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# Copper(II) Titration of Fulvic Acid Ligand Sites with Theoretical, Potentiometric, and Spectrophotometric Analysis

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**The Cu(II) titration of a fulvic acid (acid soluble soil organic fraction) is characterized by ion-selective electrode monitoring of Cu(II) and spectrophotometric monitoring of changes in the fulvic acid chromophores. The results indicate the need to recognize the polydisperse mixture character of these naturally occurring organic ligands. The theory of polyelectrolyte titration is developed to provide a common and complete description of both experiments. The titration functions emphasize the stronger binding of Cu(II) by the first sites occupied. Naturally occurring ligands are not homogeneous even after "purification".**

Recently, the titration of the mixed organic ligands occurring in natural systems with metal ions has received considerable attention. Notable examples include studies important to agriculture, natural waters, geochemical prospecting, and environmental problems (1-4). In past studies, ligands are treated according to standard methods developed for simple ligands. Since natural ligands are almost surely mixtures and are related to polymeric and colloidal organic materials (5), it seems useful to explore extensions of the theory of titrations of polymeric ligand materials specifically derived from natural sources. They can model the more complicated mixtures in soils, streams, and lakes. Humic materials such as fulvic acid are prime candidates. However, the irregular structure and mixture of components present even in a purified fulvic sample complicate the treatment of chemical and physical properties (4, 6-9). Because of this, a diverse range of experimental methods has been employed in the investigations of fulvic acid-metal ion complexing and chelation and related behavior of organic fractions of natural waters. These have included cation-exchange equilibration (2, 10), potentiometric measurements with pH glass electrodes and specific ion electrodes (10-14), water proton NMR with paramagnetic ions, and electron spin resonance spectrometry (13, 15, 16).

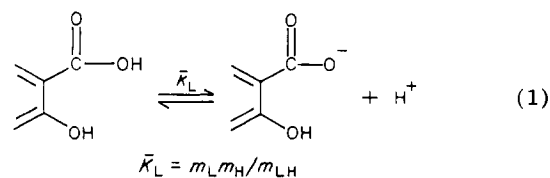
Some important work by Weber and co-workers has recently shown experimentally that the complex chemical properties of fulvic acid referred to above are manifest in the metal ion complexing equilibria (13, 14). This may contain a clue to an alternate explanation of the odd stoichiometries that have been claimed for complexes of ligands present in natural waters (1). The equilibrium functions were very clearly shown to depend on the composition of the experimental solutions. This suggests a need for reexamination and extension of the previously developed theoretical description of the fulvic acid-metal ion complexing problem (2, 3, 10, 12, 15-18). It is required not only to accommodate Weber's experimental results but also as a guide to proper exploitation of such experimental methods as UV-visible absorbance, fluorescence spectrometry, and light scattering and to provide a basis for

interpretation of titrations of natural waters. Note that the usefulness of a theoretical description depends partly on the practical calculations that may be done with it.

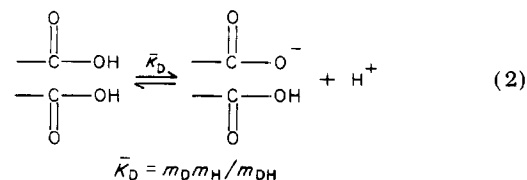
This work consists of an investigation of fulvic acid-Cu(II) complexing by specific ion electrode and photometric absorbance, in preparation for future work with fluorescence and light scattering methods. In accordance with these requirements, the objectives of this work are: (1) to expand and explain the theoretical description of the fulvic acid-divalent metal ion complexing system, and to consider in detail two special cases that appear in the literature; (2) to correlate photometric absorbance measurements with detailed Cu(II) complexing data obtained potentiometrically with pH glass and specific ion electrodes; (3) to demonstrate useful, convenient calculation procedures for the fulvic acid-Cu(II) complexing or chelation equilibria.

## THEORY

**General Formulation of the Problem.** *The Weighted Average and Differential Equilibrium Functions.* The important functional groups are assumed to be carboxyl and phenolic OH's. If the most general postulate is adopted, then at least two types of bidentate chelating sites must be considered to be possible. These are the salicylic type and the dicarboxylic type. The salicylic type is expected to react preferentially with  $\text{Cu}^{2+}$ , forming more stable chelates. Both types are freed by a first stage of  $\text{H}^+$  dissociation:



where  $m$  designates the molal concentration of the species indicated by the subscript (L = deprotonated ligand, H = proton, LH = protonated ligand), and



where D = dicarboxylate sites.

