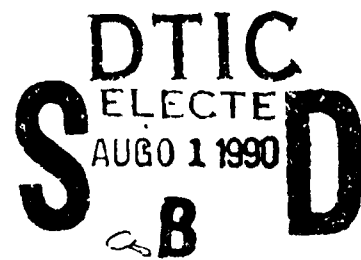


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MODEL COMPOUND INTERACTIONS  
CHARACTERIZING AQUATIC HUMIC SUBSTANCES

by

Joseph Emmanuel Castro

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A Thesis Submitted to the Faculty of the  
DEPARTMENT OF CIVIL ENGINEERING AND ENGINEERING MECHANICS

In Partial Fulfillment of the Requirements  
For the Degree of

MASTER OF SCIENCE  
WITH A MAJOR IN CIVIL ENGINEERING

In the Graduate College  
THE UNIVERSITY OF ARIZONA

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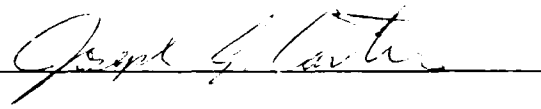
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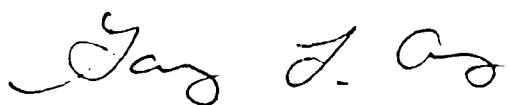
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# **ABSTRACT**

An attempt was made to simulate XAD-8 isolates of Orange County groundwater and Biscayne Aquifer groundwater using mixtures of single ligands. Mixtures of catechol, glycine, phthalic acid and salicylic acid were used to simulate potentiometric and complexometric titrations. Concentrations used for the mixtures were based on carboxylic acidity, dissolved organic carbon, and assumed values for phenolic acidity and nitrogen content. Potentiometric titrations were reproduced with mixtures of the ligands; however, complexometric titrations at pH 6.2 and pH 7.5 could not be duplicated. A stronger ligand was required to fit the pH 6.2 titrations, and higher carboxylic contents were needed for pH 7.5. At pH 6.2, 70 percent of the binding sites were attributed to phthalic acid-type groups and 20 percent to catechol-type groups. At pH 7.5 greater than 98 percent was attributed to phthalic acid-type groups.

## CHAPTER 1

### INTRODUCTION

Organic matter leaches from plants and soil matter enters natural systems and becomes dissolved organic carbon (DOC) or particulate organic carbon (POC). DOC is operationally defined as the fraction of organic carbon that passes through a 0.45-micron filter. Of the DOC, approximately 50 percent or more is typically present as humic substances. These humic substances are a concern in drinking water supplies and in the transport of trace metals in the environment.

The modeling of humic substances can only achieve limited success with fitting experimental data with model parameters. The advance in computer technology has allowed even more sophisticated statistical packages that can readily analyze a set of data.

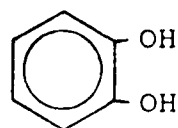
#### 1.1 Objectives

Humic substances are known to complex trace metals in the environment and increase the solubility and movement of these metals. A clear and complete structure of a humic substance is not available although representative structures have been postulated (Schnitzer and Khan, 1972;

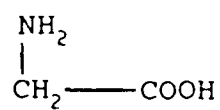
Olofsson and Allard, 1983; Steelink, 1985). Understanding the complex nature of humic substances may help predict the role they have in the fate of metals. Attempts to model metal binding by humic substances have not been successful due to unambiguous determinations of the functional groups concentrations responsible for binding. Along with that has been the overlooking of the mathematical properties of complex multi-ligand mixtures (Perdue, et al., 1984). This author attempted to develop a simple model of a humic substance by approximating the actual distribution of functional groups and the complexation behavior using model ligands. Verifying probable chemical structures of two sources of humic substances was performed by reproducing actual titration curves.

From the postulated structures of a fulvic and humic acid, carboxylic, phenolic, and amino groups were reproduced. Catechol, phthalic acid and salicylic acid represented the carboxylic and phenolic content (see Figure 1.1). Glycine was used as the amino acid due to the high binding constant for Cu(II)-glycine complexes and the high content of glycine (Thurman, 1985).

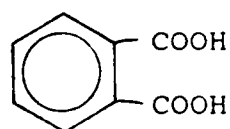
The dissolved organic matter for this research came from two groundwater sources: Orange County, California, and the Biscayne Aquifer, Florida. Orange County groundwater (OCGW) has approximately 80 percent of its DOC as humic matter and the Biscayne Aquifer (BA) has approximately 50



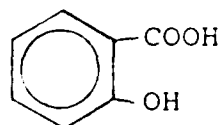
**catechol**



**glycine**



**phthalic acid**



**salicylic acid**

**Figure 1.1** Model compound structures

percent (Amy, et al., 1989). The use of these groundwaters was advantageous due to the following reasons:

- i) Accessibility of both waters to the University of Arizona Environmental Engineering Department,
- ii) OCGW has been previously investigated (Waterbury, 1990),
- iii) BA has been previously investigated (Thurman and Malcolm, 1981),
- iv) the use of two different sources may further validate the modeling effort, and
- v) the current need for the direct study of groundwater chemistry (Holm and Curtiss, 1990).

Copper was used as the trace metal of interest due to its high affinity towards ligands, its ubiquity in the environment, the numerous studies already conducted on Cu(II) speciation, and the availability of ion-selective electrodes to measure free copper(II) during titrations.

Complexometric titrations were conducted at pH 6.2 and pH 7.5 to study the effects of increasing pH while still maintaining the natural state of groundwaters, pH 6 to 8.

## 1.2 Experimental Plan

Potentiometric and complexometric titrations were first conducted on the model compounds to validate published values and experimentally-determined values under controlled pH and ionic strength. Validation of dissociation and binding constants of the model compounds was conducted by comparing experimental curves with theoretical curves. Titrations of the natural sources were then performed and

modeled with representative concentrations of the model compounds from measured carboxylic contents and assumed phenolic and nitrogen contents. Model mixtures were then titrated both potentiometrically and complexometrically to validate the proposed model humic substance.

## CHAPTER 2

### BACKGROUND

The portion of organic matter known as humic substances has been described by Schnitzer and Khan (1972) as follows:

"amorphous, brown or black, hydrophilic, acidic polydisperse substances of molecular weights ranging from several hundreds to tens of thousands."

They further subdivided humic substances into three main fractions based on solubility and acidity:

- i) humic acid (HA), which is soluble in dilute alkaline solutions but is precipitated by acidification of the alkaline extract;
- ii) fulvic acid (FA), which is that humic fraction which remains in the aqueous acidified solution; and
- iii) humin, that fraction which cannot be extracted by dilute base and acid.

#### 2.1 Elemental Composition

A description of a humic substance will depend on the source and type. Groundwater sources tend to have humic substances that are aliphatic in nature, less aromatic, less humified, and of lower molecular weight than those in soils and surface waters (Boggs, et al., 1985). They are also richer in carbon but lower in oxygen and nitrogen than soil humics. As far as the type of humic substance, humic acids contain more carbon and nitrogen and less oxygen than fulvic

acids (Schnitzer and Khan, 1972). HA also have larger molecular weights than FA and are thought to be degraded to fulvic acids.

Several elemental distributions and ratios for groundwater humic substances are shown in Table 2.1. Some of the trends discussed above can be seen in the examples shown on the table. Amino acids account for 15 percent of the nitrogen in aquatic fulvic acid and 20 percent of the nitrogen in aquatic humic acid (Thurman, 1985). Tables 2.2 and 2.3 show concentrations of amino acids from different sources and the types present.

**Table 2.1** Elemental composition and ratios of groundwater humic acids (HA) and fulvic acids (FA)

| Percentages    |            |          |          |            |          |            |                            |
|----------------|------------|----------|----------|------------|----------|------------|----------------------------|
| <u>Source:</u> | <u>C</u>   | <u>H</u> | <u>N</u> | <u>S</u>   | <u>O</u> | <u>P</u>   | <u>Ref.</u>                |
| FA Avg.        | 40-50      |          | <1-3     | 0-2        | 44-50    |            | Schnitzer and Khan (1972)  |
| Biscayne FA    | 55.44      | 4.17     | 1.77     | 1.06       | 35.39    | 0.2        | Thurman and Malcolm (1981) |
| Suwannee FA    | 54.65      | 3.71     | 0.47     | 0.5        | 39.28    | 0.2        | "                          |
| Model FA       | 45.7       | 5.4      | 2.1      | 1.9        | 44.8     |            | Schnitzer and Khan (1978)  |
| HA Avg.        | 40-60      | 4-6      | 1-6      | 0-2        | 30-50    |            | Lamy, et al., (1987)       |
| Biscayne HA    | 58.28      | 3.39     | 5.84     | 1.43       | 30.14    | 0.22       | Thurman (1981)             |
| Suwannee HA    | 57.24      | 3.94     | 1.08     | 0.63       | 39.13    | 0.2        | "                          |
| Model HA       | 56.2       | 4.7      | 3.2      | 0.8        | 35.5     |            | Schnitzer (1978)           |
| Ratios         |            |          |          |            |          |            |                            |
|                | <u>H/C</u> |          |          | <u>O/C</u> |          | <u>N/C</u> |                            |
| Biscayne FA    | 0.69       |          |          | 0.39       |          | 0.09       |                            |
| Suwannee FA    | 0.82       |          |          | 0.51       |          | 0.06       |                            |
| Biscayne HA    | 0.90       |          |          | 0.47       |          | 0.03       |                            |
| Suwannee HA    | 0.81       |          |          | 0.54       |          | 0.01       |                            |

**Table 2.2** Concentration of amino acids in soil  
and aquatic humic substances (Thurman, 1985)

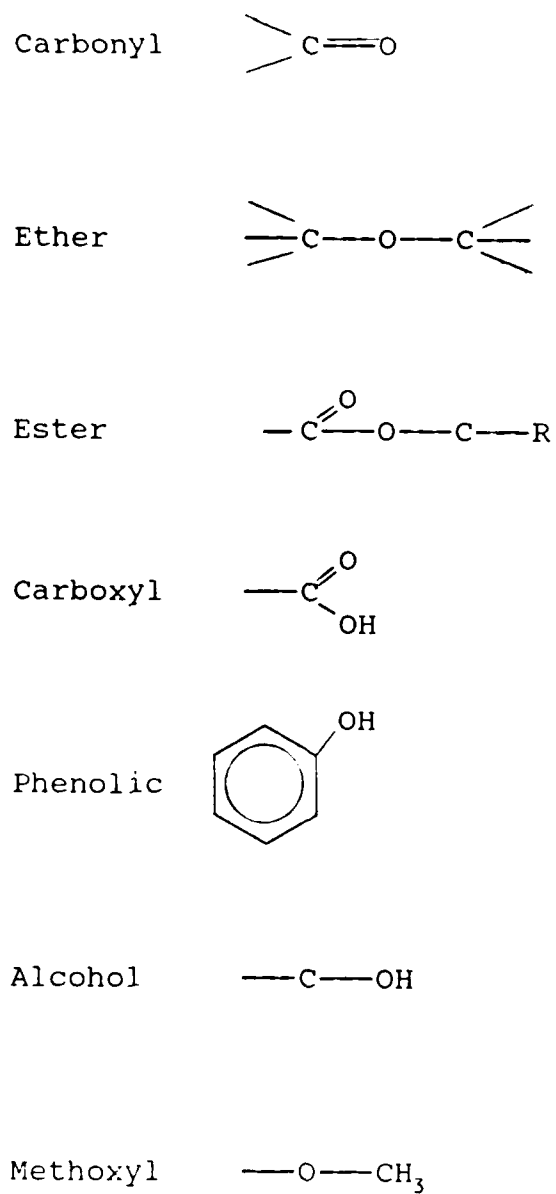
| Sample             | Amino Acids<br>(nM/mg) |
|--------------------|------------------------|
| Groundwater        |                        |
| Fulvic             | 29 - 44                |
| Humic              | 121                    |
| Streams and Rivers |                        |
| Fulvic             | 14 - 127               |
| Wetlands           |                        |
| Fulvic             | 36 - 79                |
| Humic              | 112                    |
| Soils              |                        |
| Fulvic             | 145 - 170              |
| Humic              | 478 - 707              |

**Table 2.3** Average concentration of amino acids present in humic and fulvic acids from water (Thurman, 1985)

| Amino acid     | Concentration (nM/mg) |     |
|----------------|-----------------------|-----|
|                | FA                    | HA  |
| Acidic         |                       |     |
| Aspartic acid  | 5.7                   | 12  |
| Glutamic acid  | 3.0                   | 9   |
| Adipic acid    | 0.5                   | 0.7 |
| Neutral        |                       |     |
| Glycine        | 11                    | 22  |
| Alanine        | 3                     | 10  |
| Leucine        | 1                     | 4   |
| Isoleucine     | 1                     | 3   |
| Valine         | 1                     | 5   |
| Serine         | 2                     | 5   |
| Threonine      | 2                     | 6   |
| Secondary      |                       |     |
| Proline        | 2                     | 8   |
| Hydroxyproline | 1                     | 17  |
| Aromatic       |                       |     |
| Phenylalanine  | 0.5                   | 2   |
| Tyrosine       | 0.5                   | 1   |
| Basic          |                       |     |
| Arginine       | 1                     | 1.4 |
| Lysine         | 0.5                   | 2.5 |
| Histidine      | 0.2                   | 1.3 |
| Sulfur         |                       |     |
| Cystine        | 0.2                   | 0.7 |
| Methionine     | 0.2                   | 0.7 |
| Total          | 36                    | 110 |

## 2.2 Functional Groups

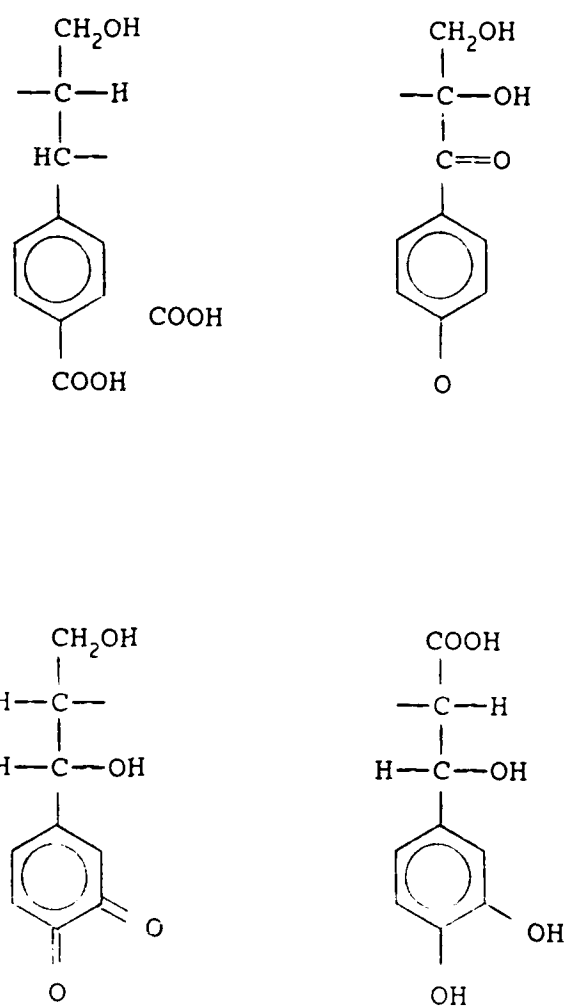
Although the actual structure of both the HA and FA fraction are unknown, it is composed of a series of functional groups; the major functional groups are shown in Figure 2.1. Functional groups of a model HA and FA determined by Schnitzer and Khan (1978) are shown in Table 2.4. Liao, et al. (1982), using gas chromatography/mass spectrometry on surface water from lakes, found that the general molecular structure of aquatic humics consisted of (a) single-ring aromatics with mainly three to six substituents as alkyl side chains, carboxylic acids, ketones, or hydroxyl groups; (b) short aliphatic carbon chains; and (c) polycyclic ring structures including polynuclear aromatics, polycyclic aromatic-aliphatics, and fused rings. In river waters and lakes, Plechanov, et al. (1983), used H-NMR (nuclear magnetic resonance) and found compounds present to be lignin-derived and of alkyl groups. Steelink (1985) has proposed basic units that are composed of postulated functional groups (see Figure 2.2). Others have postulated a representative structure for a FA and HA as shown on Figure 2.3. What is not shown in these structures are the small percentages (< 2 percent) of both nitrogen and sulfur (Perdue, 1985).



**Figure 2.1** Major functional groups in humic substances (after Snoeyink and Jenkins, 1980)

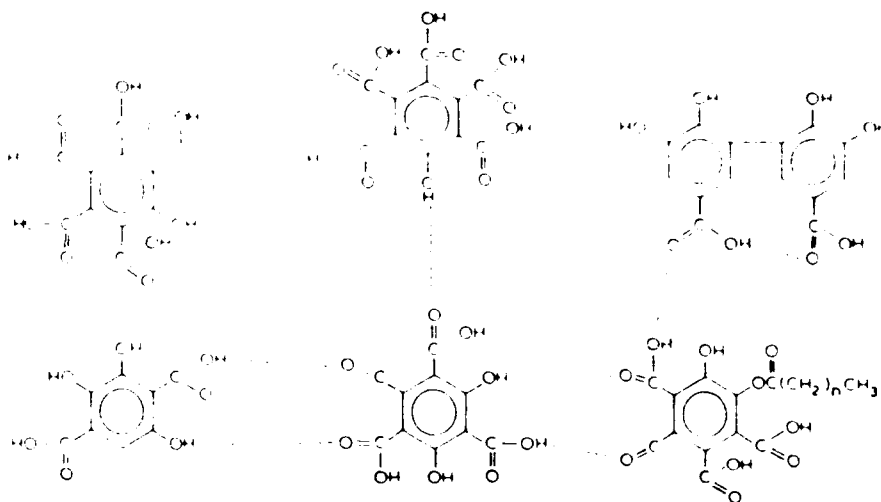
**Table 2.4** Functional group composition (Schnitzer and Khan, 1978)

| <u>Functional Groups</u>                                | <u>Model HA (meq/g)</u> | <u>Model FA (meq/g)</u> |
|---------------------------------------------------------|-------------------------|-------------------------|
| Total Acidity                                           | 6.7                     | 10.3                    |
| COOH                                                    | 3.6                     | 8.2                     |
| Phenolic -OH                                            | 3.9                     | 3.0                     |
| Alcoholic -OH                                           | 2.6                     | 6.1                     |
| Quinonoid C=O                                           | 2.9                     | 2.7                     |
| Ketonic C=O                                             |                         |                         |
| OCH <sub>3</sub>                                        | 0.6                     | 0.8                     |
| E <sub>4</sub> /E <sub>6</sub> *                        | 4.8                     | 9.6                     |
| * absorbance at 465 nm<br>-----<br>absorbance at 665 nm |                         |                         |

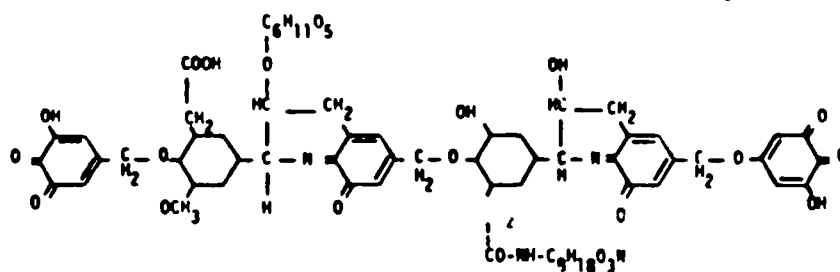


**Figure 2.2** Proposed basic units in humic acids  
(after Steelink, 1985)

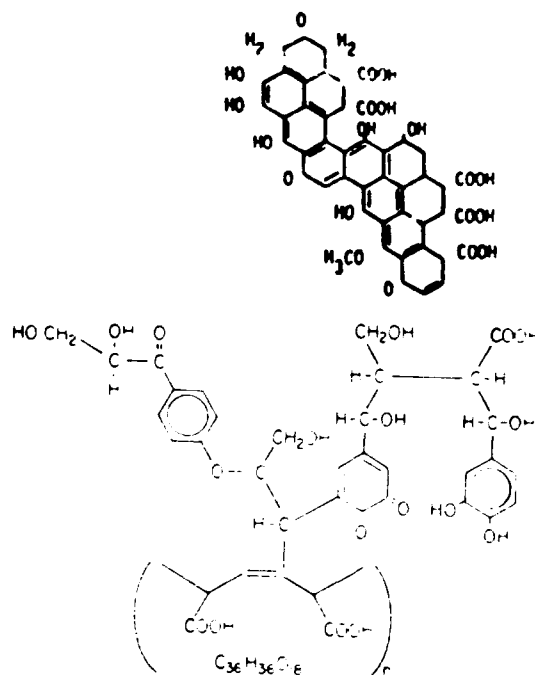
a)



b)



c)



**Figure 2.3** Postulated structure of a) fulvic acid (Schnitzer and Khan, 1972), b) humic acid (Oloffson and Allard, 1983) and c) humic acid (Steelink, 1985)

Several researchers have postulated on which types of functional groups in humic substances are important in the complexation of metals. Gamble (1970) has postulated that salicylic-type groups are involved in metal complexation while Manning and Ramamoorthy (1973) have suggested that the phthalic-type groups were responsible. Schnitzer (1972) suggested that both types of groups were important with the addition of C=O type groups and amines. Buffle, et al. (1980) refuted the idea that salicylic- and phthalic-type groups were solely responsible. By comparing the complex-formation properties of different natural water samples with the binding capacities of salicylic and phthalic acids, they showed that the binding was not high enough to satisfactorily explain the complexing properties of a fulvic acid by copper. McKnight, et al. (1983), modeled the complexation of aquatic fulvic acids by copper using two concentrations and binding constants. The most abundant ligand site ( $L_1$ ) represented both salicylic- and phthalic-type acids but only 16 percent of the total functional groups. The second most abundant ligand ( $L_2$ ) only represented 5 percent of the carboxylic and phenolic functional groups. There was also a high variability of  $L_2$  concentrations among the samples. They attributed the variable concentrations of functional groups to trace concentrations of possibly nitrogen and/or sulfur. More recently, Ephraim, et al. (1989), identified 30 - 45 percent

of the acidic sites responsible for copper binding as a salicylic acid-like moiety and 25 - 30 percent as a catechol-like moiety for an aquatic fulvic acid. Shown in Table 2.5 are dissociation and binding constants of some of the proposed types responsible for metal binding.

**Table 2.5** Dissociation and binding constants  
of possible binding groups

| Published<br>Values                                    | Model Compounds                |                    |                                |                                 |
|--------------------------------------------------------|--------------------------------|--------------------|--------------------------------|---------------------------------|
|                                                        | Catechol<br>(H <sub>2</sub> L) | Glycine<br>(HL)    | Phthalic<br>(H <sub>2</sub> L) | Salicylic<br>(H <sub>2</sub> L) |
| Potentiometric                                         |                                |                    |                                |                                 |
| pK <sub>a1</sub><br>(HL/H·L)                           | 13.0                           | 9.57               | 4.93                           | 13.6                            |
| pK <sub>a2</sub><br>(H <sub>2</sub> L/HL·H)            | 9.23 <sup>1</sup>              | 2.36 <sup>1</sup>  | 2.75 <sup>1</sup>              | 2.80 <sup>2</sup>               |
| Complexometric                                         |                                |                    |                                |                                 |
| B <sub>1</sub><br>(ML/M·L)                             | 13.58 <sup>3</sup>             | 8.27 <sup>4</sup>  | 4.00 <sup>1</sup>              | 10.80 <sup>2</sup>              |
| B <sub>2</sub><br>(ML <sub>2</sub> /M·L <sup>2</sup> ) |                                | 15.19 <sup>4</sup> | 5.31 <sup>5</sup>              | 18.45 <sup>6</sup>              |
| (MHL/M·HL)                                             |                                |                    | 1.20 <sup>1</sup>              |                                 |
| (ML·H/M·HL)                                            | 0.85 <sup>7</sup>              |                    |                                |                                 |
| (ML·H <sup>2</sup> /M·H <sub>2</sub> L)                | -8.345 <sup>7</sup>            |                    |                                |                                 |

<sup>1</sup> Smith and Martell, 1975

<sup>2</sup> Condikey and Martell, 1969

<sup>3</sup> Athavale, 1966

<sup>4</sup> Greiser and Sigel, 1971

<sup>5</sup> Lumme and Kari, 1975

<sup>6</sup> Neshkova and Sheytanov, 1985

<sup>7</sup> Jameson and Wilson, 1972

### 2.3 Metal Complexation

Humic substances are ubiquitous in the natural environment and are good ligands for metal binding. Humics can be important in the solubility of toxic metals in water sources and in the kinetics of transporting these metals (Clark and Choppin, 1990). Mantoura, et al. (1978), and Perdue (1989) described the main factors that control metal-humic interactions with the following:

- i) value of the binding constant; i.e., the nature of the metal and the binding site,
- ii) elevated pH that causes increased binding,
- iii) humic substance concentration,
- iv) elevated ionic strength that causes decreased binding, and
- v) major ion concentrations that control the competition for humic acid by magnesium and calcium, and the competition for trace metals by chloro- or sulphato- ligands.

Guy and Chakrabarti (1976) used a commercially-available humic acid (Aldrich) at pH 5 and found the stability constants of metal-organics to decrease as follows:



They also found that humic acids can maintain the binding of metal ions to as low as pH 3. Takamatsu and Yoshida (1978) also found increasing binding constants with pH for several soil humic acids, but unlike the previous authors, they found Cu(II) to have higher binding than Pb(II), and Cd(II) to have significantly lower binding at pH 5. Schnitzer and

Khan (1978), at pH 5.8 with soil-derived fulvic acids, showed the following binding trends:

$\text{Hg} = \text{Fe} = \text{Pb} = \text{Al} = \text{Cr} = \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Co} > \text{Mn} .$

Dobbs, et al. (1989), also recently showed the increase in metals bound with an increase in the number of binding sites.

Of the metals available for binding by humic substances, copper (II) is the most studied. Copper is a concern to the environment due to its toxicity to aquatic organisms. Copper toxicity is dependent not on the total copper concentration but on free copper activity (Anderson and Morel, 1978; Sunda and Guillard, 1976). Sunda and Hanson (1979) found through the UV-photooxidation of organic matter in river waters that the copper was bound predominantly to organic ligands. This directly affects the toxicity and bioavailability of copper to organisms as well as copper adsorption onto surfaces, copper precipitation, and solid solubility. It is therefore important that metal-humic interactions be part of any computational scheme in any modeling of natural water systems (Bassett and Melchior, 1990).

### 2.3.1 Mathematical Models

Some attempts to mathematically model the affinity of metals to humic substances were derived from earlier attempts of modeling proton binding to acidic polymers, ion exchange resins, and so on (Perdue, 1985). Current metal-

humate models are similar in the assumptions that follow:

- i) reactions at individual sites (ligands) are governed by mass law equations, and
- ii) microscopic mass law constants do not change with increased metal loading, i.e., there are no interactions among sites (Dzombak, et al., 1986).

Discrete and continuous multi-ligand models are currently used to describe metal-humate interactions.

The discrete ligand model uses only a few ligands (< 10) to fit experimental data. Dzombak, et al. (1986), noted that the optimal number of ligands can be estimated as one ligand for each order of magnitude of bound metal concentration observed in the titration data. Perdue (1985) described the discrete ligand model as inappropriate due to the complex mixture of nonidentical ligands that are expected in humic substances. The goal of this model though is not to represent a humic substance but to represent those sites that are important in metal binding and are of the most use (Fish, et al., 1986).

The continuous distribution models include the normal distribution model, the affinity spectrum model and the continuous stability function model. These models are based on the assumptions that the binding constant of a humic substance to a metal varies continuously and that the ligand frequency distributions can be integrated over the varying binding constant. Continuous distribution models offer an integral solution for ligand distributions, but the solution

is complex and numerical attempts to solve the integral equation are plagued by spurious oscillations (Dzombak, et al., 1986). A solution to the problems with the continuous distribution models is to assume a distribution. Such is the case with normal or Gaussian distribution models in which the probability of occurrences for a given ligand is assumed to be described by the symmetrical Gaussian distribution function (Perdue, 1985). Due to the generality of the theoretical normal distribution, the model only becomes useful as a good first approximation of the most probable acidic functional groups responsible for binding metals. The affinity spectrum model attempts to avoid the problems associated with solving an integral equation through the use of an affinity spectra. Peaks in the affinity spectrum reflect the importance of certain ligands and can be used as an aid for selecting discrete ligands from experimental data (Dzombak, et al., 1986). A similar model developed by Gamble, et al. (1972, 1973, 1980, 1983) is called the continuous stability function model. The approach in this model is to choose a dominant binding constant at each titration point and fit a ligand concentration to it. Shortfalls, however, include the characterization of only the weakest and most abundant ligand in a distribution (Dzombak, et al., 1986).

It should be recognized, though, that with metal-binding interaction, as the number of components or ligands

that bind the metal increase so does the number of sites for binding. The result is a smooth curve that can be modeled fairly easily, and if fitted, the output is only curve-fitted values.

### 2.3.2 Mathematical Applications

Current geochemical models experience difficulty incorporating humic substances into speciation calculations (Bassett and Melchior, 1990). The problem is due to the complex nature of humic substances. Classical attempts such as the Debeye-Huckel equation cannot be applied.

Perdue (1978) described the generalized reaction of a metal (M) and a protonated ligand complex (HL) to a complexed metal (ML) with the following expression:



This equation is thermodynamically equivalent to the following:



and



The knowledge of dissociation constants helps to better understand the concentration and chemical characteristics of humic substances.

Direct potentiometric titrations can give operationally-defined estimates of carboxylic groups which relate to dissociation constants for the humic substance (Perdue, 1980; Oliver, et al., 1983). Currently, operationally-defined carboxylic content is that acidity

required to titrate a solution from pH 3 to 8, and phenolic content is estimated at twice the acidity required to titrate from pH 8 to 10 (Thurman, 1985). Phenolic content taken as the difference between total acidity and carboxylic content has, however, not achieved complete certainty (Perdue, et al., 1980).

The binding of copper by DOC can assume the simplest form according to Cabaniss and Shuman (1988a) with a 1:1 complex stoichiometry, no site interactions, and a single binding site of concentration  $L_T$ . The binding constant expression (see Table 2.6 for term definitions)

$$K_{Cu} = \frac{[CuL]}{[Cu][L]} \quad (4)$$

rearranges to the form below to give the concentration of bound copper,  $[CuL]$ ,

$$[CuL] = \frac{[L_T][Cu]K_{Cu}}{1 + [Cu]K_{Cu}} \quad (5)$$

If the simplifying assumptions are dropped, the model gets more complicated.

When the assumption that all the binding sites within the humic acid are identical is dropped,  $[CuL]$  is expressed as follows (Cabaniss and Shuman, 1988a):

$$[CuL] = \frac{N \sum_{i=1} [L_i][Cu]K_{Cu}}{1 + [Cu]K_{Cu}} \quad (6)$$

Models such as the discrete ligand, continuous distribution, and normal distribution model make different assumptions of

**Table 2.6** Terms and definitions (after Cabaniss and Shuman, 1988a; Neshkova and Sheytanov, 1985)

|                 |                                                                     |
|-----------------|---------------------------------------------------------------------|
| $[Cu_T]$        | total copper concentration                                          |
| $[Cu]$          | cupric ion concentration                                            |
| $[CuL]$         | copper-organic complex concentration                                |
| $[L]$           | free ligand concentration                                           |
| $[CuOH]$        | hydrolyzed copper concentration                                     |
| $[CuOHL]$       | hydrolyzed copper-ligand complex concentration                      |
| $N, i$          | number of binding sites, site being considered                      |
| $[L_T]$         | total ligand concentration                                          |
| $[L_i]$         | concentration of ligand $i$                                         |
| $(H)$           | proton activity                                                     |
| $P, j$          | maximum coordination number, number being considered                |
| $B_j$           | copper binding constant for $j$ ligand molecules                    |
| $K_{cu}$        | copper binding constant for 1:1 complex                             |
| $K_H$           | proton binding constant                                             |
| $K_a$           | apparent $K_{cu}$ for given charge on polyelectrolyte               |
| $K_{CuH}$       | copper-proton exchange constant                                     |
| $K_{CuH^2}$     | copper-proton <sup>2</sup> exchange constant                        |
| $K_{OH}$        | copper hydrolysis constant                                          |
| $K_{CuOH}$      | hydrolyzed copper-ligand binding constant                           |
| $\alpha_{L(H)}$ | side-reaction coefficient for protonation of a ligand (see eqn. 18) |
| $T$             | temperature ( $^{\circ}K$ )                                         |

equation (6) about the number and distribution of sites.

If the assumption that the complex stoichiometry is greater than 1:1 [i.e., 1:2 to a maximum of 1:6 with Cu(II)], then a single binding site can be expressed as

$$[\text{CuL}] = \sum_{j=1}^P B_j [\text{Cu}] [\text{L}_j] \quad (7)$$

Proton dependence must be accounted for in any model. A first-order proton dependence will have the binding as shown below (Gamble, et al., 1980):

$$K_{\text{CuH}} = \frac{[\text{CuL}]}{[\text{Cu}] K_H [\text{L}]} \quad (8)$$

where

$$K_H = \frac{[\text{HL}]}{[\text{H}] [\text{L}]} \quad (9)$$

or

$$K_{\text{CuH}} = \frac{K_{\text{Cu}}}{K_H} \quad \text{for } [\text{L}] \ll [\text{HL}] \quad (10)$$

The bound copper will be

$$[\text{CuL}] = \frac{[\text{L}_T] [\text{Cu}] K_{\text{CuH}}}{[\text{H}] + [\text{Cu}] K_{\text{CuH}}} \quad (11)$$

If the dominant species of the ligand is in the form  $\text{H}_2\text{L}$ , then bound copper is expressed as

$$[\text{CuL}] = \frac{[\text{C}_T] [\text{Cu}] K_{\text{Cu}^+}}{[\text{H}] + [\text{Cu}] K_{\text{Cu}^+}} \quad (12)$$

or

$$[\text{CuL}] = \frac{[\text{C}_T] [\text{Cu}] K_{\text{CuHL}}}{\{H\}^2 + [\text{Cu}] K_{\text{CuHL}}} \quad (13)$$

If the bound copper is being hydrolyzed or a hydrolyzed copper is being bound then the binding of hydrolyzed copper can be expressed as

$$K_{\text{CuOHL}} = \frac{[\text{CuOHL}]}{[\text{CuOH}] [\text{L}]} = \frac{[\text{CuOHL}] \{H\}}{[\text{Cu}] K_{\text{OH}} [\text{L}]} \quad (14)$$

where

$$K_{\text{OH}} = \frac{[\text{CuOH}] \{H\}}{[\text{Cu}]} \quad (15)$$

and the hydrolyzed copper is

$$[\text{CuOHL}] = \frac{[\text{L}_T] K_{\text{CuOHL}} K_{\text{OH}} [\text{Cu}]}{\{H\} + K_{\text{CuOHL}} K_{\text{OH}} [\text{Cu}]} \quad (16)$$

The above equations are used for theoretical and modeling calculations, but for more applicable use, the binding constants can be determined from experimental data with the following expressions (Neshkova and Sheytanov, 1985):

$$[\text{Cu}] = [\text{Cu}_T] / \left( 1 + B_1 \frac{[\text{L}_T]}{\alpha_{\text{L(H)}}} + B_2 \frac{[\text{L}_T]^2}{\alpha_{\text{L(H)}}^2} + \dots + B_n \frac{[\text{L}_T]^n}{\alpha_{\text{L(H)}}^n} \right) \quad (17)$$

where

$$\alpha_{\text{L(H)}} = 1 + \{H\} K_H + \{H\}^2 K_H K_{2H} + \dots + \{H\}^n K_H K_{2H} \dots K_{nH} \quad (18)$$

Temperature effects for titration data can be corrected

by the following equation (Smith and Martell, 1975):

$$\log K_{Cu2} = \log K_{Cu1} + \Delta H(T_2 - T_1)/1701.3654 \text{ KJ } ^\circ\text{K/mole} \quad (19)$$

where  $\Delta H$  is the enthalpy change.

Ionic strength corrections are tabulated in Smith and Martell (1975). They found that stability constants usually decrease with increasing ionic strength and generally reach a minimum at an ionic strength of about 0.5. Stability constants were also observed to increase through an ionic strength of at least 3.0, and ionic strengths of 0.1 and 1.0 frequently had the same magnitude.

### 2.3.3 Model Fitting

Copper titration data can be fitted with any of the above modeling methods to obtain parameters. Although these fitting parameters are operational binding constants and are highly dependent on experimental conditions, comparing metal speciation that was computed with model parameters is appropriate (Holm and Curtiss III, 1990). It is, however, inappropriate to compare complexation parameters determined by different methods or for different water samples (Cabaniss and Shuman, 1988c). For this reason, only a few modeling attempts will be discussed. Van Den Berg and Kramer (1979) assumed the simplest binding of 1:1 of copper with no proton dependency, and they obtained binding constants for a fulvic acid and ligands in Lake Ontario of  $10^{7.8}$  and  $10^{8.8}$ , respectively. They calculated these constants with no knowledge of the dissociation constant of

the water sample and at a pH of 7.6.

A discrete ligand model was used by Hering and Morel (1988) for a Suwannee Stream humic acid at pH 8.2 to 8.3. They obtained the best fit with a 3-ligand system at concentrations of  $5.0 \times 10^{-5}$  M,  $2.0 \times 10^{-4}$  M and  $1.8 \times 10^{-8}$  M with binding constants of  $> 10^{11}$ ,  $10^{9.2}$  and  $10^{6.6}$ , respectively. Copper titrations were done at pH 8.2 to 8.3. In comparison, Cabaniss and Shuman (1988b) modeled Suwannee fulvic acid with a 5-ligand system for the pH range of 5 to 8.5.

Groundwater from Orange County, California, was titrated by Waterbury (1990) and the best fit was obtained using a 2-ligand system. He modeled an XAD-8 humic acid fraction with  $L_1$  at  $10^{-7.5}$  and  $L_2$  at  $10^{-11.2}$  with binding constants of  $pL_1$  at 5.2 and  $pL_2$  at 4.9 for pH 6.2 and an ionic strength of 10 mM.

## 2.4 Chemical Models

In the attempt to attribute some chemical significance to the structural and modeling work, several researchers have used different chemicals. EDTA (Dursma, 1970), nitrilotriacetic acid (Childs, 1971), salicylic acid (Morel and Morgan, 1972), and citric acid (Stumm and Brauner, 1975) were some of the single compounds tried in the modeling of a humic substance. Bresnahan (1978) attempted a 1:2 and a 1:1 mixture of salicylic and phthalic acid to simulate a soil fulvic acid but also had no success. Lamy, et al. (1987), did not try to simulate a humic substance but went directly to a commercially-available humic-like substance called PCTG (catechol + triglycine polycondensate). PCTG had the following elemental composition in percentages:

C - 45.4, H - 4.0, N - 11, O - 36.9, S - 0.5.

All of the percentages fell within the average composition of a humic acid with the exception of the nitrogen content, which was high.

Strict adherence to elemental compositions will not by itself describe a humic substance. Steelink (1985) showed that chemical formulas of humic substances can also describe the same empirical formula for whole wood. Elemental composition can help one devise hypothetical structures for humates.

## CHAPTER 3

### MATERIALS AND METHODS

The stages of this research included (1) the selection and verification of model compounds, (2) the titrations of two XAD-8 isolates, and (3) the modeling with experimental verification. The two XAD-8 isolates were groundwaters from Orange County and the Biscayne Aquifer.

#### 3.1 Materials

##### 3.1.1 Chemicals

All chemicals used for this research were reagent grade. Adjusting of pH was done with diluted concentrations of  $\text{HNO}_3$  (1.0 N, 0.1 N, and 0.01 N) and  $\text{NaOH}$  (1.0 N, 0.1 N, 0.08 N, and 0.01 N). Distilled water passing through a Millipore cartridge system (referred to as Milli-Q water) was used for dilutions.

pH control was accomplished with the zwitterion buffer MES (4-morpholineethane sulfonic acid, Aldrich) for pH 6.2 and HEPES [1,4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, Aldrich] for pH 7.5. Ionic strength was adjusted to 10 mM with sodium nitrate (Mallinckrodt). Copper (II) nitrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , Alfa] was used. Determining the concentration of the stock solution of copper was accomplished with EDTA titrations (Nutritional Biochemicals Corp.).

The model compounds used were catechol (1,2-dihydroxybenzene, Aldrich); glycine (aminoacetic acid, Baker); phthalic acid (benzene-1,2-dicarboxylic acid, Aldrich); and salicylic acid (2-hydroxybenzoic, Aldrich).

