Separation of Copper and Iron in Natural Waters by Solid-Phase Extraction

Bui

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SEPARATION OF COPPER AND IRON IN NATURAL WATERS BY SOLID-PHASE EXTRACTION

by

Charles Bui

A Thesis Submitted to the Faculty of The Graduate College in partial fulfillment of the requirements for the Degree of Master of Arts Department of Chemistry

Western Michigan University Kalamazoo, Michigan December 1993
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I am deeply indebted to Dr. Howell for his ideas, guidance, and time for this thesis. It would have been impossible to complete this thesis without his suggestions and contributions. Many thanks to Robert Sutton who provided valuable information and assistance.

I am deeply appreciative of my uncle, Thanh Nguyen, for his generous moral support. Finally, to my beloved girlfriend, To Nga, who provided financial and moral support to me in time of need.

Charles Bui
SEPARATION OF COPPER AND IRON IN NATURAL WATERS BY SOLID-PHASE EXTRACTION

Charles Bui, M.A.
Western Michigan University, 1993

A separation scheme has been developed by utilizing Solid-Phase Extraction cartridges in order to isolate and characterize the charge of metals and their complexes in natural waters. These species can be analyzed by Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma (ICP), and Ultraviolet-Visible Spectrophotometry (UV-VIS).

This separation scheme would permit the determination of the concentration of metals, as well as providing information about the forms in which the metals exist, e.g., charge of metallic complexes.

Synthetic metal complexes were prepared in the laboratory in order to study the separation scheme as well as trying to understand the binding stability of the complex under controlled pH and concentration. Lake water samples were also analyzed by the separation scheme. Different forms of metal species were detected and found distributed in different ratios for different lakes.
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INTRODUCTION

Metals in Natural Waters

The study of trace metals in natural waters is a significant environmental concern in aquatic ecosystems. The major processes that control the chemical speciation of metals in natural waters are: adsorption by particulate matter, precipitation, and complex formation with inorganic and organic ligands. These processes can be affected by the concentration of metal, pH, and concentration of metal-ligand sites associated with dissolved organic material. Adsorption by particulate material will be important in surface waters with significant levels of suspended material such as some large rivers. Precipitation of metals and formation of inorganic complexes will become more important with increasing pH, and metal concentration. Organic complexes may also be important when the concentration of dissolved organic carbon (DOC) exceeds 2–7 mg C/L and pH values of 6–8 (1).

Iron and copper are commonly found in natural waters. The concentration of these two metals in unpolluted surface waters is generally below 0.1 ppm (2). Exceptions may occur where there is a sizable influx of heavy miner
alized ground water or streams receiving large silt burdens (3). Iron has been reported to exceed this level in organic rich waters (4). It is also well known that iron exceeds this level in the deeper waters of many stratified reservoirs and lakes. As the dissolved oxygen level at greater depths in these bodies of water decreases, the reduced state of iron migrates throughout the low oxygen zone (5).

Copper, on the other hand, is listed as a priority pollutant by the U.S. Environmental Protection Agency. Traces of copper in natural waters have been studied extensively. Several scientists have shown that the toxicity of copper is more closely related to the concentration of the copper(II) ion and not necessarily to the total concentration of copper (6,7). This is very important relative to human and animal life, since, copper is extremely toxic to fish unless it is bound to organic substances (8). Mantoura and others (9) concluded that 90% of the copper is complexed by dissolved humic substances in most river waters.

Humic substances are probably the most widely distributed natural products on the earth's surface, occurring in soils, lakes, rivers, and the sea (10-12). They are amorphous, yellow-brown or black, hydrophilic, acidic, polydisperse substances of wide-ranging molecular
weight [<10,000 for fulvic acid; 10,000-30,000 for humic (13)]. Humic and fulvic acids are responsible for the yellow-brown coloration of many lakes and rivers. Based on their solubility in alkali and acid, humic substances are usually divided into three main fractions: (1) humic acid (HA), which is soluble in dilute alkaline solution but is precipitated by acidification of the alkaline extract; (2) fulvic acid (FA), which is that humic fraction which remains in the aqueous acidified solution, i.e., it is soluble in both acid and base; and (3) the humic fraction that can not be extracted by dilute base and acid which is referred to as humin (10). The classical method of extraction of humic substances is based on differences in solubility in aqueous solutions at various pH levels is shown in Figure 1.

The interactions between humic substances and metal ions have been described as ion-exchange, surface adsorption, and chelation (14). The most widely distributed groups in humic substances that have been shown to participate in metal-complexing are carboxylic acid (CO$_2$H), phenolic (OH), possibly carbonyl(C=O), and amine (NH$_2$). It is important to realize that humic substances have the capacity for binding substantial amounts of metals and that they can exert considerable control over the supply and availability of nutrient elements to plants and
animals in soils and waters. It is important to understand the chemistry and properties of metal-humate and fulvate complexes in natural waters. A better understanding of the chemistry of these complexes provides useful information on the role of humic substances in the mobility and transport mechanisms of metals in natural waters (10, 15-18).

![Diagram of extraction process]

Figure 1. Extraction of Humic Substances.

Proposed Investigation

In this study, a separation scheme is designed utilizing solid phase extraction techniques (19-22) to determine and characterize the specific nature of metals and their complexes in natural waters. This separation
scheme provides us with information about the forms in which metals exist, i.e., charge, metal to ligand ratios, and ultimately ligands. Metal-ligand complexes can exist as negative, positive, or neutral complex species. Often we do not know which species is dominant, and thus desire to separate these complexes from one another and subsequently identify the active ligands.

This separation scheme is illustrated in Figure 2. The sample is first passed through a particulate filter where the soluble metallic species are separated from the dispersed insoluble forms. Subsequently the eluant from the particulate filter is passed through a sequence of anion exchange, cation exchange, and reversed phase chromatographic extraction cartridges. The particulate filter and each of the solid phase extraction cartridges can be eluted with strong acid in order to remove the metallic species for subsequent analysis.

In order to study the feasibility of such a scheme, it was decided to consider systems of copper and iron under highly controlled conditions. Thus separations of copper and iron species in the presence of various potential ligands were carried out while varying metal concentration, ligand concentration, and pH.
Figure 2. Separation Scheme for Copper, Iron and Their Complexes.