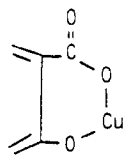
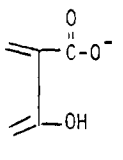
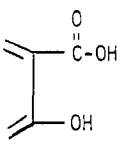
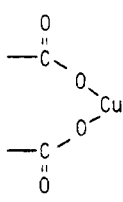
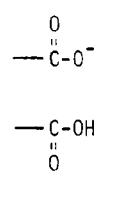
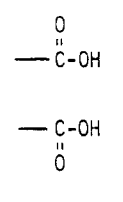
At least three classes of the dicarboxylic sites described formally by the Equations 2 must be considered as possible. These are: (a) the ortho dicarboxylic structure in Figure 1; (b) two carboxyls on the same polymer molecule, but not on the same ring; (c) two carboxyls on different polymer molecules. In this third case, this bridging of Cu(II) between two fulvic acid molecules may contribute to coagulation.

Usually, it is not experimentally practical to investigate separately metal ion chelation by the two types of sites. In-

Table I

Bidentate Chelation of Metal Ions M(II) by Fulvic Acid: Postulated General Case.

$$\text{SH}^- + \text{M}^{++} \rightleftharpoons \text{SM} + \text{H}^+$$

Type of chelation site	Chemical Form of Chelation Site					
	chelate		chelation site, singly ionized		chelation site, fully protonated	
	symbol	structure	symbol	structure	symbol	structure
salicylic	LM		LH <sup>-</sup>		LH <sub>2</sub> <sup>-</sup>	
dicarboxylic	DM		DH <sup>-</sup>		DH <sub>2</sub>	
total, (salicylic + dicarboxylic)	SM	both of the above structures	SH <sup>-</sup>	both of the above structures	SH <sub>2</sub>	both of the above structures

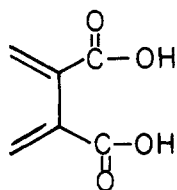
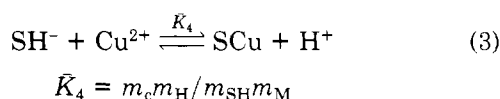


Figure 1. o-Dicarboxylic class of bidentate chelation sites

stead, it is more useful to examine them together as indicated by Table I and Equation 3;

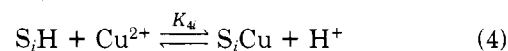


where the subscript, c, denotes complex.

There are two reasons why the bidentate chelating sites in Equation 3 must be assumed to be a mixture of sites. The first is that Table I and Equation 3 formally define a mixture of two generic types. The second reason is that fulvic acid probably has a sufficiently irregular structure so that no two of its functional groups may be assumed to be entirely chemically identical. By definition then, the equilibrium function  $\bar{K}_4$  is obtained by applying the law of mass action formally to a mixture of chelating sites. Experimentally,  $\bar{K}_4$  is measured macroscopically on the whole mixture. Not only can it not be a thermodynamic equilibrium constant, apart from the matter of activity coefficients, it cannot be any kind of real constant. In fact, it is a variable, a function of the composition of the chelation solution.

The general properties of this equilibrium function  $\bar{K}_4$  can be rigorously deduced theoretically. Essentially, this is done by relating  $\bar{K}_4$  to the properties of the components of the mixture of chelation sites. Consider the chelation equilibrium

of the  $i$ th small component of the natural polydisperse polymer called fulvic acid; we write:



$$K_{4i} = \frac{m_{ci} m_H}{m_{\text{S}_i\text{H}} m_M}$$

Simultaneously, the concentrations of total chelate and of total free sites are related to those of the components by the material balance equations,

$$m_c = \sum_{i=0}^n m_{ci} \quad (5a)$$

$$m_{\text{SH}} = \sum_{i=0}^n m_{\text{S}_i\text{H}} \quad (5b)$$

Introducing these material balance relations for the mixture into the equation for  $\bar{K}_4$  gives

$$\bar{K}_4 = \frac{m_H \sum_{i=0}^n m_{ci}}{m_M \sum_{i=0}^n m_{\text{S}_i\text{H}}} = \frac{\sum_{i=0}^n \left( \frac{m_H}{m_M} \right) m_{ci}}{\sum_{i=0}^n m_{\text{S}_i\text{H}}} \quad (6)$$

From Equation 4,

$$\left( \frac{m_H}{m_M} \right) m_{ci} = K_{4i} m_{\text{S}_i\text{H}} \quad (7)$$

Substituting this into Equation 6,

$$\bar{K}_4 = \frac{\sum_{i=0}^n K_{4i} m_{\text{S}_i\text{H}}}{\sum_{i=0}^n m_{\text{S}_i\text{H}}} \quad (8)$$

Equation 8 is an important result and should be examined carefully. It provides important insight into the chemical meaning of  $\bar{K}_4$ , the equilibrium function which is measured experimentally for the whole mixture. The points to note are: (1)  $\bar{K}_4$  is directly related to the chelation equilibrium functions,  $K_{4i}$ , of all of the components. (2)  $\bar{K}_4$  is seen to be a weighted average of the  $K_{4i}$  values of all of the components. (3) The factors  $m_{S,H}$  are the statistical weighting factors of the average,  $\bar{K}_4$ . (4)  $\bar{K}_4$  cannot in any sense be regarded as a constant. Indeed, no corresponding thermodynamic equilibrium constant exists to which it can be related by means of activity coefficients. Instead, it is a variable. This variable is a function of the composition of the sample solution. (5) The dependence of  $\bar{K}_4$  on the composition of the sample solution provides a valuable means of characterizing the chemical properties of the system.