All of the labware used was acid washed. Washing consisted of rinsing and then soaking in a 3:1 (Milli-Q:HNO<sub>3</sub>) nitric acid bath for 8 hours. Rinsing and soaking in Milli-Q followed for at least 3 hours.

### 3.1.2 Groundwater Samples

The two sources of humic substances were from groundwaters collected in five-gallon polypropylene containers in Orange County Water District, California, and the Biscayne Aquifer in Dade County, Florida. Upon receipt, samples were stored at 4° C as received. Groundwaters were filtered with prewashed 0.45- $\mu$ m filters to isolate dissolved organic matter (DOM). From analyses provided by Orange County Water District and specific conductance measurements, the ionic strength of OCGW was determined to be 3 mM (Waterbury, 1990). BA groundwater had a similar conductivity measurements and ionic strength as OCGW. Characteristics of the XAD-8 isolates are shown in Table 3.1.

**Table 3.1** Characteristics of humic fraction (Odem, 1990)

| <u>Source</u> | <u>DOC</u><br><u>(mg/L)</u> | <u>Humic</u><br><u>%</u> | <u>pH</u> | <u>Avg. MW</u> | <u>Conductivity</u><br><u>(uohms/cm)</u> | <u>COOH</u><br><u>Acidity</u><br><u>(meq/g-C)</u> |
|---------------|-----------------------------|--------------------------|-----------|----------------|------------------------------------------|---------------------------------------------------|
| <b>OCGW</b>   |                             |                          |           |                |                                          |                                                   |
| XAD-8         | 5.23                        | 80                       | 7.95      | 1700           | 420                                      | 19.7                                              |
| <b>BA</b>     |                             |                          |           |                |                                          |                                                   |
| XAD-8         | 5.66                        | 50                       | 8.05      | 1600           | 480                                      | 13.4                                              |

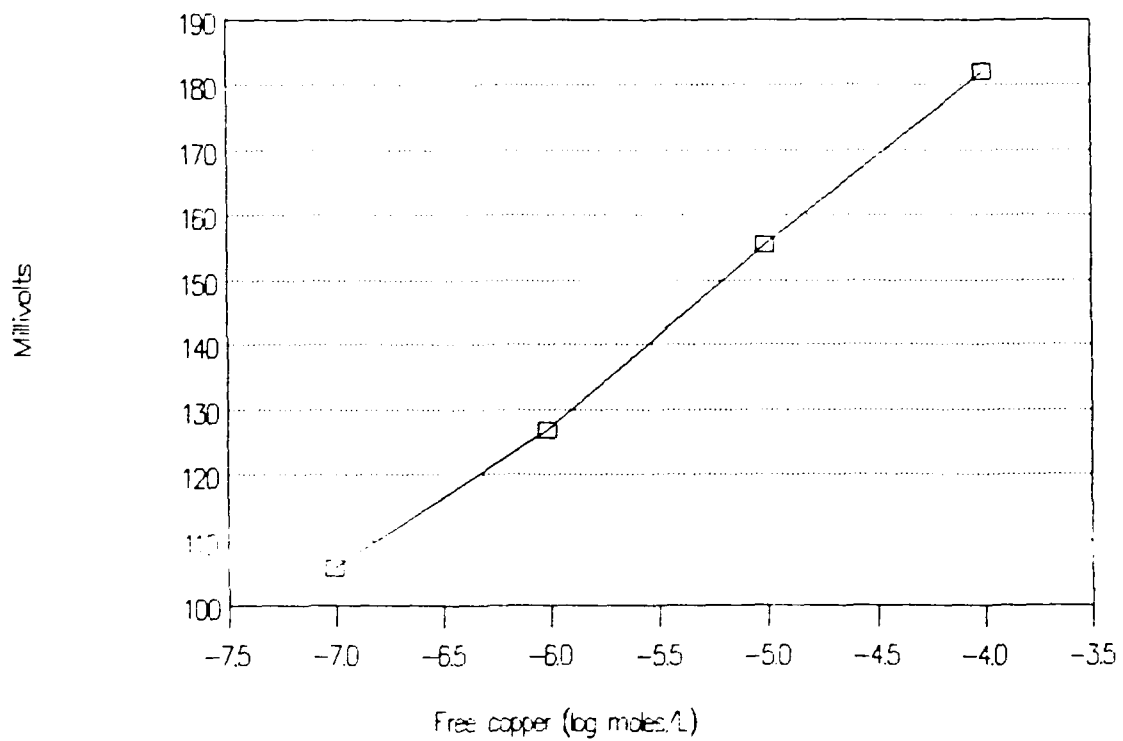
### 3.2 Analytical Methods

#### 3.2.1 Organic Carbon

Concentrations of dissolved organic carbon were measured with a Shimadzu Model TOC-500 carbon analyzer. Standards were at 5.0 and 10.0 ppm DOC. Prior to injection, a 10-ml sample was acidified to pH 2 - 3 and purged for ten minutes with  $N_2$  gas. Injection volume was 50  $\mu$ l.

#### 3.2.2 pH and $Cu^{2+}$

pH and free copper was measured with a Fisher Scientific Accumet 950 pH/ion Meter. The pH probe used was a Radiometer America pH electrode, and the copper probe was an Orion cupric electrode in combination with an Orion double junction reference electrode. The pH was calibrated with pH 4.00, 7.00, 8.00, and 10.00 buffers (Metrepack) in combination with a Fisher Scientific automatic temperature probe. Cupric electrodes were calibrated with  $10^{-6}$  M,  $10^{-5}$  M, and  $10^{-4}$  M  $Cu(NO_3)_2$  adjusted to an ionic strength of 10 mM and pH 6. Copper standards and titrants were made in polypropylene, 100-ml beakers from a stock concentration of 0.3707 M  $Cu(NO_3)_2$ . Standard were made weekly and titrants daily. The stock  $Cu(II)$  was kept refrigerated at 4° C between uses. Linear regressions from the millivolt responses of the copper standards provided a standard curve for free copper concentrations. A typical copper calibration curve is shown in Figure 3.1. For this standard curve, dilutions of  $10^{-7}$ ,  $10^{-6}$ ,  $10^{-5}$ , and  $10^{-4}$  M were measured



**Figure 3.1** Typical copper (II) calibration curve

with the copper probe and plotted. A linear regression done with Quattro spreadsheet software yielded the following expression for  $10^{-4}$  to  $10^{-7}$  M:

$$\log [\text{Cu}] = 0.038786 \text{ (mV)} - 11.0349 . \quad (20)$$

The  $r^2$  for this range was 0.996. Since the linear response of the copper probe becomes non-linear below approximately  $10^{-6.7}$  M (Orion, 1986), a three-point standard curve was used for concentrations of  $10^{-6}$ ,  $10^{-5}$ , and  $10^{-4}$  M for the complexometric titrations. For the same standard curve shown in Figure 3.1, the linear expression changed to

$$\log [\text{Cu}] = 0.0363 \text{ (mV)} - 10.6248, \quad (21)$$

and  $r^2$  was 0.999. Linearity assumed to  $10^{-7}$  M had only slight deviations.

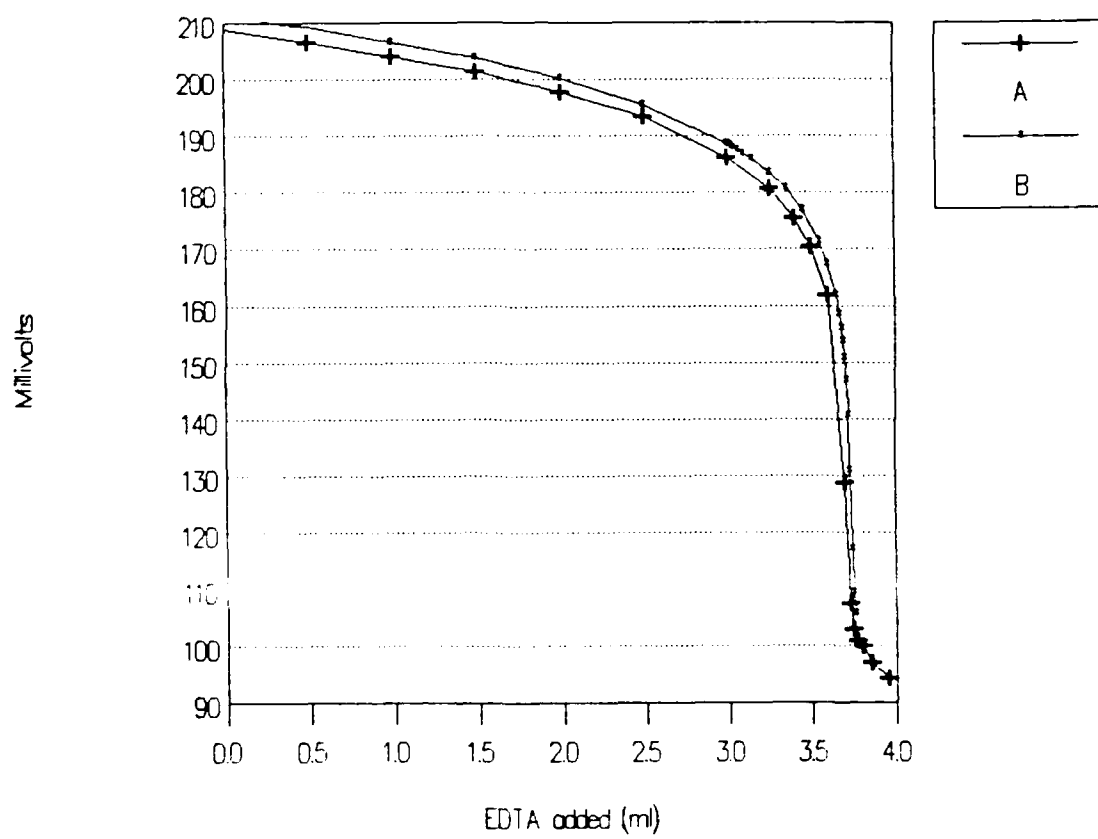
### 3.2.3 EDTA Titrations

EDTA titrations using the cupric electrode probes were performed on the diluted stock copper (II) solution as described in the cupric electrode instruction manual (Orion, 1986). Figure 3.2 shows two titrations conducted. The inflection point on the curves indicated the concentration for the stock copper (II) solution to be the following:

Titration A: 0.3680 M

Titration B: 0.3730 M

The mean of the two titration curves of 0.3707 M was used for the stock copper (II) solution concentration.



**Figure 3.2** EDTA titration curves

### 3.3 Experimental Methods

#### 3.3.1 XAD-8 Isolation

The procedure of Thurman and Malcolm (1981) for isolating humic substances was used with some modifications. The apparatus consisted of a 2-ft long, 3-inch diameter column filled a quarter from the bottom with XAD-8 resin. A separating funnel served as a reservoir for the groundwater feed and connected to the column with 1/4-inch tygon tubing along with a stopcock for flow control. Procedures used follow:

- a) Column prepared with three liters of Milli-Q water passed through until the outflow pH was between 5 and 6.
- b) 600 mls of pH 2  $\text{HNO}_3$  solution passed through the column.
- c) 0.45  $\mu\text{m}$ -filtered groundwater at pH 2 adjusted with  $\text{HNO}_3$  passed through the column at an outflow rate of  $25 \pm 2$  ml/min.
- d) 250 mls of pH 2  $\text{HNO}_3$  solution passed through until one inch of water remained in the resin.
- e) 0.1 N NaOH passed through until the outflow absorbance equaled the inflow with the eluate of humic acid collected.
- f) A hydrogen cation exchange resin was added to the collected eluate in a batch mode and stirred for 1.5 hours. The amount of resin added was determined with the following equations (Waterbury, 1990):

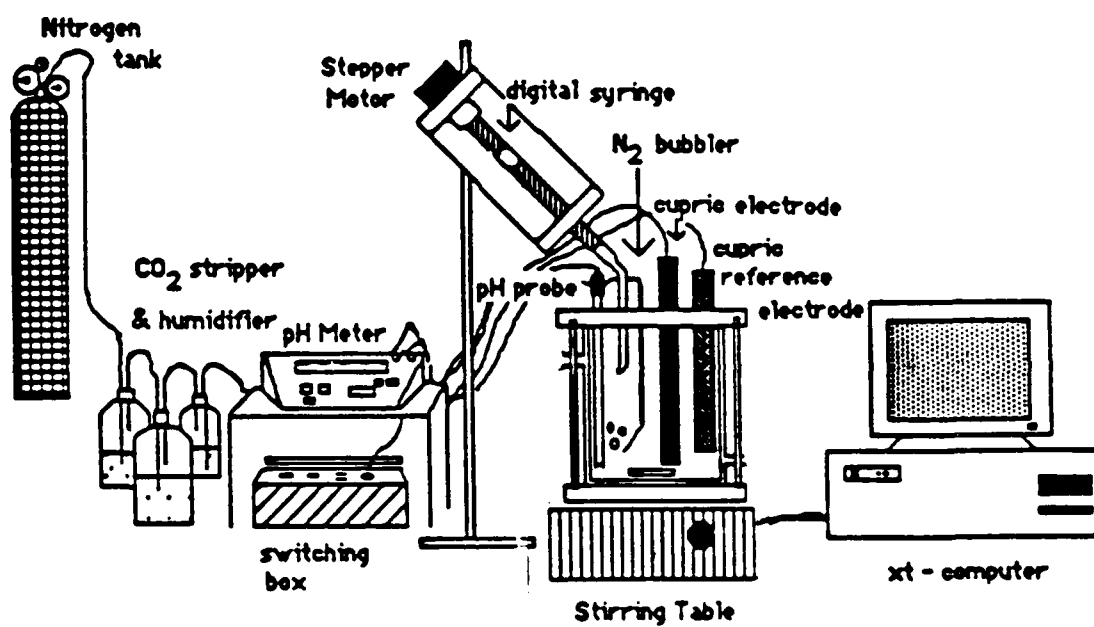
$$\begin{aligned}
 &(\text{ml of eluate}) (0.1 \text{ N NaOH}) = (\text{meq of active material}) \\
 &\frac{(\text{meq of active material})}{(5.1 \text{ meq / dry g resin})} = (\text{g of resin added}) \quad (22)
 \end{aligned}$$

g) The resin and eluate solution passed through a 0.45  $\mu\text{m}$  filter membrane to separate the resin from the dissolved humic substance.

The OCGW humic concentrate was diluted with Milli-Q then stored at its natural DOC of 5.66 mg/L. BA humic concentrate was stored in its concentrated form with a DOC of 50.2 mg/L and later diluted with Milli-Q for the titrations.

### 3.3.2 Titration Apparatus

Potentiometric and complexometric titrations for the model compounds, BA groundwater, and mixtures of model compounds were performed in 400-ml, polypropylene, jacketed beakers (see Figure 3.3). Titrations for the OCGW were performed in 150-ml, glass, jacketed beakers with temperatures controlled by recirculating water to 23° C. Titrations in polypropylene beakers were performed at room temperature (23° C  $\pm$  2). The apparatus for titrating the model compounds and BA groundwater was continually updated through this research project. Initial experiments were conducted with a Fisher Accumet 925 pH meter. A Fisher 753 electrode switch was then added to allow the measuring of



**Figure 3.3** Titration apparatus for model compounds and BA groundwater (after Waterbury, 1990)

both pH and free copper. Finally, a Fisher Accumet 950 pH/ion meter replaced both the pH meter and the electrode switch. Measurements were taken with a Radiometer America combination pH electrode and an Orion double junction reference and cupric electrode. A VWR model 310 magnetic stirrer ensured adequate mixing. A nitrogen atmosphere was used in all titrations.  $N_2$  gas was washed by bubbling through solutions of 2.0 N NaOH and Milli-Q water. An autoburette was used to add aliquots of acid or copper. The autoburette consisted of a Superior Electric Slo-syn synchronous/stepping motor, type MO61-FC02, equipped with a Breg autoburette P/N JJ-9. The motor was controlled by an IBM-compatible microcomputer through a AST Research CK 7260 multi I/O, a John Bell 86-108A Universal Parallel Interface, and a Rogers Lab R2D23 dual axis stepper motor driver board. The experimental set-up for OCGW titrations also included a Haake KT2 water temperature recirculator. A BASIC software program (see Appendix D) allowed parameter controls by the user and provided both hardcopy and printed data. For each aliquot added; time, millivolt or pH, and the volume of titrant was recorded.

Prior to starting a titration, the samples were reduced to pH 3 with  $HNO_3$  and then purged with  $N_2$  gas for at least 4 hours to remove  $CO_2$  gas.  $NaNO_3$  was added to the solutions to adjust the ionic strength to 10 mM.

### 3.3.3 Potentiometric Titrations

Potentiometric titrations were performed on catechol, glycine, phthalic, salicylic, and the XAD-8 humic acid fractions of OCGW and BA. Replicates were only performed for glycine. The XAD-8 isolates were titrated at a DOC of 5.66 mg/L for OCGW and 12.5 mg/L for BA ( a 3:1 dilution of the XAD-8 eluate). Titrations began at pH 3 and ended at pH 10. Carboxylic acidities were determined from the operational definition by Thurman (1985) with Milli-Q water corrections.

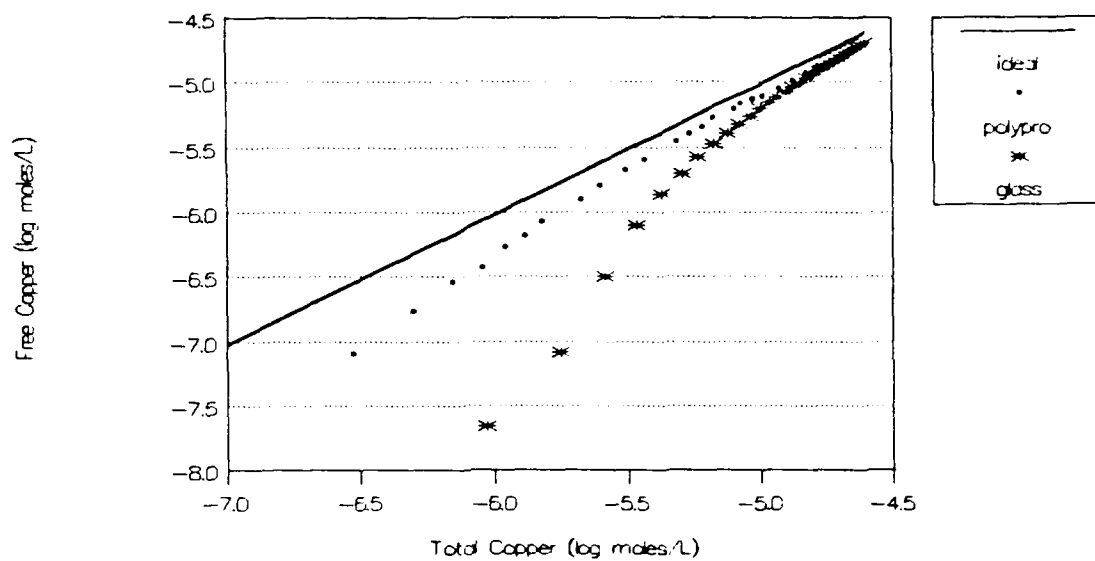
### 3.3.4 Complexometric Titrations

All complexometric titrations were conducted in the dark to prevent light interferences to the cupric electrode. A 200-ml volume of the samples at varying compound concentrations was used for the titrations. Concentrations from  $1 \times 10^{-4}$  M to  $5 \times 10^{-4}$  M was required of MES to maintain the pH at  $6.2 \pm 0.1$ . Titrations performed at pH 7.5 needed 0.5 to 5 mM HEPES to maintain the pH at  $7.5 \pm 0.01$ . DOCs of the OCGW samples were the same as the potentiometric titrations. For BA the DOC was reduced by 2.5 times to 5.02 mg/L to get complexation within the range of the copper probe. Aliquots of 1 mM copper were titrated and allowed to equilibrate for 10 minutes. Complexometric titrations for BA, however, were allowed to equilibrate for up to 30 minutes towards the end of the titrations. Replicates were again only performed on glycine at pH 6.2 and pH 7.5.

Prior to determining the binding effects of the compounds, Milli-Q blanks were titrated to show any sorption on the titrating vessels, complexation by the Milli-Q water source and buffers, and error in measurements. Shown in Figure 3.4 are Milli-Q titrations compared to an ideal blank of ultrapure water with no carbonate species at an ionic strength of 10 mM modeled with TITRATOR using Cu-OH constants from Paulson and Kester (1980). MES buffer concentration at pH 6.2 was 0.1 mM, and HEPES buffer at pH 7.5 was 5 mM. The loss in linearity of the copper probe can be seen on the curves.

OCGW XAD-8 was titrated under temperature-controlled conditions in a glass beaker; whereas, BA XAD-8 was titrated at room temperature in a polypropylene beaker.

## pH 6.2 Titrations



## pH 7.5 Titrations

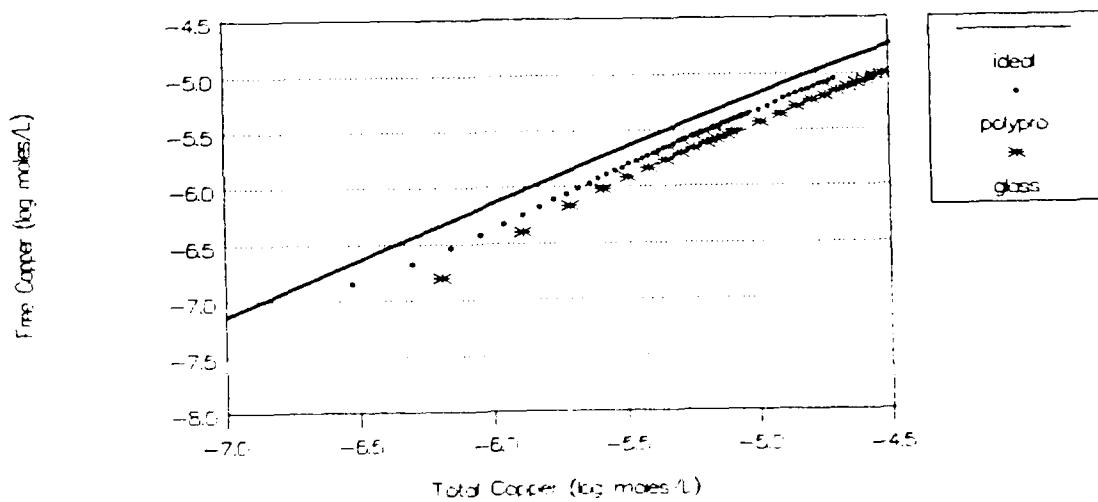


Figure 3.4 Milli-Q complexometric titrations

### 3.4 Data Analysis

Dissociation and binding constants from the titrations were verified with published constants using an interactive computer program called TITRATOR (Cabaniss, 1987). Potentiometric titrations were fitted using an iterative process with TITRATOR. Values for the model compound concentrations were based on carboxylic content, phenolic content, and nitrogen content. Complexometric data of the natural sources were initially fitted with a non-linear squares regression, statistical package (SAS, 1979) using an approach similar to Cabaniss and Shuman (1988a). Assumptions for which ligand species dominated at a certain pH were based on  $pK_a$  values. Once optimum fitting parameters were calculated, adjustments to the parameters were made using TITRATOR. Adjustments were only required for catechol and glycine (see Table 3.2).

The fitting of the complexometric data first included fitting each of the model compounds with SAS to identify the ligand and concentrations to use for further modeling. Two of the model compounds (either catechol, phthalic or salicylic acid) were then fitted to the data, and then those concentrations were used for a 3-ligand fit to the data with a set concentration of glycine based on assumed values of nitrogen content.

**Table 3.2** SAS equations and adjusted binding constants

| <u>Compound</u>                                                                                                        | <u>K*</u> | <u>Adjusted<br/>K</u> |
|------------------------------------------------------------------------------------------------------------------------|-----------|-----------------------|
| catechol:                                                                                                              |           |                       |
| $[\text{CuL}_{\text{cat}}] = \frac{[\text{L}_T] [\text{Cu}] K_{\text{CuH}}}{(\text{H})^2 + [\text{Cu}] K_{\text{Cu}}}$ | -8.345    | -7.96                 |
| glycine:                                                                                                               |           |                       |
| $[\text{CuL}_{\text{gly}}] = \frac{[\text{L}_T] [\text{Cu}] K_{\text{CuH}}}{(\text{H}) + [\text{Cu}] K_{\text{CuH}}}$  | -1.3      | -1.24                 |
| phthalic acid:                                                                                                         |           |                       |
| $[\text{CuL}_{\text{phth}}] = \frac{[\text{L}_T] [\text{Cu}] K_{\text{Cu}}}{1 + [\text{Cu}] K_{\text{Cu}}}$            | 4.0       | ----                  |
| salicylic acid:                                                                                                        |           |                       |
| $[\text{CuL}_{\text{sal}}] = \frac{[\text{L}_T] [\text{Cu}] K_{\text{CuH}}}{(\text{H}) + [\text{Cu}] K_{\text{CuH}}}$  | -2.45     | ----                  |

(after Cabaniss and Shuman, 1988a)  
 \* from published constants (see Table 2.5)

## CHAPTER 4

### RESULTS AND MODELING

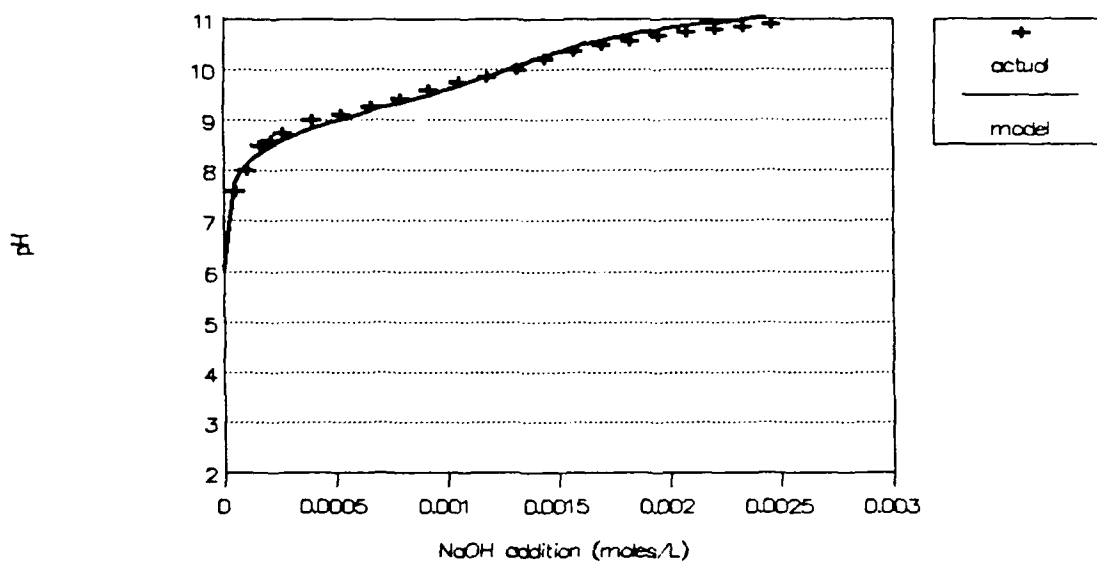
#### 4.1 Single Model Compound Titrations

Potentiometric and complexometric titrations of catechol, glycine, phthalic acid, and salicylic acid were done to verify dissociation and binding constants with the published values. The replicates performed on glycine, with error bars for the complexometric titrations, are included in the figures. Titration data are included in Appendix A.

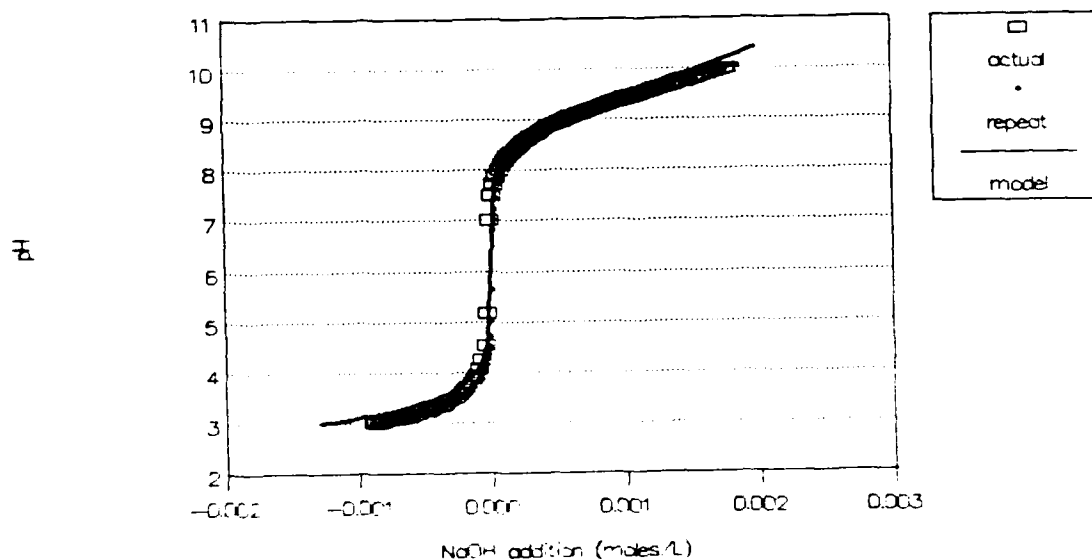
##### 4.1.1 Potentiometric Titrations

Potentiometric titrations performed on each model compound and the model fits are shown in Figures 4.1a and 4.1b. With the exception of glycine, all of the model compounds were titrated without adjusting the pH to 3. Figure 4.2 shows potentiometric titrations of all the model compounds.

## Catechol

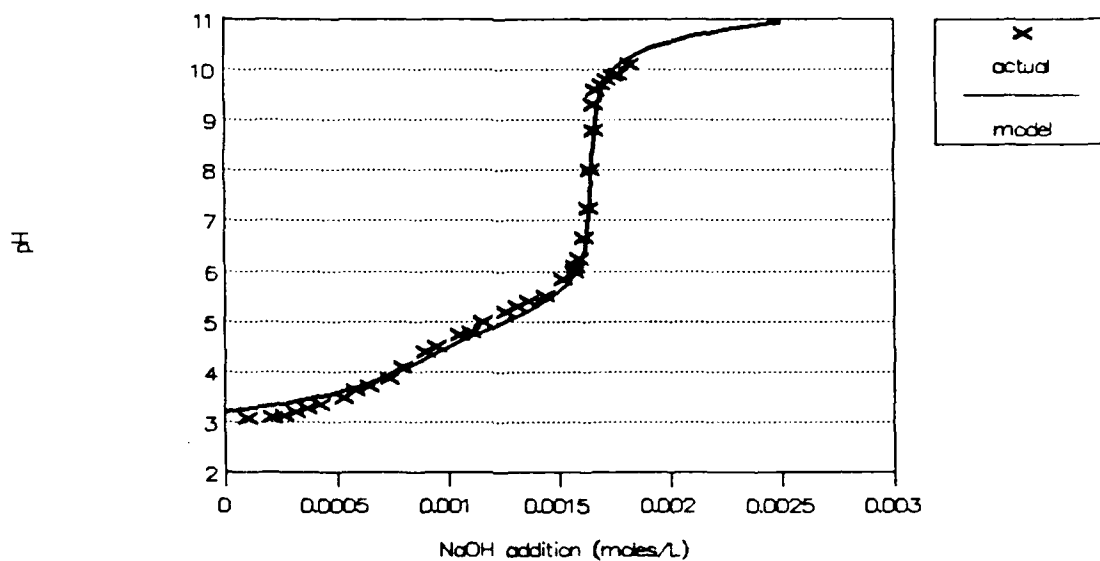


## Glycine

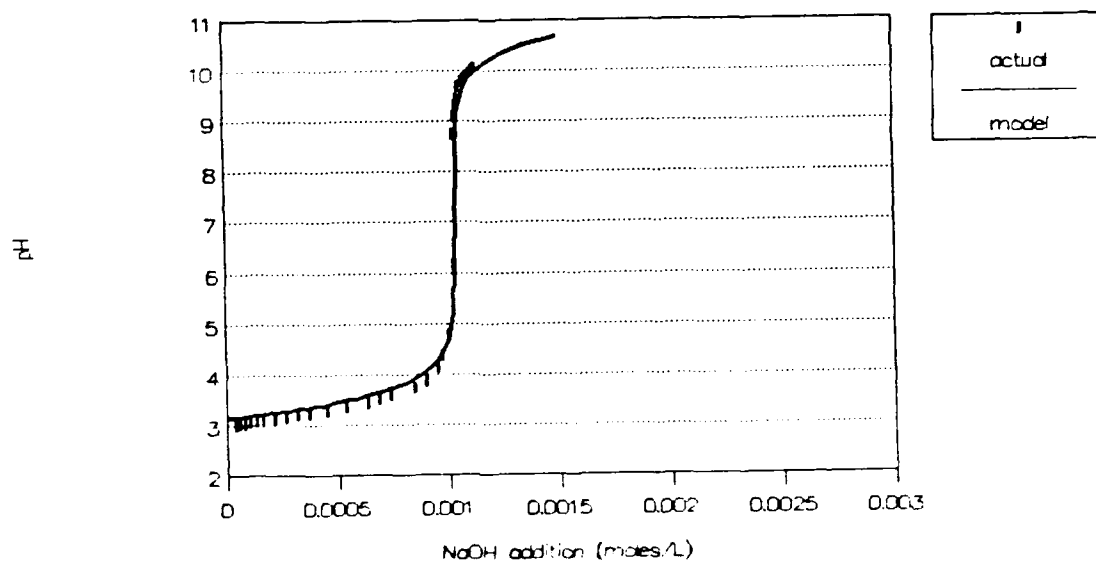


**Figure 4.1a** Potentiometric titration of model compounds - catechol ( $1.37 \times 10^{-3}$  M) and glycine ( $2.0 \times 10^{-3}$  M)

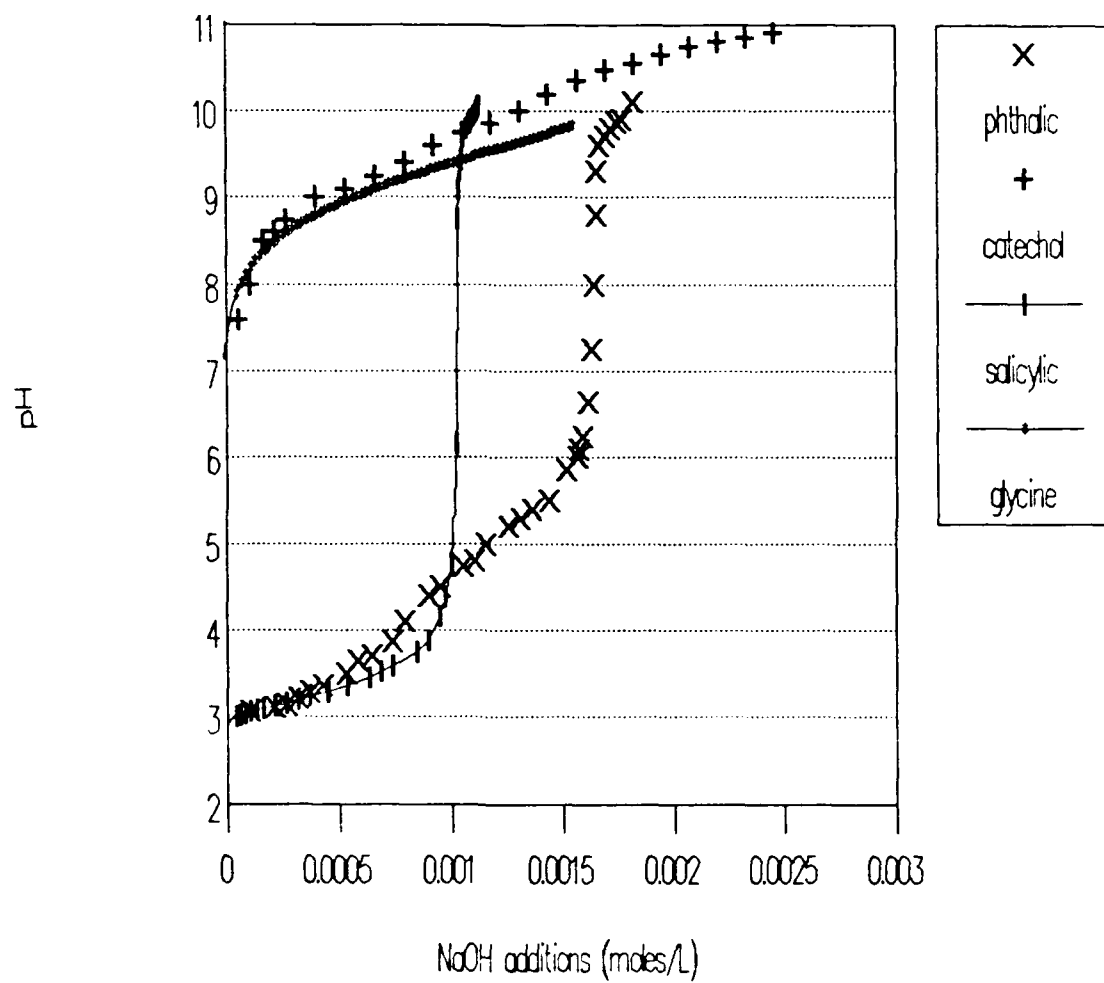
## Phthalic Acid



## Salicylic Acid



**Figure 4.1b** Potentiometric titration of model compounds - phthalic acid ( $8.25 \times 10^{-4}$  M) and salicylic acid ( $1.04 \times 10^{-3}$  M)



**Figure 4.2** All model compounds - potentiometric titrations

#### 4.1.2 Complexometric Titrations

Determining binding constants for the model compounds used required more careful attention to changes caused by temperature and ionic strength. Calculated experimental values per Neshkova and Sheytanov (1985) and temperature and ionic corrections per Smith and Martell (1975) are shown in Table 4.1.

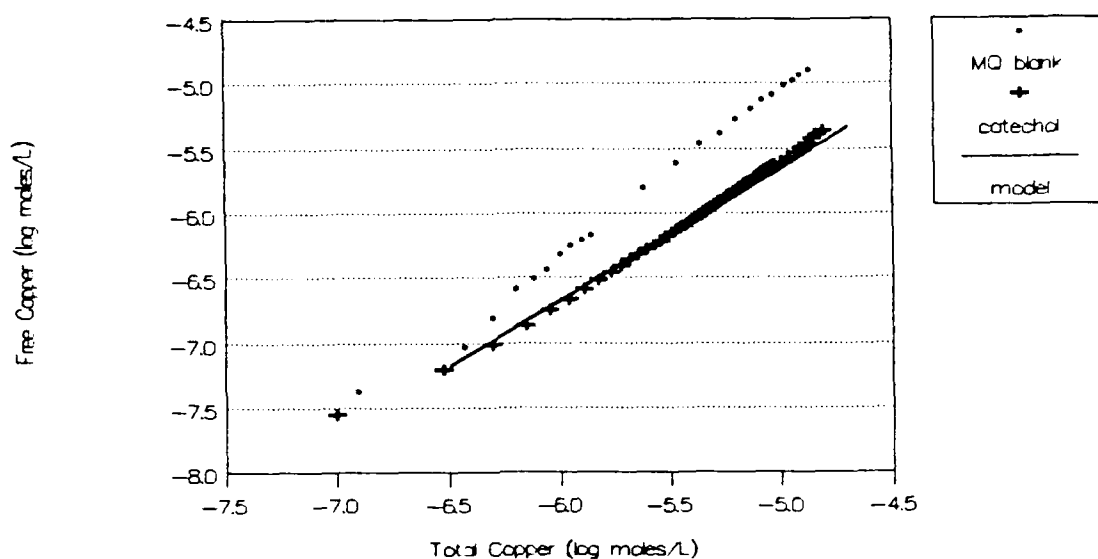
Experimental binding values calculated and summarized on Table 4.1 do not reflect all the binding that occurs. Validating binding constants was accomplished by comparing the actual experimental curves with model curves based on published values (see Table 2.5) using TITRATOR. Figures 4.3a, 4.3b and 4.3c show a good fit for the experimental and model curves of catechol, glycine and phthalic. For salicylic, the experimental curves did not fit with model curves (see Figure 4.3d). In this case, the binding constants were determined and used for further modeling. Binding constants of  $B_1$  and  $B_2$  at 11.15 and 18.96, respectively, were used as opposed to published values of 10.80 and 18.45 (see Table 2.5). Replicates of glycine performed have the error bars shown in Figure 4.4. Values normalized to the total ligand concentrations ( $L_T$ ) equal to one for all the model compounds are shown in Figure 4.5.