Complex Equilibria

For a better understanding of the nature of metal-ligand complexes in natural waters, we should review some of the theoretical equilibrium models. According to Ramette (23), the successive complexation of a metal ion by a ligand is chemically analogous to the successive protonation of the ligand:
<table>
<thead>
<tr>
<th>Complex Formation</th>
<th>Protonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 <strong>M</strong> + <strong>L</strong> = <strong>ML</strong></td>
<td><strong>L</strong> + <strong>H</strong> = <strong>HL</strong></td>
</tr>
<tr>
<td>Step 2 <strong>ML</strong> + <strong>L</strong> = <strong>ML</strong>₂</td>
<td><strong>HL</strong> + <strong>H</strong> = <strong>H</strong>₂<strong>L</strong></td>
</tr>
<tr>
<td>Step 3 <strong>ML</strong>₂ + <strong>L</strong> = <strong>ML</strong>₃</td>
<td><strong>H</strong>₂<strong>L</strong> + <strong>H</strong> = <strong>H</strong>₃<strong>L</strong></td>
</tr>
<tr>
<td>etc. etc.</td>
<td>etc. etc.</td>
</tr>
</tbody>
</table>

The metal ion is symbolized by **M**, monodentate and polydentate ligands are symbolized by **L**. It is customary to treat complex formation equilibria in terms of the equilibrium constant or formation constant. For successive complexes, the formation constants (or quotients) are numbered according to the number of ligands that have formed coordinate bonds with the metal ion. For example, the four-step complexation of copper ion by ammonia we have:

Step 1 **Cu**²⁺ + **NH**₃ = **CuNH**₃²⁺
Step 2 **CuNH**₃²⁺ + **NH**₃ = **Cu(NH)**₃₂²⁺
Step 3 **Cu(NH)**₃₂²⁺ + **NH**₃ = **Cu(NH)**₃₃²⁺
Step 4 **Cu(NH)**₃₃²⁺ + **NH**₃ = **Cu(NH)**₃₄²⁺

\[
Q_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]} = 10^{4.0}
\]
\[
Q_2 = \frac{[\text{ML}_2]}{[\text{ML}][\text{L}]} = 10^{3.5}
\]
\[
Q_3 = \frac{[\text{ML}_3]}{[\text{ML}_2][\text{L}]} = 10^{2.8}
\]
\[
Q_4 = \frac{[\text{ML}_4]}{[\text{ML}_3][\text{L}]} = 10^{1.5}
\]

The relationship between the concentration of the uncomplexed metal ion **M** and any one of its complexes is easily
found by using the product of the Q-values. These products are called the "overall" complex-formation constants or simply $B_i$ values with the subscript indicating the numbered of combined values:

$$B_2 = Q_1 Q_2 = [ML_2]/[M][L]^2$$
$$B_3 = Q_1 Q_2 Q_3 = [ML_3]/[M][L]^3$$
$$B_4 = Q_1 Q_2 Q_3 Q_4 = [ML_4]/[M][L]^4$$

The beta-values are convenient in dealing with the algebra of complex formation because the product of Q values are frequently needed.

It is also important to introduce the material-balance function $F_0$ for the metal ion. Suppose a solution contains a metal ion M at a concentration of $C_M$ moles per liter. In the absence of a complexing ligand we have

$$C_M = [M]$$

However, if the solution also contains $C_L$ moles per liter of a complexing ligand that can form four successive complexes with the metal ion, the material-balance expression may be written as

$$C_M = [M] + [ML] + [ML_2] + [ML_3] + [ML_4]$$

The individual concentrations of these species will depend strongly on the concentration of the added ligand
and upon the successive formation constants. A particu-
larly important relationship is the ratio of the total
concentration \( C_M \) to that of the uncomplexed metal \([M]\). 
This can be found by using beta-expressions to substitute
for each of the molarities of the complex species:

\[
\]

When this equation is divided by \([M]\), the result is the
material-balance function:

\[
F_0 = \frac{C_M}{[M]} = 1 + Q_1[L] + B_2[L]^2 + B_3[L]^3 + B_4[L]^4
\]

The equation above defines formation function \( F_0 \), which
is at the heart of the calculations involving successive
complexes. \( F_0 \) has a value of 1.000 in the absence of
ligand, when \([L]=0\), and increases steadily in polynomial
fashion as the ligand molarity is increased in the sys-
tem. It is possible to determine experimental values for
\( F_0 \) in a series of solutions of metal ion, usually in low
concentration, containing varying concentrations of
ligand.

Alpha-functions are also important in plotting
diagrams of the relative amounts of species present as a
function of the molarity of ligand in the solution. The
fraction of the metal that remains uncomplexed is the
reciprocal of \( F_0 \):
\[ \alpha_o = \frac{[M]}{C_M} = \frac{1}{F_0} \]

By using the \( Q_1 \) and beta-expressions it is easy to show that the fractions present as the other individual species are

\[ \alpha_1 = \frac{[ML]}{C_M} = Q_1[L]\alpha_0 = \frac{Q_1[L]}{F_0} \]
\[ \alpha_2 = \frac{[ML_2]}{C_M} = \beta_2[L]^2\alpha_0 = \frac{\beta_2[L]^2}{F_0} \]
\[ \alpha_3 = \frac{[ML_3]}{C_M} = \beta_3[L]^3/F_0 \]
\[ \alpha_4 = \frac{[ML_4]}{C_M} = \beta_4[L]^4/F_0 \]

These expressions will prove useful in plotting distribution diagrams of the relative amounts of species present as a function of the molarity of ligand in the solutions. The fraction of each species, i.e., its alpha value, is plotted versus ligand concentration. When \( \alpha_i \) values of the metal-ligand complex system of interest are plotted against ligand molarity, the dominant species for a given ligand concentration are easily identified. Practice dictates the use of a logarithmic abscissa, e.g., plotting fraction versus \( \log [L] \) to show the distribution over a wide range of ligand concentrations. Given a set of successive \( Q \) values for a certain metal-ligand system, it is a straightforward procedure to calculate the alpha values for a range of ligand molarities. The plotted values in Figure 3 show at a glance how the various nickel-ethylenediamine (Ni-en) species relate to each
other over the wide range of ethylenediamine molarities (23).

Figure 3. Various Ni-en Species Relate to Each Other Over the Wide Range of Ethylenediamine Molarity.