Equation 8 must now be further transformed for the purpose of examining the properties of  $\bar{K}_4$ , and for practical calculations. The material balance for the total chelating sites as listed in Table I is

$$c_S = m_c + m_{SH} + m_{SH_2} \quad (9)$$

Mole fractions of chelated, free, and protonated chelation sites are,

$$\chi_c = m_c/c_S \quad (10a)$$

$$\chi_{SH} = m_{SH}/c_S \quad (10b)$$

$$\chi_{SH_2} = m_{SH_2}/c_S \quad (10c)$$

Then from Equation 9,

$$\chi_c + \chi_{SH} + \chi_{SH_2} = 1 \quad (11)$$

Analogous relationships exist for the  $i$ th small component. In particular, Equation 12 defines the mole fraction of free  $i$ th component chelation sites, in the whole mixture;

$$(\Delta\chi_{SH})_i = m_{S,H}/c_S \quad (12)$$

Introducing  $c_S$  into Equation 8 via recognition that  $\sum m_{S,H} = m_{SH}$  gives

$$\bar{K}_4 = \frac{c_S}{m_{SH}} \sum_{i=0}^n K_{4i} \frac{m_{S,H}}{c_S} \quad (13a)$$

$$\bar{K}_4 = \frac{1}{\chi_{SH}} \sum_{i=0}^n K_{4i} (\Delta\chi_{SH})_i \quad (13b)$$

Fulvic acid may also behave as a polyelectrolyte. To account for its electrostatic binding of cations, Bjerrum's electrostatic factor is introduced. Because each component of the mixture will generally behave differently, it has its own separate Bjerrum electrostatic factor. For the  $i$ th component, this is

$$K_{4i} = K_{4i}^0 e^{-(\Delta G_i^e/RT)} \quad (14)$$

$$\therefore \bar{K}_4 = \frac{1}{\chi_{SH}} \sum_{i=0}^n K_{4i}^0 e^{-\Delta G_i^e/RT} (\Delta\chi_{SH})_i \quad (15)$$

An examination of Equation 15 leads to the conclusion that there are three reasons why  $\bar{K}_4$  is expected to accurately approximate a continuous function of  $\chi_{SH}$ : (a) The coefficient,  $1/\chi_{SH}$ ; (b) Large numbers of individual  $K_{4i}^0$  functions will be too similar for separate titration equivalence points to be observed experimentally; (c) The electrostatic Gibbs energy terms,  $\Delta G_i^e$ , will be increasing functions of the amount of electrostatic charge on the polymer molecules and aggregates. The existence of electric charge requires that carboxyl groups be free from both  $H^+$  and  $Cu^{2+}$ . That is,

$$\Delta G_i^e = f_i^e(\chi_{SH}) \quad (16)$$

One therefore has the continuous function

$$\bar{K}_4 = \bar{K}_4(\chi_{SH}) \quad (17)$$

Because  $\bar{K}_4$  approximates a continuous function, the summation of Equation 15 may be replaced by an integration:

$$\bar{K}_4 = \frac{1}{\chi_{SH}} \int_0^{\chi_{SH}} K_4 d\chi_{SH} = \frac{1}{\chi_{SH}} \int_0^{\chi_{SH}} K_4^0 e^{-\Delta G^e/RT} d\chi_{SH} \quad (18)$$

There are two important aspects of this equation to consider. The first is the chemical meaning of  $K_4$ . The other is the dependence of the weighted average function  $\bar{K}_4$  on the composition of the sample solution.

Equation 18 is now further transformed so that these two aspects may be examined. Rearranging,

$$\chi_{SH} \bar{K}_4 = \int_0^{\chi_{SH}} K_4 d\chi_{SH}$$

Differentiating this gives an equation for  $K_4$  in terms of the experimental quantity  $\bar{K}_4$ :

$$K_4 = \frac{d(\chi_{SH} \bar{K}_4)}{d\chi_{SH}} \quad (19)$$

The multitudes of  $K_{4i}^0$  and  $\Delta G_i^e$  functions in the summation of Equation 15 have been replaced by the corresponding continuous functions of Equation 18. These variables,  $K_4^0$  and  $\Delta G^e$ , must both be functions of  $\chi_{SH}$ . One reason for this is that they both "scan" across the components of the mixture as  $\chi_{SH}$  changes in value. The other reason in the case of  $\Delta G^e$  is that the electrostatic term generally increases with increasing ionization. The results are, therefore,