Table 4.1 Experimental constants

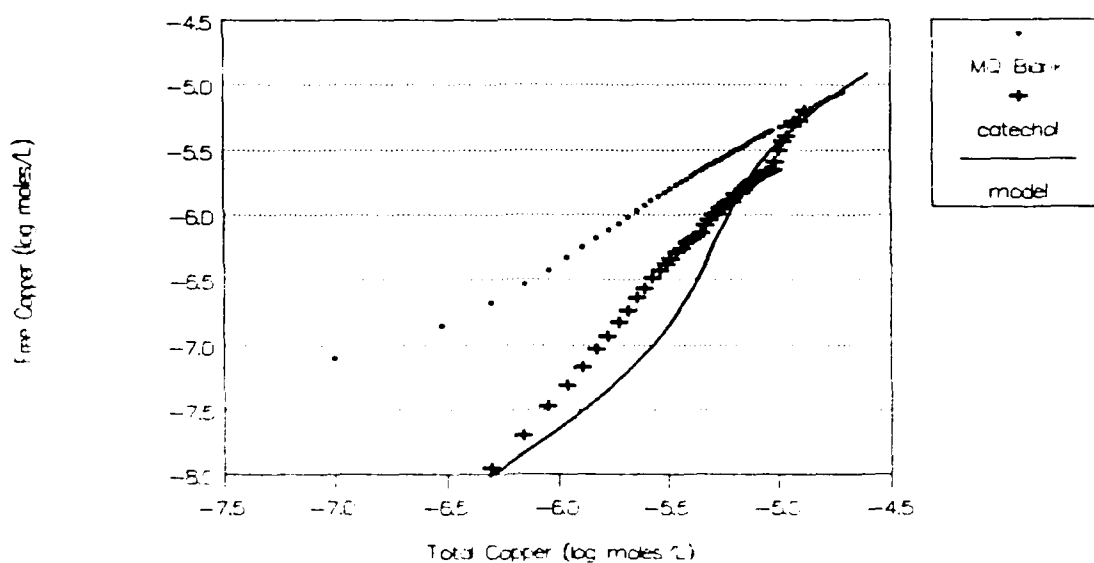
| Experimental<br>Values                    | Model Compounds                             |                                         |                                |                                 |
|-------------------------------------------|---------------------------------------------|-----------------------------------------|--------------------------------|---------------------------------|
|                                           | Catechol<br>(H <sub>2</sub> L)              | Glycine<br>(HL)                         | Phthalic<br>(H <sub>2</sub> L) | Salicylic<br>(H <sub>2</sub> L) |
| Potentiometric                            | same as published values<br>(see Table 2.5) |                                         |                                |                                 |
| Complexometric (temp. °C, ionic strength) |                                             |                                         |                                |                                 |
| B <sub>1</sub><br>pH 6.2                  | 13.59<br>(23,0.01)                          | 8.40<br>(21,0.01)<br>8.42<br>(22,0.01)  | 4.02<br>(21,0.01)              | 10.52<br>(23,0.008)             |
| B <sub>1</sub><br>pH 7.5                  | 12.6<br>(21,0.011)                          | 8.01<br>(23,0.008)<br>8.24<br>(21, .01) | 4.14<br>(23,0.01)              | 11.18<br>(22,0.01)              |
| B <sub>1</sub> = ML/M · L                 |                                             |                                         |                                |                                 |

$$B_1 = \text{ML}/\text{M} \cdot \text{L}$$

## Catechol pH 6.2



## Catechol pH 7.5

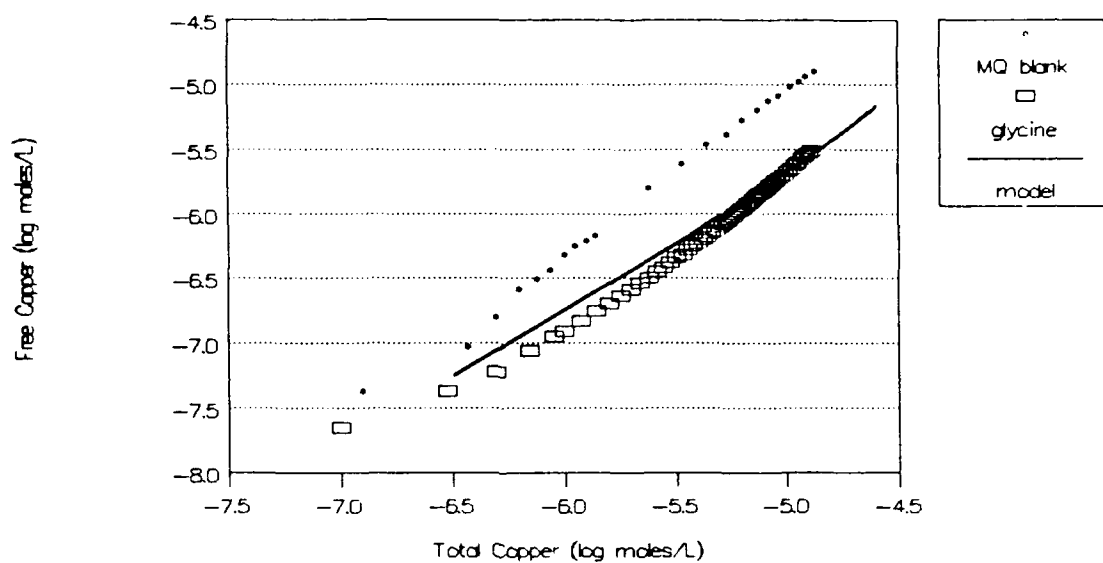


**Figure 4.3a** Model and experimental curve - catechol

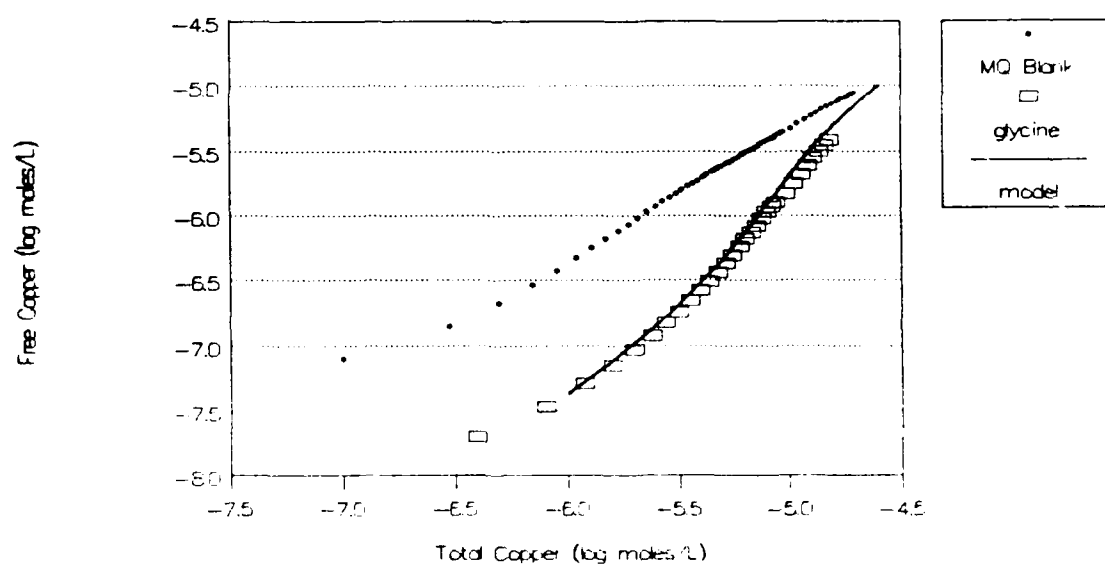
At pH 6.2 -  $1.36 \times 10^{-4}$  M,  $23^\circ$  C,  $I=0.01$

At pH 7.5 -  $4.99 \times 10^{-6}$  M,  $21^\circ$  C,  $I=0.01$

## Glycine pH 6.2



## Glycine pH 7.5

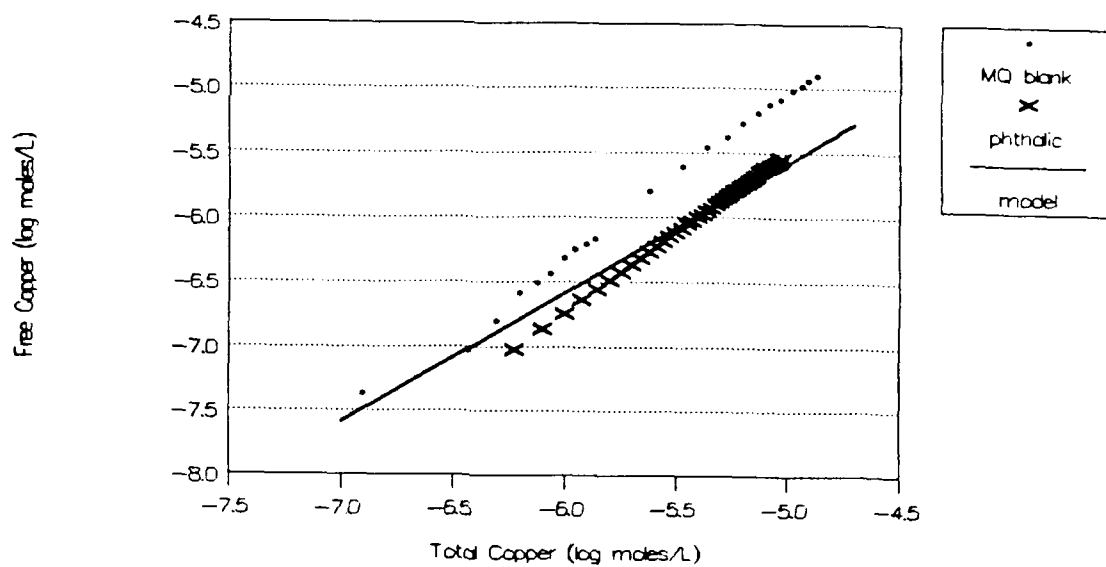


**Figure 4.3b** Model and experimental curve - glycine

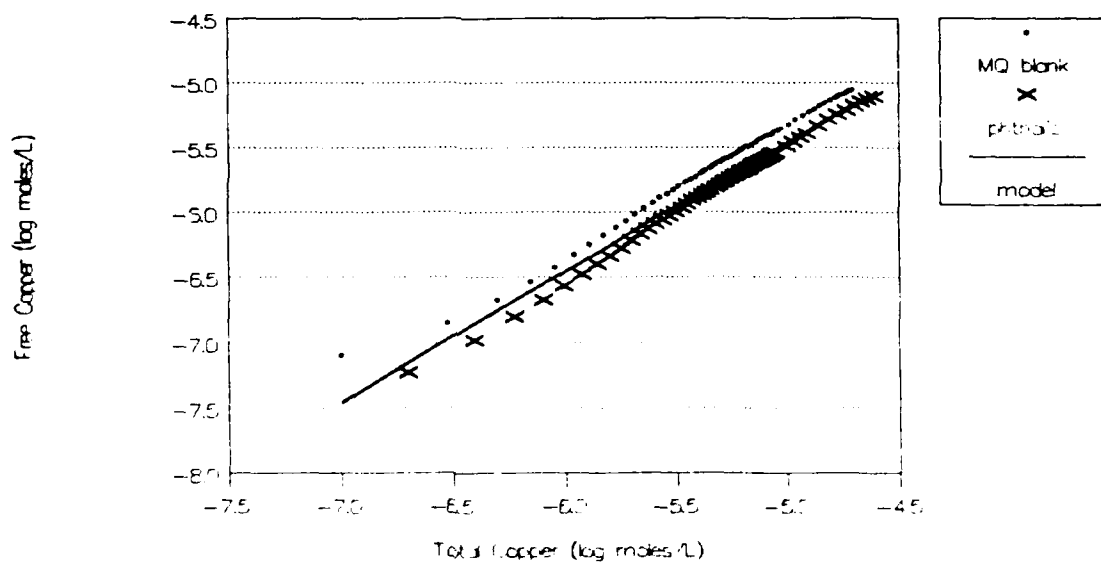
At pH 6.2 -  $1.0 \times 10^{-4}$  M,  $21^\circ$  C,  $I=0.01$

At pH 7.5 -  $1.0 \times 10^{-5}$  M,  $23^\circ$  C,  $I=0.008$

# Phthalic Acid pH 6.2

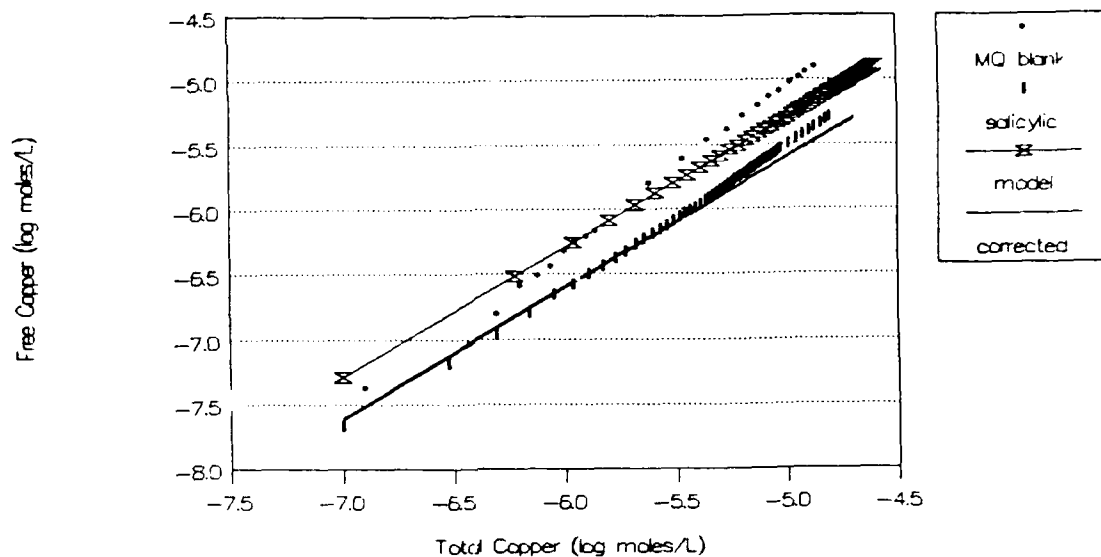


# Phthalic Acid pH 7.5

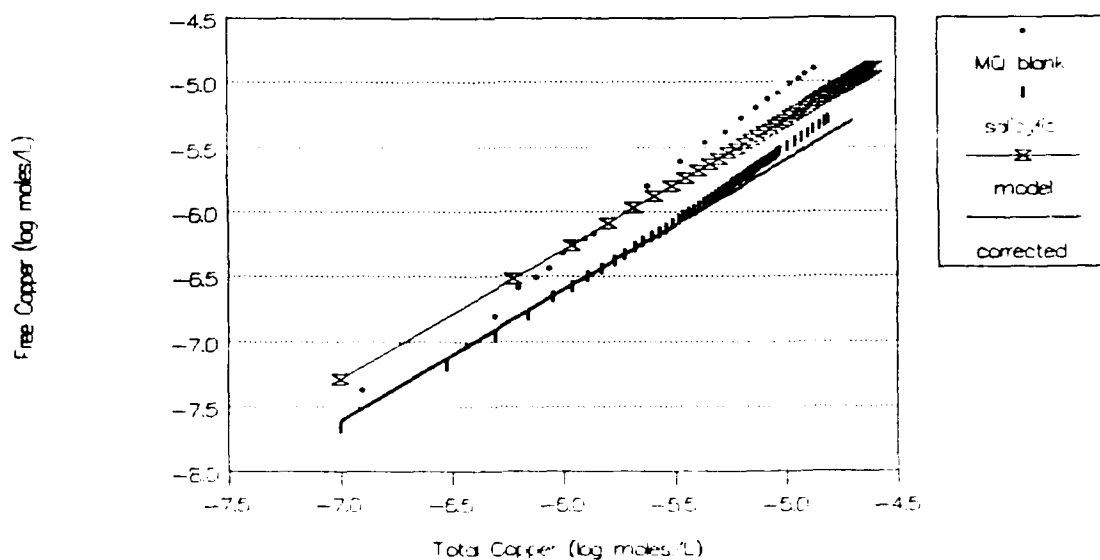


**Figure 4.3c** Model and experimental curve - phthalic acid  
 At pH 6.2 -  $2.98 \times 10^{-4}$  M,  $21^\circ$  C,  $I=0.01$   
 At pH 7.5 -  $1.5 \times 10^{-5}$  M,  $23^\circ$  C,  $I=0.01$

### Salicylic Acid pH 6.2

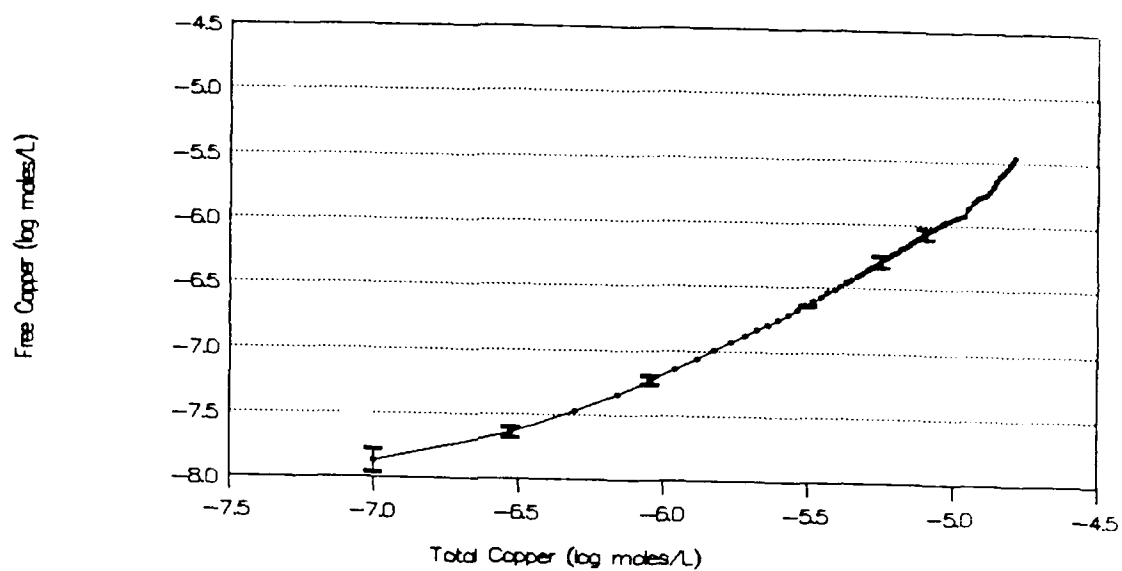


### Salicylic Acid pH 7.5



**Figure 4.3d** Model and experimental curve - salicylic acid  
 At pH 6.2 -  $5.36 \times 10^{-4}$  M,  $23^{\circ}$  C,  $I=0.008$   
 At pH 7.5 -  $1.13 \times 10^{-4}$  M,  $22^{\circ}$  C,  $I=0.01$

## pH 6.2 Titrations



## pH 7.5 Titrations

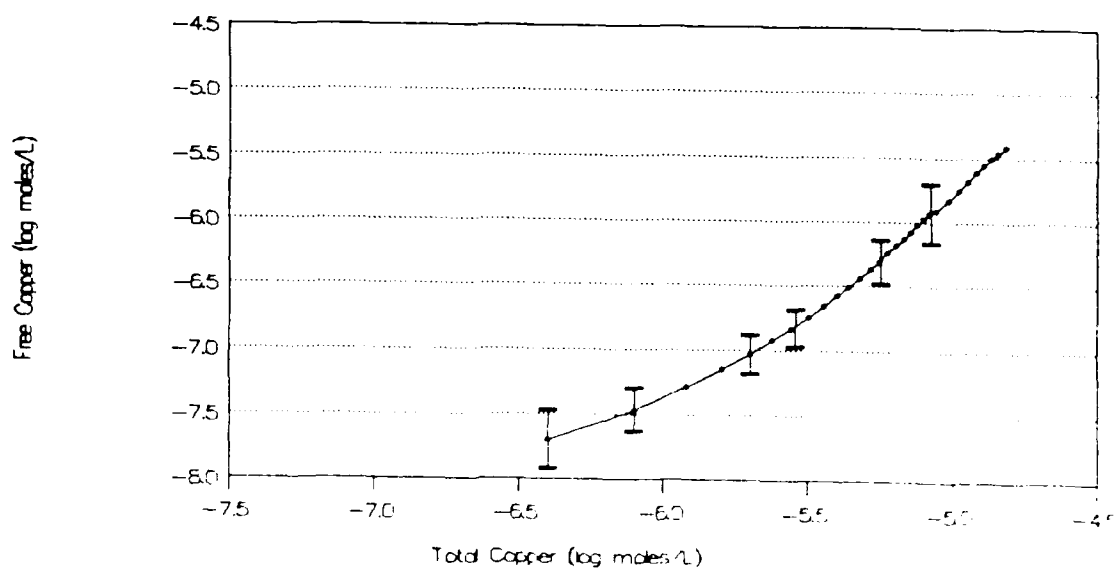
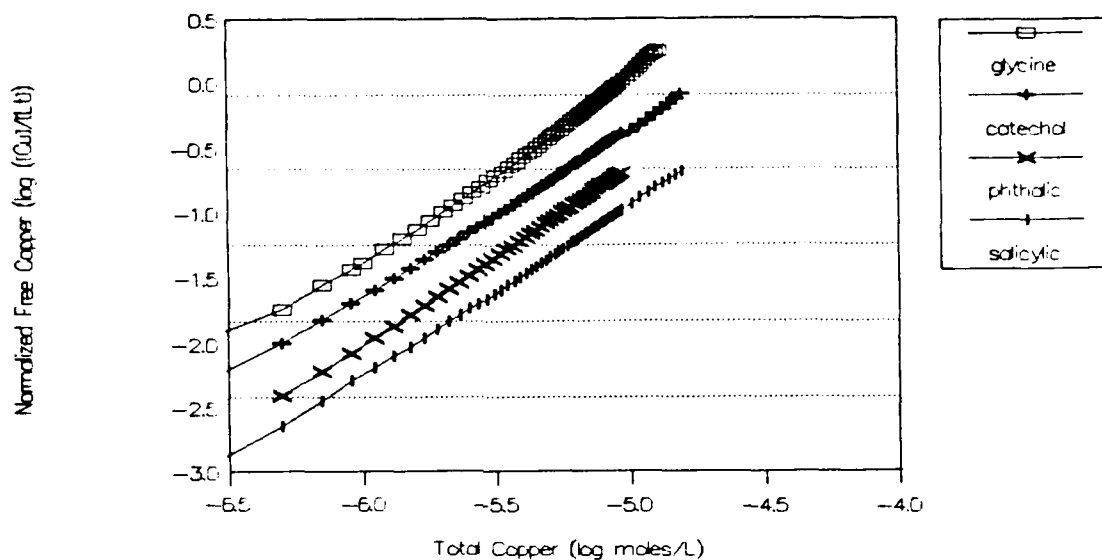
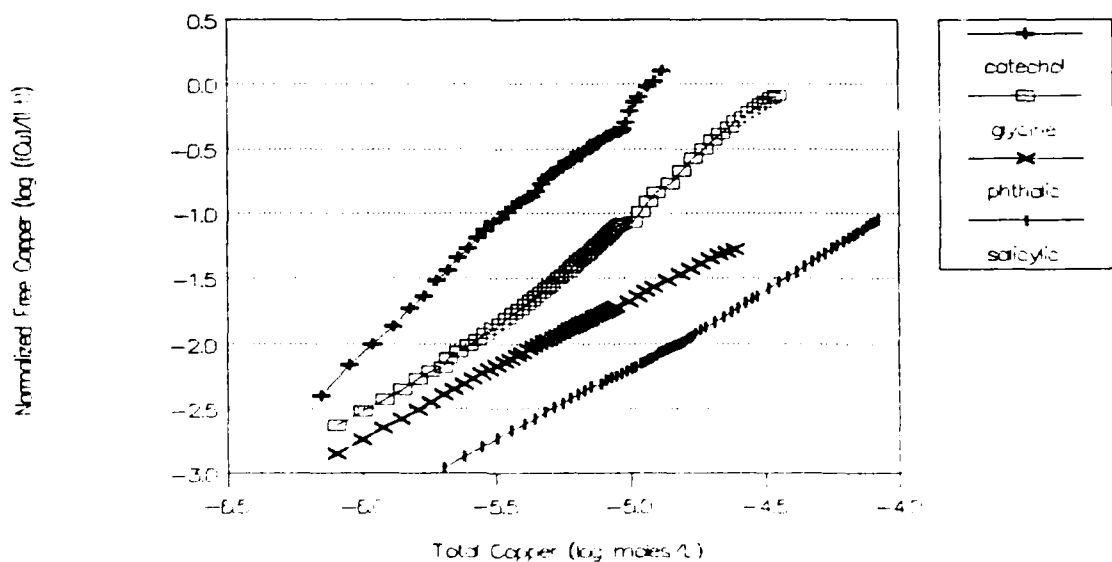


Figure 4.4 Glycine complexometric error bars

## pH 6.2 Titrations



## pH 7.5 Titrations



**Figure 4.5** All model compounds - normalized to  $[L_T] = 1$  complexometric titrations

#### 4.3 Natural Sources and Model Compound Mixtures

The XAD-8 isolates of Orange County groundwater and Biscayne Aquifer groundwater were titrated potentiometrically and complexometrically (see Appendix C).

##### 4.3.1 Potentiometric Modeling

Attempting to model each of the natural sources began by obtaining the carboxylic and phenolic acidities and DOC content of each of the solutions titrated (see Table 4.2). In keeping with the goal of using as much information about the chemical composition of the XAD-8 isolates to develop a model of a humic acid, concentrations for each of the single model compounds were calculated based on the following assumptions:

- 1) Glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ):

$$[\text{Gly}] = \text{nitrogen (N) concentration}$$

- 2) Catechol ( $\text{C}_6\text{H}_6\text{O}_2$ ):

$$[\text{Cat}] = \text{fraction (phenolic -OH concentration)}/2$$

- 3) Salicylic acid ( $\text{C}_7\text{H}_6\text{O}_3$ ):

$$[\text{Sal}] = \text{remaining phenolic -OH concentration}$$

- 4) Phthalic acid ( $\text{C}_8\text{H}_6\text{O}_4$ ):

$$[\text{Phth}] = (\text{Carboxylic conc.} - [\text{Gly}] - [\text{Sal}])/2$$

Table 4.2 Titrated XAD-8 characteristics

| <u>Source and type</u>        | <u>DOC<br/>(mg/L)</u> | <u>Carboxylic<br/>Acidity<br/>(meq/g-C)</u> | <u>Phenolic*<br/>Acidity<br/>(meq/g-C)</u> | <u>Nitrogen*<br/>Content<br/>(mg/L)</u> |
|-------------------------------|-----------------------|---------------------------------------------|--------------------------------------------|-----------------------------------------|
| OCGW XAD-8                    | 5.66                  | 19.5 $\pm$ 3.53 <sup>1</sup>                | 3.9                                        | 0                                       |
| BA XAD-8                      | 12.55                 | 11.79                                       | 2.5                                        | 0.11                                    |
| * assumed per Thurman (1985)  |                       |                                             |                                            |                                         |
| <sup>1</sup> Waterbury (1990) |                       |                                             |                                            |                                         |

To verify that reasonable concentrations were calculated, elemental compositions were compared to the ranges of measured compositions from different water sources.

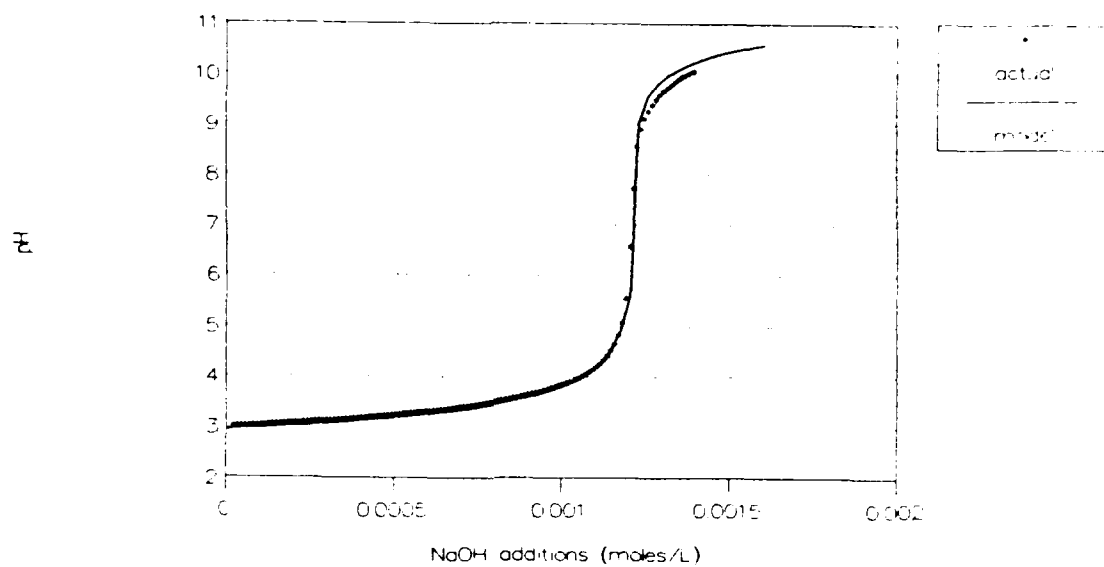
DOC and the carboxylic content were experimentally determined. Values for phenolic and nitrogen content, however, were assumed using typical ranges (Thurman, 1985). The fraction of phenolic content present as catechol was varied with assumption (2) to obtain a good fit.

OCGW fitting was first attempted with no glycine and a catechol fraction of 1/2 the phenolic -OH content of 2 meq/g-C at  $2.83 \times 10^{-5}$  M. Increasing the catechol fraction had the effect of fitting the upper portion of the titration curve better (the phenolic portion), but too high a fraction (greater than 7/8) increased the error in the lower portion of the potentiometric fit (the carboxylic portion). The optimum fraction for catechol was determined at 75 percent of the phenolic -OH content. Next, the phenolic content was increased to better fit the upper portion of the curve. With increasing phenolic -OH content the error was reduced in the upper portion of the curve. However, concentrations of greater than 10 meq/g-C were needed to reduce the error. Schnitzer (1978) suggested a value of 3.9 meq/g-C as more appropriate. The addition glycine had little effect improving the potentiometric fit; therefore, it was assumed that nitrogen concentration in the form of glycine was present at 0.005 mg/L. The effect of these changes are

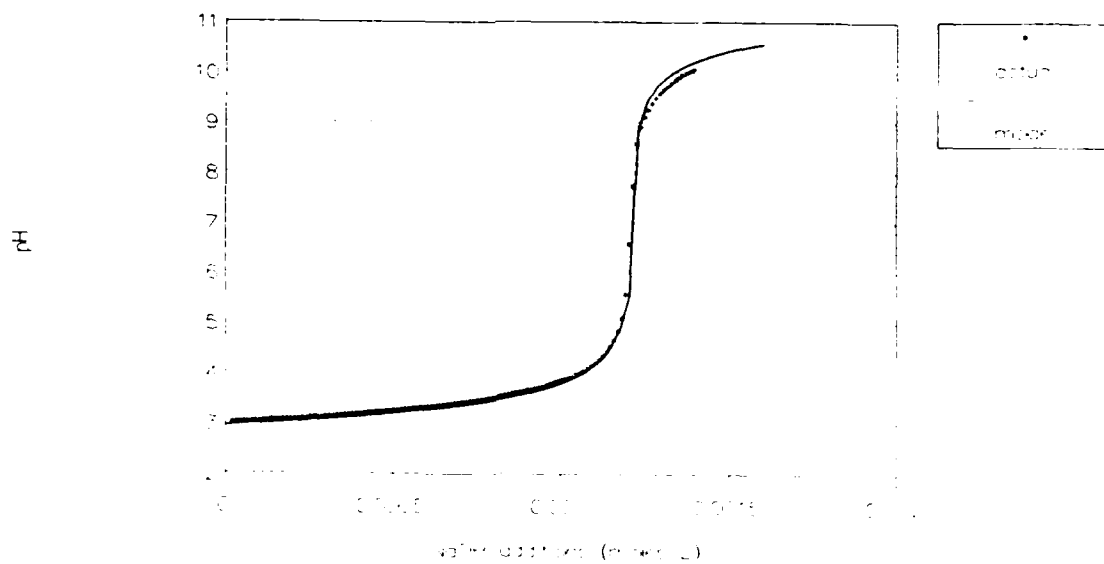
shown in Figures 4.6a and 4.6b.

For BA groundwater, the process of obtaining a good fit to the potentiometric titration data was similar to that performed on OCGW. Results are shown in Figure 4.7 and Table 4.3. Since the addition of salicylic acid did not help the fit, all the phenolic content at 2.5 meq/g-C was attributed to catechol. For the concentration of glycine, two concentrations were investigated: a low value of 121 nM/mg (0.1 percent), representing the concentration of amino acids present in BA humic acid, and a high of 5.8 percent nitrogen (Thurman, 1985). A value in between these two ranges provided the best fit. Phenolic -OH content was assumed to be constant at 2.5 meq/g-C per Thurman (1985).

### High Catechol Fraction

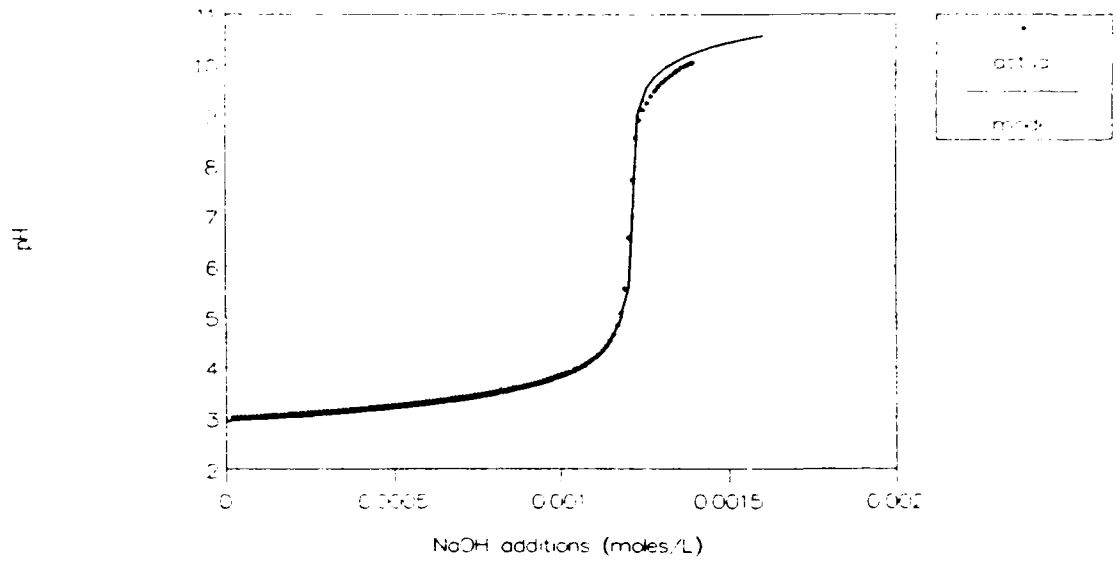


### High Phenolic OH Content



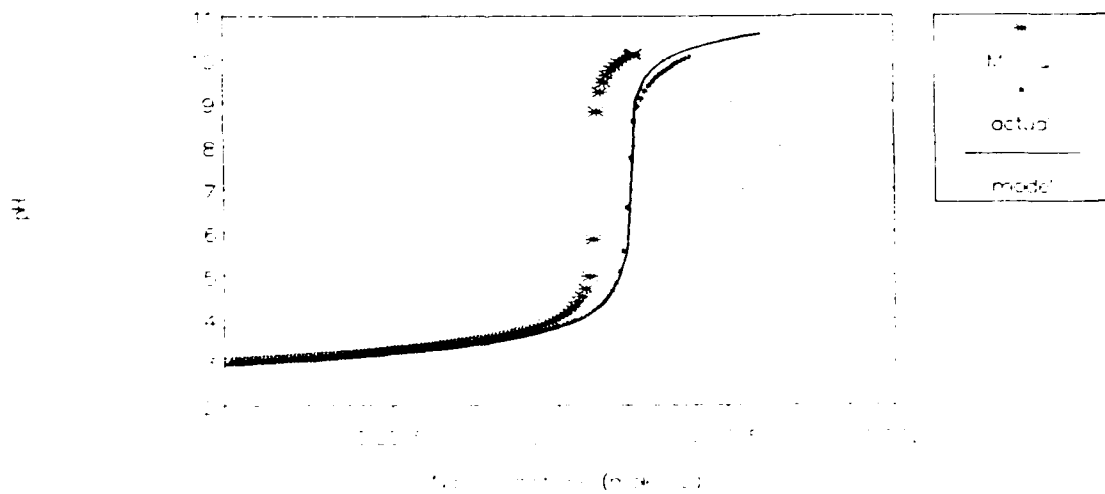
**Figure 4.6a** Potentiometric modeling of OCGW XAD-8 - catechol and phenolic effects (see text)

## Nitrogen Addition



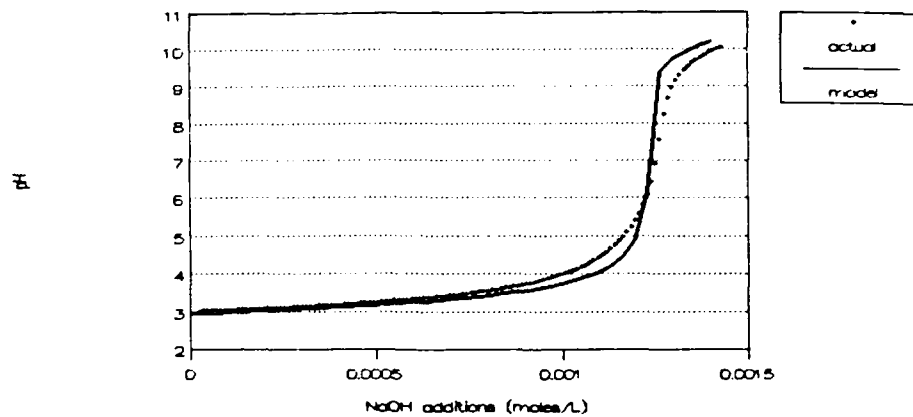
## Final Potentiometric Fit

$\text{COOH} = 19.7 \text{ meq/g-C}$ ;  $\text{OH} = 3.9 \text{ meq/g-C}$ ;  $\text{Cat} = 3/4$

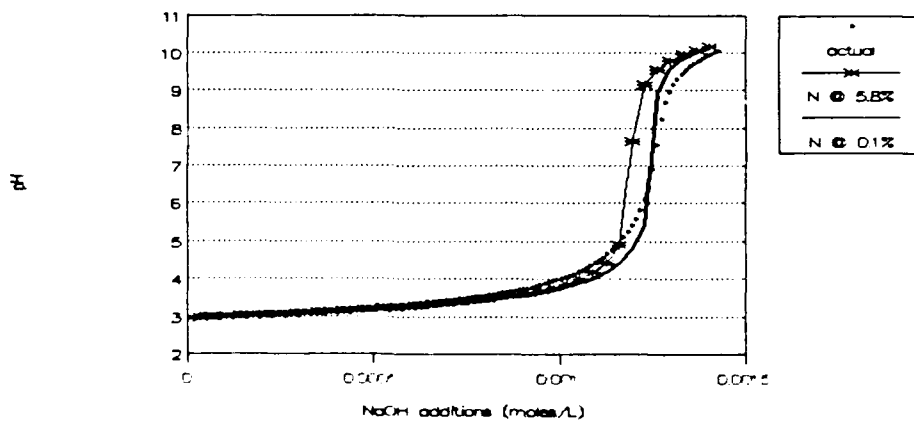


**Figure 4.6b** Potentiometric modeling of OCGW XAD-8 - nitrogen effects and final fitting (see text)

## All Salicylic Acid



## Nitrogen Effects



## Final Potentiometric Fit

Cat=100% of OH: N @ 2.0%

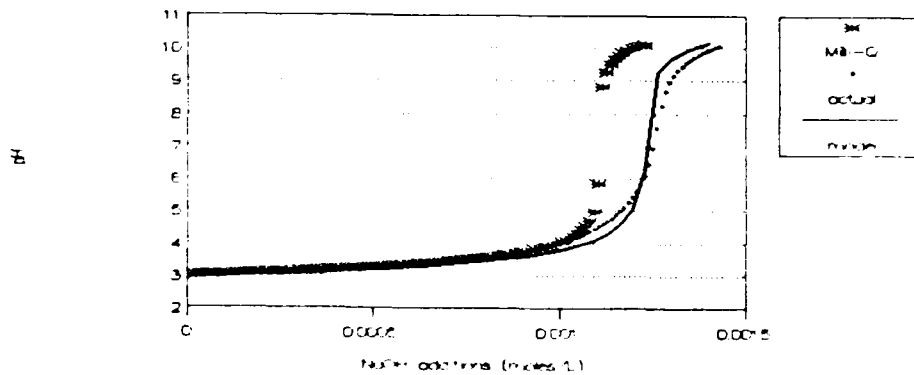


Figure 4.7 Potentiometric modeling of BA XAD-8  
(see text)

**Table 4.3** Assumed concentrations (pL) of model compounds

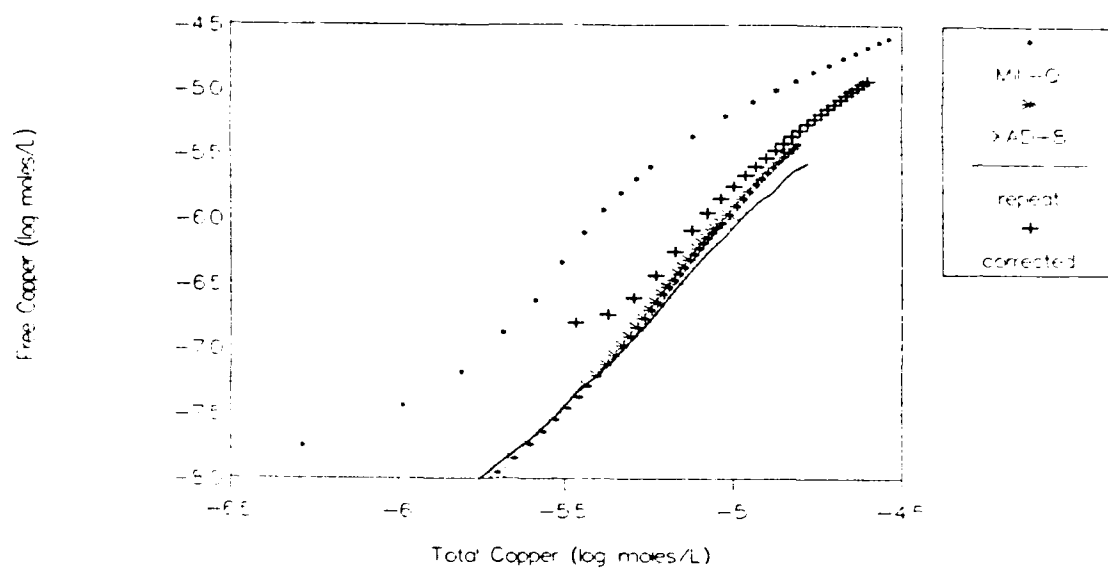
| <u>Source</u> | <u>Catechol</u> | <u>Glycine</u> | <u>Phthalic<br/>Acid</u> | <u>Salicylic<br/>Acid</u> |
|---------------|-----------------|----------------|--------------------------|---------------------------|
| OCGW          | 5.082           | ----           | 4.276                    | 5.258                     |
| BA            | 4.804           | 4.699          | 4.194                    | ----                      |

#### 4.3.2 Complexometric Modeling

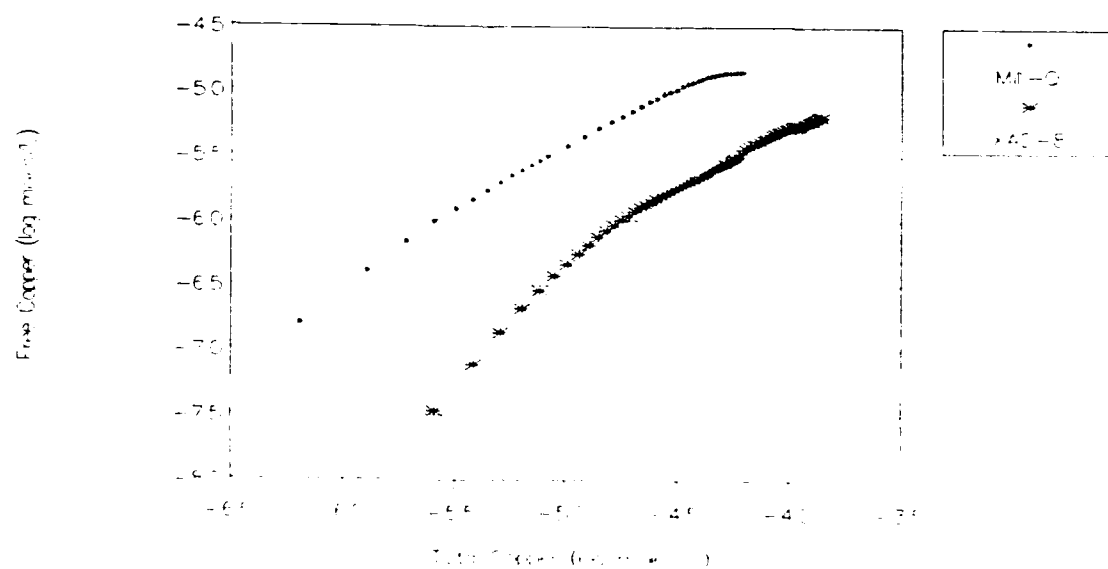
Figures 4.8 and 4.9 show complexometric titration curves of OCGW XAD-8 and BA XAD-8, respectively. As shown on Figure 4.8, the pH 6.2 titration of OCGW showed problems with the Milli-Q blank titration. Values for the OCGW XAD-8 titration at pH 6.2 were corrected by subtracting the difference from the ideal Milli-Q titration and the actual from the XAD-8 titration. Since total copper concentrations for the data points did not match, a fitted model data set derived from Waterbury (1990) was used. No significant problem was noted for the other blank titrations of pH 6.2 in polypropylene and pH 7.5 in polypropylene or glass; therefore, the data was used without correcting for the blank (see Appendix C).