The Affect of pH: Protonation of the Ligand

The bonding sites (unshared electron pairs) on ligands that form metal complexes have affinities for hydrogen ions also. If the pH is high enough, this effect will be negligible because too little of the ligand will be converted to the HL form to make any difference in the free ligand (L⁻) concentration. But at lower pH values, the ligand will be increasingly forced to form its conjugate acid and therefore will not be as readily available
for complexation with the metal ion. The equilibrium scheme is

\[ M + L \rightarrow ML, ML_2 \]
\[ H^+ + L \rightarrow HL, H_2L \]

**Competition Between Ligands for the Metal Ion**

When a solution contains a metal ion and two potential ligands, each of which can form complexes, pH may often determine which one predominates. At high pH condition, for example, the hydroxide ion may compete more effectively in binding to the metal compared to another ligand.

This distribution diagram and its concepts helps us to predict the relative concentration of the metal ion and its complexes at certain pH values. By providing \( \beta_i \) values, we are able to calculate and plot the \( \alpha_i \) values versus log [L]. This concept can be applied to any metal-ligand complex for which we have the necessary thermodynamic data.

**Analysis Technique**

There are several detection methods for trace metal analysis. Spectrophotometric methods are generally used for the analysis of many metals in industrial waste waters. For example, 2,9-dimethyl-1,10-phenanthroline,
commonly called neocuproine, coordinates with copper(I) at a pH of 3-10 to form a bright orange color. Neocuproine forms a 2:1 ligand to metal complex with copper(I) in isoamyl alcohol. When absorbance is measured at 545 nm, 0.05-20 ppm of copper can be determined (24).

The spectrophotometric method has also been applied successfully to the detection and determination of iron. 1,10-Phenanthroline reacts with iron(II) in a solution of pH 4 to give an intense red-orange colored complex. The wavelength of maximum absorption is 508 nm (25).

\[
\text{Neocuproine} + \text{Cu(I)} \rightarrow \text{Cu(I)} \quad \lambda_{\text{max}} = 508 \text{ nm}
\]

\[
\text{Fe}^{2+} + 3 \text{ o-Phenanthroline} \quad \lambda_{\text{max}} = 508 \text{ nm}
\]

However, these methods are cumbersome, often requiring solvent extraction before the spectrophotometric measurements can be made. In addition, they may be sub-
ject to serious interferences by even moderate concentrations of certain other cations and anions (26). Spectrophotometric methods do not apply to some stable metal-ligand complexes. For instance, Fe(CN)$_6^{3-}$ (hexacyanoferrate(III) anion), is such a stable complex that the iron will not coordinate with o-phenanthroline. Nevertheless, spectrophotometric methods offer good sensitivity and better precision compared to that of many other techniques.

Atomic absorption and emission spectroscopy are well suited for the analysis of metals in natural waters. The technique is widely recognized for its ability to rapidly analyze complex samples for trace metals. If the metal concentrations are below the detection limit, pre-concentration methods can be used. Different types of pre-concentration steps, e.g., extraction (27,28), ion exchange or co-precipitation (29), have been employed.

In atomic spectroscopy, the sample may be atomized by a flame, an electrically powered graphite furnace, or an inductively coupled plasma (ICP). Trace metal concentrations can be detected by atomic absorption at part per million (ppm) levels. Graphite furnaces offer greater sensitivity than that afforded by flames and require less sample than a flame, but often give poorer precision. They also require greater effort to ascertain the opti-
mum conditions for each type of sample. The inductively coupled plasma reaches much higher temperatures than that of ordinary combustion flames and is useful for emission spectroscopy. The high temperature and stability of the plasma eliminates many interferences and often provides greater sensitivity than conventional flame technique. The major advantage of these atomic spectroscopic techniques over spectrophotometric methods lie in their inherent greater sensitivity to metal concentrations and their relative insensitivity on the ligand species present.
EXPERIMENTAL PROCEDURE

Instrumentation

All spectrophotometric measurements were made using a Beckman Model DU-6 UV-VIS Spectrophotometer or a Hewlett Packard Corporation Model 8451A Diode Array Spectrophotometer. Both are single beam instruments with holographic gratings configured for spectral bandwidth of 2 nm. The diode array instrument was used to obtain spectra for the purpose of locating wavelength maxima while the Beckman instrument was employed for making quantitative absorbance measurements.

Atomic absorption measurements were made with a Jarrel-Ash Model 82-536 Atomic Absorption-Atomic Emission Spectrometer. This instrument employs a 0.5 meter Ebert 5.0 cm x 5.0 cm curved grating with 1180 lines/mm. All measurements were made with a Jarrel Ash Co. R212 photomultiplier tube with an S-5 response at 480 v. dc, a HETCO premixed laminar flow burner with air-acetylene, single pass optics, entrance and exit slits of 100 and 150 µm respectively. The air supply was from filtered house air operated at 40 psi while the acetylene was obtained from AGA Gas Inc., Kalamazoo, MI. as reagent grade (99.8%) in
a tank supplied with a two stage regulator set at 150 and 5 psi. Other operating conditions for copper and iron are illustrated in Table 1.

Table 1

| Operating Conditions for Copper and Iron by Jarrel-Ash Spectrophotometer |
|----------------------------------------------------------|-----------------|
| Burner Height (cm)                                      | Copper | Iron |
| Hollow Cathode Lamp (Westinghouse)                      | WL22837 | WL22606 |
| Lamp Current (ma)                                       | 4.0    | 28.0 |
| Wavelength (A)                                          | 3247   | 2483 |
| Gain (%)                                                 | 30.0   | 50.0 |
| Damping (%)                                              | 100    | 100 |
| Air Flow Rate (LPM)                                     | 7.3    | 7.3 |
| Acetylene Flow Rate (LPM)                               | 2.1    | 2.1 |

ICP atomic emission data was collected by the Western Michigan University Institute of Water Science's Water Quality Laboratory. The instrument used was a Leeman Labs Inc., Model No. PS 1000 (sequential) Inductively Coupled Plasma (ICP)/Echelle Spectrometer. The spectrometer is a fixed echelle grating with a quartz prism for order sorting operated with an argon plasma
torch. Reagent grade argon (prepurified) obtained from Michigan Airgas Inc., Saginaw MI. was employed throughout. The torch was operated at 1.0 kW, 11 LPM of coolant, and 40 psi nebulizer pressure for all samples. Copper and iron were analyzed at 324.754 and 259.940 nm respectively.