$$\Delta G^e = f^e(\chi_{SH}) \quad (20a)$$

$$K_4^0 = f_4^0(\chi_{SH}) \quad (20b)$$

$$K_4 = K_4(\chi_{SH}) \quad (20c)$$

It is clearly seen in Equations 18 and 19 that  $K_4$  is defined as a differential function;

$$K_4 = K_4^0 e^{-\Delta G^e/RT} \quad (21a)$$

$$K_4 = \frac{\delta m_c m_H}{\delta m_{SH} m_M} \quad (21b)$$

$K_4$  has both theoretical and practical importance and should be noted with care. In particular, its chemical meaning is that it is a differential equilibrium function defined by Equation 21, for an infinitesimal portion of the mixture of chelating sites. The quantities  $\delta m_c$  and  $\delta m_{SH}$  are the equilibrium concentrations of the chelated and free chelating sites of this infinitesimal portion of the mixture. The differential equilibrium function  $K_4$  and the weighted average equilibrium function  $\bar{K}_4$  therefore have fundamentally different chemical meanings. Their practical properties will also usually be quite different.

*Composition Dependence of the Equilibrium, and State Functions.* The second question about Equation 18 will now be examined. The first point about the effects of solution composition is that  $\bar{K}_4$  can be expected to show some sort of dependence on fulvic acid concentration. Saar and Weber have recently demonstrated experimentally a concentration dependence for the  $Cd^{2+}$ -fulvic acid equilibrium function (14). They suspect that conformational changes may be responsible but a specific mechanism is not required. Earlier, it had been shown both theoretically and experimentally that the acid dissociation  $\bar{K}$  of fulvic is concentration dependent (9). This is a precisely parallel phenomenon. In addition to total fulvic acid concentration, the composition of the solution is described by the mole fractions, in Equation 11. From it we get

$$\chi_{SH} = 1 - \chi_c - \chi_{SH_2} \quad (22a)$$

$$d\chi_{SH} = d\chi_c - d\chi_{SH_2} \quad (22b)$$

It is now seen from this discussion and the Equations 22 that Equation 17 does not describe a state function. Instead, Equation 23 shows that three independent variables are required for describing the total dependence of  $\bar{K}_4$  on the composition of the solution:

$$\bar{K}_4 = \bar{f}_4(\chi_c, \chi_{SH_2}, c_S) \quad (23)$$

The concentration of total chelation sites is taken here as the most convenient means of describing the total fulvic acid concentration.

The effects of concentration on  $\bar{K}_4$  are sufficiently important to warrant a complete theoretical discussion. This is a substantial task, however, and is outside the scope of the present work. Instead, constant concentration systems will be discussed here. With this restriction, Equations 22 are substituted into Equation 19.

$$K_4 = \frac{d[(1 - \chi_c - \chi_{SH_2})\bar{K}_4]}{-(d\chi_c + d\chi_{SH_2})} \quad (24)$$

$$d[(1 - \chi_c - \chi_{SH_2})\bar{K}_4] = -K_4 d\chi_c + K_4 d\chi_{SH_2} \quad (25)$$

This is now integrated, recognizing that  $\bar{K}_4$  does not exist at  $\chi_c = 0$ ;

$$(1 - \chi_c - \chi_{SH_2})\bar{K}_4 = -\int_0^{\chi_c} K_4 d\chi_c - \int_0^{\chi_{SH_2}} K_4 d\chi_{SH_2} \quad (26)$$

Rearranging this,

$$\bar{K}_4 = -\frac{1}{(1 - \chi_c - \chi_{SH_2})} \int_0^{\chi_c} K_4 d\chi_c - \frac{1}{(1 - \chi_c - \chi_{SH_2})} \int_0^{\chi_{SH_2}} K_4 d\chi_{SH_2} \quad (27)$$

At constant temperature and constant fulvic acid concentration, Equation 27 is the basic working equation describing the  $\text{Cu}^{2+}$ -fulvic acid chelation equilibrium.  $\bar{K}_4$  is now seen to depend on two independent variables. The two variables used in Equation 27 for specifying  $\bar{K}_4$  were chosen not only for convenience but also because they are chemically the most interesting. It is now obvious that the integral of Equation 18 is not a state function. That is, its numerical value will depend on the pathway by which  $\bar{K}_4$  gets from 0 to  $\chi_{SH}$ .