The same concentrations for the single model compounds were used to try to fit the complexometric curves. As shown on Figure 4.10a and 4.10b, there was not a good correspondence between fitted and actual values. Curve-fitting was attempted using SAS (see Appendix D). To an extent this effort was considered to be a divergence from the chemically approach being used.

## pH 6.2 Titrations

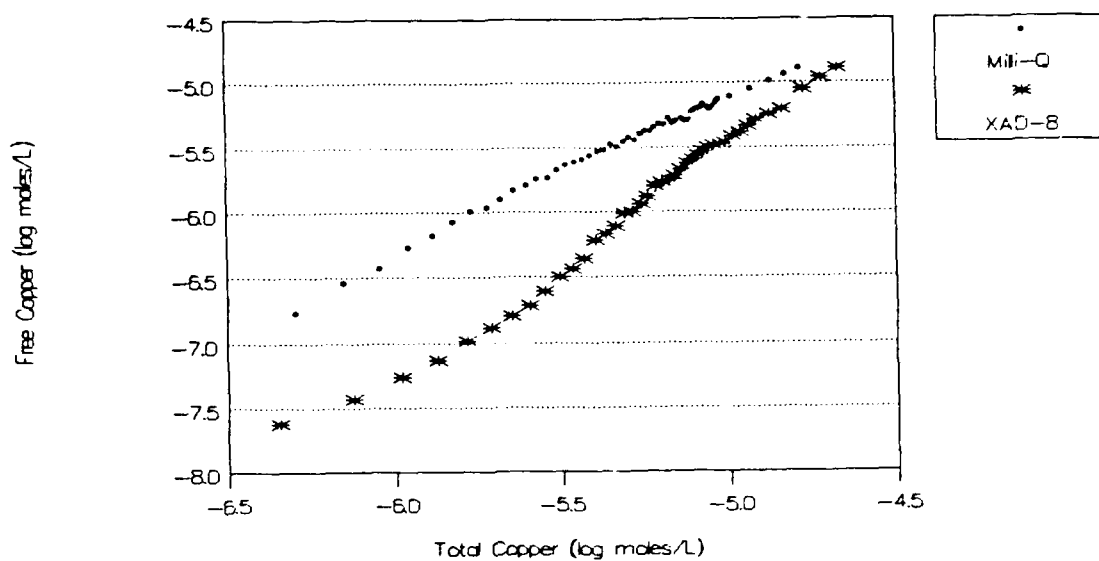


## pH 7.5 Titrations

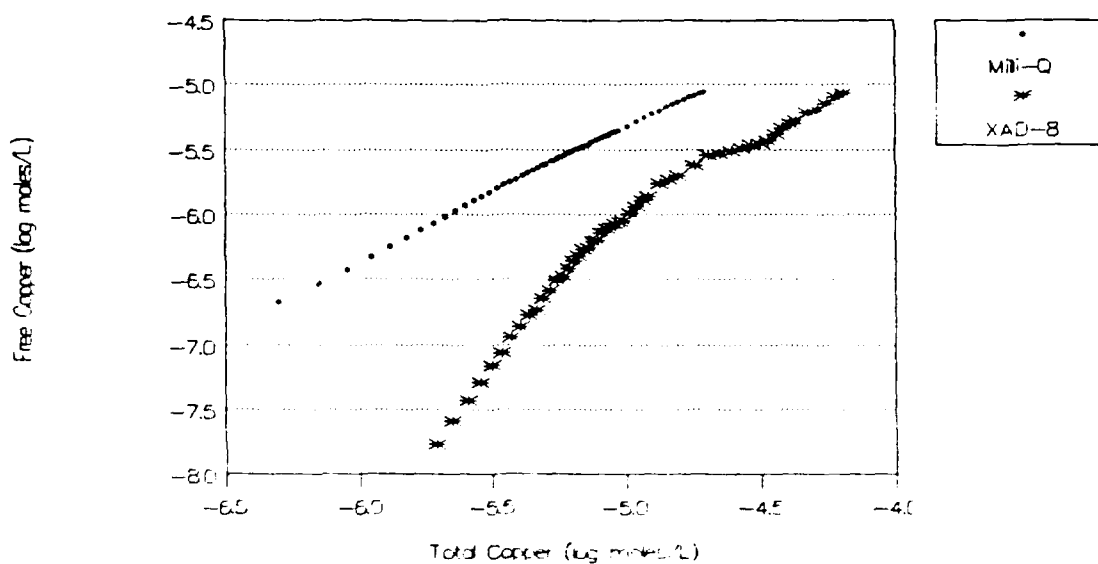


**Figure 4.8** OCGW XAD-8 complexometric titrations

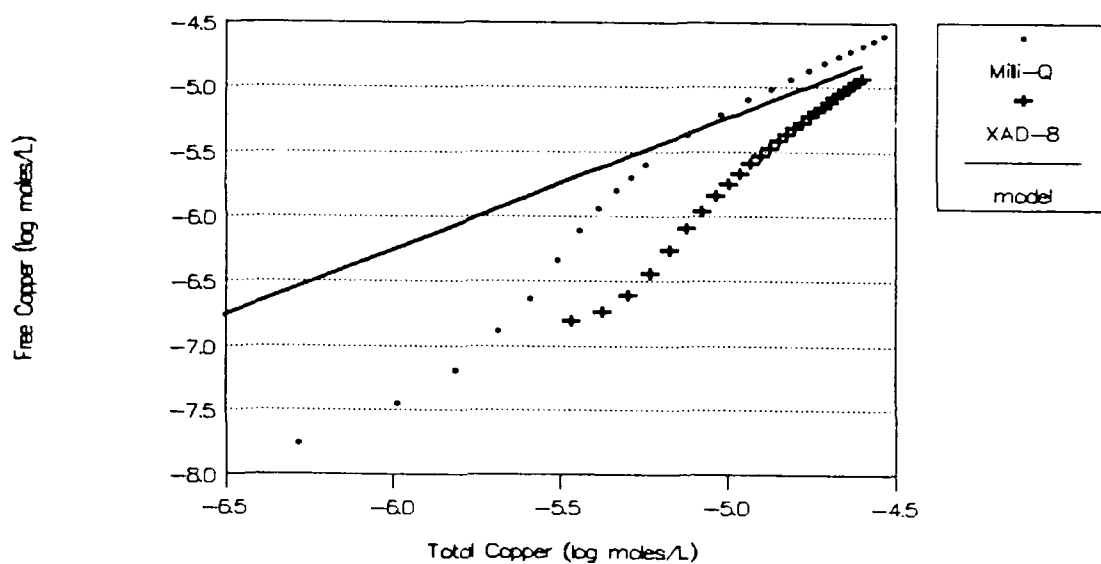
## pH 6.2 Titrations



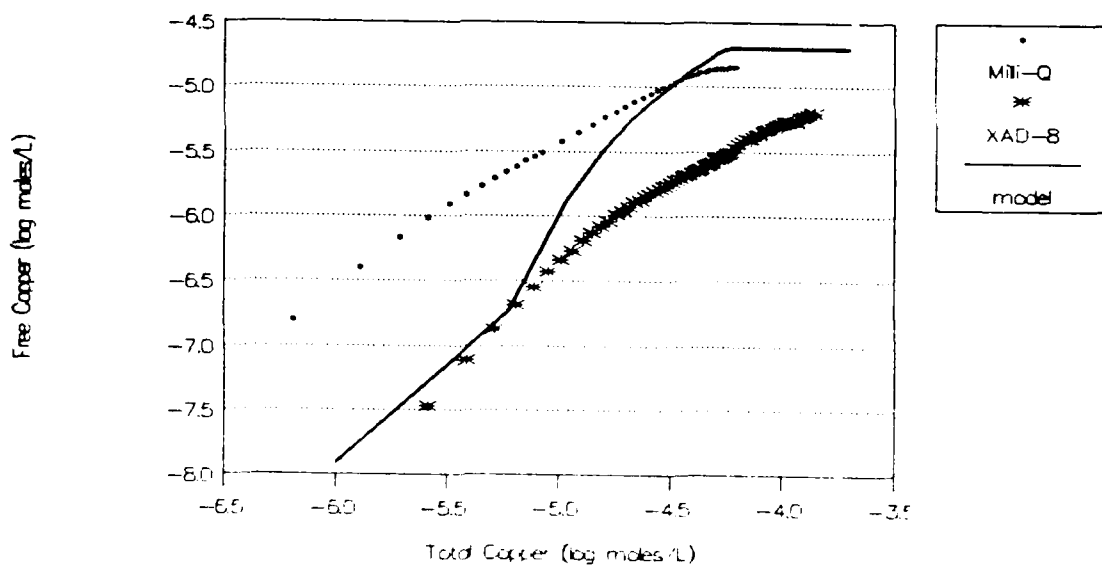
## pH 7.5 Titrations

**Figure 4.9** BA XAD-8 complexometric titrations

### OCGW XAD-8 pH 6.2 Titrations

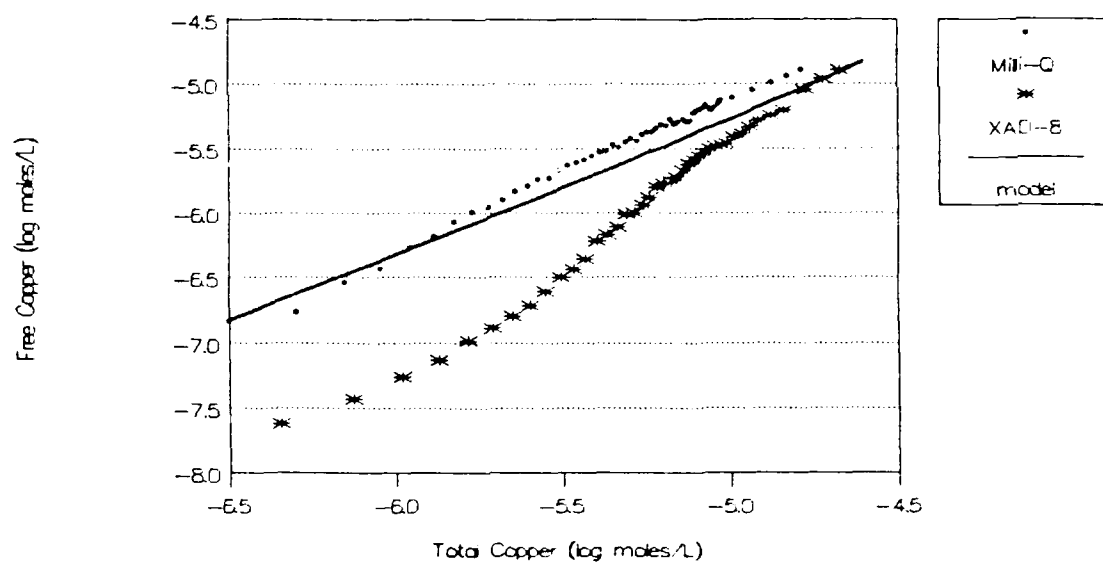


### OCGW XAD-8 pH 7.5 Titrations

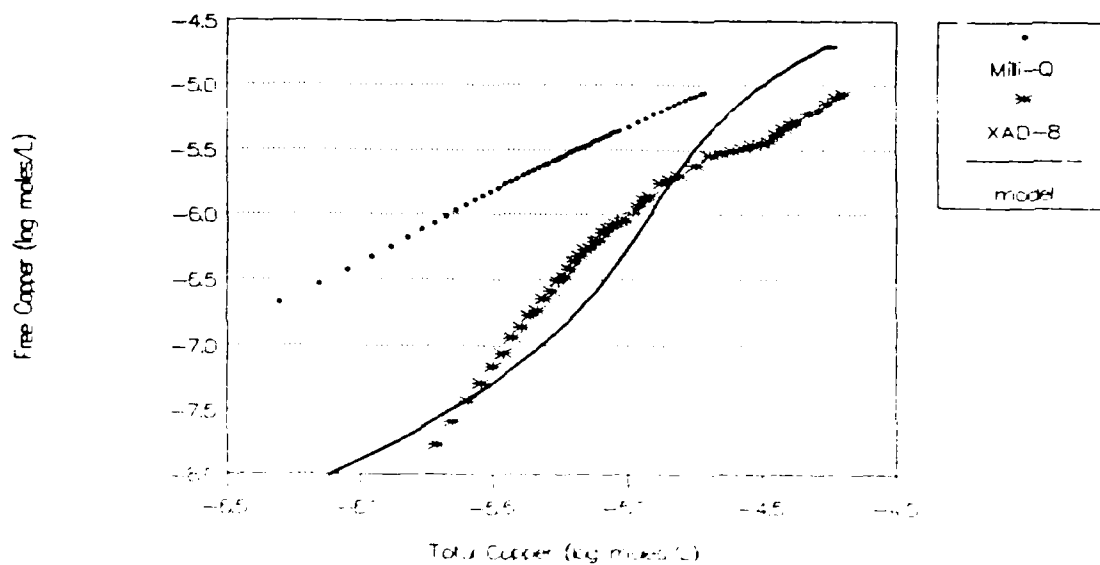


**Figure 4.10a** Complexometric curve fits with potentiometric mixture of model compounds - OCGW

### BA XAD-8 pH 6.2 Titrations



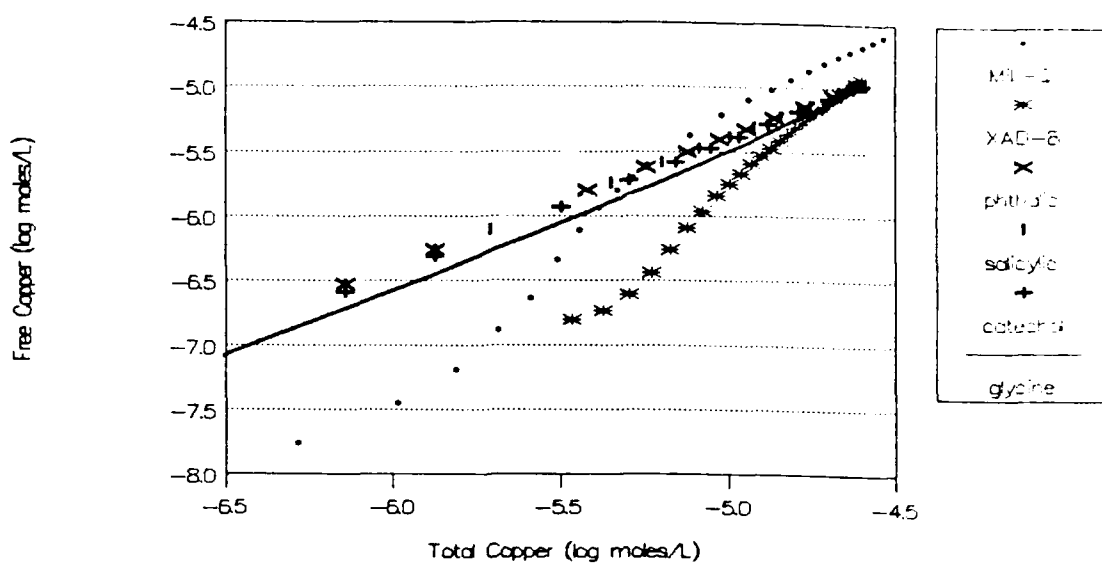
### BA XAD-8 pH 7.5 Titrations



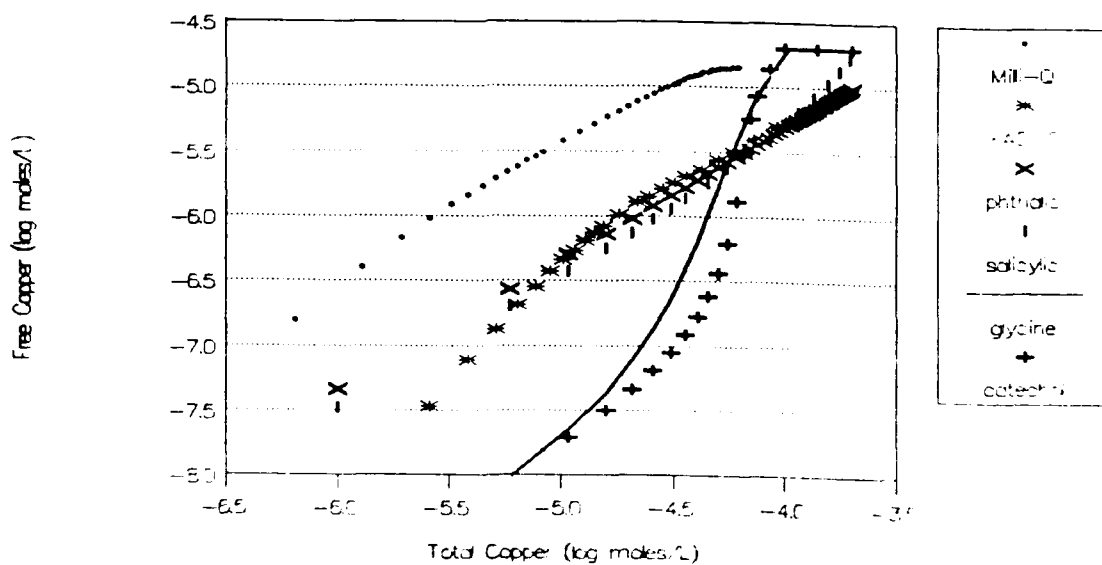
**Figure 4.10b** Complexometric curve fits with potentiometric mixture of model compounds - BA

For both XAD-8 isolates at pH 6.2, single-ligand concentrations of catechol, phthalic and salicylic acid were similar. Attempts at pH 7.5 had phthalic and salicylic acid with similar curves (see Figures 4.11 and 4.12). Since using both concentrations of salicylic acid and catechol would exceed the assumed phenolic -OH content, phthalic acid and catechol were chosen for the two-ligand fitting. After the concentrations of the two ligands were obtained on SAS, a reasonable guess was made for the three-ligand fitting. Results of the SAS outputs are shown on Table 4.4. Even though the best possible combination of elements was fitted with SAS, the elemental composition and acidities resulted in too high an estimate for carboxylic acidities (see Table 4.5) nor were the actual curves properly fitted with the sum of squares errors unacceptably large - OCGW pH 6.2 at  $6.39 \times 10^{-9}$ , OCGW pH 7.5 at  $4.03 \times 10^{-7}$ , BA pH 6.2 at  $3.05 \times 10^{-9}$ , and BA 7.5 at  $2.97 \times 10^{-8}$  (see Figure 4.13a and 4.13b).

## pH 6.2 1-Ligand Models

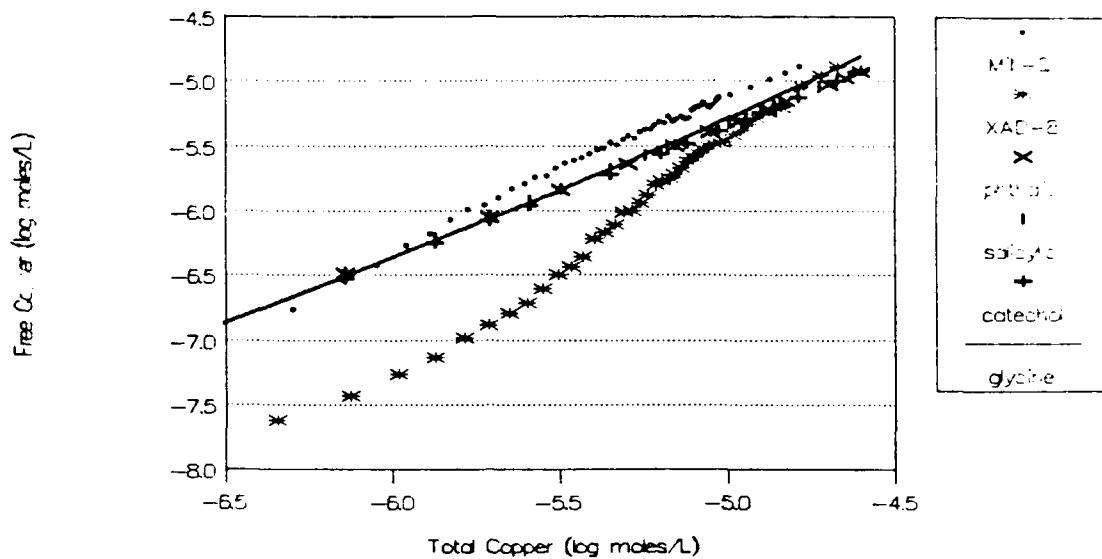


## pH 7.5 1-Ligand Models



**Figure 4.11** OCGW XAD-8 single model compound SAS fitting (see Table 4.4)

## pH 6.2 1-Ligand Models



## pH 7.5 1-Ligand Models

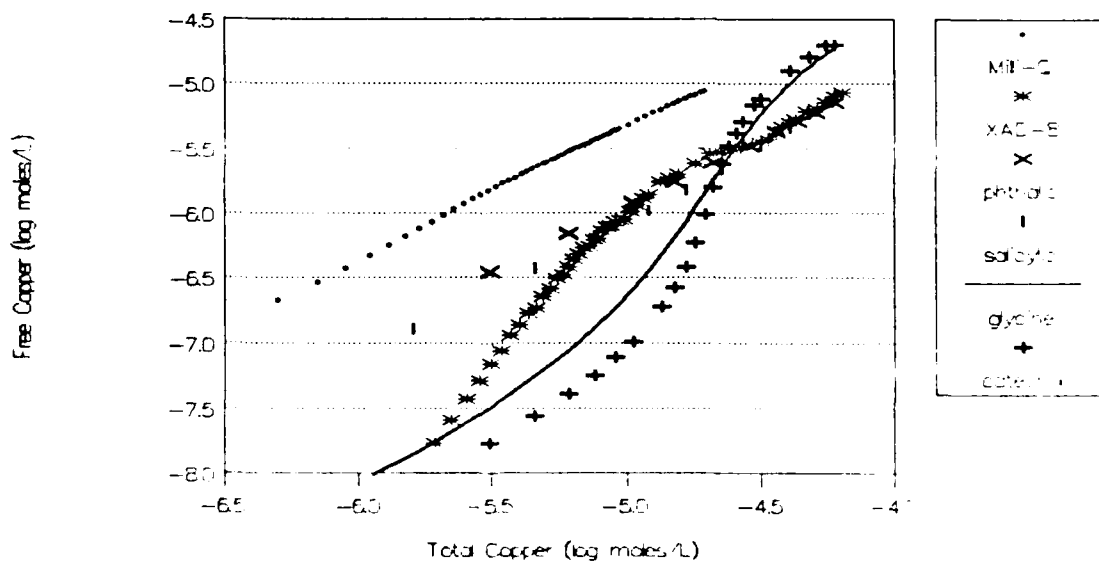


Figure 4.12 BA XAD-8 single model compound SAS fitting (see Table 4.4)

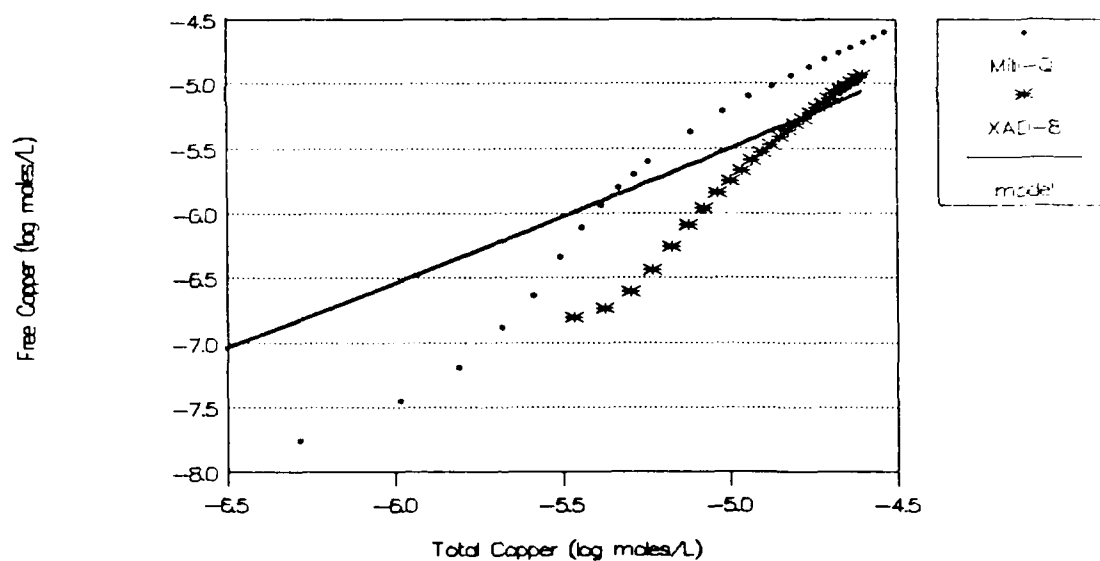
**Table 4.4** SAS modeling concentrations

| CONCENTRATIONS (pL) |                      |               |                    |               |
|---------------------|----------------------|---------------|--------------------|---------------|
|                     | OCGW (DOC=5.66 mg/L) |               | BA (DOC=5.02 mg/L) |               |
|                     | <u>pH 6.2</u>        | <u>pH 7.5</u> | <u>pH 6.2</u>      | <u>pH 7.5</u> |
| <b>1-ligand Fit</b> |                      |               |                    |               |
| catechol            | 4.2                  | 4.2           | 4.3                | 4.7           |
| glycine             | 4.5                  | 4.1           | 4.8                | 4.55          |
| phthalic acid       | 3.83                 | 2.703         | 3.9                | 3.13          |
| salicylic acid      | 3.6                  | 3.595         | 3.7                | 4.0           |
| <b>2-ligand Fit</b> |                      |               |                    |               |
| catechol            | 4.2                  | 4.6           | 4.2                | 5.03          |
| phthalic acid       | 4.25                 | 2.86          | 4.6                | 3.25          |
| <b>3-ligand Fit</b> |                      |               |                    |               |
| catechol            | 4.434                | 5.3           | 4.91               | 5.3           |
| phthalic acid       | 4.4                  | 2.78          | 8.02               | 3.3           |
| glycine             | 5.0                  | 5.0           | 5.1                | 5.1           |

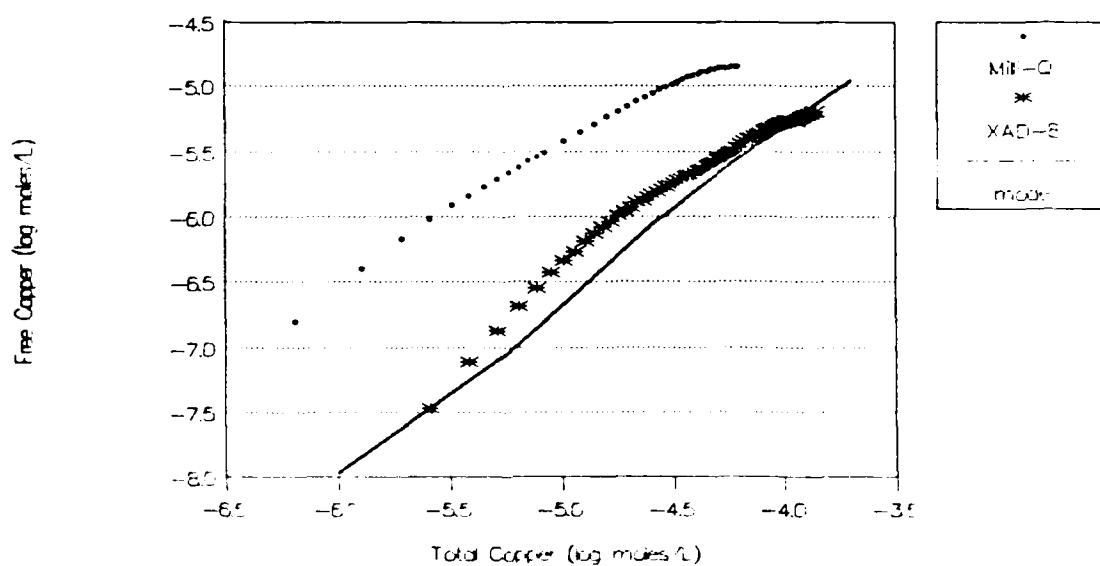
**Table 4.5** Composition of SAS modeling  
three ligand fits

| <u>Elemental Percentages</u>                   | <u>OCGW (DOC=5.66 mg/L)</u> |               | <u>BA (DOC=5.02 mg/L)</u> |               |
|------------------------------------------------|-----------------------------|---------------|---------------------------|---------------|
|                                                | <u>pH 6.2</u>               | <u>pH 7.5</u> | <u>pH 6.2</u>             | <u>pH 7.5</u> |
| C                                              | 66.5 +                      | 43.6          | 60.6                      | 57.7          |
| H                                              | 5.0                         | 27.3 +        | 5.7                       | 3.7           |
| O                                              | 27.1 +                      | 29.0 -        | 31.0                      | 38.5          |
| N                                              | 1.2                         | 0.04 --       | 2.7                       | 0.1 --        |
| Total                                          | 99.8                        | 99.94         | 100                       | 100           |
| <u>Ratios</u>                                  |                             |               |                           |               |
| H/C                                            | 0.90                        | 7.48 ++       | 1.11 +                    | 0.76 -        |
| O/C                                            | 0.31 -                      | 0.50          | 0.38 -                    | 0.50          |
| N/C                                            | 0.02                        | 0.0008 -      | 0.04                      | 0.002 -       |
| <u>Acidity (meq/g-C)</u>                       |                             |               |                           |               |
| Carboxylic                                     | 16.03 -                     | 586.4 ++      | 0.004 --                  | 199.7++       |
| Phenolic -OH                                   | 14.12 +                     | 1.77 -        | 4.92                      | 1.20 -        |
| + high<br>++ very high<br>- low<br>-- very low |                             |               |                           |               |

### pH 6.2 3-Ligand Model

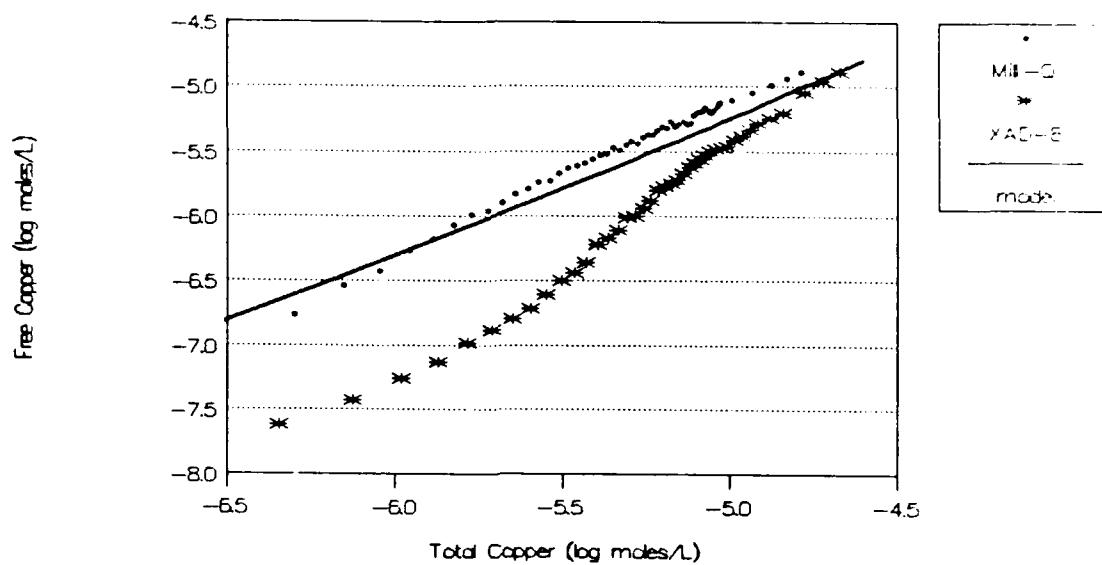


### pH 7.5 3-Ligand Model

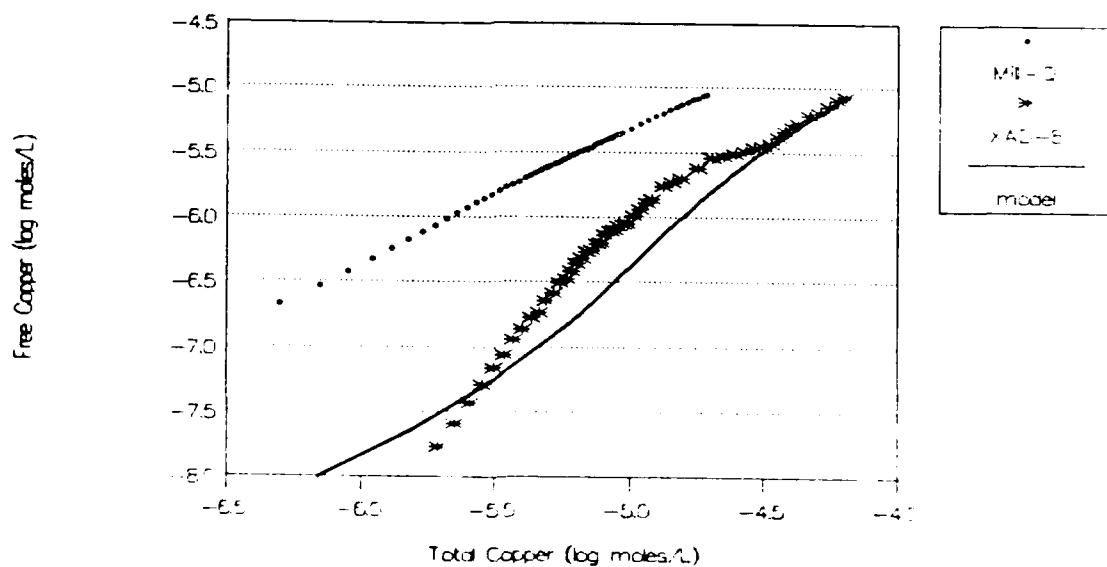


**Figure 4.13a** OCGW XAD-8 3-ligand SAS fitting  
(pH 6.2 XAD-8 corrected for blank)

### pH 6.2 3-Ligand Model



### pH 7.5 3-Ligand Model



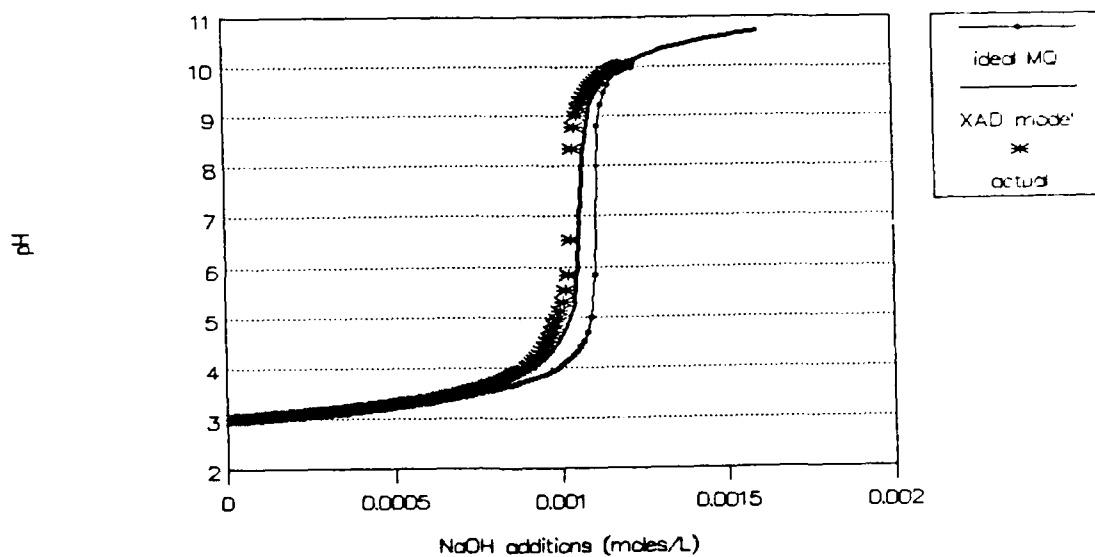
**Figure 4.13b** BA XAD-8 3-ligand SAS fitting

To show that modeling mixtures were as expected for the actual titrations, the OCGW model mixture for pH 6.2 was titrated (see Table 4.6). Figure 4.14 shows the results of the potentiometric and complexometric titrations with the outcome as expected. For the potentiometric curve, the titration is positioned to the left of the Milli-Q titration due to the basic condition caused by the presence of glycine.