Total Organic Carbon (TOC) analyses were also carried out by the Western Michigan University Institute of Water Science's Water Quality Laboratory with a UIC Inc. Model 5011 CO₂ Coulometer. Since the reader may not be familiar with this type of instrumentation, its principles of operation will be briefly described. A small aliquot of the sample is first quantitatively measured and placed in a combustion system where the solvent is carefully evaporated. Next the sample is combusted in a stream of scrubbed oxygen which is then bubbled through a trapping solution held in the coulometer cell. The trapping solution is a partially aqueous medium containing ethanolamine and color pH indicator. When the combustion gases are passed into the coulometer cell, any CO₂ will react with the ethanolamine and be quantitatively absorbed. Due to the neutralization of the ethanolamine, the indicator changes color which is detected by an internal colorimeter. The coulometer is turned on for a time sufficient to generate base in order to maintain the
original indicator color. The system operates at 100% current efficiency for microgram quantities of carbon with a linearity and accuracy up to 0.1%.

Procedure

All reagents used were ACS grade or better unless indicated otherwise.

Colorimetric Determination of Copper

The procedure followed for the determination of copper is described by Welcher and Boschman (24). This method employs 2,9-dimethyl-1,10-phenanthroline (neocuprone) as the chromogenic reagent followed by extraction with chloroform and subsequent measurement of the absorbance at 457 nm (\( \epsilon = 7,950 \text{ Lmol}^{-1}\text{cm}^{-1} \)).

Colorimetric Determination of Iron

The procedure for the determination of iron is described by Day and Underwood (30). Iron(III) is reduced to iron(II) with hydroxylamine hydrochloride and complexed by o-phenanthroline to form an intensively orange-red colored complex. The wavelength of the absorption maximum of this complex is 508 nm (\( \epsilon = 11,100 \text{ Lmol}^{-1}\text{cm}^{-1} \)).
Separation of Copper and Iron Complexes by Solid Phase Extraction

0.45 µm HA (47 mm diameter) and 0.45 µm PTFE (13 mm diameter) pore size filters were purchased from Millipore, Inc. HA filter type is made of mixed cellulose acetate and nitrate. PTFE filters are made of polytetrafluoroethylene. The Swinny stainless steel filter holder, 13 mm diameter, was equipped with a Teflon gasket and O-ring. It is designed for filtering small volumes of liquids, usually less than 10 ml, from a hypodermic syringe. An all-glass filter holder, 47 mm diameter, in conjunction with a one liter side arm filtering flask was used for vacuum filtration. A 50 ml sample or more can be easily filtered with this apparatus. All these items were obtained from Millipore, Inc. The Alltech vacuum manifold permits column loading, extraction, and subsequent elution for up to 12 SPE (solid phase extraction) cartridges. Opening a nylon stopcock causes sample to be drawn through the cartridge and the eluate collected in test tubes. The attached vacuum bleed valve and gauge allows the control and monitoring of vacuum.

The SPE cartridges were purchased from Alltech Associates, Inc. These cartridges are high quality polypropylene tubes filled with specific sorbents and fitted with a male luer hub. They are designed to work with
vacuum systems to achieve rapid sample eluant collection. The SPE procedure used in this separation scheme is based on well established liquid chromatography separation mechanisms. These include ion-exchange and reverse-phase columns. SAX (anion) and SCX (cation) SPE cartridges were used to trap anionic and cationic species on the active exchange sites. These species may be subsequently eluted by means of specific eluting solvents. SAX cartridges contained 100 mg of a quaternary triethylamino bonded phase resin. SCX cartridges contain 100 mg of a butyl sulphonate bonded phase resin. The volume of resin for each cartridge is approximately 1 ml. The reverse-phase (LC-CN) cartridge is packed with 100 mg of a cyanopropyl bonded phase and its packing volume is also about 1 ml.

Inorganic ligands used were obtained from salts of ACS reagent grade or better wherever possible. Inorganic salts used to form complexes with copper and iron included sodium chloride (Cl\textsuperscript{-}), potassium thiocyanate (SCN\textsuperscript{-}), sodium acetate (C\textsubscript{2}H\textsubscript{3}O\textsubscript{2}\textsuperscript{-}), potassium ferrocyanide (Fe(CN)\textsubscript{6}\textsuperscript{4-}), potassium ferricyanide (Fe(CN)\textsubscript{6}\textsuperscript{3-}), sodium fluoride (F\textsuperscript{-}), sodium sulfate (SO\textsubscript{4}\textsuperscript{2-}), anhydrous dibasic sodium phosphate (H\textsubscript{2}PO\textsubscript{4}\textsuperscript{-}, HPO\textsubscript{4}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}), and anhydrous sodium carbonate (HCO\textsubscript{3}\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}). Organic ligands used included catechol (certified technical grade, Fisher Scientific), resorcinol (technical grade, Fisher Scien-
tific), hydroquinone (purified technical grade, Fisher Scientific), gallic acid (technical grade, 97% purified, Aldrich Chemical Co.), and tannic acid (technical grade powder, Matheson Coleman & Bell Co.).

Copper(II) standard solutions were prepared from cleaned copper foil dissolved in concentrated nitric acid. Iron(III) standard solutions were made by dissolving iron wire (99.54% analytical reagent, Mallinckrodt) in concentrated hydrochloric acid. Iron(II) secondary standard solutions were prepared from ferrous perchlorate hexahydrate. Metal concentrations were determined by atomic absorption measurements utilizing calibration plots made from standard solutions. Metal-ligand complexes were prepared in the laboratory in order to study the separation scheme as well as trying to understand the binding stability of the complex under conditions of controlled pH and concentration.

Generally, metal concentrations of 10 ppm were initially tested although in some instances solutions of 5 ppm were prepared and tested. Ligand concentrations were usually in an excess of at least 1:6 molar ratio with respect to metal ion concentration. The actual excess of free ligand varies according to the nature of the complex as seen in Table 1, 3, and 5.

