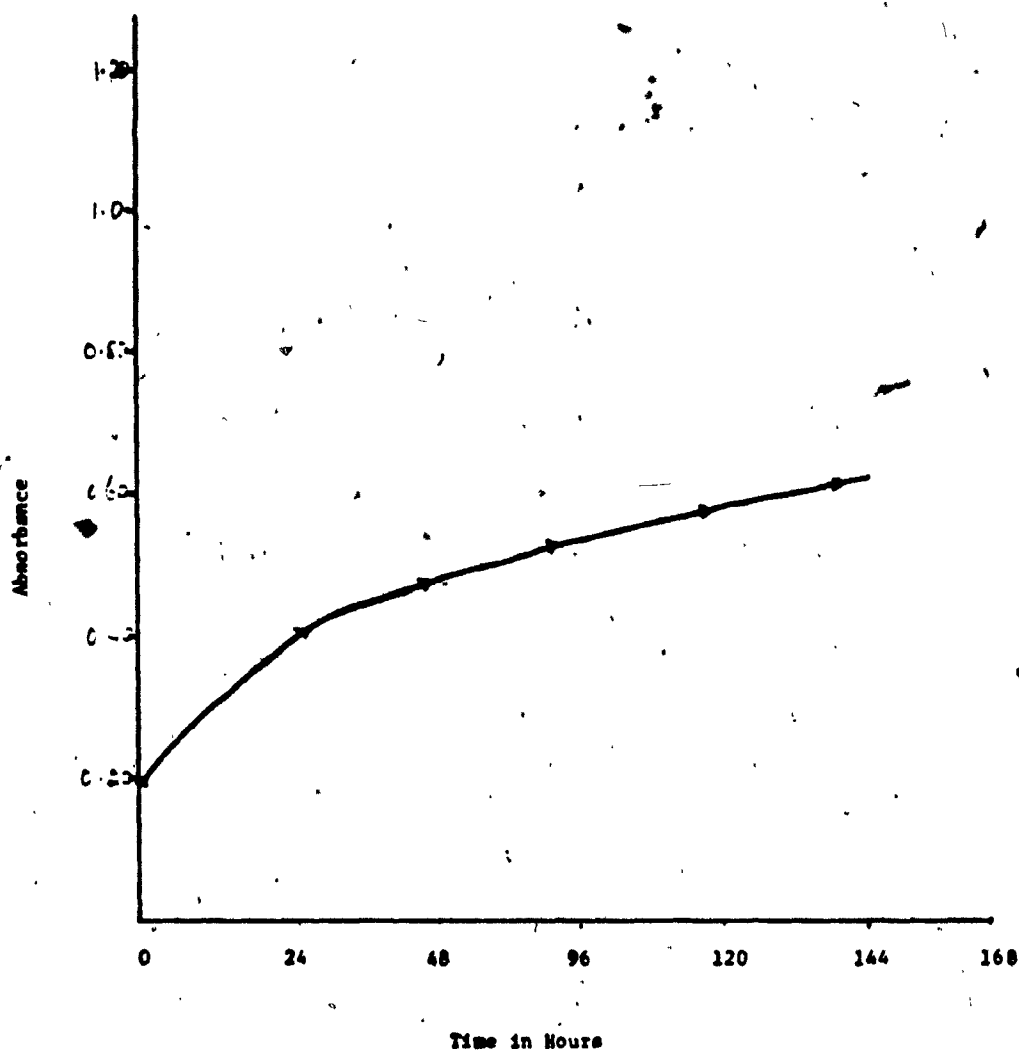


Figure 19. A plot of Absorbance vs Time

For Fe(II)/Fe(III)-FA mixture Fe(II)/Fe(III)  $2.5 \times 10^{-3} M$ ,  
FA  $1.67 \times 10^{-3} M$ , Ferrozine  $3.0 \times 10^{-3} M$ ,  $NH_4OH \cdot HCl$   $6.0 \times 10^{-3} M$   
 $HClO_4$   $1.0 \times 10^{-2} M$ .

The two slowly reacting components could both be Fe(III) species as is reasonable in these oxygenated solutions. However, it is also possible that Fe(II) ions could be incorporated into the Fe(III) hydrous oxide colloid since  $\text{Fe}_2\text{O}_3$  is well known to coprecipitate divalent cations. In this context, see the experiment below in which no Fe(II) was originally added.

The second sample studied Fe(III)-FA, the reaction is complete within three hours and two distinct slowly reacting components are resolved and are fitted to first order rate constants  $7.4 \times 10^{-2} \text{sec}^{-1}$  and  $3.2 \times 10^{-3} \text{sec}^{-1}$

Figure 17. Observe the absence of a "fast" x component which we attributed to Fe(II) above.

The third sample studied Fe(II)/Fe(III)-FA is similar to the first in the sense that Fe(II) and Fe(III) both went into the mixture. But, since the solutions are aerated, if Skogerboe and Wilson (39) are correct in their notion that FA is at a redox equilibrium with the metal ions we might expect the sample to resemble the second made up with Fe(III) and FA. Clearly, neither parallel applies. The rate constants and proportions of the third components that can be identified are unique to this sample.

There is a fast component which looks like Fe(II) and slower components unlike those above. It cannot be said that the two methods of making Fe-FA solutions exposed to  $\text{O}_2$  lead to the same species. This is consistent with the electrochemical evidence that Fe(II)/Fe(III) equilibrium is not rapidly established in FA complexes.

## SUMMARY

Fulvic acid was extracted from soil with 0.5N NaOH solution using fractionation scheme shown in Figure 1.

The fulvate salt was purified by repeated passage through cation exchange resin columns. A brown powdered product was isolated and characterized as fulvic acid (FA). This work documents the otherwise largely "oral" tradition of preparation of this widely used Armadale Prince Edward Island sample.

The redox behaviour of fulvic acid with iron was studied as a function of pH at 25°C. Use of polarographic and Kinetic techniques were demonstrated in order to answer the fundamental question of the usefulness of equilibrium methods in the theory of metal-fulvate redox interactions.

The Dpp peak potentials of Fe(III)-FA complexes were found to shift cathodically with increased pH, also the peaks broaden while the current decreases.

Adsorption on the electrode is a factor which prevents the system from behaving in a simple reversible fashion.

The dependence of Fe(III)-FA cyclic voltammograms on pH was studied. All the electrochemical results can be given a consistent interpretation which focuses on colloidal size particles where Fe rather than one on FA is the electroactive center.

A study of the Kinetics of dissociation of Fe(II)/Fe(III)-FA and Fe(III)-FA complexes at pH = 6 at 25°C was done using Kinetic spectrometry. Applications of these methods show three components for the release of iron from fulvic acid, but the three components differ according to sample history. The Fe-FA system in the presence of O<sub>2</sub> does not reach redox equilibrium.

The objective of this work was achieved. The experiments with two independent methods, both showed the lack of reversibility. This type of information requires that equilibrium model not be used. For future work the similar Kinetic spectrum method may be applied.

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