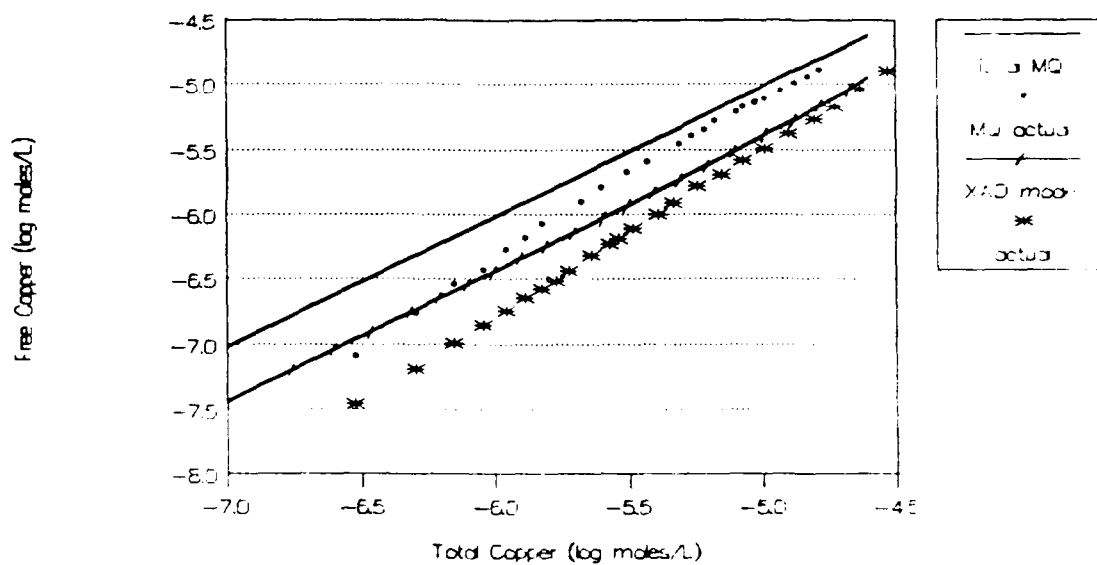
**Table 4.6** Composition of titrated mixture

| <u>OCGW Model (DOC=5.66 mg/L)</u>   |       | <u>Average HA</u><br>(Lamy, et al., 1987;<br>Steelink, 1985;<br>Thurman, 1985) |
|-------------------------------------|-------|--------------------------------------------------------------------------------|
| <u>Compound concentrations (pL)</u> |       |                                                                                |
| catechol                            | 4.849 |                                                                                |
| phthalic acid                       | 4.254 |                                                                                |
| glycine                             | 5.00  |                                                                                |
| <u>Elemental percentages</u>        |       |                                                                                |
| C                                   | 57.2  | 40-60                                                                          |
| H                                   | 4.1   | 4-6                                                                            |
| O                                   | 37.5  | 30-50                                                                          |
| N                                   | 1.2   | 1-6                                                                            |
| <u>Ratios</u>                       |       |                                                                                |
| H/C                                 | 0.85  | 0.91                                                                           |
| O/C                                 | 0.49  | 0.50                                                                           |
| N/C                                 | 0.02  | 0.04                                                                           |
| <u>Acidity (meq/g-C)</u>            |       |                                                                                |
| Carboxylic                          | 19.7  |                                                                                |
| Phenolic                            | 5.0   |                                                                                |

## Potentiometric Titrations



## pH=6.2 Complexometric



**Figure 4.14** Titration of OCCW model mixture

#### 4.4 Other Modeling Attempts

Without any further titrations, each of the natural sources were modeled with other amino acids because glycine did not provide enough binding capacity.

##### 4.4.1 OCGW XAD-8 Modeling

Using the pH 6.2 complexometric data and concentrations of catechol and glycine, the SAS program was allowed to fit for a third ligand concentration and binding constant. The result was a pL of 5.20 and a binding constant of 9.00 for a non-protonated binding site. In Smith and Martell (1975), two possible compounds were found that fit the binding constant requirement: N-N-glycine and N-Uridoiiminodiacetic acid (N-U acid). Properties of these two amines are shown in Table 4.7.

Using assumptions (1) to (4), concentrations of phthalic acid and catechol were modeled with SAS for both amino acids at pH 6.2 and 7.5. The results are shown in Table 4.8 with calculated chemical compositions. Figure 4.15 shows the potentiometric and complexometric plots of the mixtures with better results than the previous ligand used, glycine.

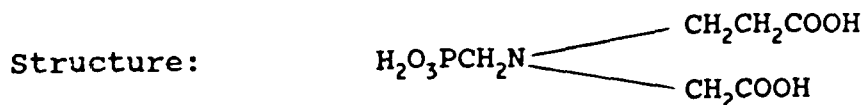
For both pH models, the potentiometric plots fit close to one another but not near to the actual XAD-8 titration. In Figure 4.15 the pH 6.2 model mixture fit better on the upper portion of the complexometric curve but had too much binding at the lower portions of the curve. The pH 6.2

Table 4.7 Other amino acids (Smith and Martell, 1975)

**Name:**

N-(Phosphonomethyl)-N-(2-carboxethyl) glycine or  
(N-(phosphonomethyl) glycine-N-propanoic acid  
(H<sub>4</sub>L)

Chemical formula: C<sub>6</sub>H<sub>12</sub>O<sub>7</sub>NP



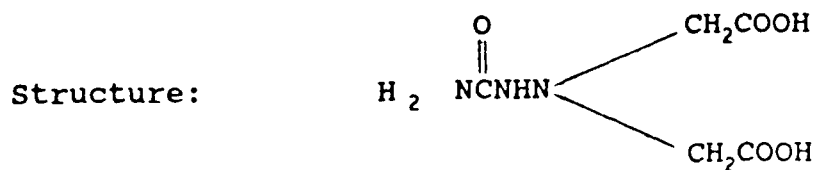
Constants (log K):

|                                     |       |
|-------------------------------------|-------|
| HL/H.L                              | 10.41 |
| H <sub>2</sub> L/HL.H               | 5.59  |
| H <sub>3</sub> L/H <sub>2</sub> L.H | 3.48  |
| H <sub>4</sub> L/H <sub>3</sub> L.H | 2.72  |
| CuL/Cu.L                            | 13.0  |
| CuHL/CuL.H                          | 4.71  |

**Name:**

N-Uriodoiminodiacetic acid (H<sub>2</sub>L)

Chemical Formula: C<sub>5</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub>



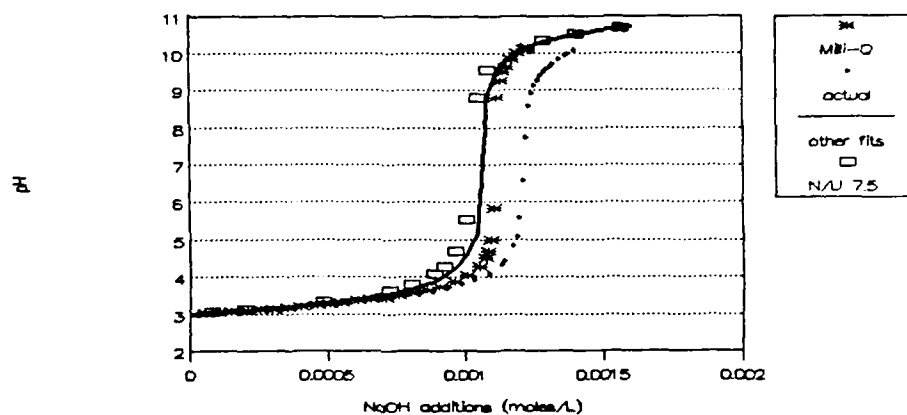
Constants (log K)

|                       |      |
|-----------------------|------|
| HL/H.L                | 4.04 |
| H <sub>2</sub> L/HL.H | 2.96 |
| CuL/Cu.L              | 8.40 |

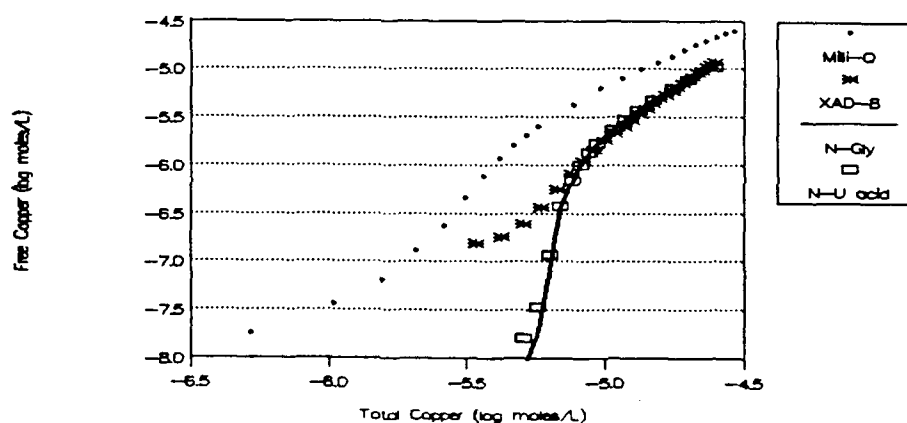
**Table 4.8** Amino acid modeling elemental compositions  
and ratios - OCGW XAD-8

| OCGW XAD-8                                     |        |          |                |                 |
|------------------------------------------------|--------|----------|----------------|-----------------|
| pH 6.2 with                                    |        |          | pH 7.5 with    |                 |
| <u>N-N-gly</u> <u>N-U acid</u>                 |        |          | <u>N-N-gly</u> | <u>N-U acid</u> |
| Mixture (pL - %)-the same for both amino acids |        |          |                |                 |
| amine                                          | 5.2    | - 8.9 %  |                | 4.35            |
| catechol                                       | 4.85   | - 20.0 % |                | 4.85            |
| phthalic                                       | 4.3    | - 71.0 % |                | 4.96            |
| Percentages                                    |        |          |                |                 |
| C                                              | 55.1   | 45.4     | 37.4 -         | 39.9            |
| H                                              | 4.1    | 4.3      | 4.9            | 4.7             |
| O                                              | 38.3   | 39.4     | 43.5           | 39.7            |
| N                                              | 0.8 -  | 10.8 +   | 4.4            | 15.7 +          |
| P                                              | 1.7 +  | ---      | 9.8 ++         | ---             |
| Ratios                                         |        |          |                |                 |
| H/C                                            | 0.88   | 1.14 +   | 1.56 +         | 1.39 +          |
| O/C                                            | 0.52   | 0.65 +   | 0.87 +         | 0.75 +          |
| N/C                                            | 0.01 - | 0.20 +   | 0.10 +         | 0.34 +          |
| + high                                         |        |          |                |                 |
| ++ very high                                   |        |          |                |                 |
| - low                                          |        |          |                |                 |
| -- very low                                    |        |          |                |                 |

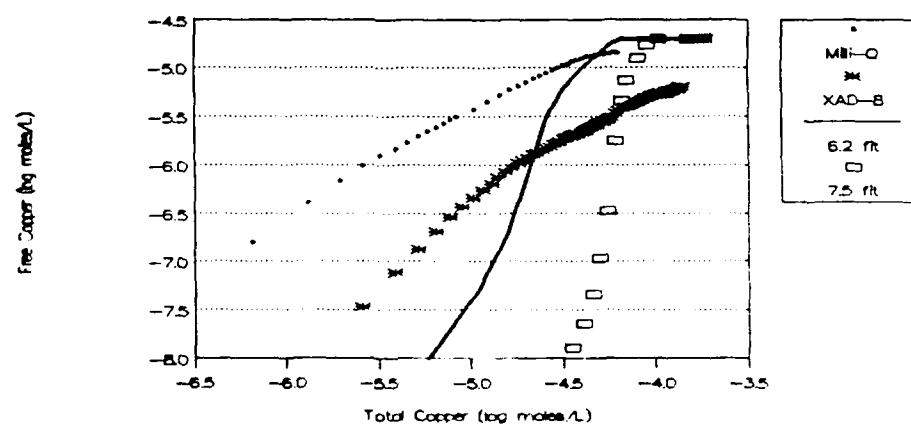
# Amine Potentiometric Models



## pH 6.2 Amine Models



## pH 7.5 Amine Models



**Figure 4.15** OCGW XAD-8 amine titration models (with pH 6.2 model mixture shown on the pH 7.5 graph)

modeling concentrations were compared to the 7.5 concentrations and showed no match nor a fit to the actual titration.

#### 4.4.2 BA XAD-8 Modeling

Concentrations for the two amines were determined similarly to OCGW modeling (see Table 4.9). Also similar to OCGW modeling, only the pH 6.2 titration showed a good fit with the stronger amine models (see Figure 4.16) but with too much binding occurring at the lower portions of the curves.

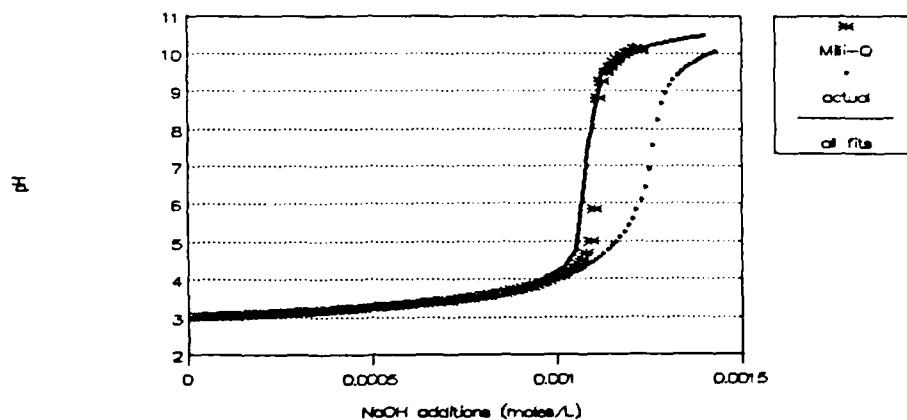
#### 4.4.3 Fitting pH 7.5 Titrations

The fitting of each of the pH 7.5 titrations came about by using the concentrations of catechol and phthalic acid obtained from the 3-ligand fitting with SAS (see Table 4.5) and substituting the stronger binding amines of N-N-glycine and N-U acid for glycine. The pL concentration of each amine required to fit the data was 5.4 for both water sources. The results of the fitting are shown in Figure 4.17. Acidities for the model mixtures to fit the pH 7.5 titrations were even higher than that shown in Table 4.5.

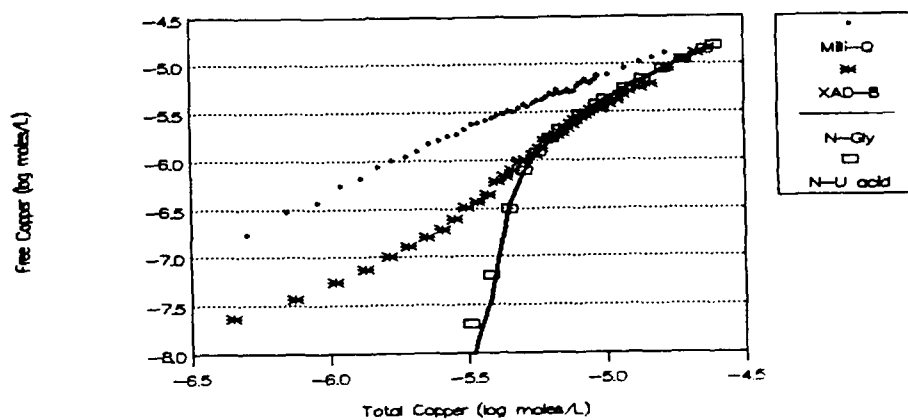
**Table 4.9** Amino acid modeling elemental compositions  
and ratios - BA XAD-8

| BA XAD-8                                       |        |                |                 |                                |
|------------------------------------------------|--------|----------------|-----------------|--------------------------------|
|                                                |        | pH 6.2 with    |                 | pH 7.5 with                    |
|                                                |        | <u>N-N-gly</u> | <u>N-U acid</u> | <u>N-N-gly</u> <u>N-U acid</u> |
| Mixture (pL - %)-the same for both amino acids |        |                |                 |                                |
| amine                                          | 5.4    | -              | 12.0 %          | 5                              |
| catechol                                       | 5.2    | -              | 19.0 %          | 5.2                            |
| phthalic                                       | 4.64   | -              | 69.0 %          | 4.77                           |
| Percentages                                    |        |                |                 |                                |
| C                                              | 53.9   |                | 55.0            | 47.3 49.5                      |
| H                                              | 4.1    |                | 4.0             | 4.5 4.3                        |
| O                                              | 38.7   |                | 37.8            | 40.6 38.4                      |
| N                                              | 1.0    |                | 3.28            | 2.4 7.8 +                      |
| P                                              | 2.3 ++ |                | ---             | 5.2 ++ ---                     |
| Ratios                                         |        |                |                 |                                |
| H/C                                            | 0.91   |                | 0.88            | 1.11 + 1.03 +                  |
| O/C                                            | 0.54   |                | 0.52            | 0.64 + 0.58 +                  |
| N/C                                            | 0.02   |                | 0.05            | 0.04 0.01 -                    |
| + high<br>++ very high<br>- low<br>-- very low |        |                |                 |                                |

## Amine Potentiometric Models



## pH 6.2 Amine Models



## pH 7.5 Amine Models

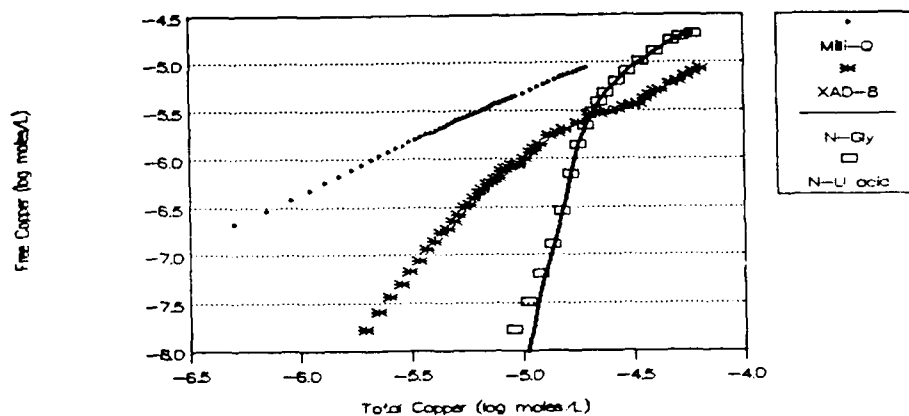
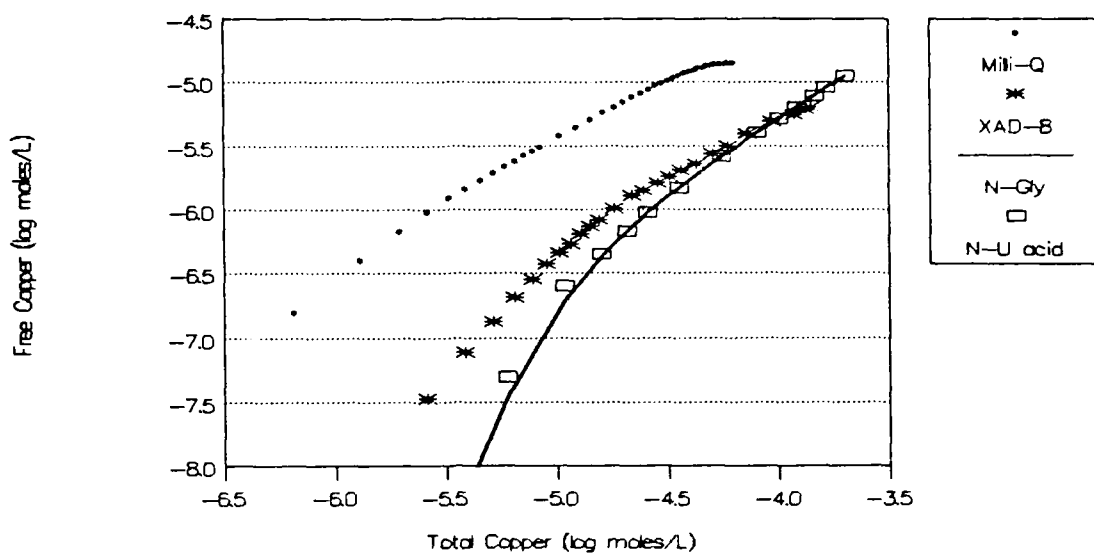


Figure 4.16 BA XAD-8 amine titration models

# OCGW XAD-8 pH 7.5 Amine



# BA XAD-8 pH 7.5 Amine

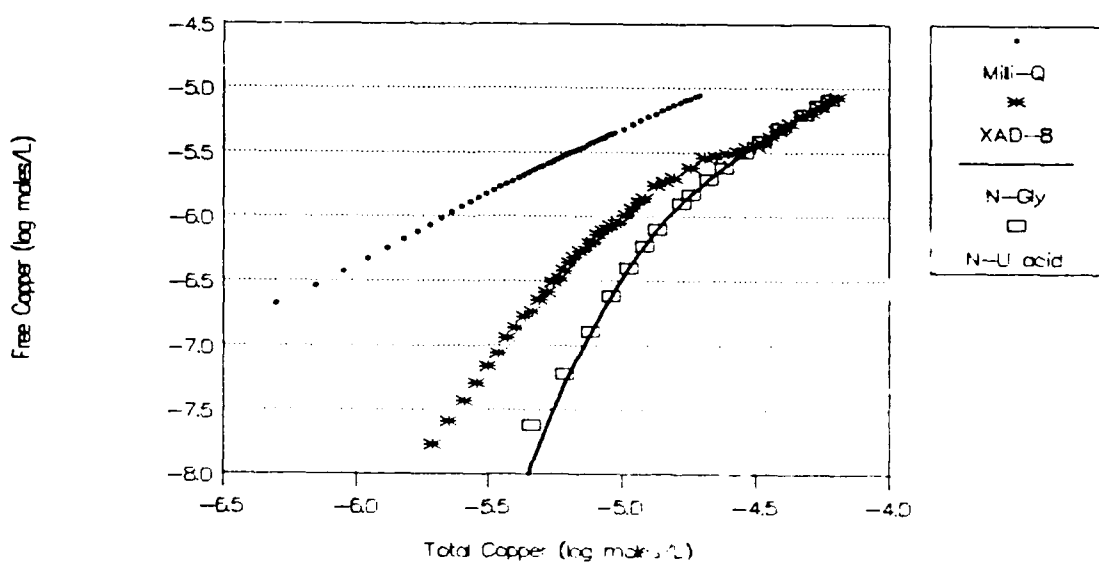


Figure 4.17 pH 7.5 fitting

## CHAPTER 5

## DISCUSSION

Although the results of the experimentation and modeling did not achieve the objective of developing a model of a humic substance based on a combination of ligands, it does give further insight into the behavior of a humic substance in an experiment protocol.

### 5.1 Titration Experiments

#### 5.1.1 Model Compound Binding Constants

Verifying published binding constants for each of the model compounds to those experimentally obtained was necessary because of the dependence on temperature and ionic strength. Although experimental temperatures and ionic strengths did change the binding by no more than 1/2 an order of magnitude, modeled curves fitted well with experimental curves. Temperature and ionic strength corrections were inherent in TITRATOR and were, therefore, not required for modeling. Salicylic acid was the only compound which did not agree with the published binding constants. In this case, experimental values were used since the published values did not fit either complexometric titration at pH 6.2 or 7.5.

Compared to Ephraim's, et al. (1989), work identifying 30 - 45 percent of acidic sites responsible for copper

binding to a salicylic acid-like group and 25 - 30 percent as a catechol-like group for an aquatic fulvic acid, this research found for the models that fit the complexometric curves at pH 6.2, 70 percent of the copper binding was by phthalic acid groups, 20 percent for catechol, and 10 percent by amines for an aquatic humic acid. Work at pH 7.5 showed less than 1 - 2 percent of the groups responsible for copper binding were of the catechol and amine type, and a large percentage (> 98 percent) characterized a phthalic acid-type group.

#### 5.1.2 Titration Vessel Interferences

As shown in Figure 3.4, the type of titration vessel used will effect complexometric results. The decrease of free copper with glass was observed by Cabaniss and Shuman (1988c) along with no decrease observed in opaque, teflon beakers. This study showed slight interferences with polypropylene which may have not been due to adsorption. In comparing glass and polypropylene titrations, though, glass had much higher adsorption of copper (II) occurring.

#### 5.1.3 Titration Reliability

Repeats done on glycine showed good repeatability for potentiometric titrations. Error bars for complexometric titrations did not, however, show as good a repeatability. At the lower portions of the titration curve, where free copper was less than  $10^{-7}$  M, some error was expected due to the loss of linearity with the copper probes. The error for

the titration was at its lowest at a total copper concentration of  $10^{-5.5}$  M, and increased from that point with increasing total copper concentration. This trend can be explained by the number of binding sites for the ligands being occupied decreasing as more copper is introduced. The remaining ligand sites take a longer time to be occupied by the free copper; therefore, enough time should pass before further copper additions. In this research, titrations were automated, and ten minutes were allowed between copper additions. Cabaniss and Shuman (1988a) allowed 3 to 30 minutes between additions, depending on the total copper concentration. Holm and Curtiss (1990) equilibrated for 60 minutes.

Between the two pH titrations, the pH 7.5 titrations had greater error than the pH 6.2 titrations. This could be due to the presence of another ligand ( $\text{OH}^-$ ) requiring even longer equilibration times. It may have been also due to the difficulty experienced in maintaining a constant pH at 7.5. A HEPES concentration of 5 mM was found to be adequate to maintain the pH to  $\pm .01$  units. Holm and Curtiss (1990) buffered their titrations with HEPES at 6.7 mM.

## 5.2 Model Compound Mixtures

The selection of the model compounds used - catechol, phthalic acid and salicylic acid - was partially based on previous work that attributed binding sites of humic substances to these groups on humic substance molecules (see Section 2.2). Of the previous work, this research effort agreed with Buffle, et al. (1980), in showing that salicylic and phthalic acids do not have high enough binding capacities to explain a humic substance. Also in this research, catechol and glycine were not adequate. What was also shown is that if it is assumed that phenolic and carboxyl groups are responsible for the majority of the complexation of metals that occurs, then phenolic acidity measurements limit the use of salicylic acid and catechol quantities. With the similarity in behaviors of salicylic acid and phthalic acid in modeling each of the groundwater sources, chemical constraints of phenolic -OH content required the use of phthalic acid and catechol to describe the complexation of copper (II) by a humic substance. In previous work that had carboxylic acidities closer to phenolic acidities, salicylic acid-type groups may have been more appropriate.

### 5.2.1 OCGW XAD-8 Mixtures

For this groundwater source, phthalic acid and catechol did not adequately model the complexometric curves. The addition of glycine was also not successful. The

substitution of glycine with N-N-glycine and N-U acid did fit the titration at pH 6.2, but there too much binding occurring at the lower portions of the curve. This indicated that the nitrogen content used was excessive. Problems occurred when concentrations of phthalic acid, catechol and the higher binding amino acids were modeled to the pH 7.5 titrations. The parameters which provided a good fit at pH 6.2 titrations were not adequate to explain pH 7.5 titrations. Only by using the high phthalic acid concentrations from the 3-ligand fitting was a good fit approached with the higher binding amino acids. The result though of using the higher concentration of phthalic acid was a mixture that did not contain a reasonable carboxylic acidity. Use of the higher binding amino acids also caused a poor fit of the potentiometric curves due to the loss in overall acidity.

#### 5.2.2 BA XAD-8 Mixtures

Modeling of the BA XAD-8 groundwater had the same results as OCGW. Final fitting of the pH 5.2 complexometric titration was possible with catechol, phthalic acid and N-N-glycine or N-U acid; but this combination of ligands gave a poor fit to potentiometric data. The same concentrations did not fit the pH 7.5 titrations, and fitting was possible by using high concentrations of phthalic acid. The phthalic acid concentration was not as high for BA as OCGW due to the lower carboxylic content of BA.

### 5.2.3 Possible Other Functional Groups

The results indicated that the complexation behavior of a humic acid is best modeled by a strong amino acid at pH 6.2 and with carboxylic and phenolic groups. Titrations at pH 7.5 needed a strong carboxylic-type group for proper fitting. For a model mixture to fit at both pHs, the carboxylic-type group would need to have a strong unprotonated binding ligand at pH 7.5 that dominates the speciation. At pH 6.2, a relatively-weak, protonated ligand would need to dominate. This suggests a site with an acid dissociation constant between 6.2 and 7.5 and a multidentate character.

Even if such a ligand was available, the necessity of also fitting potentiometric curves and satisfying reasonable concentrations and elemental percentages and ratios may not be possible. For example, the carboxylic acidities may be exceeded by such a ligand to fit the pH 7.5 titrations. An increased binding with pH might be due to another minor functional group such as the sulfur groups. However, at this point the model system begins to mirror the complexity of the item being modeled.

## CHAPTER 6

### CONCLUSIONS

#### 6.1 Chemical Modeling of a Humic Acid

This research project set out to find a simple model mixture for a highly complex system. The model had to fit the constraints of being chemically-valid and of being able to describe experimental data. In attempting to characterize a groundwater humic/fulvic acid with simple model compounds, some of the constraints were satisfied for some of the conditions. The modeling of a humic substance was possible at pH 6.2 with phthalic acid, catechol and N-N-glycine, but the presence of N-N-glycine reduced the mixture acidity and caused an improper characterization of potentiometric data. At pH 7.5, experimental fitting of the complexometric curves was possible with the same compounds, but with high concentrations of phthalic acid, resulting in carboxylic acidities that were excessive. Carboxylic and phenolic acidities occurring as multidentate ligands would better model the complexation behavior of humic substances than the excessive binding observed by nitrogen present as amino acids. The low concentrations of highly complexing nitrogen did not characterize the behavior of the humic substances properly.

## 6.2 Recommendations for Future Work

Future work of finding a simple model for a humic substance should begin with a systematic approach of modeling a proposed model mixture with the computer programs available prior to expending time in the laboratory. Experimental verification is the final and necessary step to the modeling process of the model compound constants and the model mixtures. The apparatus for complexometric titrations should include the use of appropriate, non-adsorbing titration vessels. Polypropylene or opaque teflon should be adequate. Temperature control of complexometric titrations is not as vital as for potentiometric titrations, but for consistency, a jacketed, temperature-controlled, vessel would be ideal. The DOC of the titrated natural sources should be kept between 4 - 6 mg/L to ensure adequate response for the titration range of copper (II). The titrant additions are also important and should be between  $2 \times 10^{-5}$  M and  $2 \times 10^{-4}$  M per addition of copper (II). One item not fully recognized in this research was the long equilibration times required as total copper concentration increases. Automated programs can be adjusted so that longer times are allowed as the titration progresses. An increase in time will likely result in the need for greater buffering capacity. The effects of increasing buffering should be examined as buffer concentrations begin to overwhelm the ligand concentrations.

**APPENDICES****Appendix A Titration Data of Single Model Compounds**

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 Model Compound Potentiometric Titrations  
 -----

(Phth, Cat, Sal-by Len Rothfield) (Glyc-Castro)

| Phthalic Acid<br>[NaOH] | pH   | Catechol<br>[NaOH] | pH    |
|-------------------------|------|--------------------|-------|
| 0                       | 2.95 | 0                  | 6.5   |
| 0.000107                | 3.07 | 5.33E-05           | 7.6   |
| 0.000213                | 3.11 | 0.000107           | 8     |
| 0.000266                | 3.14 | 0.00016            | 8.5   |
| 0.000319                | 3.21 | 0.000213           | 8.6   |
| 0.000372                | 3.29 | 0.000266           | 8.74  |
| 0.000424                | 3.36 | 0.000398           | 9     |
| 0.00053                 | 3.5  | 0.00053            | 9.1   |
| 0.000582                | 3.64 | 0.000641           | 9.25  |
| 0.000645                | 3.71 | 0.000792           | 9.4   |
| 0.00074                 | 3.86 | 0.000923           | 9.6   |
| 0.000792                | 4.1  | 0.001053           | 9.75  |
| 0.000897                | 4.4  | 0.001182           | 9.85  |
| 0.000949                | 4.5  | 0.001311           | 10    |
| 0.001053                | 4.75 | 0.00144            | 10.2  |
| 0.001105                | 4.8  | 0.001569           | 10.35 |
| 0.001156                | 5    | 0.001697           | 10.48 |
| 0.00126                 | 5.2  | 0.001824           | 10.55 |
| 0.001311                | 5.3  | 0.001951           | 10.65 |
| 0.001363                | 5.4  | 0.002078           | 10.75 |
| 0.00144                 | 5.5  | 0.002204           | 10.8  |
| 0.001517                | 5.85 | 0.00233            | 10.85 |
| 0.001569                | 6    | 0.002456           | 10.9  |
| 0.001579                | 6.1  | 0.002581           | 10.95 |
| 0.001594                | 6.25 |                    |       |
| 0.00162                 | 6.65 |                    |       |
| 0.001633                | 7.25 |                    |       |
| 0.001645                | 8    |                    |       |
| 0.001656                | 8.8  |                    |       |
| 0.001658                | 9.3  |                    |       |
| 0.001671                | 9.6  |                    |       |
| 0.001697                | 9.7  |                    |       |
| 0.001722                | 9.8  |                    |       |
| 0.001748                | 9.87 |                    |       |
| 0.001773                | 9.9  |                    |       |
| 0.001824                | 10.1 |                    |       |

| Salicylic Acid<br>[NaOH] | pH    |
|--------------------------|-------|
| 0                        | 2.9   |
| 5.33E-06                 | 2.93  |
| 1.07E-05                 | 2.95  |
| 1.6E-05                  | 2.97  |
| 4.26E-05                 | 3     |
| 5.86E-05                 | 3.02  |
| 7.99E-05                 | 3.04  |
| 0.000107                 | 3.06  |
| 0.000133                 | 3.08  |
| 0.00016                  | 3.09  |
| 0.000213                 | 3.13  |
| 0.000266                 | 3.16  |
| 0.000319                 | 3.2   |
| 0.000372                 | 3.24  |
| 0.000451                 | 3.29  |
| 0.000535                 | 3.36  |
| 0.000635                 | 3.45  |
| 0.000687                 | 3.52  |
| 0.00074                  | 3.59  |
| 0.000844                 | 3.75  |
| 0.000895                 | 3.88  |
| 0.000949                 | 4.16  |
| 0.000975                 | 4.39  |
| 0.001001                 | 4.78  |
| 0.001027                 | 6.17  |
| 0.001032                 | 8.76  |
| 0.001037                 | 9.1   |
| 0.001042                 | 9.32  |
| 0.001047                 | 9.44  |
| 0.001053                 | 9.69  |
| 0.001068                 | 9.8   |
| 0.001084                 | 9.85  |
| 0.001094                 | 9.9   |
| 0.001105                 | 9.94  |
| 0.001115                 | 9.99  |
| 0.00112                  | 10.01 |
| 0.001125                 | 10.03 |
| 0.00113                  | 10.06 |

| Glycine<br>[NaOH] | pH       | Glycine Repeat<br>[NaOH] | pH    |
|-------------------|----------|--------------------------|-------|
| 1.06E-05          | 3.001    | 1.07E-05                 | 3     |
| 2.11E-05          | 3.006    | 2.13E-05                 | 3.005 |
| 4.26E-05          | 3.015    | 3.2E-05                  | 3.01  |
| 6.48E-05          | 3.025    | 4.26E-05                 | 3.014 |
| 8.51E-05          | 3.036    | 5.33E-05                 | 3.019 |
| 0.000106          | 3.046    | 6.39E-05                 | 3.024 |
| 0.000128          | 3.058    | 7.45E-05                 | 3.029 |
| 0.000149          | 3.069    | 8.52E-05                 | 3.033 |
| 0.00017           | 3.081    | 9.58E-05                 | 3.039 |
| 0.000191          | 3.092    | 0.000106                 | 3.044 |
| 0.000212          | 3.105    | 0.000117                 | 3.05  |
| 0.000234          | 3.118    | 0.000128                 | 3.055 |
| 0.000255          | 3.131    | 0.000138                 | 3.06  |
| 0.000276          | 3.145    | 0.000149                 | 3.065 |
| 0.000297          | 3.16     | 0.00016                  | 3.071 |
| 0.000318          | 3.174    | 0.00017                  | 3.076 |
| 0.000339          | 3.19     | 0.000181                 | 3.083 |
| 0.000381          | 3.225    | 0.000191                 | 3.089 |
| 0.000403          | 3.242    | 0.000202                 | 3.094 |
| 0.000424          | 3.26     | 0.000213                 | 3.101 |
| 0.000445          | 3.282    | 0.000223                 | 3.106 |
| 0.000466          | 3.303    | 0.000234                 | 3.113 |
| 0.000487          | 3.324    | 0.000244                 | 3.119 |
| 0.000508          | 3.348    | 0.000255                 | 3.126 |
| 0.000529          | 3.372    | 0.000266                 | 3.133 |
| 0.00055           | 3.399    | 0.000276                 | 3.14  |
| 0.000571          | 3.427    | 0.000287                 | 3.146 |
| 0.000592          | 3.459    | 0.000297                 | 3.152 |
| 0.000613          | 3.491    | 0.000308                 | 3.159 |
| 0.000634          | 3.528    | 0.000318                 | 3.166 |
| 0.000655          | 3.569    | 0.000329                 | 3.174 |
| 0.000676          | 3.613    | 0.00034                  | 3.182 |
| 0.000697          | 3.664    | 0.00035                  | 3.189 |
| 0.000718          | 3.722    | 0.000361                 | 3.196 |
| 0.000738          | 3.787    | 0.000371                 | 3.205 |
| 0.000759          | 3.867    | 0.000382                 | 3.212 |
| 0.00078           | 3.962    | 0.000392                 | 3.221 |
| 0.000801          | 4.088    | 0.000403                 | 3.229 |
| 0.000822          | 4.264    | 0.000414                 | 3.238 |
| 0.000843          | 4.547    | 0.000424                 | 3.247 |
| 0.000864          | 5.183    | 0.000435                 | 3.255 |
| 0.000885          | 7.01     | 0.000445                 | 3.264 |
| 0.000905          | 7.497    | 0.000456                 | 3.275 |
| 0.000926          | 7.771    | 0.000466                 | 3.283 |
| 0.000947          | 7.891    | 0.000477                 | 3.294 |
| 0.000968          | 8.006    | 0.000487                 | 3.304 |
| 0.000988          | 8.105    | 0.000498                 | 3.315 |
| 0.001009          | 8.186    | 0.000508                 | 3.325 |
| 0.00103           | 8.258001 | 0.000519                 | 3.337 |
| 0.001051          | 8.321    | 0.000529                 | 3.348 |
| 0.001071          | 8.376001 | 0.00054                  | 3.36  |
| 0.001092          | 8.428001 | 0.00055                  | 3.372 |
| 0.001113          | 8.474    | 0.000561                 | 3.385 |
| 0.001134          | 8.517    | 0.000571                 | 3.398 |
| 0.001154          | 8.559    | 0.000582                 | 3.412 |
| 0.001175          | 8.596    | 0.000592                 | 3.426 |
| 0.001196          | 8.632    | 0.000603                 | 3.44  |