A typical procedure, with some variations to accom-
modate adequate concentration levels, is described as follows: a solution of 50 ppm of metal ion and an excess of ligand (at least 1:6 mole ratio) was prepared in a 100 ml volumetric flask. A six fold excess of ligand was added to insure attainment of equilibrium for the complex. The solution was adjusted to pH 5 with sodium hydroxide or perchloric acid solution as needed and measured with a pH meter. Several hours were allowed for the attainment of equilibrium. Approximately 10 ml of this solution was applied to the particulate filter. A 10 ml syringe with stainless steel Swinny was used to force the sample through a 13 mm diameter 0.45 μm PTFE filter. The eluate from the filter subsequently passes through the SAX, SCX, and LC-CN cartridges. The insoluble metal ion species collected on the filter were washed with 10 ml of 3M nitric acid. This fraction, particulate species, was collected and diluted to 50 ml with Milli-Q water. The metal species from each cartridge were treated in a similar fashion. All fractions were then analyzed by atomic absorption spectrophotometric measurements. The concentration of each metal fraction was determined based on the calibration plot of standard metal solutions. Similar trials were repeated for a pH of 8.

Since only relative amounts of metal on the different separation media were of interest in order to study
separation scheme, no effort was made to employ exact 10 ml aliquot using simulated samples. However, exact 50 ml aliquot of surface water was employed so that quantitative measurements could be made.

Surface water samples were collected from four different lakes chosen to be free of industrial inputs in southwest Michigan area. The samples were collected in glass bottles and stored at 14 °C in the dark. They were subsequently analyzed within one day of collection by the solid phase extraction technique. Table 7 describes the source of lake samples.

The procedure for the separation of metal species in natural waters is similar to that described for the simulated samples. However, due to lower metal ion concentration, lake samples were applied as 50.00 ml aliquot. Fractions were collected and diluted to 50 ml with Milli-Q water and trace metals of copper and iron were determined by the inductively coupled plasma (ICP).
RESULTS AND DISCUSSION

Simulated Samples

General Observations

Careful examination of Tables 2 through 7 reveals reasonably good agreement of predicted and observed charged species. The predicted species are determined by calculating the log of the free ligand concentration (Table 2, 4, and 6) and then examining the appropriate alpha or distribution plot (See Appendix). The observed dominant species were consistent with the predicted species for the copper(II) systems with chloride, thiocyanate, acetate, fluoride, and carbonate. The iron(II) system was found to be in agreement only for cyanide. A lack of thermodynamic data for the organic ligands with iron(II) prevented any predictions from being made. The iron(III) systems were in agreement for cyanide, fluoride (pH 8.0) and sulfate (pH 5.0). On first examination, however, a number of apparent anomalies seem to be evident. Upon reflection these are often easily resolved. For example in several instances a secondary species was predicted but not found. This is probably due to the fact
### Table 2

Cu(II)-Ligand Complex Data

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Conc.(mM)</th>
<th>pH</th>
<th>Conc.(mM)</th>
<th>Conc.(mM)</th>
<th>Cu(II) Particulate*</th>
<th>SAX*</th>
<th>SCX*</th>
<th>LC-CN*</th>
<th>Eluate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chloride</td>
<td>10.0</td>
<td>3.0</td>
<td>100</td>
<td>100</td>
<td>0.254</td>
<td>0.3</td>
<td>0.7</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2a. Thiocyanate</td>
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ND = Not Detectable

* All standard deviations were ± 0.2
Table 3

Summary of Data for Cu(II) Complexes

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<th>Ligand</th>
<th>Free Ligand</th>
<th>Concentration (mM)</th>
<th>pH</th>
<th>Predicted Dominant Species</th>
<th>Predicted Secondary Species</th>
<th>Found Dominant Cartridge</th>
<th>Found Secondary Cartridge</th>
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0 = neutral species and/or neutral cartridge
* = Stability constant is not available
ppt = particulate on filter
Table 4
Fe(II)-Ligand Complex Data

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<th>Ligand</th>
<th>Ligand Conc. (mM)</th>
<th>pH</th>
<th>Free Ligand Conc. (mM)</th>
<th>Fe(II) Conc. (mM)</th>
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<th>SAX* (ppm Fe)</th>
<th>SCX* (ppm Fe)</th>
<th>LC-CN* (ppm Fe)</th>
<th>Eluate* (ppm Fe)</th>
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ND = Not Detectable
* All standard deviations were ± 0.2
Table 5

Summary of Data for Fe(II) Complexes

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<th>Ligand</th>
<th>Free Ligand Conc. (mM)</th>
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<th>Predicted Secondary Species</th>
<th>Found Dominant Cartridge</th>
<th>Found Secondary Cartridge</th>
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0 = neutral species and/or neutral cartridge
* = stability constant is not available
ppt = particulate on filter
Table 6

Fe(III)-Ligand Complex Data

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<th>SCX* (ppm Fe)</th>
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</tr>
<tr>
<td>3b. Fluoride</td>
<td>35.8</td>
<td>8.09</td>
<td>35.8</td>
<td>0.406</td>
<td>6.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>4a. Sulfate</td>
<td>17.9</td>
<td>5.03</td>
<td>17.9</td>
<td>0.406</td>
<td>4.0</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>4b. Sulfate</td>
<td>17.9</td>
<td>7.87</td>
<td>17.9</td>
<td>0.406</td>
<td>ND</td>
<td>4.0</td>
<td>0.3</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>5. Catechol</td>
<td>13.6</td>
<td>5.0</td>
<td>4.83E-04</td>
<td>0.406</td>
<td>ND</td>
<td>ND</td>
<td>4.5</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND = Not Detectable

* All standard deviations were ± 0.2
Table 7

Summary of Data for Fe(III) Complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Free Ligand Conc. (mM)</th>
<th>pH</th>
<th>Predicted Dominant Species</th>
<th>Predicted Secondary Species</th>
<th>Found Dominant Cartridge</th>
<th>Found Secondary Cartridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cyanide</td>
<td>3.70E-03</td>
<td>5.0</td>
<td>-</td>
<td>None</td>
<td>-</td>
<td>None</td>
</tr>
<tr>
<td>2. Acetate</td>
<td>6.37</td>
<td>5.0</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>None</td>
</tr>
<tr>
<td>3a. Fluoride</td>
<td>35.3</td>
<td>5.07</td>
<td>0</td>
<td>+</td>
<td>ppt</td>
<td>None</td>
</tr>
<tr>
<td>3b. Fluoride</td>
<td>35.8</td>
<td>8.09</td>
<td>ppt</td>
<td>None</td>
<td>ppt</td>
<td>None</td>
</tr>
<tr>
<td>4a. Sulfate</td>
<td>17.9</td>
<td>5.03</td>
<td>ppt</td>
<td>None</td>
<td>ppt</td>
<td>None</td>
</tr>
<tr>
<td>4b. Sulfate</td>
<td>17.9</td>
<td>7.87</td>
<td>ppt</td>
<td>None</td>
<td>-</td>
<td>None</td>
</tr>
<tr>
<td>5. Catechol</td>
<td>4.83E-04</td>
<td>5.0</td>
<td>*</td>
<td>*</td>
<td>+</td>
<td>None</td>
</tr>
</tbody>
</table>