It will be recalled that the two independent variables of Equation 27 are both mole fractions. These are  $\chi_c$ , the mole fraction of the bidentate sites occupied by  $\text{Cu(II)}$ , and  $\chi_{SH_2}$ , the mole fraction of sites occupied by two protons. They are emphasized again here because they are of experimental interest. By taking one of these variables as an experimental constant, the system may be characterized by scanning across the mixture experimentally with the other. In principle, either  $\chi_c$  or  $\chi_{SH_2}$  may be taken as the parameter of a family of experimental curves. The differential equilibrium function  $K_4$  is more interesting than the weighted average  $\bar{K}_4$  for these purposes, first because it reveals chemical detail more distinctly. This is because the averaging process always tends to obscure detailed structure. Another important reason is that  $\bar{K}_4$ , being measured for a mixture, is not related in any simple or conventional way to a Gibbs standard energy. Unlike the concentration quotient for an equilibrium system of pure reagent species, it cannot be related to a thermodynamic equilibrium constant by means of activity coefficients. The differential equilibrium function  $K_4$  has an important advantage in this respect. Because an infinitesimally small portion of a continuous mixture has the attributes of a single chemical species,  $K_4$  may be related to a thermodynamic equilibrium constant in the conventional way. With complete rigor we may therefore write,

$$K_4 = K_4 \frac{\gamma_c \gamma_H}{\gamma_{SH} \gamma_M} \quad (28a)$$

$$\Delta G^\circ_4 = -RT \ln K_4 = -RT \ln K_4 - RT \ln \frac{\gamma_c \gamma_H}{\gamma_{SH} \gamma_M} \quad (28b)$$

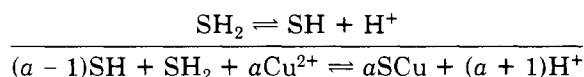
In most practical cases, there will be no activity coefficient data available. When this precludes the calculation of  $\Delta F^\circ_4$ , the closely related expression in Equation 29 will be very useful:

$$RT \ln K_4 = -(\Delta G^\circ_4 + RT \ln \Gamma_4) \quad (29a)$$

$$\Gamma_4 = \frac{\gamma_c \gamma_H}{\gamma_{SH} \gamma_M} \quad (29b)$$

For dilute solutions such as soil solutions or fresh waters,  $\Gamma_4$  is expected to differ little from unity.

*The Effects of Equilibrium Shifts on the Distribution of Complexing Sites among Species.* At equilibrium, the bidentate complexing sites are distributed among the chemical species SH, SCu, and  $\text{SH}_2$ . A shift in the complexing equilibrium will generally change the concentrations of all of these. This can be formally represented by Equations 30.



By differentiating the mole fraction Equation 11, one gets,

$$\frac{d\chi_c}{d\chi_{SH_2}} + \frac{d\chi_{SH}}{d\chi_{SH_2}} = -1 \quad (31)$$

This equation may be used for describing the manner in which the distribution of bidentate sites among species will change with shifts in the complexing equilibrium. From Equations 30 one may construct the following sum;

$$\begin{array}{rcl} \frac{d\chi_c}{d\chi_{SH_2}} & = & -a \\ \frac{d\chi_{SH}}{d\chi_{SH_2}} & = & +(a-1) \\ \hline \text{total} & = & -1 \end{array} \quad (32)$$

According to this scheme, the relative changes in the concentrations of the species SH and  $\text{SH}_2$  during a change in the concentration of the complex SCu, may be calculated from simple mole fraction plots. The chemical meaning of these derivatives should be noted,  $d\chi_c/d\chi_{SH_2}$  and  $d\chi_{SH}/d\chi_{SH_2}$  measure the rates at which  $\text{Cu(II)}$  complex or chelate and free bidentate sites are used up as  $\text{SH}_2$  sites react.

*Variable Loading of Chelation Sites with Cu(II) and Constant Mole Fraction Protonation.* With  $\chi_{SH_2}$  experimentally held constant,  $\chi_{SH_2} = \chi'_{SH_2}$ , then the general working Equation 27 reduces to a simpler form:

$$\bar{K}_4 = \bar{f}_4(\chi_c, \chi'_{SH_2}) \quad (33a)$$

$$\bar{K}_4 = -\frac{1}{(1 - \chi_c - \chi'_{SH_2})} \int_0^{\chi_c} K_4 d\chi_c \quad (33b)$$

Note that the constant  $\chi'_{SH_2}$  may now be used as the parameter of a family of experimental curves. Equation 33 is readily solved for  $K_4$ .

$$\int_0^{\chi_c} K_4 d\chi_c = -(1 - \chi_c - \chi'_{SH_2})\bar{K}_4 \quad (34)$$

$$K_4 = -\frac{d[(1 - \chi_c - \chi'_{SH_2})\bar{K}_4]}{d\chi_c} \quad (35)$$

$$K_4 = f_4(\chi_c, \chi'_{SH_2}) \quad (36)$$

Assuming the activity coefficients to have relatively unimportant effects, it follows approximately that:

$$\Delta G^\circ_4 \approx \Delta G^\circ_4(\chi_c, \chi'_{SH}) \quad (37)$$

The mixture of chelation sites may therefore be characterized in detail with experimental scans of both  $K_4$  and the expression of Equation 29.