| Glycine<br>[NaOH] | pH       | Glycine Repeat<br>[NaOH] | pH       |
|-------------------|----------|--------------------------|----------|
| 0.001237          | 8.698    | 0.000624                 | 3.47     |
| 0.001258          | 8.729999 | 0.000634                 | 3.486    |
| 0.001278          | 8.759    | 0.000645                 | 3.503    |
| 0.001299          | 8.788999 | 0.000655                 | 3.521    |
| 0.001319          | 8.814999 | 0.000666                 | 3.54     |
| 0.00134           | 8.840999 | 0.000676                 | 3.559    |
| 0.001361          | 8.866999 | 0.000687                 | 3.58     |
| 0.001381          | 8.892    | 0.000697                 | 3.6      |
| 0.001402          | 8.917    | 0.000708                 | 3.623    |
| 0.001422          | 8.939999 | 0.000718                 | 3.647    |
| 0.001443          | 8.962    | 0.000729                 | 3.672    |
| 0.001463          | 8.984999 | 0.000739                 | 3.7      |
| 0.001484          | 9.007    | 0.00075                  | 3.728    |
| 0.001504          | 9.028    | 0.00076                  | 3.759    |
| 0.001525          | 9.049    | 0.000771                 | 3.792    |
| 0.001545          | 9.068    | 0.000781                 | 3.83     |
| 0.001566          | 9.089    | 0.000791                 | 3.87     |
| 0.001586          | 9.109    | 0.000802                 | 3.914    |
| 0.001607          | 9.128    | 0.000812                 | 3.964    |
| 0.001627          | 9.148    | 0.000823                 | 4.018    |
| 0.001648          | 9.165    | 0.000833                 | 4.083    |
| 0.001668          | 9.185001 | 0.000844                 | 4.159    |
| 0.001688          | 9.203    | 0.000854                 | 4.249    |
| 0.001709          | 9.222    | 0.000864                 | 4.363    |
| 0.001729          | 9.239001 | 0.000875                 | 4.509    |
| 0.00175           | 9.257    | 0.000885                 | 4.705    |
| 0.00177           | 9.274999 | 0.000896                 | 5.009    |
| 0.00179           | 9.292    | 0.000906                 | 5.624    |
| 0.001811          | 9.311    | 0.000917                 | 6.801    |
| 0.001831          | 9.326    | 0.000927                 | 7.229    |
| 0.001851          | 9.343001 | 0.000937                 | 7.451    |
| 0.001872          | 9.359999 | 0.000948                 | 7.605    |
| 0.001892          | 9.377    | 0.000958                 | 7.723    |
| 0.001912          | 9.392999 | 0.000969                 | 7.816    |
| 0.001933          | 9.409001 | 0.000979                 | 7.89     |
| 0.001953          | 9.425999 | 0.000989                 | 7.956    |
| 0.001973          | 9.441    | 0.001                    | 8.029    |
| 0.001993          | 9.458    | 0.001021                 | 8.113    |
| 0.002014          | 9.474    | 0.001041                 | 8.199001 |
| 0.002034          | 9.49     | 0.001062                 | 8.273    |
| 0.002054          | 9.505    | 0.001083                 | 8.337    |
| 0.002074          | 9.522001 | 0.001104                 | 8.395001 |
| 0.002094          | 9.537    | 0.001124                 | 8.446999 |
| 0.002115          | 9.552    | 0.001145                 | 8.496    |
| 0.002135          | 9.569    | 0.001166                 | 8.54     |
| 0.002155          | 9.583999 | 0.001186                 | 8.58     |
| 0.002175          | 9.599    | 0.001207                 | 8.617001 |
| 0.002195          | 9.614001 | 0.001228                 | 8.655    |
| 0.002216          | 9.627    | 0.001248                 | 8.689    |
| 0.002236          | 9.646    | 0.001269                 | 8.722    |
| 0.002256          | 9.662    | 0.00129                  | 8.754    |
| 0.002276          | 9.678001 | 0.00131                  | 8.783    |

| Glycine<br>[NaOH] | pH       | Glycine Repeat<br>[NaOH] | pH       | Glycine Repeat<br>[NaOH] | pH       |
|-------------------|----------|--------------------------|----------|--------------------------|----------|
| 0.002295          | 9.692    | 0.001331                 | 8.812    | 0.002248                 | 9.644    |
| 0.002316          | 9.708    | 0.001352                 | 8.839    | 0.002288                 | 9.675    |
| 0.002336          | 9.724    | 0.001372                 | 8.866    | 0.002328                 | 9.707    |
| 0.002356          | 9.741    | 0.001393                 | 8.891    | 0.002368                 | 9.739001 |
| 0.002376          | 9.755999 | 0.001413                 | 8.916001 | 0.002409                 | 9.771    |
| 0.002396          | 9.771    | 0.001434                 | 8.941    | 0.002449                 | 9.802    |
| 0.002416          | 9.786    | 0.001454                 | 8.963    | 0.002489                 | 9.833    |
| 0.002436          | 9.802    | 0.001475                 | 8.986    | 0.002529                 | 9.864001 |
| 0.002456          | 9.818    | 0.001496                 | 9.008001 | 0.002569                 | 9.896    |
| 0.002476          | 9.833999 | 0.001516                 | 9.03     | 0.002608                 | 9.928001 |
| 0.002496          | 9.850001 | 0.001537                 | 9.050999 | 0.002648                 | 9.958999 |
| 0.002516          | 9.865    | 0.001557                 | 9.071999 | 0.002688                 | 9.991    |
| 0.002536          | 9.88     | 0.001578                 | 9.092    |                          |          |
| 0.002556          | 9.896    | 0.001598                 | 9.113    | 0.002728                 | 10.022   |
| 0.002576          | 9.912    | 0.001619                 | 9.130999 | 0.002768                 | 10.053   |
| 0.002596          | 9.927    | 0.001639                 | 9.151    |                          |          |
| 0.002616          | 9.944    | 0.001659                 | 9.17     |                          |          |
| 0.002636          | 9.958999 | 0.00168                  | 9.189    |                          |          |
| 0.002656          | 9.974    | 0.0017                   | 9.208    |                          |          |
| 0.002676          | 9.99     | 0.001721                 | 9.225001 |                          |          |
| 0.002696          | 10.004   | 0.001741                 | 9.244001 |                          |          |
|                   |          | 0.001762                 | 9.260999 |                          |          |
|                   |          | 0.001782                 | 9.279    |                          |          |
|                   |          | 0.001802                 | 9.295999 |                          |          |
|                   |          | 0.001823                 | 9.313    |                          |          |
|                   |          | 0.001843                 | 9.332    |                          |          |
|                   |          | 0.001863                 | 9.347999 |                          |          |
|                   |          | 0.001884                 | 9.365    |                          |          |
|                   |          | 0.001904                 | 9.380999 |                          |          |
|                   |          | 0.001924                 | 9.397001 |                          |          |
|                   |          | 0.001945                 | 9.413999 |                          |          |
|                   |          | 0.001965                 | 9.43     |                          |          |
|                   |          | 0.001985                 | 9.446    |                          |          |
|                   |          | 0.002005                 | 9.461001 |                          |          |
|                   |          | 0.002026                 | 9.475001 |                          |          |
|                   |          | 0.002046                 | 9.487001 |                          |          |
|                   |          | 0.002086                 | 9.517999 |                          |          |
|                   |          | 0.002127                 | 9.549    |                          |          |
|                   |          | 0.002167                 | 9.581001 |                          |          |
|                   |          | 0.002207                 | 9.613    |                          |          |

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 Milli-Q Complexometric Titrations @ pH = 6.2  
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| Milli-Q Blank @ pH 6.2<br>Polypyrrolene<br>log [CuT]log [CuF] | Milli-Q Blank @ pH 6.2<br>Glass (Waterbury, 1990)<br>log [CuT]log [CuF] | Ideal Milli-Q<br>@ pH 6.2<br>log [CuT]Blank |
|---------------------------------------------------------------|-------------------------------------------------------------------------|---------------------------------------------|
| -7.000                                                        | -7.532                                                                  | -7 -7.01963                                 |
| -6.523                                                        | -7.089                                                                  | -6.03152 -6.05117                           |
| -6.301                                                        | -6.767                                                                  | -5.75449 -5.77416                           |
| -6.155                                                        | -6.535                                                                  | -5.5867 -5.60639                            |
| -6.046                                                        | -6.431                                                                  | -5.46597 -5.48568                           |
| -5.959                                                        | -6.272                                                                  | -5.37161 -5.39133                           |
| -5.886                                                        | -6.182                                                                  | -5.29414 -5.31388                           |
| -5.824                                                        | -6.072                                                                  | -5.22841 -5.24817                           |
| -5.770                                                        | -5.995                                                                  | -5.17134 -5.19112                           |
| -5.722                                                        | -5.957                                                                  | -5.1209 -5.1407                             |
| -5.678                                                        | -5.902                                                                  | -5.07572 -5.09554                           |
| -5.639                                                        | -5.833                                                                  | -5.0348 -5.05463                            |
| -5.603                                                        | -5.788                                                                  | -4.9974 -5.01726                            |
| -5.570                                                        | -5.746                                                                  | -4.96297 -4.98284                           |
| -5.539                                                        | -5.736                                                                  | -4.93107 -4.95096                           |
| -5.510                                                        | -5.677                                                                  | -4.90136 -4.92127                           |
| -5.481                                                        | -5.636                                                                  | -4.87354 -4.89347                           |
| -5.457                                                        | -5.618                                                                  | -4.84741 -4.86735                           |
| -5.433                                                        | -5.594                                                                  | -4.82275 -4.84272                           |
| -5.410                                                        | -5.559                                                                  | -4.79942 -4.81941                           |
| -5.389                                                        | -5.535                                                                  | -4.77728 -4.79728                           |
| -5.368                                                        | -5.525                                                                  | -4.75622 -4.77624                           |
| -5.349                                                        | -5.480                                                                  | -4.73613 -4.75617                           |
| -5.330                                                        | -5.494                                                                  | -4.71693 -4.73698                           |
| -5.312                                                        | -5.459                                                                  | -4.69854 -4.71861                           |
| -5.294                                                        | -5.424                                                                  | -4.68089 -4.70099                           |
| -5.278                                                        | -5.442                                                                  | -4.66394 -4.68405                           |
| -5.262                                                        | -5.400                                                                  | -4.64762 -4.66776                           |
| -5.246                                                        | -5.373                                                                  | -4.63119 -4.65205                           |
| -5.231                                                        | -5.376                                                                  | -4.61672 -4.63689                           |
| -5.217                                                        | -5.348                                                                  | -4.60206 -4.62225                           |
| -5.203                                                        | -5.314                                                                  |                                             |
| -5.190                                                        | -5.331                                                                  |                                             |
| -5.177                                                        | -5.279                                                                  |                                             |
| -5.164                                                        | -5.314                                                                  |                                             |
| -5.152                                                        | -5.300                                                                  |                                             |
| -5.140                                                        | -5.279                                                                  |                                             |
| -5.128                                                        | -5.296                                                                  |                                             |
| -5.117                                                        | -5.283                                                                  |                                             |
| -5.106                                                        | -5.227                                                                  |                                             |
| -5.095                                                        | -5.206                                                                  |                                             |
| -5.084                                                        | -5.193 log [CuT]log [CuF]                                               |                                             |
| -5.074                                                        | -5.172                                                                  |                                             |
| -5.064                                                        | -5.189 -4.827 -4.943                                                    |                                             |
| -5.054                                                        | -5.203 -4.784 -4.888                                                    |                                             |
| -5.045                                                        | -5.182                                                                  |                                             |
| -5.035                                                        | -5.161                                                                  |                                             |
| -5.024                                                        | -5.134                                                                  |                                             |
| -5.026                                                        | -5.127                                                                  |                                             |
| -4.921                                                        | -5.110                                                                  |                                             |
| -4.929                                                        | -5.047                                                                  |                                             |
| -4.929                                                        | -4.985                                                                  |                                             |

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 COMPLEXOMETRIC TITRATIONS @ pH = 6.2 OF MODEL COMPOUNDS  
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Phthalic Acid (2.58E-4M)

MED = .0001 M EDTA

log[CuT] log[CuF]

|        |        |
|--------|--------|
| -6.222 | -7.024 |
| -6.097 | -6.862 |
| -6.000 | -6.741 |
| -5.921 | -6.640 |
| -5.854 | -6.559 |
| -5.797 | -6.485 |
| -5.746 | -6.423 |
| -5.700 | -6.366 |
| -5.659 | -6.319 |
| -5.621 | -6.268 |
| -5.586 | -6.229 |
| -5.554 | -6.191 |
| -5.524 | -6.152 |
| -5.496 | -6.121 |
| -5.470 | -6.086 |
| -5.445 | -6.055 |
| -5.422 | -6.032 |
| -5.400 | -6.000 |
| -5.379 | -5.977 |
| -5.358 | -5.950 |
| -5.339 | -5.931 |
| -5.321 | -5.904 |
| -5.303 | -5.884 |
| -5.286 | -5.865 |
| -5.270 | -5.845 |
| -5.254 | -5.826 |
| -5.239 | -5.807 |
| -5.224 | -5.791 |
| -5.210 | -5.776 |
| -5.197 | -5.756 |
| -5.183 | -5.744 |
| -5.170 | -5.725 |
| -5.158 | -5.710 |
| -5.146 | -5.698 |
| -5.134 | -5.682 |
| -5.122 | -5.659 |
| -5.111 | -5.646 |
| -5.100 | -5.625 |
| -5.090 | -5.628 |
| -5.079 | -5.616 |
| -5.069 | -5.605 |
| -5.059 | -5.593 |
| -5.050 | -5.582 |
| -5.040 | -5.570 |
| -5.031 | -5.558 |
| -5.026 | -5.547 |

| Glycine (5F-5H) |          |          |          | Gly (1c-4H)     |          |          |          |
|-----------------|----------|----------|----------|-----------------|----------|----------|----------|
| [HFS] = 0.0001H |          |          |          | [HFS] = 0.0001H |          |          |          |
| log[CuT]        | log[CuT] | log[CuT] | log[CuT] | log[CuT]        | log[CuT] | log[CuT] | log[CuT] |
| -7.000          | -7.653   | -4.975   | -5.649   | -7.000          | -7.867   | -4.975   | -5.963   |
| -6.923          | -7.374   | -4.960   | -5.624   | -6.923          | -7.639   | -4.960   | -5.917   |
| -6.801          | -7.224   | -4.944   | -5.599   | -6.801          | -7.465   | -4.944   | -5.867   |
| -6.155          | -7.066   | -4.930   | -5.578   | -6.155          | -7.337   | -4.930   | -5.817   |
| -6.046          | -6.959   | -4.915   | -5.553   | -6.046          | -7.227   | -4.916   | -5.778   |
| -6.001          | -6.916   | -4.902   | -5.531   | -5.959          | -7.139   | -4.902   | -5.807   |
| -5.921          | -6.830   | -4.888   | -5.511   | -5.887          | -7.060   | -4.889   | -5.764   |
| -5.855          | -6.758   |          |          | -5.825          | -6.997   | -4.876   | -5.729   |
| -5.797          | -6.694   |          |          | -5.770          | -6.936   | -4.863   | -5.689   |
| -5.746          | -6.637   |          |          | -5.722          | -6.886   | -4.851   | -5.654   |
| -5.700          | -6.583   |          |          | -5.679          | -6.837   | -4.839   | -5.618   |
| -5.659          | -6.537   |          |          | -5.639          | -6.791   | -4.828   | -5.580   |
| -5.621          | -6.494   |          |          | -5.603          | -6.751   | -4.817   | -5.554   |
| -5.586          | -6.451   |          |          | -5.570          | -6.712   | -4.806   | -5.523   |
| -5.554          | -6.415   |          |          | -5.539          | -6.677   | -4.795   | -5.494   |
| -5.524          | -6.379   |          |          | -5.510          | -6.641   | -4.785   | -5.462   |
| -5.496          | -6.343   |          |          | -5.483          | -6.606   |          |          |
| -5.470          | -6.315   |          |          | -5.458          | -6.577   |          |          |
| -5.445          | -6.283   |          |          | -5.434          | -6.542   |          |          |
| -5.422          | -6.254   |          |          | -5.411          | -6.517   |          |          |
| -5.400          | -6.225   |          |          | -5.389          | -6.485   |          |          |
| -5.379          | -6.200   |          |          | -5.369          | -6.460   |          |          |
| -5.359          | -6.175   |          |          | -5.349          | -6.435   |          |          |
| -5.339          | -6.150   |          |          | -5.330          | -6.407   |          |          |
| -5.321          | -6.125   |          |          | -5.312          | -6.386   |          |          |
| -5.303          | -6.104   |          |          | -5.295          | -6.361   |          |          |
| -5.286          | -6.079   |          |          | -5.278          | -6.336   |          |          |
| -5.270          | -6.061   |          |          | -5.262          | -6.315   |          |          |
| -5.254          | -6.039   |          |          | -5.247          | -6.297   |          |          |
| -5.239          | -6.018   |          |          | -5.232          | -6.277   |          |          |
| -5.225          | -6.000   |          |          | -5.218          | -6.254   |          |          |
| -5.210          | -5.979   |          |          | -5.204          | -6.233   |          |          |
| -5.197          | -5.961   |          |          | -5.190          | -6.215   |          |          |
| -5.183          | -5.943   |          |          | -5.177          | -6.194   |          |          |
| -5.171          | -5.925   |          |          | -5.164          | -6.176   |          |          |
| -5.158          | -5.907   |          |          | -5.152          | -6.158   |          |          |
| -5.146          | -5.893   |          |          | -5.140          | -6.141   |          |          |
| -5.134          | -5.875   |          |          | -5.128          | -6.123   |          |          |
| -5.123          | -5.857   |          |          | -5.117          | -6.105   |          |          |
| -5.111          | -5.843   |          |          | -5.106          | -6.091   |          |          |
| -5.100          | -5.828   |          |          | -5.095          | -6.073   |          |          |
| -5.090          | -5.814   |          |          | -5.085          | -6.055   |          |          |
| -5.079          | -5.800   |          |          | -5.074          | -6.041   |          |          |
| -5.069          | -5.785   |          |          | -5.064          | -6.027   |          |          |
| -5.059          | -5.771   |          |          | -5.055          | -6.013   |          |          |
| -5.050          | -5.757   |          |          | -5.045          | -5.998   |          |          |
| -5.040          | -5.746   |          |          | -5.036          | -5.981   |          |          |
| -5.029          | -5.738   |          |          | -5.027          | -5.970   |          |          |
| -5.009          | -5.699   |          |          | -5.009          | -6.073   |          |          |
| -4.992          | -5.674   |          |          | -4.992          | -6.020   |          |          |

## Salicylic Acid (5.35766E-4M)

[MES]=.00052M I=.0008

log[CuT] log[CuF]

|        |        |
|--------|--------|
| -6.999 | -7.657 |
| -6.522 | -7.178 |
| -6.301 | -6.968 |
| -6.155 | -6.796 |
| -6.045 | -6.660 |
| -5.958 | -6.576 |
| -5.886 | -6.502 |
| -5.824 | -6.440 |
| -5.770 | -6.382 |
| -5.721 | -6.324 |
| -5.678 | -6.272 |
| -5.639 | -6.227 |
| -5.602 | -6.191 |
| -5.569 | -6.159 |
| -5.538 | -6.126 |
| -5.509 | -6.094 |
| -5.482 | -6.065 |
| -5.457 | -6.036 |
| -5.433 | -6.010 |
| -5.410 | -5.987 |
| -5.388 | -5.958 |
| -5.368 | -5.935 |
| -5.348 | -5.913 |
| -5.329 | -5.890 |
| -5.311 | -5.871 |
| -5.294 | -5.851 |
| -5.277 | -5.829 |
| -5.261 | -5.812 |
| -5.246 | -5.793 |
| -5.231 | -5.777 |
| -5.217 | -5.757 |
| -5.203 | -5.741 |
| -5.189 | -5.725 |
| -5.176 | -5.712 |
| -5.163 | -5.696 |
| -5.151 | -5.683 |
| -5.139 | -5.670 |
| -5.128 | -5.654 |
| -5.116 | -5.641 |
| -5.105 | -5.628 |
| -5.094 | -5.615 |
| -5.084 | -5.605 |
| -5.074 | -5.592 |
| -5.064 | -5.583 |
| -5.054 | -5.570 |
| -5.044 | -5.560 |
| -5.035 | -5.547 |
| -5.026 | -5.537 |
| -4.991 | -5.495 |
| -4.959 | -5.460 |
| -4.929 | -5.424 |
| -4.901 | -5.392 |
| -4.875 | -5.362 |
| -4.850 | -5.333 |
| -4.827 | -5.307 |
| -4.805 | -5.282 |

## Catechol (1.36125E-4M)

[MES]=.00048 I=.0008

log[CuT] log[CuF]

|        |        |
|--------|--------|
| -7.000 | -7.545 |
| -6.523 | -7.205 |
| -6.302 | -7.011 |
| -6.156 | -6.862 |
| -6.046 | -6.751 |
| -5.959 | -6.662 |
| -5.887 | -6.585 |
| -5.825 | -6.522 |
| -5.771 | -6.461 |
| -5.722 | -6.407 |
| -5.679 | -6.363 |
| -5.640 | -6.322 |
| -5.603 | -6.283 |
| -5.570 | -6.249 |
| -5.539 | -6.217 |
| -5.510 | -6.182 |
| -5.483 | -6.153 |
| -5.458 | -6.125 |
| -5.434 | -6.099 |
| -5.411 | -6.071 |
| -5.389 | -6.048 |
| -5.369 | -6.026 |
| -5.349 | -6.001 |
| -5.330 | -5.982 |
| -5.312 | -5.963 |
| -5.295 | -5.940 |
| -5.278 | -5.921 |
| -5.262 | -5.905 |
| -5.247 | -5.886 |
| -5.232 | -5.867 |
| -5.218 | -5.851 |
| -5.204 | -5.836 |
| -5.190 | -5.820 |
| -5.177 | -5.804 |
| -5.164 | -5.791 |
| -5.152 | -5.775 |
| -5.140 | -5.762 |
| -5.129 | -5.747 |
| -5.117 | -5.734 |
| -5.106 | -5.721 |
| -5.095 | -5.708 |
| -5.085 | -5.696 |
| -5.075 | -5.683 |
| -5.065 | -5.670 |
| -5.055 | -5.658 |
| -5.045 | -5.648 |
| -5.036 | -5.639 |
| -5.027 | -5.626 |
| -4.992 | -5.616 |
| -4.960 | -5.578 |
| -4.930 | -5.537 |
| -4.902 | -5.499 |
| -4.876 | -5.461 |
| -4.851 | -5.426 |
| -4.828 | -5.394 |
| -4.806 | -5.365 |

-----  
 Ni(II)-O Complexometric Titrations @ pH 7.5  
 -----

Ni(II)-O Blank  
 Polypropylene  
 log [CuT]log [CuF]

-7.000 -7.104  
 -6.923 -6.856  
 -6.801 -6.680  
 -6.655 -6.539  
 -6.646 -6.425  
 -6.959 -6.331  
 -6.887 -6.249  
 -6.825 -6.181  
 -6.771 -6.119  
 -6.722 -6.066  
 -6.679 -6.018  
 -6.640 -5.972  
 -6.603 -5.933  
 -6.570 -5.897  
 -6.539 -5.864  
 -6.510 -5.832  
 -6.483 -5.806  
 -6.458 -5.776  
 -6.434 -5.751  
 -6.411 -5.731  
 -6.389 -5.704  
 -6.369 -5.685  
 -6.349 -5.665  
 -6.330 -5.646  
 -6.312 -5.626  
 -6.295 -5.610  
 -6.278 -5.597  
 -6.262 -5.581  
 -6.247 -5.564  
 -6.232 -5.551  
 -6.218 -5.535  
 -6.204 -5.522  
 -6.190 -5.509  
 -6.177 -5.496  
 -6.164 -5.483  
 -6.152 -5.473  
 -6.140 -5.463  
 -6.127 -5.447  
 -6.117 -5.437  
 -6.106 -5.427  
 -6.095 -5.417  
 -6.085 -5.403  
 -6.074 -5.398  
 -6.064 -5.391  
 -6.055 -5.378  
 -6.045 -5.369  
 -6.036 -5.362  
 -6.027 -5.355  
 -6.019 -5.326  
 -6.009 -5.390  
 -6.940 -5.258  
 -6.902 -5.228  
 -6.876 -5.205

Ni(II)-O Blank  
 Glass  
 log [CuT]log [CuF]

-6.18795 -6.80266  
 -5.88695 -6.39791  
 -5.71088 -6.17343  
 -5.58597 -6.01697  
 -5.48909 -5.91493  
 -5.40993 -5.84011  
 -5.34301 -5.77208  
 -5.28505 -5.71426  
 -5.23392 -5.65984  
 -5.18819 -5.61903  
 -5.14683 -5.57821  
 -5.10907 -5.5442  
 -5.07433 -5.51019  
 -4.98391 -5.42856  
 -4.90936 -5.35713  
 -4.84577 -5.29251  
 -4.79034 -5.23809  
 -4.7412 -5.19727  
 -4.69708 -5.15646  
 -4.65704 -5.11904  
 -4.6204 -5.08503  
 -4.58662 -5.05782  
 -4.55529 -5.03061  
 -4.52609 -5.0068  
 -4.49873 -4.9864  
 -4.473 -4.96599  
 -4.44873 -4.94558  
 -4.42574 -4.93198  
 -4.40392 -4.91837  
 -4.38315 -4.90477  
 -4.36334 -4.89116  
 -4.3444 -4.88436  
 -4.32625 -4.87415  
 -4.30884 -4.87075  
 -4.29211 -4.86395  
 -4.276 -4.86055  
 -4.26048 -4.86055  
 -4.2455 -4.85715  
 -4.23102 -4.85375  
 -4.21701 -4.85375  
 -4.20345 -4.85375

log [CuT]log [CuF]

-----  
 -4.851 -5.179  
 -4.828 -5.157  
 -4.806 -5.137  
 -4.785 -5.114  
 -4.765 -5.095  
 -4.746 -5.088  
 -4.727 -5.072  
 -4.710 -5.056

Ideal Blank  
 @ pH 7.5  
 log [CuT]log [CuF]

-7.000 -7.13629  
 -5.585 -5.73417  
 -5.293 -5.45304  
 -5.120 -5.29045  
 -4.996 -5.1769  
 -4.900 -5.0902  
 -4.821 -5.02041  
 -4.755 -4.96223  
 -4.697 -4.91248  
 -4.646 -4.86912  
 -4.601 -4.83078  
 -4.560 -4.79646  
 -4.522 -4.76543  
 -4.487 -4.73715  
 -4.455 -4.7112  
 -4.425 -4.7  
 -4.397 -4.7  
 -4.371 -4.7  
 -4.346 -4.7  
 -4.323 -4.7  
 -4.301 -4.7  
 -4.279 -4.7  
 -4.259 -4.7  
 -4.240 -4.7  
 -4.222 -4.7  
 -4.204 -4.7  
 -4.187 -4.7  
 -4.170 -4.7  
 -4.155 -4.7  
 -4.139 -4.7  
 -4.125 -4.7  
 -4.111 -4.7  
 -4.097 -4.7  
 -4.083 -4.7  
 -4.071 -4.7  
 -4.058 -4.7  
 -4.046 -4.7  
 -4.034 -4.7  
 -4.022 -4.7  
 -4.011 -4.7  
 -4.000 -4.7

-----  
 Model Compounds Complexometric Titrations @ pH 7.5  
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Phthalic Acid

HEPES 0.0005M [L] + 1.5E-4M

log [CuT] log [CuF] log [CuT] log [CuF]

|        |        |        |        |
|--------|--------|--------|--------|
| -6.700 | -7.231 | -4.668 | -5.147 |
| -6.399 | -6.980 | -4.638 | -5.124 |
| -6.223 | -6.803 | -4.610 | -5.104 |
| -6.098 | -6.673 |        |        |
| -6.001 | -6.565 |        |        |
| -5.922 | -6.477 |        |        |
| -5.855 | -6.402 |        |        |
| -5.797 | -6.337 |        |        |
| -5.746 | -6.275 |        |        |
| -5.700 | -6.220 |        |        |
| -5.659 | -6.171 |        |        |
| -5.621 | -6.132 |        |        |
| -5.587 | -6.093 |        |        |
| -5.555 | -6.060 |        |        |
| -5.525 | -6.027 |        |        |
| -5.497 | -5.998 |        |        |
| -5.470 | -5.969 |        |        |
| -5.446 | -5.943 |        |        |
| -5.422 | -5.916 |        |        |
| -5.400 | -5.894 |        |        |
| -5.379 | -5.871 |        |        |
| -5.359 | -5.851 |        |        |
| -5.340 | -5.832 |        |        |
| -5.321 | -5.812 |        |        |
| -5.304 | -5.796 |        |        |
| -5.287 | -5.776 |        |        |
| -5.270 | -5.760 |        |        |
| -5.255 | -5.744 |        |        |
| -5.240 | -5.727 |        |        |
| -5.225 | -5.711 |        |        |
| -5.211 | -5.698 |        |        |
| -5.197 | -5.685 |        |        |
| -5.184 | -5.672 |        |        |
| -5.171 | -5.659 |        |        |
| -5.158 | -5.646 |        |        |
| -5.146 | -5.636 |        |        |
| -5.134 | -5.623 |        |        |
| -5.123 | -5.613 |        |        |
| -5.112 | -5.600 |        |        |
| -5.101 | -5.590 |        |        |
| -5.090 | -5.581 |        |        |
| -5.080 | -5.571 |        |        |
| -5.070 | -5.561 |        |        |
| -5.060 | -5.551 |        |        |
| -5.050 | -5.541 |        |        |
| -5.005 | -5.499 |        |        |
| -4.972 | -5.460 |        |        |
| -4.941 | -5.424 |        |        |
| -4.912 | -5.395 |        |        |
| -4.860 | -5.339 |        |        |
| -4.814 | -5.290 |        |        |
| -4.772 | -5.248 |        |        |

Glycine  
HIES .0600 [L] IF-5M  
log [CuT]log [CuF]

|        |        |
|--------|--------|
| -6.097 | -7.466 |
| -5.921 | -7.293 |
| -5.796 | -7.152 |
| -5.700 | -7.032 |
| -5.621 | -6.924 |
| -5.554 | -6.810 |
| -5.496 | -6.742 |
| -5.445 | -6.657 |
| -5.399 | -6.578 |
| -5.358 | -6.503 |
| -5.321 | -6.435 |
| -5.286 | -6.366 |
| -5.254 | -6.305 |
| -5.224 | -6.243 |
| -5.196 | -6.184 |
| -5.170 | -6.128 |
| -5.146 | -6.076 |
| -5.122 | -6.024 |
| -5.100 | -5.975 |
| -5.079 | -5.929 |
| -5.059 | -5.907 |
| -5.013 | -5.835 |
| -4.979 | -5.753 |
| -4.948 | -5.682 |
| -4.919 | -5.616 |
| -4.891 | -5.558 |
| -4.866 | -5.505 |
| -4.842 | -5.460 |
| -4.819 | -5.417 |

Glycine repeat  
[L] IF-5M HIES .0  
log [CuT]log [CuF]

| log [CuT] | log [CuF] | log [CuT] | log [CuF] |
|-----------|-----------|-----------|-----------|
| -6.398    | -7.919    | -4.727    | -5.502    |
| -6.222    | -7.759    | -4.693    | -5.437    |
| -6.097    | -7.629    | -4.661    | -5.382    |
| -6.000    | -7.521    | -4.632    | -5.336    |
| -5.921    | -7.430    | -4.604    | -5.290    |
| -5.854    | -7.348    | -4.579    | -5.254    |
| -5.796    | -7.273    | -4.554    | -5.219    |
| -5.745    | -7.208    | -4.532    | -5.189    |
| -5.700    | -7.179    | -4.510    | -5.160    |
| -5.678    | -7.117    | -4.489    | -5.134    |
| -5.639    | -7.061    | -4.470    | -5.108    |
| -5.603    | -7.015    | -4.451    | -5.085    |
| -5.570    | -6.970    |           |           |
| -5.539    | -6.924    |           |           |
| -5.510    | -6.885    |           |           |
| -5.483    | -6.843    |           |           |
| -5.457    | -6.800    |           |           |
| -5.433    | -6.768    |           |           |
| -5.410    | -6.732    |           |           |
| -5.389    | -6.699    |           |           |
| -5.368    | -6.667    |           |           |
| -5.348    | -6.637    |           |           |
| -5.330    | -6.611    |           |           |
| -5.312    | -6.582    |           |           |
| -5.294    | -6.552    |           |           |
| -5.278    | -6.523    |           |           |
| -5.262    | -6.500    |           |           |
| -5.246    | -6.474    |           |           |
| -5.231    | -6.448    |           |           |
| -5.217    | -6.422    |           |           |
| -5.203    | -6.396    |           |           |
| -5.190    | -6.373    |           |           |
| -5.177    | -6.350    |           |           |
| -5.164    | -6.324    |           |           |
| -5.152    | -6.305    |           |           |
| -5.140    | -6.282    |           |           |
| -5.128    | -6.259    |           |           |
| -5.117    | -6.239    |           |           |
| -5.105    | -6.220    |           |           |
| -5.095    | -6.200    |           |           |
| -5.084    | -6.177    |           |           |
| -5.074    | -6.158    |           |           |
| -5.064    | -6.141    |           |           |
| -5.054    | -6.119    |           |           |
| -5.045    | -6.102    |           |           |
| -5.035    | -6.086    |           |           |
| -5.026    | -6.076    |           |           |
| -4.992    | -6.070    |           |           |
| -4.959    | -5.988    |           |           |
| -4.930    | -5.910    |           |           |
| -4.902    | -5.841    |           |           |
| -4.851    | -5.776    |           |           |

## Salicylic Acid

HEPES=0.005M (I)-1.13E-4M

log [CuT] log [CuI] log [CuT] log [CuF]

|        |        |        |        |
|--------|--------|--------|--------|
| -6.398 | -7.678 | -4.351 | -5.353 |
| -6.097 | -7.356 | -4.324 | -5.320 |
| -6.021 | -7.154 | -4.298 | -5.284 |
| -5.796 | -7.014 | -4.274 | -5.252 |
| -5.699 | -6.903 | -4.251 | -5.219 |
| -5.620 | -6.815 | -4.230 | -5.193 |
| -5.554 | -6.740 | -4.210 | -5.164 |
| -5.496 | -6.672 | -4.190 | -5.141 |
| -5.445 | -6.616 | -4.172 | -5.118 |
| -5.399 | -6.564 | -4.154 | -5.092 |
| -5.358 | -6.522 | -4.138 | -5.073 |
| -5.320 | -6.476 | -4.121 | -5.050 |
| -5.286 | -6.437 | -4.106 | -5.030 |
| -5.254 | -6.405 | -4.091 | -5.014 |
| -5.224 | -6.369 | -4.077 | -5.001 |
| -5.196 | -6.340 |        |        |
| -5.170 | -6.307 |        |        |
| -5.145 | -6.281 |        |        |
| -5.111 | -6.258 |        |        |
| -5.089 | -6.232 |        |        |
| -5.069 | -6.209 |        |        |
| -5.049 | -6.200 |        |        |
| -5.031 | -6.177 |        |        |
| -5.013 | -6.157 |        |        |
| -4.995 | -6.141 |        |        |
| -4.979 | -6.125 |        |        |
| -4.963 | -6.102 |        |        |
| -4.948 | -6.086 |        |        |
| -4.933 | -6.073 |        |        |
| -4.919 | -6.056 |        |        |
| -4.905 | -6.040 |        |        |
| -4.891 | -6.024 |        |        |
| -4.878 | -6.011 |        |        |
| -4.866 | -5.998 |        |        |
| -4.854 | -5.985 |        |        |
| -4.842 | -5.968 |        |        |
| -4.830 | -5.959 |        |        |
| -4.819 | -5.949 |        |        |
| -4.808 | -5.936 |        |        |
| -4.797 | -5.926 |        |        |
| -4.787 | -5.913 |        |        |
| -4.777 | -5.903 |        |        |
| -4.767 | -5.890 |        |        |
| -4.757 | -5.871 |        |        |
| -4.739 | -5.845 |        |        |
| -4.721 | -5.822 |        |        |
| -4.687 | -5.783 |        |        |
| -4.656 | -5.740 |        |        |
| -4.627 | -5.705 |        |        |
| -4.600 | -5.672 |        |        |
| -4.574 | -5.636 |        |        |
| -4.550 | -5.601 |        |        |
| -4.527 | -5.581 |        |        |
| -4.486 | -5.529 |        |        |
| -4.449 | -5.477 |        |        |
| -4.411 | -5.434 |        |        |

## Catechol

HEPES=0.005M (I)-4.989E-6M

log [CuT] log [CuF]

|        |        |
|--------|--------|
| -6.700 | -8.612 |
| -6.399 | -8.341 |
| -6.302 | -7.949 |
| -6.156 | -7.703 |
| -6.047 | -7.466 |
| -5.960 | -7.310 |
| -5.888 | -7.171 |
| -5.826 | -7.032 |
| -5.771 | -6.939 |
| -5.723 | -6.821 |
| -5.680 | -6.737 |
| -5.640 | -6.640 |
| -5.604 | -6.567 |
| -5.571 | -6.491 |
| -5.540 | -6.428 |
| -5.511 | -6.376 |
| -5.484 | -6.341 |
| -5.458 | -6.289 |
| -5.434 | -6.255 |
| -5.412 | -6.213 |
| -5.390 | -6.192 |
| -5.369 | -6.171 |
| -5.350 | -6.137 |
| -5.331 | -6.078 |
| -5.313 | -6.039 |
| -5.296 | -6.005 |
| -5.279 | -5.987 |
| -5.263 | -5.953 |
| -5.248 | -5.946 |
| -5.233 | -5.907 |
| -5.218 | -5.894 |
| -5.204 | -5.897 |
| -5.191 | -5.838 |
| -5.178 | -5.841 |
| -5.165 | -5.828 |
| -5.153 | -5.803 |
| -5.141 | -5.782 |
| -5.129 | -5.758 |
| -5.118 | -5.741 |
| -5.107 | -5.734 |
| -5.096 | -5.723 |
| -5.085 | -5.706 |
| -5.075 | -5.703 |
| -5.063 | -5.689 |
| -5.055 | -5.671 |
| -5.046 | -5.668 |
| -5.041 | -5.675 |
| -5.032 | -5.668 |
| -5.023 | -5.650 |
| -5.014 | -5.598 |
| -4.997 | -5.505 |
| -4.980 | -5.435 |
| -4.964 | -5.397 |
| -4.934 | -5.317 |
| -4.906 | -5.280 |
| -4.880 | -5.200 |

Appendix B Titration Data of Model Mixture

POTENTIOMETRIC TITRATION OF OCGW XAD-8 MODEL MIXTURE

| Titrator |          | Model    | Actual          |          |
|----------|----------|----------|-----------------|----------|
| [NaOH]   | MODEL MQ | OCGW-SAS | Model Titration |          |
|          | pH       | pH       | [NaOH]          | pH       |
| 2.67E-05 | 2.96727  | 3.01618  | 7.97E-06        | 3        |
| 5.35E-05 | 2.97818  | 3.02822  | 1.59E-05        | 3.004    |
| 8.02E-05 | 2.98937  | 3.0406   | 2.15E-04        | 3.1      |
| 0.000107 | 3.00086  | 3.05334  | 3.81E-04        | 3.202    |
| 0.000134 | 3.01266  | 3.06645  | 5.07E-04        | 3.3      |
| 0.000161 | 3.02479  | 3.07998  | 5.62E-04        | 3.351    |
| 0.000187 | 3.03726  | 3.09393  | 6.09E-04        | 3.4      |
| 0.000214 | 3.05011  | 3.10833  | 6.56E-04        | 3.457    |
| 0.000241 | 3.06335  | 3.12323  | 6.95E-04        | 3.506    |
| 0.000268 | 3.077    | 3.13865  | 7.27E-04        | 3.555    |
| 0.000294 | 3.0911   | 3.15463  | 7.58E-04        | 3.61     |
| 0.000321 | 3.10567  | 3.17121  | 7.81E-04        | 3.657    |
| 0.000348 | 3.12075  | 3.18845  | 8.05E-04        | 3.709    |
| 0.000375 | 3.13637  | 3.20638  | 8.20E-04        | 3.747    |
| 0.000401 | 3.15257  | 3.22508  | 8.75E-04        | 3.919    |
| 0.000428 | 3.1694   | 3.24461  | 8.83E-04        | 3.95     |
| 0.000455 | 3.1869   | 3.26505  | 8.98E-04        | 4.021    |
| 0.000482 | 3.20515  | 3.28648  | 9.61E-04        | 4.499    |
| 0.000508 | 3.22419  | 3.30901  | 9.92E-04        | 4.975    |
| 0.000535 | 3.24411  | 3.33275  | 1.01E-03        | 5.529    |
| 0.000562 | 3.26498  | 3.35785  | 1.02E-03        | 5.843    |
| 0.000589 | 3.28691  | 3.38446  | 1.03E-03        | 6.531    |
| 0.000615 | 3.31001  | 3.41279  | 1.04E-03        | 8.334    |
| 0.000642 | 3.3344   | 3.44306  | 1.05E-03        | 8.767999 |
| 0.000669 | 3.36024  | 3.47555  | 1.05E-03        | 8.998999 |
| 0.000696 | 3.38772  | 3.51063  | 1.07E-03        | 9.281    |
| 0.000722 | 3.41706  | 3.54872  | 1.09E-03        | 9.534001 |
| 0.000749 | 3.44852  | 3.59039  | 1.10E-03        | 9.596    |
| 0.000776 | 3.48244  | 3.63642  | 1.11E-03        | 9.649999 |
| 0.000803 | 3.51923  | 3.68772  | 1.12E-03        | 9.699001 |
| 0.000829 | 3.55944  | 3.74565  | 1.12E-03        | 9.744001 |
| 0.000856 | 3.60374  | 3.81214  | 1.13E-03        | 9.783    |
| 0.000883 | 3.65307  | 3.89     | 1.14E-03        | 9.819    |
| 0.00091  | 3.70882  | 3.98365  | 1.15E-03        | 9.852999 |
| 0.000936 | 3.77272  | 4.10036  | 1.16E-03        | 9.915    |
| 0.000963 | 3.84767  | 4.25285  | 1.18E-03        | 9.967    |
| 0.00099  | 3.93831  | 4.46408  | 1.19E-03        | 9.991    |
| 0.001017 | 4.053    | 4.77284  | 1.19E-03        | 10.014   |
| 0.001043 | 4.20926  | 5.25762  |                 |          |
| 0.00107  | 4.4558   | 8.21701  |                 |          |
| 0.001097 | 5.0829   | 9.28201  |                 |          |
| 0.001124 | 9.26697  | 9.61777  |                 |          |
| 0.00115  | 9.65553  | 9.81881  |                 |          |
| 0.001177 | 9.85728  | 9.9602   |                 |          |
| 0.001204 | 9.9945   | 10.0685  |                 |          |