0 = neutral species and/or neutral cartridge
*
= stability constant is not available
ppt = particulate on filter
that the concentration of the secondary species under the conditions of the experiment was too small to be detected. It will be noted that the studies were generally conducted at two pH values ca. 5 and 8. At high pH values (pH ~ 8) hydroxide precipitates were anticipated where the product $\alpha_0$ and the free metal ion concentration exceeded the maximum metal ion concentration calculated from the solubility product and pH values. In some instances, particularly with organic ligands, it was not always possible to make predictions since the needed thermodynamic data could not be found in the literature.

Cu(II)-Thiocyanate

While copper(II) was tested with thiocyanate, it was found that an anionic copper(I) complex was formed as a result of the following reactions:

\[
\begin{align*}
2\text{Cu}^{2+} + 2\text{SCN}^- & \rightarrow 2\text{Cu}^+ + (\text{SCN})_2 \uparrow \\
\text{Cu}^+ + \text{SCN}^- & \rightarrow \text{CuSCN} \downarrow \\
\text{CuSCN} \downarrow + \text{SCN}^- & \rightarrow \text{Cu(SCN)}_2^- 
\end{align*}
\]

It is likely that consumption of the thiocyanate ion to form thiocyanogen reduced the thiocyanate ion concentration to a point where there was no longer a sufficient excess of the ligand and consequently some positively charged copper(I) and possibly unreacted copper(II)
remained after reaction.

**Cu(II)-Sulfate**

At pH 5.00 it was anticipated that metal fractions $(\alpha_0 = 0.31, \alpha_1 = 0.64)$ of $\text{Cu}^{2+}$ and $\text{CuSO}_4$ would be found. However only the positively charged species, presumably $\text{Cu}^{2+}$, was found. No plausible explanation can be put forth, other than perhaps the thermodynamic data (temperature, ionic strength, etc.) used for calculation were not applicable to the conditions under which the test was carried out. Further study is indicated.

**Cu(II)-Phosphate**

The phosphate system for copper(II) did not seem to behave as expected, giving a precipitate and a neutral species at pH 8.00 when only a precipitate was anticipated. This was likely due to complex formation, $\text{CuHPO}_4$, with free copper(II) from incomplete precipitation as the hydroxide. At pH 5.02 a neutral species was anticipated but a positive species and a precipitate were observed. The precipitate at this pH should not have been copper(II) hydroxide, but may be a mixed salt of copper(II) and phosphate species such as $\text{Cu}_2(\text{H}_2\text{PO}_4)_2(\text{HPO}_4)$. This could have reduced the phosphate levels too low to produce the anticipated neutral species, $\text{CuHPO}_4$, and there-
fore leave some positively charged uncomplexed copper(II) ion.

**Cu(II)-Catechol**

Catechol, 1,2-dihydroxy benzene, was expected to form a negatively charged complex with copper(II), e.g., Cu(C₆H₄O₂)₂⁻ and possibly a neutral CuC₆H₄O₂ species. However, only a positive and a neutral species were observed. The catechol reagent used was technical grade and its purity may be somewhat questionable. Hence, the free ligand concentration might not have been as large as anticipated thus permitting only the 1:1 complex to form and leaving some excess copper(II) ion.

**Cu(II)-Resorcinol, Hydroquinone, Gallic Acid, and Tannic Acid**

Thermodynamic data for these ligands was not available so predictions could not be made. Since all of the reagents were of technical grade, purity was in question. Based on color changes, it seemed that some complexation was occurring. This was further evidenced by observation of negatively charged species in the case of resorcinol (pH 5.0) and gallic acid (pH 5.0 and 8.0). However, precipitate formation at pH 8.0 in the cases of resorcinol and hydroquinone tends to suggest the organic complex is less stable than copper(II) hydroxide under these
conditions. Due to the complexity of tannic acid (a complex natural substance), it is not possible to even intelligently speculate as to the identity of the species present.

**Fe(II)-Phosphate**

At both pH 5.0 and 8.0, the neutral FeHPO$_4$ was anticipated but precipitates were encountered. The iron(II) hydroxide precipitate was not expected in either instance. Here, as was the case with copper(II), one might consider that some insoluble complex mixed phosphate salt was formed in lieu of the anticipated complex ions.

**Fe(II)-Catechol, Resorcinol, Hydroquinone, Gallic Acid, and Tannic Acid**

As was seen in the case with the copper(II) complexes, thermodynamic data were not available to permit prediction of species. Complexation seems to be occurring in the cases of catechol (pH 8.0), gallic acid, and tannic acid (both at pH 5.0 and 8.0). If complexation was occurring with resorcinol and hydroquinone, positive species were formed. However, in view of the fact that iron(II) hydroxide was observed to form, one might question whether any stable complex was forming at lower pH values and consequently only uncomplexed iron(II) ions
were being observed.

**Iron(III)-Acetate**

Thermodynamic data would suggest the formation of the neutral iron(III)-acetate \( \alpha_3 = 0.61 \), and cationic species \( \text{Fe(C}_2\text{H}_3\text{O}_2)_2^+ \) \( \alpha_2 = 0.25 \), \( \text{Fe(C}_2\text{H}_3\text{O}_2)_2^+ \) \( \alpha_1 = 0.07 \). However, only a positively charged species was observed. Consequently, one must assume the species collected on the SCX cartridge is one or more of the following species: \( \text{Fe}^{3+} \), \( \text{Fe(C}_2\text{H}_3\text{O}_2)_2^+ \), or \( \text{Fe(C}_2\text{H}_3\text{O}_2)_2^+ \). Since there is no reason to suspect the validity of the thermodynamic data, no explanation for the apparent anomaly can be put forth. This is obviously a case for which future study should be considered.