*Variable Protonation of Chelation Sites Obtained with Very Small Constant Loading with Cu(II).* In most geochemical systems such as soil solutions of surface waters, Cu(II) is present only at the trace level. In such a case, the properties of the Cu(II) fulvic system will be dominated by  $H^+$  instead of by Cu(II). The relevant method of characterizing the system is therefore to scan across the mixture of sites with variable protonation, at constant trace level of Cu(II) loading. That is, it is assumed that

$$\chi_c \approx \text{constant}; d\chi_c \approx 0 \quad (38a)$$

$$\chi_c \ll \chi_{SH_2}; (1 - \chi_c - \chi_{SH_2}) \approx (1 - \chi_{SH_2}) \quad (38b)$$

The working Equation 27 then reduces to,

$$\bar{K}_4 = -\frac{1}{(1 - \chi_{SH_2})} \int_0^{\chi_{SH_2}} K_4 d\chi_{SH_2} \quad (39)$$

Because Equation 39 now presents the problem in acid dissociation form, it is convenient to introduce  $\alpha_i$ , the familiar degree of ionization for the carboxyl group in the salicylic type structure of Table I. This requires the postulate that with trace Cu(II) loading, the salicylic type sites are preferentially occupied. From Equation 11, we have

$$\begin{aligned} \chi_{SH} &= (1 - \chi_c - \chi_{SH_2}) \\ &\approx (1 - \chi_{SH_2}) \end{aligned} \quad (40)$$

$$d\chi_{SH} = -d\chi_{SH_2}$$

Equation 33 now becomes,

$$\bar{K}_4 = \frac{1}{\chi_{SH}} \int_0^{\chi_{SH}} K_4 d\chi_{SH} \quad (41)$$

By definition,

$$\chi_{SH} = \frac{m_{LH}}{c_s} \quad (42a)$$

$$\alpha_1 = \frac{m_{LH}}{c_L} \quad (42b)$$

Let  $m_{SH} = Bm_{LH}$ , where  $B$  is simply the fraction of ionized carboxyl groups belonging to the salicylic type sites in Table I.

Then,  $m_{SH} = Bc_L\alpha_1$

$$\chi_{SH} = \frac{Bc_L}{c_s} \alpha_1 \quad (43a)$$

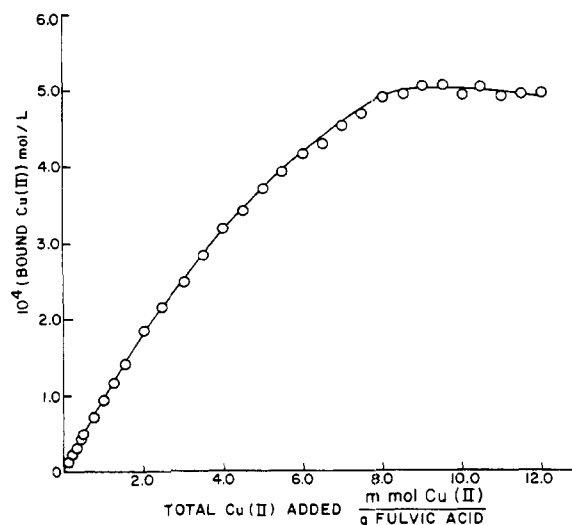
$$d\chi_{SH} = \frac{Bc_L}{c_s} d\alpha_1 \quad (43b)$$

Substituting into Equation 42 therefore gives the required result in Equations 44 and 45.

$$\bar{K}_4 = \frac{1}{\alpha_1} \int_0^{\alpha_1} K_4 d\alpha_1 \quad (44)$$

$$K_4 = \frac{d(\alpha_1 \bar{K}_4)}{d\alpha_1} \quad (45)$$

Equations 44 and 45 were first presented by Gamble, Schnitzer, and Hoffman, who were concerned with the applied



**Figure 2.** Titration of fulvic acid with Cu(II) at 25.0 °C. Determination of bound Cu(II) and the total chelation capacity of the fulvic acid

problem of trace Cu(II) in soil solutions (10). This geochemical system may be characterized simply by an experimental plot of

$$K_4 = f_4(\alpha_1, \chi'_c) \quad (46)$$

where  $\chi'_c$  is the constant, low Cu(II) loading of the salicylic type sites. It should be noted that in the original work by Gamble et al., the ion exchange method employed for chelation measurements was not fully successful in fulfilling the experimental requirement of very low loading of the sites by Cu(II). It should now be possible to avoid this experimental problem, because of the specific ion electrodes that are now commercially available.

## EXPERIMENTAL

**Chemical Materials** The fulvic acid was the previously described Armadale Bh horizon material prepared according to the literature (7, 8, 19, 20). Water was redistilled under  $N_2$ , and other chemicals were all of reagent grade.