-----  
 OCGW Model and Model Titration @ pH 6.2  
 -----

| Model<br>of OCGW @ pH 6.2<br>log <sub>a</sub> [CuT]log [CuF] | Actual Model<br>Titration<br>log [CuT]log [CuF] | Actual Model<br>Titration<br>log [CuT]log [CuF] |
|--------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| -7 -7.44448                                                  | -7.000 -7.883                                   | -5.064 -5.560                                   |
| -6.03152 -6.47197                                            | -6.523 -7.463                                   | -5.054 -5.553                                   |
| -5.75449 -6.19098                                            | -6.301 -7.196                                   | -5.045 -5.546                                   |
| -5.58667 -6.01932                                            | -6.155 -6.998                                   | -5.036 -5.546                                   |
| -5.46597 -5.89479                                            | -6.046 -6.859                                   | -5.031 -5.543                                   |
| -5.37161 -5.7967                                             | -5.959 -6.748                                   | -4.992 -5.498                                   |
| -5.29414 -5.71558                                            | -5.887 -6.647                                   | -4.959 -5.453                                   |
| -5.22841 -5.64627                                            | -5.825 -6.574                                   | -4.930 -5.428                                   |
| -5.17134 -5.58568                                            | -5.770 -6.519                                   | -4.902 -5.376                                   |
| -5.1209 -5.5318                                              | -5.722 -6.435                                   | -4.851 -5.331                                   |
| -5.07572 -5.48323                                            | -5.679 -6.369                                   | -4.805 -5.269                                   |
| -5.0348 -5.43899                                             | -5.639 -6.317                                   | -4.764 -5.209                                   |
| -4.9974 -5.39833                                             | -5.603 -6.269                                   | -4.727 -5.164                                   |
| -4.96297 -5.36071                                            | -5.570 -6.227                                   | -4.693 -5.119                                   |
| -4.93107 -5.32567                                            | -5.539 -6.185                                   | -4.632 -5.043                                   |
| -4.90136 -5.29287                                            | -5.510 -6.137                                   | -4.579 -4.963                                   |
| -4.87354 -5.26203                                            | -5.483 -6.109                                   | -4.532 -4.904                                   |
| -4.84741 -5.23292                                            | -5.457 -6.071                                   | -4.489 -4.848                                   |
| -4.82275 -5.20535                                            | -5.433 -6.046                                   | -4.451 -4.793                                   |
| -4.79942 -5.17915                                            | -5.411 -6.039                                   |                                                 |
| -4.77728 -5.15419                                            | -5.389 -6.001                                   |                                                 |
| -4.75622 -5.13035                                            | -5.368 -5.980                                   |                                                 |
| -4.73613 -5.10754                                            | -5.349 -5.932                                   |                                                 |
| -4.71693 -5.08566                                            | -5.330 -5.911                                   |                                                 |
| -4.69854 -5.06464                                            | -5.312 -5.876                                   |                                                 |
| -4.68089 -5.04441                                            | -5.295 -5.887                                   |                                                 |
| -4.66394 -5.02491                                            | -5.278 -5.852                                   |                                                 |
| -4.64762 -5.00609                                            | -5.262 -5.821                                   |                                                 |
| -4.6319 -4.98779                                             | -5.247 -5.786                                   |                                                 |
| -4.61672 -4.9703                                             | -5.232 -5.769                                   |                                                 |
| -4.60206 -4.95324                                            | -5.217 -5.762                                   |                                                 |
|                                                              | -5.203 -5.755                                   |                                                 |
|                                                              | -5.190 -5.748                                   |                                                 |
|                                                              | -5.177 -5.734                                   |                                                 |
|                                                              | -5.164 -5.706                                   |                                                 |
|                                                              | -5.152 -5.689                                   |                                                 |
|                                                              | -5.140 -5.668                                   |                                                 |
|                                                              | -5.128 -5.654                                   |                                                 |
|                                                              | -5.117 -5.640                                   |                                                 |
|                                                              | -5.106 -5.626                                   |                                                 |
|                                                              | -5.095 -5.616                                   |                                                 |
|                                                              | -5.085 -5.605                                   |                                                 |
|                                                              | -5.074 -5.598                                   |                                                 |

## Appendix C Titration Data of Natural Sources

-----  
 Potentiometric Titration of OCGW XAD-B  
 -----

(by W. Odem & J. Taylor)

DOC = 5.66 mg/L

| Bili-Q Blank |          | OCGW XAD-B |          |
|--------------|----------|------------|----------|
| [NaOH]       | pH       | [NaOH]     | pH       |
| 1.15E-05     | 3.002    | 2.31E-05   | 3.003    |
| 5.97E-05     | 3.022    | 6.92E-05   | 3.022    |
| 1.04E-04     | 3.043    | 1.04E-04   | 3.035    |
| 1.50E-04     | 3.065    | 1.50E-04   | 3.056    |
| 2.07E-04     | 3.092    | 2.07E-04   | 3.082    |
| 2.53E-04     | 3.114    | 2.53E-04   | 3.104    |
| 2.99E-04     | 3.139    | 3.11E-04   | 3.132    |
| 3.56E-04     | 3.171    | 3.33E-04   | 3.145    |
| 4.02E-04     | 3.199    | 3.68E-04   | 3.163    |
| 4.59E-04     | 3.235    | 4.36E-04   | 3.203    |
| 5.05E-04     | 3.267    | 4.71E-04   | 3.224    |
| 5.50E-04     | 3.301    | 5.39E-04   | 3.269    |
| 6.07E-04     | 3.349    | 5.73E-04   | 3.293    |
| 6.53E-04     | 3.389    | 6.30E-04   | 3.336    |
| 7.10E-04     | 3.447    | 6.87E-04   | 3.385    |
| 7.55E-04     | 3.5      | 7.32E-04   | 3.428    |
| 8.00E-04     | 3.56     | 7.89E-04   | 3.489    |
| 8.57E-04     | 3.65     | 8.34E-04   | 3.542    |
| 9.02E-04     | 3.738    | 8.79E-04   | 3.606    |
| 9.58E-04     | 3.881    | 9.36E-04   | 3.698    |
| 1.00E-03     | 4.041    | 9.81E-04   | 3.79     |
| 1.05E-03     | 4.298    | 1.03E-03   | 3.895    |
| 1.07E-03     | 4.523    | 1.08E-03   | 4.077    |
| 1.08E-03     | 4.698    | 1.13E-03   | 4.319    |
| 1.09E-03     | 4.986    | 1.14E-03   | 4.405    |
| 1.10E-03     | 5.848    | 1.17E-03   | 4.817    |
| 1.12E-03     | 8.798001 | 1.18E-03   | 5.078    |
| 1.13E-03     | 9.245    | 1.19E-03   | 5.558    |
| 1.14E-03     | 9.472999 | 1.21E-03   | 6.568    |
| 1.15E-03     | 9.627    | 1.22E-03   | 7.712    |
| 1.17E-03     | 9.838    | 1.23E-03   | 8.559    |
| 1.19E-03     | 9.983    | 1.24E-03   | 8.897001 |
| 1.22E-03     | 10.093   | 1.25E-03   | 9.100001 |
| 1.22E-03     | 10.09    | 1.26E-03   | 9.252    |
| 1.23E-03     | 10.128   | 1.27E-03   | 9.371    |
| 1.24E-03     | 10.128   | 1.28E-03   | 9.477    |
| 1.24E-03     | 10.125   | 1.29E-03   | 9.564    |
| 1.23E-03     | 10.124   | 1.31E-03   | 9.639    |
| 1.23E-03     | 10.12    | 1.32E-03   | 9.708    |
| 1.23E-03     | 10.12    | 1.34E-03   | 9.829001 |
| 1.23E-03     | 10.118   | 1.36E-03   | 9.929    |
| 1.23E-03     | 10.118   | 1.37E-03   | 9.976    |
| 1.23E-03     | 10.116   | 1.39E-03   | 10.055   |

-----  
 OCGW XAD-B Complexometric Titrations @ pH 6.2  
 -----(after Waterbury, 1990)-----

| OCGW XAD-B         | Repeat             | (Castro)                                             |
|--------------------|--------------------|------------------------------------------------------|
| log [CuT]log [CuF] | log [CuT]log [CuF] | Corrected for<br>Milli-Q Blank<br>log [CuT]log [CuF] |
| -6.60217 -9.35777  | -6.60206 -9.14822  | -5.46597 -6.80693                                    |
| -6.30125 -9.01557  | -6.60114 -8.80608  | -5.37161 -6.74058                                    |
| -6.12526 -8.73855  | -6.12516 -8.57795  | -5.29414 -6.60931                                    |
| -6.00041 -8.52671  | -6.00033 -8.38783  | -5.22841 -6.43878                                    |
| -5.90363 -8.35154  | -5.90352 -8.23574  | -5.17134 -6.25661                                    |
| -5.82456 -8.2008   | -5.82445 -8.12167  | -5.1209 -6.09253                                     |
| -5.75772 -8.07044  | -5.75761 -8.0076   | -5.07572 -5.95679                                    |
| -5.69984 -7.95637  | -5.69973 -7.89354  | -5.0348 -5.84512                                     |
| -5.64879 -7.84638  | -5.60293 -7.70342  | -4.9974 -5.75107                                     |
| -5.60314 -7.74046  | -5.52396 -7.51331  | -4.96297 -5.66965                                    |
| -5.56186 -7.64269  | -5.45723 -7.32319  | -4.93107 -5.59753                                    |
| -5.52418 -7.54899  | -5.39946 -7.20913  | -4.90136 -5.5325                                     |
| -5.48953 -7.45937  | -5.34852 -7.05703  | -4.87354 -5.47303                                    |
| -5.45745 -7.37789  | -5.30298 -6.94297  | -4.84741 -5.41809                                    |
| -5.42759 -7.29234  | -5.2618 -6.8289    | -4.82275 -5.36692                                    |
| -5.39967 -7.21086  | -5.22423 -6.71483  | -4.79942 -5.31901                                    |
| -5.37345 -7.12938  | -5.18968 -6.60076  | -4.77728 -5.27391                                    |
| -5.34874 -7.05198  | -5.12775 -6.41065  | -4.75622 -5.23136                                    |
| -5.32536 -6.97865  | -5.07383 -6.25856  | -4.73613 -5.19109                                    |
| -5.3032 -6.9024    | -5.02595 -6.14449  | -4.71693 -5.15292                                    |
| -5.28212 -6.84014  | -4.9727 -5.9924    | -4.69854 -5.11666                                    |
| -5.26202 -6.77089  | -4.92546 -5.87833  | -4.68089 -5.08221                                    |
| -5.24282 -6.7057   | -4.88297 -5.80228  | -4.66394 -5.04941                                    |
| -5.22445 -6.6446   | -4.84435 -5.68821  | -4.64762 -5.01817                                    |
| -5.20683 -6.58349  | -4.80897 -5.61217  | -4.6319 -4.98839                                     |
| -5.1899 -6.52646   | -4.77634 -5.57414  | -4.61672 -4.95996                                    |
| -5.17362 -6.47349  |                    | -4.60206 -4.93282                                    |
| -5.15793 -6.42054  |                    |                                                      |
| -5.1428 -6.37165   |                    |                                                      |
| -5.12818 -6.31869  |                    |                                                      |
| -5.11405 -6.27388  |                    |                                                      |
| -5.10037 -6.22907  |                    |                                                      |
| -5.08711 -6.18833  |                    |                                                      |
| -5.07426 -6.14759  |                    |                                                      |
| -5.06177 -6.11092  |                    |                                                      |
| -5.04965 -6.07426  |                    |                                                      |
| -5.03708 -6.03759  |                    |                                                      |
| -5.02533 -5.99241  |                    |                                                      |
| -4.9885 -5.90723   |                    |                                                      |
| -4.96827 -5.84612  |                    |                                                      |
| -4.94896 -5.79317  |                    |                                                      |
| -4.93049 -5.73613  |                    |                                                      |
| -4.9128 -5.69539   |                    |                                                      |
| -4.89581 -5.64651  |                    |                                                      |
| -4.87948 -5.60577  |                    |                                                      |
| -4.86375 -5.56503  |                    |                                                      |
| -4.84859 -5.52836  |                    |                                                      |
| -4.83326 -5.48763  |                    |                                                      |
| -4.81921 -5.45911  |                    |                                                      |
| -4.80613 -5.42652  |                    |                                                      |

TOUGH XAD-8 PH 7.5 COMPLEXOMETRIC TITRATION

| log [CuT] | log [CuF] | log [CuT] | log [CuF] |
|-----------|-----------|-----------|-----------|
| -5.28505  | -6.87068  | -4.01019  | -5.28911  |
| -5.18812  | -6.68702  | -3.99901  | -5.2857   |
| -5.10907  | -6.54757  | -3.98812  | -5.2755   |
| -5.04217  | -6.43192  | -3.97751  | -5.2687   |
| -4.98424  | -6.34349  | -3.96715  | -5.2653   |
| -4.93314  | -6.26526  | -3.95704  | -5.2687   |
| -4.88744  | -6.19384  | -3.94716  | -5.2755   |
| -4.8461   | -6.13261  | -3.93751  | -5.2653   |
| -4.80836  | -6.0816   | -3.92807  | -5.25169  |
| -4.77365  | -6.03738  | -3.91884  | -5.24829  |
| -4.74152  | -5.99316  | -3.90928  | -5.23809  |
| -4.71161  | -5.96255  | -3.90095  | -5.23128  |
| -4.68364  | -5.92854  | -3.89229  | -5.22448  |
| -4.65737  | -5.89453  | -3.88379  | -5.21768  |
| -4.6326   | -5.87752  | -3.87547  | -5.21428  |
| -4.60917  | -5.85711  | -3.8673   | -5.20407  |
| -4.58695  | -5.8333   | -3.85929  | -5.19727  |
| -4.56581  | -5.8095   | -3.85143  | -5.19387  |
| -4.54566  | -5.79249  |           |           |
| -4.52641  | -5.77548  |           |           |
| -4.50798  | -5.75848  |           |           |
| -4.49031  | -5.74147  |           |           |
| -4.47333  | -5.72787  |           |           |
| -4.45699  | -5.71426  |           |           |
| -4.44125  | -5.69725  |           |           |
| -4.42607  | -5.68365  |           |           |
| -4.4114   | -5.68025  |           |           |
| -4.39721  | -5.66664  |           |           |
| -4.38348  | -5.65304  |           |           |
| -4.37017  | -5.64283  |           |           |
| -4.35726  | -5.62923  |           |           |
| -4.34472  | -5.61562  |           |           |
| -4.33254  | -5.60542  |           |           |
| -4.32069  | -5.59182  |           |           |
| -4.30917  | -5.58161  |           |           |
| -4.29794  | -5.56801  |           |           |
| -4.287    | -5.5578   |           |           |
| -4.27633  | -5.5578   |           |           |
| -4.26592  | -5.5476   |           |           |
| -4.25575  | -5.5374   |           |           |
| -4.24582  | -5.52379  |           |           |
| -4.23612  | -5.51699  |           |           |
| -4.22662  | -5.50679  |           |           |
| -4.20825  | -5.47277  |           |           |
| -4.19063  | -5.44556  |           |           |
| -4.1737   | -5.42516  |           |           |
| -4.15742  | -5.40815  |           |           |
| -4.14173  | -5.40475  |           |           |
| -4.1266   | -5.38774  |           |           |
| -4.11199  | -5.37414  |           |           |
| -4.09785  | -5.36393  |           |           |
| -4.08417  | -5.35033  |           |           |
| -4.07092  | -5.33672  |           |           |
| -4.05906  | -5.32652  |           |           |
| -4.04558  | -5.31632  |           |           |
| -4.03345  | -5.30251  |           |           |
| -4.02166  | -5.29931  |           |           |

-----  
 Potentiometric Titration of BA XAD-8  
 -----

(By W. Odum & J. Taylor)

| Blank    |       | DOC-12.66 mg/L<br>BA XAD-8 |       |
|----------|-------|----------------------------|-------|
| [NaOH]   | pH    | [NaOH]                     | pH    |
| 1.15E-05 | 3.002 | 1.15E-05                   | 2.996 |
| 2.31E-05 | 3.007 | 2.31E-05                   | 3.001 |
| 3.46E-05 | 3.011 | 3.46E-05                   | 3.005 |
| 4.62E-05 | 3.017 | 4.62E-05                   | 3.009 |
| 5.77E-05 | 3.022 | 5.77E-05                   | 3.013 |
| 6.92E-05 | 3.027 | 6.92E-05                   | 3.018 |
| 8.08E-05 | 3.032 | 8.08E-05                   | 3.022 |
| 9.23E-05 | 3.037 | 9.23E-05                   | 3.026 |
| 0.000104 | 3.043 | 0.000104                   | 3.031 |
| 0.000115 | 3.048 | 0.000115                   | 3.036 |
| 0.000127 | 3.054 | 0.000127                   | 3.041 |
| 0.000138 | 3.059 | 0.000138                   | 3.046 |
| 0.00015  | 3.065 | 0.00015                    | 3.05  |
| 0.000161 | 3.07  | 0.000161                   | 3.054 |
| 0.000173 | 3.074 | 0.000173                   | 3.059 |
| 0.000184 | 3.08  | 0.000184                   | 3.065 |
| 0.000196 | 3.087 | 0.000196                   | 3.07  |
| 0.000207 | 3.092 | 0.000207                   | 3.075 |
| 0.000219 | 3.097 | 0.000219                   | 3.081 |
| 0.00023  | 3.103 | 0.00023                    | 3.086 |
| 0.000242 | 3.109 | 0.000242                   | 3.092 |
| 0.000253 | 3.114 | 0.000253                   | 3.098 |
| 0.000265 | 3.121 | 0.000265                   | 3.104 |
| 0.000276 | 3.127 | 0.000276                   | 3.109 |
| 0.000288 | 3.133 | 0.000288                   | 3.115 |
| 0.000299 | 3.139 | 0.000299                   | 3.121 |
| 0.000311 | 3.146 | 0.000311                   | 3.128 |
| 0.000322 | 3.151 | 0.000322                   | 3.132 |
| 0.000333 | 3.158 | 0.000333                   | 3.139 |
| 0.000345 | 3.164 | 0.000345                   | 3.145 |
| 0.000356 | 3.171 | 0.000356                   | 3.15  |
| 0.000368 | 3.178 | 0.000368                   | 3.156 |
| 0.000379 | 3.184 | 0.000379                   | 3.161 |
| 0.000391 | 3.191 | 0.000391                   | 3.169 |
| 0.000402 | 3.199 | 0.000402                   | 3.173 |
| 0.000414 | 3.206 | 0.000414                   | 3.18  |
| 0.000425 | 3.214 | 0.000425                   | 3.187 |
| 0.000436 | 3.22  | 0.000436                   | 3.195 |
| 0.000448 | 3.228 | 0.000448                   | 3.203 |
| 0.000459 | 3.235 | 0.000459                   | 3.211 |
| 0.000471 | 3.243 | 0.000471                   | 3.219 |
| 0.000482 | 3.251 | 0.000482                   | 3.226 |
| 0.000493 | 3.259 | 0.000493                   | 3.234 |
| 0.000505 | 3.267 | 0.000505                   | 3.243 |
| 0.000516 | 3.275 | 0.000516                   | 3.252 |
| 0.000528 | 3.284 | 0.000528                   | 3.26  |
| 0.000539 | 3.292 | 0.000539                   | 3.269 |
| 0.00055  | 3.301 | 0.00055                    | 3.278 |
| 0.000562 | 3.31  | 0.000562                   | 3.287 |
| 0.000573 | 3.32  | 0.000573                   | 3.297 |
| 0.000585 | 3.329 | 0.000585                   | 3.307 |
| 0.000596 | 3.338 | 0.000596                   | 3.317 |
| 0.000607 | 3.349 | 0.000607                   | 3.327 |

-----  
 Potentiometric Titration of BA XAD-8  
 -----

(by W. Odem & J. Taylor)

| Milli-Q Blank |       | DOC=12.66 mg/L<br>BA XAD-8 |       |
|---------------|-------|----------------------------|-------|
| [NaOH]        | pH    | [NaOH]                     | pH    |
| -----         |       |                            |       |
| 0.000619      | 3.358 | 0.000619                   | 3.337 |
| 0.00063       | 3.369 | 0.00063                    | 3.348 |
| 0.000641      | 3.378 | 0.000641                   | 3.359 |
| 0.000653      | 3.389 | 0.000653                   | 3.37  |
| 0.000664      | 3.4   | 0.000664                   | 3.382 |
| 0.000675      | 3.412 | 0.000675                   | 3.392 |
| 0.000687      | 3.424 | 0.000687                   | 3.405 |
| 0.000698      | 3.435 | 0.000698                   | 3.417 |
| 0.00071       | 3.447 | 0.00071                    | 3.43  |
| 0.000721      | 3.46  | 0.000721                   | 3.443 |
| 0.000732      | 3.473 | 0.000732                   | 3.457 |
| 0.000744      | 3.487 | 0.000744                   | 3.471 |
| 0.000755      | 3.5   | 0.000755                   | 3.485 |
| 0.000766      | 3.515 | 0.000766                   | 3.5   |
| 0.000777      | 3.529 | 0.000777                   | 3.516 |
| 0.000789      | 3.544 | 0.000789                   | 3.53  |
| 0.0008        | 3.56  | 0.0008                     | 3.547 |
| 0.000811      | 3.577 | 0.000811                   | 3.564 |
| 0.000823      | 3.594 | 0.000823                   | 3.582 |
| 0.000834      | 3.611 | 0.000834                   | 3.6   |
| 0.000845      | 3.631 | 0.000845                   | 3.619 |
| 0.000857      | 3.65  | 0.000857                   | 3.638 |
| 0.000868      | 3.67  | 0.000868                   | 3.658 |
| 0.000879      | 3.692 | 0.000879                   | 3.68  |
| 0.00089       | 3.715 | 0.00089                    | 3.702 |
| 0.000902      | 3.738 | 0.000902                   | 3.725 |
| 0.000913      | 3.763 | 0.000913                   | 3.75  |
| 0.000924      | 3.79  | 0.000924                   | 3.775 |
| 0.000936      | 3.817 | 0.000936                   | 3.802 |
| 0.000947      | 3.849 | 0.000947                   | 3.831 |
| 0.000958      | 3.881 | 0.000958                   | 3.86  |
| 0.000969      | 3.916 | 0.000969                   | 3.892 |
| 0.000981      | 3.954 | 0.000981                   | 3.925 |
| 0.000992      | 3.996 | 0.000992                   | 3.96  |
| 0.001003      | 4.041 | 0.001003                   | 3.998 |
| 0.001014      | 4.093 | 0.001014                   | 4.037 |
| 0.001026      | 4.152 | 0.001026                   | 4.079 |
| 0.001037      | 4.22  | 0.001037                   | 4.125 |
| 0.001048      | 4.298 | 0.001048                   | 4.174 |
| 0.001059      | 4.398 | 0.001059                   | 4.226 |
| 0.001071      | 4.523 | 0.001071                   | 4.283 |

-----  
 Potentiometric Titration of BA XAD-8  
 -----

(by W. Odem & J. Taylor)

| Blank    |          | DOC: 12.66 mg/L |          |
|----------|----------|-----------------|----------|
| [NaOH]   | pH       | BA XAD-8        | pH       |
| [NaOH]   | pH       | [NaOH]          | pH       |
| 0.001082 | 4.698    | 0.001082        | 4.344    |
| 0.001093 | 4.986    | 0.001093        | 4.41     |
| 0.001104 | 5.848    | 0.001104        | 4.484    |
| 0.001116 | 8.728001 | 0.001116        | 4.563    |
| 0.001127 | 9.245    | 0.001127        | 4.642    |
| 0.001138 | 9.472999 | 0.001138        | 4.745    |
| 0.001149 | 9.627    | 0.001149        | 4.849    |
| 0.00116  | 9.745    | 0.00116         | 4.964    |
| 0.001172 | 9.838    | 0.001172        | 5.05     |
| 0.001183 | 9.916001 | 0.001183        | 5.235    |
| 0.001194 | 9.983    | 0.001194        | 5.398    |
| 0.001205 | 10.042   | 0.001205        | 5.584    |
| 0.001216 | 10.093   | 0.001216        | 5.807    |
| 0.001216 | 10.092   | 0.001228        | 6.077    |
| 0.001216 | 10.091   | 0.001239        | 6.421    |
| 0.001216 | 10.09    | 0.00125         | 6.893    |
| 0.001216 | 10.09    | 0.001261        | 7.542    |
| 0.001216 | 10.088   | 0.001272        | 8.222    |
| 0.001228 | 10.128   | 0.001283        | 8.665    |
| 0.001228 | 10.128   | 0.001295        | 8.943    |
| 0.001228 | 10.128   | 0.001306        | 9.142999 |
| 0.001228 | 10.127   | 0.001317        | 9.295    |
| 0.001228 | 10.126   | 0.001328        | 9.417    |
| 0.001228 | 10.125   | 0.001339        | 9.521    |
| 0.001228 | 10.125   | 0.00135         | 9.612001 |
| 0.001228 | 10.124   | 0.001361        | 9.692001 |
| 0.001228 | 10.124   | 0.001373        | 9.762999 |
| 0.001228 | 10.122   | 0.001384        | 9.829001 |
| 0.001228 | 10.121   | 0.001395        | 9.887    |
| 0.001228 | 10.12    | 0.001406        | 9.939999 |
| 0.001228 | 10.12    | 0.001417        | 9.989001 |
| 0.001228 | 10.118   | 0.001428        | 10.032   |

'BISCAYNE AQUIFER XAD-8 PH 6.2 COMPLEXOMETRIC TITRATION'  
log [CuT]      log [CuF]

|        |        |
|--------|--------|
| -5.784 | -6.989 |
| -5.711 | -6.887 |
| -5.649 | -6.798 |
| -5.595 | -6.714 |
| -5.504 | -6.496 |
| -5.464 | -6.442 |
| -5.428 | -6.360 |
| -5.395 | -6.221 |
| -5.364 | -6.170 |
| -5.335 | -6.109 |
| -5.308 | -6.011 |
| -5.283 | -5.997 |
| -5.259 | -5.943 |
| -5.236 | -5.882 |
| -5.214 | -5.807 |
| -5.194 | -5.770 |
| -5.174 | -5.749 |
| -5.155 | -5.719 |
| -5.137 | -5.675 |
| -5.120 | -5.627 |
| -5.104 | -5.596 |
| -5.088 | -5.563 |
| -5.072 | -5.532 |
| -5.057 | -5.505 |
| -5.043 | -5.484 |
| -5.022 | -5.474 |
| -5.009 | -5.464 |
| -4.984 | -5.413 |
| -4.960 | -5.383 |
| -4.937 | -5.332 |
| -4.916 | -5.291 |
| -4.876 | -5.243 |
| -4.840 | -5.209 |
| -4.775 | -5.050 |
| -4.719 | -4.958 |
| -4.670 | -4.887 |

'BISCAYNE AQUIFER XAD-8 PH 7.5 COMPLEXOMETRIC TITRATION'  
log [CuT] log [CuF]

|        |        |
|--------|--------|
| -5.428 | -6.942 |
| -5.395 | -6.866 |
| -5.364 | -6.773 |
| -5.335 | -6.732 |
| -5.308 | -6.649 |
| -5.283 | -6.590 |
| -5.259 | -6.507 |
| -5.236 | -6.473 |
| -5.215 | -6.417 |
| -5.194 | -6.359 |
| -5.174 | -6.321 |
| -5.156 | -6.269 |
| -5.138 | -6.255 |
| -5.120 | -6.207 |
| -5.104 | -6.196 |
| -5.088 | -6.138 |
| -5.073 | -6.110 |
| -5.058 | -6.096 |
| -5.043 | -6.069 |
| -5.023 | -6.062 |
| -5.009 | -6.055 |
| -4.984 | -5.996 |
| -4.960 | -5.937 |
| -4.938 | -5.896 |
| -4.916 | -5.858 |
| -4.876 | -5.761 |
| -4.840 | -5.733 |
| -4.806 | -5.702 |
| -4.746 | -5.626 |
| -4.694 | -5.547 |
| -4.647 | -5.533 |
| -4.605 | -5.512 |
| -4.567 | -5.499 |
| -4.532 | -5.464 |
| -4.500 | -5.450 |
| -4.470 | -5.436 |
| -4.443 | -5.385 |
| -4.417 | -5.333 |
| -4.392 | -5.305 |
| -4.369 | -5.281 |
| -4.327 | -5.219 |
| -4.289 | -5.198 |
| -4.254 | -5.146 |
| -4.222 | -5.098 |
| -4.193 | -5.063 |

## Appendix D Computer Programs

```

19  REMD: PROGRAM FOR POTENTIOMETRIC TITRATIONS
20  TL = .01
21  INPUT "OUTPUT FILE NAME (***.dat) ==>";FILES$
22  INPUT "ENTER EXPERIMENT ID ==>";ID$
23  INPUT "ENTER pH SET POINT ==>";SPH
24  INPUT "ENTER PRINT INTERVAL IN MINUTES==>";PI
25  INPUT "ALiquOT SIZE FOR ACID";M1
26  INPUT "STRENGTH OF ACID IN (M) ==>";C1
27  INPUT "ALiquOT SIZE FOR BASE ==>";M2
28  INPUT "STRENGTH OF BASE IN (M)==>";C2
29  INPUT "pH TOLERANCE ==>";TL
30  ACD = M1 * .00025 * C1 / 10001
31  BAS = M2 * .00025 * C2 / 10001
32  DS = CHR$(4)
33  WS = CHR$(23)
34  PRINT DS:OPEN "lpt1:" FOR OUTPUT AS #1
35  PRINT #1,"EXPERIMENT ID,FILE and DATE ==>";ID$,FILES$,DATE$
36  PRINT #1,"MOLES OF ACID PER ADDITION ==>";ACD
37  PRINT #1,"MOLES OF BASE PER ADDITION ==>";BAS
38  PRINT #1,"pH TOLERANCE ==>";TL
39  PRINT #1,"SET POINT pH ==>";SPH
40  PRINT #1,;PRINT #1,;PRINT #1,;PRINT #1,
41  PRINT #1,"TIME(SEC)          #ACID          #BASE          #pH"
42  PRINT #1,"-----"
43  PRINT DS:CLOSE #1
44  OPEN FILES$ FOR OUTPUT AS #2
45  PRINT #2, "EXPERIMENT ID and FILE ==> ";ID$,FILES$
46  PRINT #2, "DATE OF EXPERIMENT ==> ";DATE$
47  PRINT #2, "MOLES OF ACID PER ADDITION ==> ";ACD
48  PRINT #2, "MOLES OF BASE PER ADDITION ==> ";BAS
49  PRINT #2, "pH SET POINT ==> ";SPH
50  PRINT #2, "pH TOLERANCE ==> ";TL
51  PRINT #2,"time","#acid","#base","pH"
52  CLOSE #2
53  GOSUB 2000
54  GOSUB 3000
55  T0 = MIN + SEC / 60 + HR * 60
56  GOSUB 6000
57  CLS
58  GOSUB 5000
59  K = PEEK(1048) AND 128
60  IF K = 128 THEN GOSUB 8000
61  IF FI = 0 GOTO 140
62  GOSUB 2000
63  DF = ABS(SPH-PH)
64  IF (PH - SPH) > = TL THEN GOSUB 4000
65  IF (SPH - PH) > = TL THEN GOSUB 10000
66  GOSUB 3000
67  TIME = MIN + SEC/60 +HR*60
68  IF (TIME - T0) < PI GOTO 280
69  GOSUB 6000
70  T0 = TIME
71  GOSUB 5000
72  GOTO 192
73  PRINT DS:OPEN "COM1:600,n,7,2,C5,DS,CD" FOR INPUT AS #2
74  LOCATE 24,1
75  INPUT #2, PH$: CLOSE #2
76  CLS
77  PRINT DS
78  PH = VAL(LEFT$(PH$,7))
79  PH = INT(PH*1000 + .5)/1000

```

```

3045 IF PH <= 0 THEN GOTO 10080
3046 RETURN
3047 TS = TIMES
3048 HR = VAL(MID$(TS,1,2))
3049 MIN = VAL(MID$(TS,4,2))
3050 SEC = VAL(MID$(TS,7,2))
3051 IF F1 < > 0 GOTO 3078
3052 IHR = HR:IMIN = MIN
3053 ISEC = SEC
3054 F1 = 1
3055 IF SEC >= ISEC GOTO 3082
3056 MIN = MIN - 1:SEC = 60 + SEC - ISEC
3057 GOTO 3084
3058 SEC = SEC - ISEC
3059 IF MIN >= IMIN GOTO 3088
3060 HR = HR - 1:MIN = 60 + MIN - IMIN
3061 GOTO 3090
3062 MIN = MIN - IMIN
3063 GOSUB 9100
3064 OS = RIGHT$(TS,8):D7$ = LEFT$(TS,11)
3065 RETURN
3066 OUT DDDB,136
3067 FOR I = 1 TO M1
3068 OUT PB,I
3069 JJ = 0
3070 OUT PB,0
3071 NEXT I
3072 AC=AC + 1
3073 RETURN
3074 CLS
3075 PRINT D7$
3076 LOCATE 10,1
3077 PRINT " pH ELAPSED TIME TIME #ADD"
3078 PRINT
3079 TS = TIME * 60!
3080 PRINT PH; TAB(13);HR;":":MIN;":":SEC;TAB(26);OS
3081 LOCATE 12,36: PRINT AC;"/":AB
3082 LOCATE 20,1
3083 PRINT "TO INTERRUPT THE PROGRAM: PRESS 'Ins' key (num lock light must be
off!) RELEASE KEY ONLY AFTER MENU APPEARS"
3084 RETURN
3085 PRINT D$:OPEN "lpt1:" AS #1
3086 IF F1 < > 0 GOTO 6010
3087 PRINT #1,: PRINT #1,: PRINT #1,: PRINT #1, D$:PRINT #1,: PRINT #1,
PRINT #1," pH ELAPSED TIME #ADD"
3088 F1 = 1: PRINT #1,
3089 PRINT #1,TS; TAB(15);AC; TAB(25);AB; TAB(35); PH
3090 PRINT #1, D$: CLOSE #1
3091 OPEN FILES FOR APPEND AS #2
3092 PRINT#2, TS,AC,AB,PH
3093 CLOSE#2
3094 RETURN
3095 PRINT D$:OPEN "lpt1:" AS #1
3096 PRINT #1,:PRINT #1,
3097 PRINT #1,D7$
3098 PRINT #1,: PRINT #1,: PRINT #1,D$: CLOSE #1
3099 RETURN
3100 K=0:CLS:COLOR 0,7
3101 PRINT "PARAMETER CHANGE MENU":PRINT:PRINT
3102 PRINT "1) FILL/EMPTY SYRINGE"

```

```

8020 PRINT "2) SET POINT pH"
8030 PRINT "3) SET PRINT INTERVAL"
8040 PRINT "4) RESET ELAPSED TIME"
8050 PRINT "5) RESET ALIQUOT SIZE"
8060 PRINT "6) RETURN TO PROGRAM"
8070 PRINT "7) EXIT"
8075 PRINT "8) SET TOLERANCE"
8080 PRINT: INPUT "ENTER THE NUMBER OF YOUR CHOICE =>";K9
8081 OPEN FILES FOR APPEND AS #2
8082 PRINT #2, "CHANGE #":K9
8083 CLOSE #2
8084 CLS:COLOR 7,0
8085 IF K9 = 6 THEN RETURN
8090 ON K9 GOSUB 8300,8330,8350,8370,8380,8320,8200,8220
8100 GOTO 8000
8120 RETURN
8130 INPUT "ENTER pH SET POINT =>";SPH
8140 RETURN
8150 INPUT "ENTER PRINT INTERVAL IN MINUTES =>";PI
8160 RETURN
8170 INPUT "ENTER NUMBER OF ELAPSED DAYS =>";DAY
8172 INPUT "ENTER INITIAL HOUR =>";IHR
8173 INPUT "ENTER INITIAL MINUTES =>";MIN
8174 INPUT "ENTER INITIAL SECONDS =>";ISEC
8175 RETURN
8180 INPUT "ENTER ALIQUOT SIZE FOR ACID":M1
8190 RETURN
8200 COLOR 7,0:END
8220 INPUT "ENTER TOLERANCE IN pH UNITS =>";TI
8230 RETURN
8300 M=200
8400 OUT DDDB,136
8430 PRINT "EMPTY(1)  FILL(2)"
8440 INPUT N
8441 IF N=1 THEN GOTO 8445
8442 IF N=2 THEN GOTO 8545
8443 RETURN
8445 FOR I=1 TO M
8450 OUT PB,1
8460 J=0
8470 OUT PB,0
8480 NEXT I
8490 GOTO 8430
8545 FOR I=1 TO M
8550 OUT PB,3
8560 J=0
8570 OUT PB,2
8580 NEXT I
8590 GOTO 8430
9100 IF HR > = IHR GOTO 9160
9110 IF F3 = 1 GOTO 9170
9120 DAY = DAY + 1
9130 F3 = 1
9150 GOTO 9170
9160 F3 = 0
9170 HR = HR + DAY*24 - IHR
9180 RETURN
10000 OUT DDDB,136
10005 PRINT "*****"
10010 FOR I = 1 TO M2

```

```
10015  JJ = 0
10020  OUT PB,1
10030  JJ = 0
10040  OUT PB,0
10050  NEXT I
10060  AB = AB + 1
10070  RETURN
10080  END
10010  FOR I = 1 TO M2
10015  JJ = 0
10020  OUT PB,1
10030  JJ = 0
10040  OUT PB,0
10050  NEXT I
10060  AB = AB + 1
10070  RETURN
10080  END
```