**Iron(III)-Fluoride**

The thermodynamic data available predicts the formation of a neutral \( \text{FeF}_3 \) and a cation complex of \( \text{FeF}_2^+ \) at pH 5.0. However negative and a positive species were observed. One might speculate that the negative species could be a \( \text{FeF}_4^- \) although thermodynamic data for this complex were not found in a search of the common data bases for this type of information. The positively charged species might be \( \text{Fe}^{3+} \), \( \text{FeF}^2+ \), or \( \text{FeF}_2^+ \) with the latter two species more probable. No explanation for the
lack of a neutral FeF$_3$ is immediately obvious. Further study of this system is suggested.

**Iron(III)-Sulfate**

From theoretical considerations one must consider precipitate formation to be the dominant process at both pH 5.0 and 8.0. Precipitate was found at pH 5.0, however, a negatively charged species was found at pH 8.0 with no precipitate. One possible explanation of this might be to consider the possibility of colloid formation with iron(III) hydroxide, a well known phenomenon. Under these conditions, it is reasonable to assume the colloid to be negatively charged and hence not retained by the particulate filter but retained on the SAX cartridge.

**Natural Water Samples**

As described earlier, four lake samples were collected for analysis by the newly developed SPE separation scheme. The sample collection data can be found in Table 8. In addition to the analysis for iron an copper species collected on the different SPE cartridges, pH and total organic carbon (TOC) measurements were made on the samples. Due to the low levels of metals encountered in these samples, inductively coupled plasma (ICP) emission analysis was carried out. The data for these analyses can
be found in Table 9. The four lakes sampled were chosen for their suspected organic content based on initial visual aerial observations. Two were chosen, Howard and Baseline Lakes, on the supposition that they would have low levels of TOC. Brandywine and Goose Lakes were chosen because their dark red coloration which suggested that they likely had high levels of TOC. It was felt that high levels of organic matter would provide possible species to function as ligands for complexation of iron and copper and thus a correlation between TOC and concentration of metal should exist. As can be seen from Table 8, this supposition is borne out by the fact that Goose Lake with the highest TOC, 65.39 mg C/L, contained the highest levels of iron and copper.

**Howard Lake**

Copper levels, while detected, were below the limit of quantitation (0.019 ppm) and thus it was not possible to draw any conclusions regarding the nature of any copper complexes present. Iron, however, was present at levels sufficient to quantitate and it can be seen from the table that approximately 35% of the iron is in a dispersed or suspended form. The bulk of the iron, ca. 45%, was present as a positively charged species while about 10% each was as negatively charged and neutral species.
Baseline Lake

None of the levels of iron or copper in this lake were sufficient to even reach the detection limits of 0.0023 and 0.0057 ppm respectively. The unusually high pH was found to be consistent on two different sampling dates approximately one month apart. This anomalous pH is probably not characteristic of the entire lake since it is a popular sports fishing lake.

Brandywine Lake

Copper was only detected at levels below the quantitation limits thus preventing conclusions from being drawn regarding the nature of the species present. The levels of iron indicated that nearly half the iron present was adsorbed to suspended particulates or other precipitate matter. Approximately 16, 19, and 20 percent of the iron was present as negative, positive, and neutral species respectively.

Goose Lake

The levels of copper again were too low to draw any firm conclusions as to the nature of the soluble copper species. However, it is obvious that the bulk of the copper in this lake tends to be dispersed as particulate matter. Interestingly, the iron levels in this lake were
primarily in the form of soluble species, e.g., negative, positive, and neutral at about 28, 36, and 22 percent respectively with the dispersed iron at only 15%. The very low pH of 4.21 might be playing a significant role in maintaining the iron in soluble forms. There appeared to be no evidence of any fishing in this lake.
### Table 8
Sample Collection Data

<table>
<thead>
<tr>
<th>Sample I.D. No.</th>
<th>Lake</th>
<th>Time:Date</th>
<th>County</th>
<th>Township Coordinates</th>
<th>Site Location</th>
<th>pH</th>
<th>Temp. Degree C</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-1 Baseline</td>
<td>Allegan</td>
<td>1415:6/3/93</td>
<td>Allegan</td>
<td>T.1N;R.13W Sect.32&amp;34</td>
<td>Public Dock</td>
<td>9.43</td>
<td>25.4</td>
<td>Overcast &amp; strong breeze</td>
</tr>
<tr>
<td>BR-1 Brandywine</td>
<td>Van Buren</td>
<td>1500:6/13/93</td>
<td>Van Buren</td>
<td>T.1S;R.13W Sect.29</td>
<td>Public Dock</td>
<td>7.10</td>
<td>26.2</td>
<td>Clear &amp; calm</td>
</tr>
<tr>
<td>GO-2 Goose</td>
<td>St. Joseph</td>
<td>1745:7/30/93</td>
<td>St. Joseph</td>
<td>T.5S;R.11W Sect.3</td>
<td>S. Boat Dock</td>
<td>4.21</td>
<td>24.3</td>
<td>Cloudy &amp; gentle breeze</td>
</tr>
<tr>
<td>HO-1 Howard</td>
<td>Kalamazoo</td>
<td>1845:6/3/93</td>
<td>Kalamazoo</td>
<td>T.4S;R.11W Sect.33&amp;34</td>
<td>SW. Boat Ram</td>
<td>8.25</td>
<td>17.8</td>
<td>Overcast &amp; light breeze</td>
</tr>
<tr>
<td>HO-2 Howard</td>
<td>Kalamazoo</td>
<td>1715:7/30/93</td>
<td>Kalamazoo</td>
<td>T.4S;R.11W Sect.33&amp;34</td>
<td>SW. Boat Ram</td>
<td>8.49</td>
<td>19.2</td>
<td>Clear &amp; calm</td>
</tr>
</tbody>
</table>
Table 9