**Equipment.** Potentiometric measurements were made using an Orion model 701 Digital Ionanalyzer meter using a Beckman #41263 glass electrode, an Orion model 94-29A cupric ion selective electrode, and a Fisher #13-639 KCl reference electrode. Fisher Scientific pH 3, pH 7, standard buffers were used for the glass electrode measurements. The error in the cupric ion electrode was  $\pm 2$  mV.

Visible absorption spectra were obtained between 650 and 350 nm on a Cary 14 recording spectrophotometer; 1-cm quartz sample cells were used. The absorbance curves had biases of 3%, but the shapes were reproducible with scatter of about  $\pm 0.3\%$ .

**Experimental Samples.** Sample solutions contained 0.1000 g fulvic acid/L; 100.0 mL aliquots of these were used for titrations.

## RESULTS AND DISCUSSION

The functional group analyses reported by Schnitzer et al. for Armadale BH horizon fulvic acid include a phenolic OH value of 3.0 mmol/g fulvic acid (2, 6). The total number of carboxyl groups determined by potentiometric titration is 7.71 mmol/g fulvic acid (2, 7, 8). The bidentate complexing capacity postulated according to Table I is therefore approximately 5.4 mmol/g fulvic acid. The potentiometric Cu(II) titration curve in Figure 2 has a plateau indicating a bidentate Cu(II) complexing capacity of 5.43 mmol/g fulvic acid, when corrected for dilution effects. This is in satisfactory agreement with the former value.

Bidentate Cu(II) complexing equilibrium results calculated from the Cu(II) titration curve are given in Table II. The first two columns give  $H^+$  molality estimated from pH measurements and total Cu(II) added by titration. Three mole

Table II. Cu(II)-Fulvic Acid Chelation Equilibrium at 25.0 °C, No Background Electrolyte

mmol Cu(II) g fulvic acid	$m_H$	$\bar{K}_4 \pm 10\%$	$\chi_{SH}$	$\chi_c$	$\chi_{SH_2}$
0.100	$1.84 \times 10^{-4}$	$1.54 \times 10^3$	0.609	$1.81 \times 10^{-2}$	0.373
0.200	$1.94 \times 10^{-4}$	$3.93 \times 10^2$	0.592	$3.63 \times 10^{-2}$	0.372
0.300	$2.01 \times 10^{-4}$	$1.97 \times 10^2$	0.576	$5.40 \times 10^{-2}$	0.370
0.400	$2.06 \times 10^{-4}$	97.6	0.560	$7.17 \times 10^{-2}$	0.369
0.500	$2.14 \times 10^{-4}$	66.9	0.545	$8.96 \times 10^{-2}$	0.365
0.750	$2.24 \times 10^{-4}$	34.6	0.517	0.132	0.350
1.000	$2.34 \times 10^{-4}$	24.7	0.488	0.175	0.337
1.250	$2.43 \times 10^{-4}$	18.2	0.462	0.214	0.324
1.500	$2.51 \times 10^{-4}$	15.8	0.435	0.256	0.309
2.000	$2.63 \times 10^{-4}$	12.5	0.388	0.328	0.284
2.500	$2.69 \times 10^{-4}$	11.4	0.345	0.400	0.255
3.000	$2.75 \times 10^{-4}$	10.3	0.307	0.466	0.228
3.500	$2.82 \times 10^{-4}$	10.4	0.268	0.532	0.201
4.000	$2.88 \times 10^{-4}$	11.5	0.228	0.600	0.172
4.500	$2.95 \times 10^{-4}$	11.1	0.198	0.650	0.152
5.000	$2.95 \times 10^{-4}$	8.96	0.166	0.706	0.128
5.500	$3.02 \times 10^{-4}$	12.6	0.139	0.754	0.107
6.000	$3.06 \times 10^{-4}$	15.0	0.111	0.802	0.0861