## BASIC PROGRAM FOR CATHODIC REDUCTION

```

1  DEF SEG = 0: CLS : F1 = 0: F2 = 0: DAY = 0
2  M = 10:29 = - 16384
3  DDBP = 547: AC = 0
4  PB = 544
5  AB = 0
6  TL = 0
7  INPUT "OUTPUT FILE NAME =>": FILES$
8  INPUT "ENTER EXPERIMENT ID =>": IDS$
9  INPUT "ENTER NUMBER OF COPPER SOLUTION ADDITIONS =>": SPH
10 INPUT "ENTER PRINT INTERVAL IN MINUTES=>": PI
11 INPUT "ALQUOT SIZE FOR COPPER SOLUTION": M1
12 INPUT "CONCENTRATION OF COPPER IN (M) =>": C1
13 ACD = M1 * .00025 * C1 / 1000!
14 DS = CHR$(4)
15 WS = CHR$(23)
16 PRINT DS: OPEN "lpt1:" FOR OUTPUT AS #1
17 PRINT #1, "EXPERIMENT ID, FILE and DATE =": IDS$, FILES$, DATE$
18 PRINT #1, "MOLES OF COPPER PER ADDITION =": ACD
19 PRINT #1, "NUMBER OF COPPER SOLUTION ADDITIONS =": SPH
20 PRINT #1, ":PRINT #1, :PRINT #1, :PRINT #1, ~
21 PRINT #1, "TIME(SEC)          #COPPER SOLUTION          #MV"
22 PRINT #1, "-----"
23 PRINT DS: CLOSE #1
24 OPEN FILES FOR OUTPUT AS #2
25 PRINT #2, "EXPERIMENT ID and FILE ==> ": IDS$, FILES$
26 PRINT #2, "DATE OF EXPERIMENT ==> ": DATE$
27 PRINT #2, "MOLES OF COPPER PER ADDITION ==> ": ACD
28 PRINT #2, "NUMBER OF COPPER SOLUTION ADDITIONS ==> ": SPH
29 PRINT #2, "time", "# COPPER SOLUTION", "MV"
30 CLOSE #2
31 GOSUB 2000
32 GOSUB 3000
33 T0 = MIN + SEC / 60 + HR * 60
34 GOSUB 6000
35 CLS
36 GOSUB 5000
37 K = PEEK(1048) AND 128
38 IF K = 128 THEN GOSUB 8000
39 IF F1 = 0 GOTO 140
40 GOSUB 2000
41 GOSUB 4000
42 GOSUB 3000
43 TIME = MIN + SEC/60 + HR*60
44 IF (TIME - T0) < PI GOTO 280
45 GOSUB 6000
46 T0 = TIME
47 GOSUB 5000
48 GOTO 192
49 PRINT DS: OPEN "COM1:600,s,7,2,CS,DS,CD" FOR INPUT AS #2
50 LOCATE 24,1
51 INPUT #2, MV$: CLOSE #2
52 CLS
53 PRINT LS
54 MV = VAL(LEFT$(MV$,7))
55 MV = INT(MV*1000 + .5)/1000
56 RETURN
57 TS = TIMES
58 HR = VAL(MID$(TS,1,2))
59 MIN = VAL(MID$(TS,4,2))
60 SEC = VAL(MID$(TS,7,2))

```

```

3072 IF F1 < > 0 GOTO 3078
3074 1HR = HR:IMIN = MIN
3075 ISEC = SEC
3076 F1 = 1
3078 IF SEC > = ISEC GOTO 3082
3080 MIN = MIN - 1:SEC = 60 + SEC - ISEC
3081 GOTO 3084
3082 SEC = SEC - ISEC
3084 IF MIN > = IMIN GOTO 3088
3086 HR = HR - 1:MIN = 60 + MIN - IMIN
3087 GOTO 3090
3088 MIN = MIN - IMIN
3090 GOSUB 9100
3095 O$ = RIGHT$(T$,8):D7$ = LEFT$(T$,11)
3100 RETURN
4000 IF TL >= SPH THEN GOTO 10020
4001 OUT DDRB,136
4005 FOR I = 1 TO M1
4010 OUT PB,1
4020 JJ = 0
4030 OUT PB,0
4040 NEXT I
4045 AC=AC + 1
4046 TL = TL + 1
4050 RETURN
5000 CLS
5005 PRINT D7$
5010 LOCATE 10,1
5020 PRINT " MV          ELAPSED TIME      TIME      #ADD"
5030 PRINT
5035 TS = TIME * 60!
5040 PRINT MV; TAB(13);HR;";";MIN;";";SEC;TAB(26);O$
5050 LOCATE 12,36: PRINT AC;"/";AB
5055 LOCATE 20,1
5056 PRINT "TO INTERRUPT THE PROGRAM: PRESS 'Ins' key (num lock light must be
off!) RELEASE KEY ONLY AFTER MENU APPEARS"
5060 RETURN
6000 PRINT D$:OPEN "lpt1:" AS #1
6003 IF F1 < > 0 GOTO 6010
6004 PRINT #1,: PRINT #1,: PRINT #1,: PRINT #1, D$:PRINT #1,: PRINT #1,
6005 PRINT #1," MV          ELPSD T TIME      #ADD"
6007 F1 = 1: PRINT #1,
6010 PRINT #1,TS: TAB(25);AC: TAB(35); MV
6020 PRINT #1, D$: CLOSE #1
6025 OPEN FILES FOR APPEND AS #2
6026 PRINT#2, TS,AC,MV
6027 CLOSE#2
6030 RETURN
7000 PRINT D$:OPEN "LPT1:" AS #1
7010 PRINT #1,:PRINT #1,
7020 PRINT #1,D7$
7030 PRINT #1,: PRINT #1,: PRINT #1,D$: CLOSE #1
7040 RETURN
8000 K=0:CLS:COLOR 0,7
8010 PRINT "PARAMETER CHANGE MENU":PRINT:PRINT
8015 PRINT "1) FILL/EMPTY SYRINGE"
8020 PRINT "2) NUMBER OF COPPER SOLUTION ADDITIONS"
8030 PRINT "3) SET PRINT INTERVAL"
8040 PRINT "4) RESET ELAPSED TIME"
8050 PRINT "5) RESET ALIQUOT SIZE"

```

```

8060 PRINT "6) RETURN TO PROGRAM"
8070 PRINT "7) EXIT"
8080 PRINT: INPUT "ENTER THE NUMBER OF YOUR CHOICE =>";K9
8081 OPEN FILE$ FOR APPEND AS #2
8082 PRINT #2, "CHANGE #";K9
8083 CLOSE #2
8084 CLS:COLOR 7,0
8085 IF K9 = 6 THEN RETURN
8090 ON K9 GOSUB 8300,8130,8150,8170,8180,8120,8200
8100 GOTO 8000
8120 RETURN
8130 INPUT "ENTER NUMBER OF COPPER SOLUTION ADDITIONS =>";SPH
8140 RETURN
8150 INPUT "ENTER PRINT INTERVAL IN MINUTES =>";PI
8160 RETURN
8170 INPUT "ENTER NUMBER OF ELAPSED DAYS =>";DAY
8172 INPUT "ENTER INITIAL HOUR =>";IHR
8173 INPUT "ENTER INITIAL MINUTES =>";MIN
8174 INPUT "ENTER INITIAL SECONDS =>";ISEC
8175 RETURN
8180 INPUT "ENTER ALIQUOT SIZE FOR COPPER SOLUTION";M1
8190 RETURN
8200 COLOR 7,0:END
8300 M=200
8400 OUT DDRB,136
8430 PRINT "EMPTY(1)  FILL(2)"
8440 INPUT N
8441 IF N=1 THEN GOTO 8445
8442 IF N=2 THEN GOTO 8545
8443 RETURN
8445 FOR I=1 TO M
8450 OUT PB,1
8460 J=0
8470 OUT PB,0
8480 NEXT I
8490 GOTO 8430
8545 FOR I=1 TO M
8550 OUT PB,3
8560 J=0
8570 OUT PB,2
8580 NEXT I
8590 GOTO 8430
9100 IF HR > = IHR GOTO 9160
9110 IF F3 = 1 GOTO 9170
9120 DAY = DAY + 1
9140 F3 = 1
9150 GOTO 9170
9160 F3 = 0
9170 HR = HR + DAY*24 - IHR
9180 RETURN
10010 JJ = 0
10020 OPEN "LPT1:" AS #1
10030 PRINT #1,TS; TAB(25);AC; TAB(35); NV
10040 CLOSE #1
10050 END

```

```
'SAS PROGRAM CALCULATING 1-LIGAND CONCENTRATION FITTING FOR  
'0000' XAD-8 PH 6.2 COMPLEXOMETRIC TITRATIONS WITH PHTHALIC ACID'
```

```
libname joe '[mconklin.stat]';  
filename file1 'sascorr.dat';
```

```
title 'cphth.dat 1 parameter fit of c1';
```

```
data joe.temp;  
  infile file1;  
  input cut 2-12 cu 13-21;  
  cut=10**cut;  
  cu=10**cu;  
  keep cut cu;
```

```
proc nlin best=10 plot method=marquardt;  
  parm c1=-3.83;  
  bounds c1<0;  
  h=6.31e-7;  
  k1=4.0;  
  g1=10**c1*10**k1*cu/(1+cu*10**k1);  
  model cut=cu+g1;  
  der.c1=g1/10**c1;  
  output out=b p=yhat r=yresid;  
plot data=b;  
plot cut*cu='a' yhat*cu='p' /overlay vpos=25;  
plot yresid*cu / vref=0 vpos=25;
```

'SAS PROGRAM CALCULATING 2-LIGAND CONCENTRATIONS OF PHTHALIC ACID AND  
CATECHOL FOR OCGW XAD-8 PH 6.2 COMPLEXOMETRIC TITRATIONS'

```
libname joe '[mconklin.stat]';
filename file1 'sascorr.dat';

title 'cphthcat.dat 2 parameter fit: c1,c3';

data joe.temp;
  infile file1;
  input cut 2-12 cu 13-21;
  cut=10**cut;
  cu=10**cu;
  keep cut cu;
proc nlin best=10 plot method=marquardt;
  parm      c1=-4.25
            c3=-4.2;
  bounds c1<0,c3<0;
  h=6.31e-7;
  k1=4.0;
  k3=-7.96;

  g1=10**c1*10**k1*cu/(1+cu*10**k1);
  g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
  model cut=cu+g1+g3;

  der.c1=g1/10**c1;
  der.c3=g3/10**c3;
  output out=b p=yhat r=yresid;
proc plot data=b;
  plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
  plot yresid*cu / vref=0 vpos=25;
```

'SAS PROGRAM CALCULATING CONCENTRATIONS OF PHTHALIC ACID AND  
CATCHOL WITH A FIXED CONCENTRATION OF GLYCINE FOR BA XAD-8  
COMPLEXOMETRIC TITRATIONS AT PH 7.5'

```
libname joe '[mconklin.stat]';
filename file1 'ba7.dat';
```

```
title 'BA73lig.dat 2 parameter fit: c1,c3';
```

```
data joe.temp;
  infile file1;
  input cut 2-12 cu 13-21;
  cut=10**cut;
  cu=10**cu;
  keep cut cu;
```

```
proc nlin best=10 plot method=marquardt;
  parm c1=-3.3
        c3=-5.3;
  bounds c1<0,c3<0;
  h=3.16228e-8;
  c4=-5.095;
  k1=4.0;
  k3=-7.96;
  k4=-1.24;
```

```
g1=10**c1*10**k1*cu/(1+cu*10**k1);
g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
g4=10**c4*10**k4*cu/(h+cu*10**k4);
model cut=cu*g1+g3+g4;
```

```
der.c1=g1/10**c1;
der.c3=g3/10**c3;
output out=b p=yhat r=yresid;
```

```
proc plot data=b;
  plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
  plot yresid*cu / vref=0 vpos=25;
```

'SAS PROGRAM CALCULATING CONCENTRATIONS OF PHTHALIC ACID AND  
CATFCHOL WITH A FIXED CONCENTRATION OF GLYCINE FOR BA XAD-8  
COMPLEXOMETRIC TITRATIONS AT PH 7.5'

```
libname joe '[mconklin.stat]';
filename file1 'ba7.dat';
```

```
title 'BA73lig.dat 2 parameter fit: c1,c3';
```

```
data joe.temp;
  infile file1;
  input cut 2-12 cu 13-21;
  cut=10**cut;
  cu=10**cu;
  keep cut cu;
```

```
proc nlin best=10 plot method=marquardt;
  parm      c1=-3.3
            c3=-5.3;
  bounds c1<0,c3<0;
  h=3.16228e-8;
  c4=-5.095;
  k1=4.0;
  k3=-7.96;
  k4=-1.24;
```

```
  g1=10**c1*10**k1*cu/(1+cu*10**k1);
  g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
  g4=10**c4*10**k4*cu/(h+cu*10**k4);
  model cut=cu+g1+g3+g4;
```

```
  der.c1=g1/10**c1;
  der.c3=g3/10**c3;
  output out=b p=yhat r=yresid;
```

```
proc plot data=joe.temp;
  plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
  plot yresid*cu / vref=0 vpos=25;
```

'END PROGRAM CALCULATING A THIRD LIGAND CONCENTRATION AND  
 BINDING CONSTANT FOR OCGW XAD-8 PH 7.5 COMPLEXOMETRIC TITRATION'

```
libname joe '[mconklin.stat]';
filename file1 'ocgw7.dat';

title 'OC7flo.dat 2 parameter fit: c9,k9';

data joe.temp;
  infile file1;
  input cut 2-12 cu 13-21;
  cut=10**cut;
  cu=10**cu;
  keep cut cu;

proc nlin best=10 plot method=marquardt maxiter=30;
  parm c9=-4.4 to -4.3 by 0.01
        k9=10;
  bounds c9<0,k9>5;
  h=3.16228e-8;
  c1=-4.3;
  c3=-4.85;
  k1=4.0;
  k3=-7.96;
  g1=10**c1*10**k1*cu/(1+cu*10**k1);
  g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
  g9=10**c9*10**k9*cu/(1+cu*10**k9);
  model cut=cu*g1+g3+g9;

  der.c9=g9/10**c9;
  der.k9=g9/10**k9-(g9**k9/((10**k9)**2*10**c9));
  output out=b p=yhat r=yresid;
proc plot data=b;
  plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
  plot yresid*cu / vref=0 vpos=25;
```

'SAS PROGRAM CALCULATING N-N-GLYCINE CONCENTRATION FOR  
 RISCOYNE AQUIFER XAD-8 PH 6.2 COMPLEXOMETRIC TITRATION  
 WITH CATECHOL AND PHTHALIC ACID '

```
libname joe '[mconklin.stat]';
filename file1 'ba6.dat';

title 'BA63ngly.dat 1 parameter fit: c8';

data joe.temp;
  infile file1;
  input cut 2-12 cu 13-21;
  cut=10**cut;
  cu=10**cu;
  keep cut cu;

proc nlin best=10 plot method=marquardt maxiter=10;
  parm c8=-5.4 to -4.4 by .02;

  bounds c8<0;
  h=6.30957e-7;
  c1=-4.6395;
  c3=-5.2006;
  k1=4.0;
  k3=-7.96;
  k8=8.4;
  g1=10**c1*10**k1*cu/(1+cu*10**k1);
  g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
  g8=10**c8*10**k8*cu/(1+cu*10**k8);
  model cut=cu*g1+g3+g8;

  der.c8=g8/10**c8;
  output out=b p=y.at r=yresid;
proc plot data=b;
  plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
  plot yresid*cu / vref=0 vpos=25;
```

TECHNICAL CASE PROGRAM OUTPUT

BA63ngly.dat 1 parameter fit:  
NON-LINEAR LEAST SQUARES GRID SEARCH DEFEH

| C8    | RESIDUAL SS      |
|-------|------------------|
| -5.40 | 3.6742351307E-11 |
| -5.38 | 3.7244576549E-11 |
| -5.36 | 4.0456504235E-11 |
| -5.34 | 4.6764982353E-11 |
| -5.32 | 5.6600092189E-11 |
| -5.30 | 7.0439597964E-11 |
| -5.28 | 8.8813838906E-11 |
| -5.26 | 1.1231110703E-10 |
| -5.24 | 1.4158355818E-10 |
| -5.22 | 1.7735370838E-10 |

BA63ngly.dat 1 parameter fit:  
NON-LINEAR LEAST SQUARES ITERATIVE  
DEPENDENT VARIABLE: CUT METHOD: MAP

| ITERATION | C8   | FFC     |
|-----------|------|---------|
| 0         | -5.4 | 3.67423 |
| 1         | -5.4 | 3.67423 |

NOTE: CONVERGENCE CRITERION MET.

BA63ngly.dat 1 parameter fit: c8

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS

| SOURCE            | DF | SUM OF SQUARES | MEAN SQUARE  | DEPENDENT VARIABLE C8 |
|-------------------|----|----------------|--------------|-----------------------|
| REGRESSION        | 1  | 3.015437E-09   | 3.015437E-09 |                       |
| RESIDUAL          | 35 | 3.674233E-11   | 1.04981E-12  |                       |
| UNCORRECTED TOTAL | 36 | 3.052180E-09   |              |                       |
| (CORRECTED TOTAL) | 35 | 7.819497E-10   |              |                       |

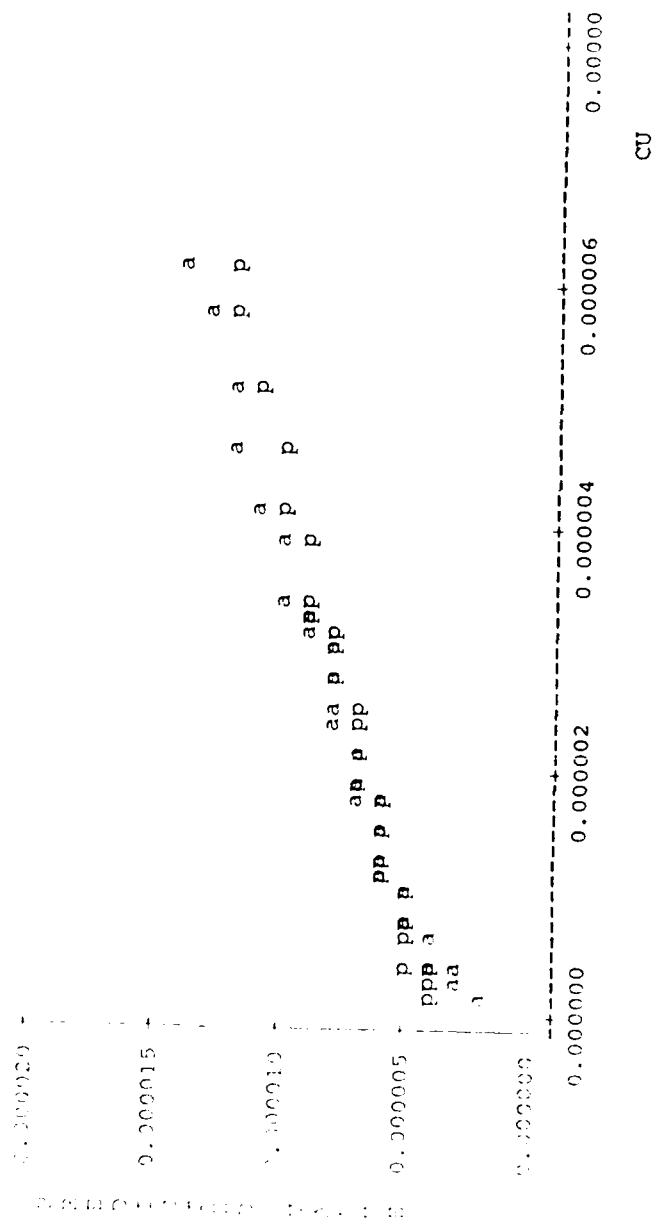
| PARAMETER | ESTIMATE     | ASYMPTOTIC<br>STD. ERROR | ASYMPTOTIC 95%<br>CONFIDENCE INTERVAL<br>LOWER | UPPER         |
|-----------|--------------|--------------------------|------------------------------------------------|---------------|
| C8        | -5.399999944 | 1.717317E-07             | -5.4000002925                                  | -5.3999996952 |

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

|    | C8     |
|----|--------|
| C8 | 1.0000 |

BA63ngly.dat 1 parameter fit:

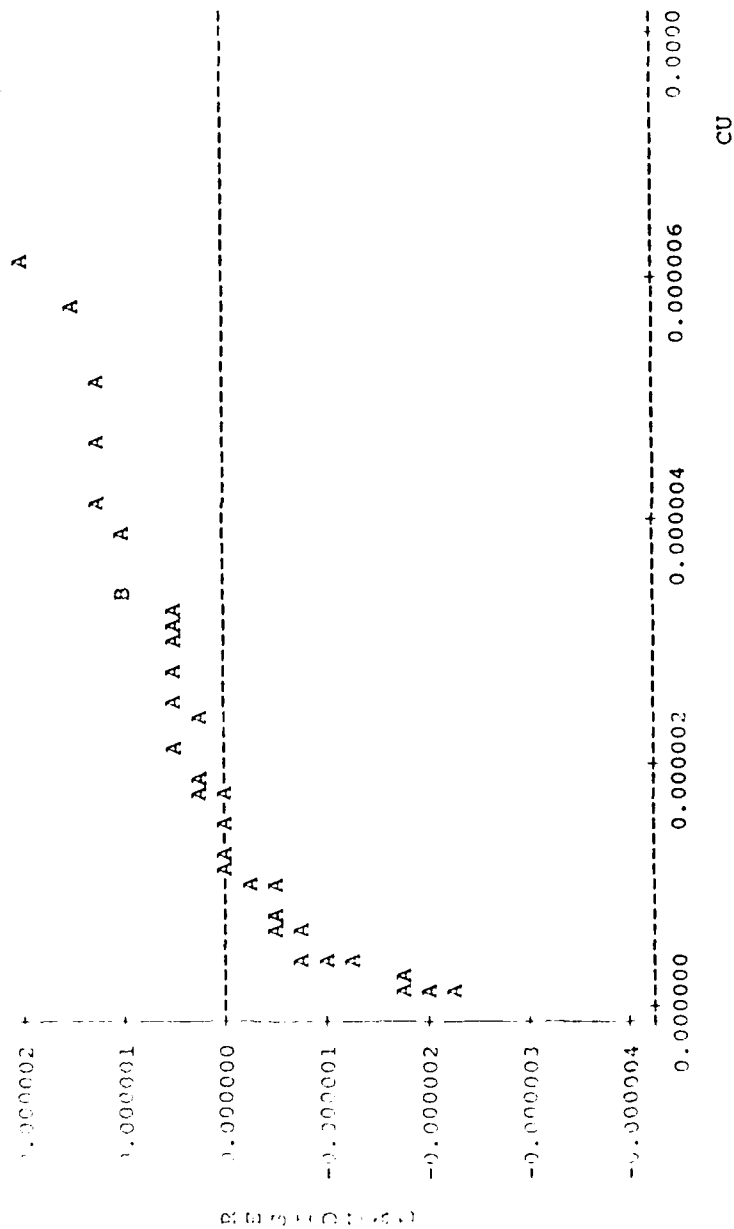
PLOT OF CUT\*CU      SYMBOL USED :  
 PLOT OF YHAT\*CU      SYMBOL USED :



NOTE: 13 OBS HIDDEN

BA63ngly.dat 1 parameter fit:

PLOT OF YRESID\*CU      LEGEND: A = 1 OBS. B



## TITRATOR DATA FILE - POTENTIOMETRIC TITRATION

DCGW 3Lig Poten

8:06 pm March 13, 1990

[gly]=1E-5M

[Phth]=5.5751E-5M [Cat]=1.415E-5M

Org-N=0.17 mg/L -OH=5 -COOH=19.7 meq/g C

## Chemical Components: DCGW 3Lig Poten

| # | Name   | C1 | Charge | Total       | Initial | Log Free | Error       |
|---|--------|----|--------|-------------|---------|----------|-------------|
| 1 | H2Phth | 1  | 0      | 5.57510E-05 | 0.000   | 0.000    | 0.00000E+00 |
| 2 | OH-    | 1  | -1     | -1.1050E-03 | -11.000 | 0.000    | 0.00000E+00 |
| 3 | Na+    | 1  | 1      | 1.00000E-02 | 0.000   | 0.000    | 0.00000E+00 |
| 4 | NO3-   | 1  | -1     | 1.00000E-02 | 0.000   | 0.000    | 0.00000E+00 |
| 5 | H2Cat  | 1  | 0      | 1.41500E-05 | 0.000   | 0.000    | 0.00000E+00 |
| 6 | HGly   | 1  | 0      | 1.00000E-05 | 0.000   | 0.000    | 0.00000E+00 |

Ionic Strength = 0.00000  
 Maximum iterations -- no convergence

## Equilibrium Species: DCGW 3Lig Poten

| # | Name   | C1 | H | O  | N | N | H | H | Log K   | Molarity   |
|---|--------|----|---|----|---|---|---|---|---------|------------|
|   |        |    | 2 | H  | a | 0 | 2 | G |         |            |
|   |        |    | P | -  | + | 3 | C | 1 |         |            |
|   |        |    | h |    |   | - | a | y |         |            |
| 1 | H+     | 1  | 0 | -1 | 0 | 0 | 0 | 0 | -14.000 | 0.0000E+00 |
| 2 | HPhth- | 1  | 1 | 1  | 0 | 0 | 0 | 0 | 11.250  | 0.0000E+00 |
| 3 | Phth-- | 1  | 1 | 2  | 0 | 0 | 0 | 0 | 20.320  | 0.0000E+00 |
| 4 | HCat-  | 1  | 0 | 1  | 0 | 0 | 1 | 0 | 4.770   | 0.0000E+00 |
| 5 | Cat--  | 1  | 0 | 2  | 0 | 0 | 1 | 0 | 5.770   | 0.0000E+00 |
| 6 | H2Gly+ | 1  | 0 | -1 | 0 | 0 | 0 | 1 | -11.770 | 0.0000E+00 |
| 7 | Gly-   | 1  | 0 | 1  | 0 | 0 | 0 | 1 | 4.420   | 0.0000E+00 |

DCGW 3-Lig

8:06 pm March 19, 1990

[Phth]=5.5751E-5M [Cat]=1.415E-5M

[Gly]=1E-5M @ Org-N=0.17mg/L

carboxylic=19.7meq/g C phenolic=5 meq/g C

## Chemical Components: DCGW 3-Lig

| # | Name   | C1 | Charge | Total       | Initial | Log Free | Error       |
|---|--------|----|--------|-------------|---------|----------|-------------|
| 1 | Cu++   | 1  | 2      | 1.00000E-07 | -12.000 | 0.000    | 0.00000E+00 |
| 2 | NO3-   | 1  | -1     | 1.00000E-02 | 0.000   | 0.000    | 0.00000E+00 |
| 3 | Na+    | 1  | 1      | 1.00000E-02 | 0.000   | 0.000    | 0.00000E+00 |
| 4 | Gly-   | 1  | -1     | 1.00000E-05 | 0.000   | 0.000    | 0.00000E+00 |
| 5 | Phth-- | 1  | -2     | 5.57510E-05 | 0.000   | 0.000    | 0.00000E+00 |
| 6 | Cat--  | 1  | -2     | 1.41500E-05 | 0.000   | 0.000    | 0.00000E+00 |
| 7 | H+     | 2  | 1      | 6.20360E-07 | -6.200  | 0.000    | 0.00000E+00 |

Ionic Strength = 0.00000

Maximum iterations -- no convergence

## Equilibrium Species: DCGW 3-Lig

| #  | Name     | C1 | C | N | N | G | P | C | H  | Log K   | Molarity   |
|----|----------|----|---|---|---|---|---|---|----|---------|------------|
|    |          |    | u | 0 | a | l | h | a | +  |         |            |
|    |          |    | + | 3 | + | y | t | t |    |         |            |
|    |          |    | + | - | - | - | h | - |    |         |            |
| 1  | OH-      | 1  | 0 | 0 | 0 | 0 | 0 | 0 | -1 | -14.000 | 0.0000E+00 |
| 2  | CuOH+    | 1  | 1 | 0 | 0 | 0 | 0 | 0 | -1 | -8.040  | 0.0000E+00 |
| 3  | Cu(OH)2  | 1  | 1 | 0 | 0 | 0 | 0 | 0 | -2 | -16.330 | 0.0000E+00 |
| 4  | Cu(OH)3- | 1  | 1 | 0 | 0 | 0 | 0 | 0 | -3 | -26.300 | 0.0000E+00 |
| 5  | Cu(OH)4- | 1  | 1 | 0 | 0 | 0 | 0 | 0 | -4 | -39.400 | 0.0000E+00 |
| 6  | (CuOH)2+ | 1  | 2 | 0 | 0 | 0 | 0 | 0 | -2 | -10.950 | 0.0000E+00 |
| 7  | CuHNO3+  | 1  | 1 | 1 | 0 | 0 | 0 | 0 | 0  | 0.500   | 0.0000E+00 |
| 8  | Cu(NCO)2 | 1  | 1 | 2 | 0 | 0 | 0 | 0 | 0  | -0.400  | 0.0000E+00 |
| 9  | H2SiO4   | 1  | 0 | 0 | 0 | 1 | 0 | 0 | 2  | 11.900  | 0.0000E+00 |
| 10 | HSiO3-   | 1  | 0 | 0 | 0 | 1 | 0 | 0 | 1  | 9.570   | 0.0000E+00 |
| 11 | CuSiO3   | 1  | 1 | 0 | 0 | 1 | 0 | 0 | 0  | 8.270   | 0.0000E+00 |
| 12 | CuSiO3.2 | 1  | 1 | 0 | 0 | 2 | 0 | 0 | 0  | 15.13   | 0.0000E+00 |
| 13 | HSiO3H-  | 1  | 0 | 0 | 0 | - | 1 | 0 | 1  | 4.93    | 0.0000E+00 |
| 14 | HSiO3H+  | 1  | 0 | 0 | 0 | - | 1 | 0 | 2  | 7.02    | 0.0000E+00 |
| 15 | SiO4--   | 1  | 1 | 0 | 0 | - | 1 | - | 0  | 4.00    | 0.0000E+00 |

## REFERENCES

- Anderson, D. M. and Morel, F. M. M. Copper sensitivity of gonyaulax tamarensis. Limnol Oceanog, 23, 283-295 (1978).
- Athavale, V. T.; Prabhu, L. H.; and Vartak, D. G. Solution stability constants of some metal complexes of derivatives of catechol. J Inorg Nucl Chem, 28, 1237-1249 (1966).
- Bassett, R. L. and Melchior, D. C. Chemical modeling of aqueous systems. In Chemical Modeling of Aqueous Systems II, ed. Melchior, D. C. and Bassett, R. L., Amer Chem Soc, Wash D. C., 1-14 (1990).
- Bresnahan, W. T.; Grant, C. L.; and Weber, J. H. Stability constants for the complexation of copper (II) ions with water and soil fulvic acids measured by ion selective electrode. Anal Chem, 50, 12, 1675-1679 (1978).
- Buffle, J., et al. Study of the complex formation of copper (II) by humic and fulvic substances. Anal Chim Acta, 116, 255-274 (1980).
- Cabaniss, S. E. Titrator: An interactive program for aquatic equilibrium calculation. Env Sci & Tech, 21, 2, 209-210 (1987).
- Cabaniss, S. E. and Shuma M. S. Copper binding by dissolved organic matter: I. Suwannee River fulvic acid equilibria. Geoch Cosmo Acta, 52, 185-193 (1988a).
- Cabaniss, S. E. and Shuman, M. S. Copper binding by dissolved organic matter: II. Variation in type and source of organic matter. Geoch Cosmo Acta, 52, 195-200 (1988b).
- Cabaniss, S. E. and Shuman, M. S. Fluorescence quenching measurements of copper-fulvic acid binding. Anal Chem, 60, 2418-2421 (1988c).
- Childs, C. W. Chemical equilibrium models for lake water which contains nitrilotriacetic acid and for normal lake water. Proc. of 14th Conference on Great Lakes Research, 198-210 (1971).

Clark, S. B. and Choppin, G. R. Kinetics of rare earth metal binding to aquatic humic acids. In Chemical Modeling of Aqueous Systems II, ed. Melchior, D. C. and Bassett, R. L., Amer Chem Soc, Wash D. C., 519-525 (1990).

Condikey, G. F. and Martell, A. E. Mixed ligand chelates of copper (II). Inorg Nucl Chem, 31, 2455-2466 (1969).

Dobbs, J. C., et al. Characterization of metal binding sites in fulvic acids by lanthanide ion probe spectroscopy. Anal Chem, 61, 483-488 (1989).

Duursma, E. K. Organic chelation of  $^{60}\text{Co}$  and  $^{65}\text{Zn}$  by leucine in relation to sorption by sediments. In Symposium on Organic Matter in Natural Waters, ed. Hood, D. W., Univ. of Alaska, 387-397 (1970).

Dzombak, D. A.; Fish, W.; and Morel, F. M. M. Metal-humate interactions. 1. Discrete ligand and continuous distribution models. Env Sci & Tech, 20, 7, 669-675 (1986).

Ephraim, J. H., et al. A novel description of the acid-base properties of an aquatic fulvic acid. Env Sci & Tech, 23, 3, 356-362 (1989).

Fish, W.; Dzombak, D. A.; and Morel, F. M. M. Metal-humate interaction. 2. Application and comparison of models. Env Sci & Tech, 20, 7, 676-682 (1986).

Gamble, D. S. Potentiometric titration of fulvic acid: equivalence point calculations and acidic functional groups. Can J Chem, 50, 2680-2687 (1972).

Gamble, D. S. Titration curves of fulvic acid: the analytical chemistry of a weak acid polyelectrolyte. Can J Chem, 48, 2662-2669 (1970).

Gamble, D. S. and Schnitzer, M. The chemistry of fulvic acid and its reactions with metal ions. In Trace Metals and Metal-Organic Interactions in Natural Waters, ed. Singer, P. C., Ann Arbor Sci, Ann Arbor, Mich, 265-302 (1973).

Gamble, D. S.; Schnitzer, M.; Kerndorff, H.; and Langford, C. H. Multiple metal ion exchange equilibria with humic acid. Geoch Cosmo Acta, 47, 7, 1311-1323 (1983).

Gamble, D. S.; Underdow, A. W.; and Langford, C. H. Copper (II) titration of fulvic acid ligand sites with theoretical, potentiometric, and spectrophotometric analysis. Anal Chem, 52, 12, 1901-1908 (1980).

Greisser, R. and Sigel, H. Ternary complexes in solution. XI. Complexation between the cobalt (II)-, nickel (II)-, copper (II)-, and zinc (II)-2, 2'-bipyridyl 1:1 complexes and ethylenediamine, glycinate, or pyrocatecholate. Inorg Chem, 10, 10, 2229-2232 (1971).

Guy, R. D. and Chakrabarti, C. L. Studies of metal-organic interactions in model systems pertaining to natural waters. Can J Chem, 54, 2600-2611 (1976).

Hering, J. G. and Morel, F. M. M. Humic acid complexation of calcium and copper. Env Sci & Tech, 22, 10, 1234-1237 (1988).

Holm, T. R. and Curtiss III, C. D. Copper complexation by natural organic matter in ground water. In Chemical Modeling of Aqueous Systems II, ed. Melchior, D. C. and Bassett, R. L., Amer Chem Soc, Wash, D. C., 508-518 (1990).

Jameson, R. F. and Wilson, M. F. Thermodynamics of the interactions of catechol with transition metals. Part II. Copper and nickel complexes of catechol. J Chem Soc Dalton Transactions, 23, 2614-2616 (1972).

Kragten, J. Atlas of Metal-Ligand Equilibria in Aqueous Solution, John Wiley & Sons, New York (1978).

Larry, I.; Cromer, M.; and Scharff, J. P. Binding strength evaluation of Cu(II) complexation with organic ligands of environmental interest. The Science of the Total Env, 62, 271-274 (1987).

Liao, W., et al. Structural characterization of aquatic humic material. Env Sci & Tech, 16, 403-410 (1982).

Lumme, P. and Kari, E. Phthalic acid as a reagent in inorganic qualitative analysis of metal ions. Part IV. Thermodynamics of the complexation of phthalate ion with divalent copper, nickel, and cobalt ions in aqueous sodium perchlorate solutions. Acta Chem Scand, 29, 125-135 (1975).

Manning, P. G. and Ramamoorthy S. Equilibrium studies of metal-ion complexes of interest to natural waters - VII. Mixed-ligand complexes of Cu(II) involving fulvic acid as primary ligand. J Inorg Nucl Chem, 35, 1577-1581 (1973).

Mantoura, R. F. C.; Dickson, A.; and Riley, J. P. The complexation of metals with humic materials in natural waters. Estuarine Cos Mar Sci, 6, 387-408 (1978).

McKnight, D. M., et al. Complexation of copper by aquatic humic substances from different environments. The Science of the Total Env, 28, 65-76 (1983).

Morel, F. M. M. and Morgan, J. A numerical method for computing equilibria in aqueous chemical systems. Env Sci & Tech, 6, 58-67 (1972).

Neshkova, M. and Sheytanov, H. The behavior of two types of copper ion-selective electrodes in different copper (II)-ligand systems. Talanta, 32, 10, 937-947 (1985).

Odem, W. Department of Environmental Engineering, University of Arizona, Tucson, AZ, Verbal communication (1990).

Oliver, B. G.; Thurman, E. M.; and Malcolm, R. L. The contribution of humic substances to the acidity of colored natural waters. Geoch Cosmo Acta, 47, 2031-2035 (1983).

Olofsson, U. and Allard, B. Complexing of Actinides with Naturally Occurring Organic Substance - Literature survey, SKBF/KBS Teknisk Report 83-09, 27 p. (1983).

Orion. Model 94-29 Cupric Electrode Instruction Manual, Orion Research Inc., 33 p. (1986).

Paulson, A.J. and Kester, D. R. Copper (II) ion hydrolysis in aqueous solution. J Soln Chem, 9, 4, 269-277 (1980).

Perdue, E. M. Acidic functional groups of humic substances. In Humic Substances in Soil, Sediment, and Water, ed. Aiken, G. R.; McKnight, D. M.; Wershaw, R. L.; and MacCarthy, P.; John Wiley & Sons, New York, 493-526 (1985).

Perdue, E. M. Effects of humic substances on metal speciation. In Aquatic Humic Substances. ed. Buffet and MacCarthy, Amer Chem Soc, 281-295 (1989).

Perdue, E. M. Solution thermochemistry of humic substances - I. Acid-base equilibria of humic acid. Geoch Cosmo Acta, 42, 1351-1358 (1978).

Perdue, E. M.; Reuter, J. H.; and Ghosal, M. The operational nature of acidic functional group analyses and its impact on mathematical descriptions of acid-base equilibria in humic substances. Geoch Cosmo Acta, 44, 1841-1851 (1980).

Perdue, E. M.; Reuter, J. H.; and Parrish, R. S. A statistical model of proton binding by humus. Geoch Cosmo Acta, 48, 1257-1263 (1984).

Plechanov, N., et al. Investigations on humic substances in natural waters. In Aquatic and Terrestrial Humic Materials, ed. Christman, R. F. and Gjessing, E. T., Ann Arbor Science, Ann Arbor, Mich., 387-405 (1983).

SAS Institute Inc. SAS User's Guide: Basics, Version 5 edition, Cary, N. C. (1985).

Schnitzer, M. and Khan, S. U. Humic Substances in the Environment, Marcel Dekker, Inc., New York, 327 p. (1972).

Schnitzer, M. and Khan, S. U. (eds.). Soil Organic Matter, Developments in Soil Science 8, Elsevier Sci Publ Co, New York, 319 p. (1978).

Smith, R. M. and Martell, E. E. Critical Stability Constants, Plenum Press, New York (1975).

Snoeyink, V. L. and Jenkins, D. Water Chemistry, John Wiley & Sons, New York, 463 p. (1980).

Steelink, C. Implications of elemental characteristics of humic substances. In Humic Substances in Soil, Sediment, and Water, ed. Aiken, G. R.; McKnight, D. M.; Wershaw, R. L.; and MacCarthy, P.; John Wiley & Sons, New York, 457-476 (1985).

Stumm, W. and Brauner, P. A. Chemical Speciation. In Chemical Oceanography, ed. Riley, J.P. and Skirrow, G., 2nd ed., I, Academic Press, London, 173-234 (1975).

Sunda, W. G. and Guillard, R. R. L. The relationship between cupric ion activity and toxicity of copper to phytoplankton. J Water Res, 34, 513-529 (1976).

Sunda, W. G. and Hanson, P. J. Chemical speciation of copper in river water. In Chemical Modeling in Aqueous Systems, ed. Jenne, E. A., Amer Chem Soc, 147-180 (1979).

Takamatsu, T. and Yoshida, T. Determination of stability constants of metal-humic acid complexes by potentiometric titration and ion-selective electrode. Soil Science, 125, 6, 377-386 (1978).

Thurman, E. M. Organic Geochemistry of Natural Waters, Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht, 497 p. (1985).

Thurman, E. M. and Malcolm, R. L. Preparative isolation of aquatic humic substances. Env Sci & Tech, 15, 4, 463-468 (1981).

Thurman, E. M. and Malcolm, R. L. Structural study of humic substances: new approaches and methods. In Aquatic Terrestrial Humic Matter, ed. Christman, R. F. and Gjessing, E. T., Ann Arbor Sci, Ann Arbor, Mich, 1-23 (1983).

Van Den Berg, C. M. G. and Kramer, J. R. Conditional stability constants for copper ions with ligands in natural waters. In Chemical Modeling in Aqueous Systems, ed. Jenne, E. A., Amer Chem Soc, Wash D.C., 115-132 (1979).

Waterbury, M. J. M. S. Thesis. The effects of natural organic matter on the speciation and transport of Cu(II) in groundwater, Dept of Hydrology, Univ. of Arizona, Tucson, 160 p. (1990).