Results of Metals Determination on Lake Samples

<table>
<thead>
<tr>
<th>Lake</th>
<th>pH</th>
<th>Total Organic Carbon (mg C/L)</th>
<th>Total (ppm)</th>
<th>Particulate (ppm)</th>
<th>SAX (ppm)</th>
<th>SCX (ppm)</th>
<th>LC-CN (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Howard</td>
<td>8.49</td>
<td>12.04</td>
<td>Copper &lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron 0.102</td>
<td>0.0359</td>
<td>0.0104</td>
<td>0.0456</td>
<td>0.0102</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100% 35.2%</td>
<td>100% 10.2%</td>
<td>100% 44.7%</td>
<td>100% 9.99%</td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>9.43</td>
<td>15.08</td>
<td>Copper ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Brandywine</td>
<td>6.85</td>
<td>38.04</td>
<td>Copper &lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron 0.570</td>
<td>0.263</td>
<td>0.0893</td>
<td>0.1068</td>
<td>0.1111</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100% 46.1%</td>
<td>100% 15.7%</td>
<td>100% 18.7%</td>
<td>100% 19.5%</td>
<td></td>
</tr>
<tr>
<td>Goose</td>
<td>4.21</td>
<td>65.39</td>
<td>Copper 0.0211</td>
<td>0.0211</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
<td>&lt;0.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron 0.636</td>
<td>0.0947</td>
<td>0.1761</td>
<td>0.2262</td>
<td>0.1392</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100% 14.9%</td>
<td>100% 27.7%</td>
<td>100% 35.5%</td>
<td>100% 21.9%</td>
<td></td>
</tr>
</tbody>
</table>

ND = Not Detectable

Limit of Detection: Cu = 0.0057 ppm; Fe = 0.0023 ppm
Limit of Quantitation: Cu = 0.019 ppm; Fe = 0.008 ppm
CONCLUSIONS AND RECOMMENDATIONS

The studies with simulated samples employing the SPE separation scheme in the great majority of cases seems to support the original supposition that the data can provide useful information regarding the charges of metals and their complexes in water samples. Further evidence of this can be seen from the studies done on the four lake samples since in the instances where metal concentrations were high enough, one could definitely see that different forms of the metals were present in the samples. Furthermore, not only were metals found in the four defined states (suspended, negative, positive, and neutral), but they were found in different ratios for different lakes. The fact that all four forms were present is not too surprising considering the high levels of TOC present in some of the lakes. Much of the organic matter is likely to be that of humic substances which are quite diverse and complex, providing the potential to react with metal ions and producing a wide variety of complex species of different size and charge.

The results from the lake samples tend to support the proposition that high levels of TOC provide organic species which have the ability to coordinate metal ions.
Further it can be seen that the mobility of iron in waters such as Brandywine Lake is likely to occur through the movement of solids by physical turbulence caused by wind, rapid water flow and man's activities. However, in lakes such as Goose Lake, it appears that the movement of iron is primarily by diffusion and normal water flow. Copper, on the other hand, in this lake would seem to be transported primarily by physical forces creating turbulence.

The next logical extension of this work would be to develop techniques for identifying the potential ligands by analyzing the eluted materials from each of the cartridges. Since most of these ligands are likely to be phenolic substances and carboxylic acids, one approach might be to derivatize them with an appropriate derivatizing agent and then to separate and identify them using the gas chromatography-mass spectrometry (GC-MS) technique. Once the identity of the ligands is known, UV-visible and electrochemical techniques might be used to identify the species in an intact natural sample.
Appendix

Alpha Plots of Metal versus Log [Ligand]
Cu(II)-Chloride Complexes

![Graph showing fraction vs. log [chloride] for Cu(II)-chloride complexes]

- Cu$^{2+}$
- CuCl$^+$
- CuCl$^-$
- CuCl$_2^-$
Cu(I)-Thiocyanate Complexes

![Graph showing the fraction of Cu⁺, Cu(SCN)₂⁻, and CuSCN as a function of log [Thiocyanate].]
Cu(II)-Acetate Complexes

Fraction

Log [Acetate]
Cu(II)-Fluoride Complexes

![Graph showing the fraction of Cu(II) and CuF+ as a function of log [Fluoride].](image)
Cu(II)-Sulfate Complexes

Fraction

Log [Sulfate]
Cu(II)-Carbonate Complexes

- \( \text{Cu}^{2+} \)
- \( \text{CuCO}_3 \)
- \( \text{Cu}(_2\text{CO}_3)^{2-} \)

Fraction vs. Log [Carbonate]
Cu(II)-Monohydrogen Phosphate Complexes

\[ \log [\text{Monohydrogen Phosphate}] \]

Fraction

\( \text{Cu}^{2+} \)  \( \text{CuHPO}_4 \)

Log [Monohydrogen Phosphate]
Cu(II)-Catechol Complexes

![Graph showing Cu(II) and Catechol complexes](image-url)
Copper(II)-Hydroxide Complexes

Fraction

pH

\[ \text{Cu}^{2+} \]

\[ \text{CuOH}^+ \]
Fe(II)-Cyano complexes
(Ferrocyanide)
Fe(II)-Monohydrogen Phosphate Complexes

Fraction

\[ \text{Log [Monohydrogen Phosphate]} \]

\[ \text{Fe}^{2+} \]  \[ \text{FeHPO}_4^- \]
Iron(II)-Catechol Complexes

Fraction

Log [Catechol]
Fe(II)-Hydroxide Complexes

Fraction

pH

Fe$^{2+}$

Fe(OH)$^+$
Iron(III)-Cyano Complexes

Ferricyanide

Fe$^{3+}$

Fe(CN)$_6^{3-}$

Fraction

Log [Cyano]

-9 -8.5 -8 -7.5 -7 -6.5 -6 -5.5 -5
Iron(III)-Acetate Complexes

Fraction

Log [Acetate]
Iron(III)-Fluoride Complexes

![Graph showing the formation of iron(III)-fluoride complexes as a function of log [fluoride]. The graph includes species such as Fe$^{3+}$, FeF$^{2+}$, FeF$_3$, and FeF$_2^+$.](image-url)
Iron(III)-Sulfate Complexes

\[ \text{Fraction} \]

\[ \text{Log [Sulfate]} \]

\[ \text{Fe}^{3+} \]

\[ \text{Fe}(\text{SO}_4)^{2-} \]

\[ \text{FeSO}_4^+ \]
Iron(III)-Hydroxide Complexes

Fraction

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

pH

0 2 4 6 8 10 12 14

Fe(OH)$_2^+$

Fe$^{3+}$

Fe(OH)$_2^+$

Fe(OH)$_3^+$
REFERENCES