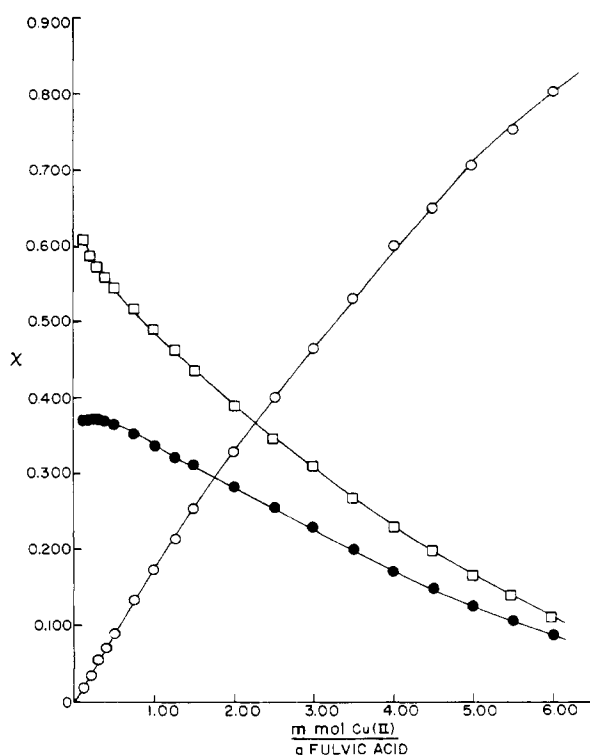


Figure 3. Mole fractions of un-ionized, ionized, and complexed chelation sites. (●)  $\chi_{SH_2}$  = mole fraction of un-ionized bidentate chelation sites. (□)  $\chi_{SH}$  = mole fraction of bidentate chelation sites free from 1st proton and from Cu(II). (○)  $\chi_c$  = mole fraction of bidentate sites occupied by chelated Cu(II).

fractions,  $\chi$ , are listed for the purpose of describing the composition of the system. Together with temperature and fulvic acid concentration, any two of the three mole fractions will totally specify the sample composition. According to Equation 27, the most useful choice for this purpose is the use of  $\chi_c$  and  $\chi_{SH_2}$ . That is, the composition of the experimental sample is specified in terms of bidentate sites occupied by Cu(II) and by two protons.  $H^+$  concentration is of course required operationally for experimental control, even though Equation 27 does not use it for specifying the sample composition. The behavior of the three mole fractions during the Cu(II) titration is shown in Figure 3.  $\chi_{SH}$  and  $\chi_{SH_2}$  are seen to decrease differently with increasing  $\chi_c$ .

With Cu(II) loadings from  $\chi_c = 1.8 \times 10^{-2}$  to  $\chi_c = 0.8$ , the  $\bar{K}_4$  values in Table II and Figure 4 decrease by two orders of

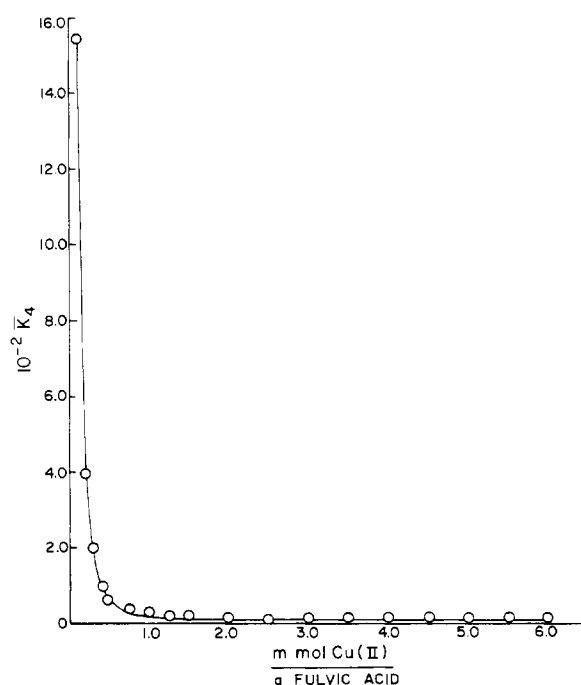
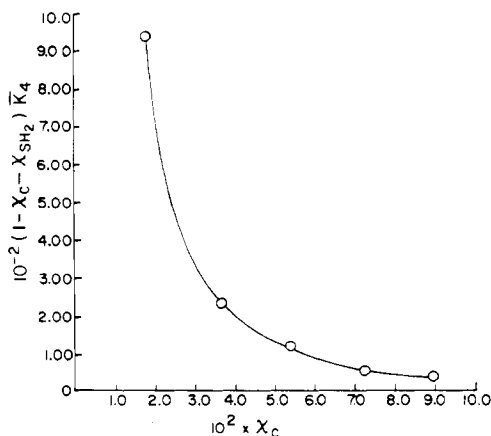


Figure 4.  $\bar{K}_4$ , the weighted average mass action quotient for Cu(II)-fulvic acid chelation equilibrium

magnitude.  $\bar{K}_4$  determinations previously reported by Gamble et al. for approximately the same fulvic acid concentration fall almost completely within this range (2, 10). The earlier results were calculated according to Equations 39 to 45 for the low loading-variable protonation experiment, however. An exact comparison would therefore require some additional calculations. It seems evident nonetheless, that the two sets of results are mutually consistent.

Two types of  $K_4$  calculations are now seen theoretically to be possible, and each is expected to have its own uses. Both use constant temperature and fulvic acid concentration. The first of these calculations uses Equations 35 and 36 to calculate  $K_4$  as a state function having constant  $\chi_{SH_2}$ . That is, protonation is constant while Cu(II) loading varies. The practical importance of this calculation is that it makes possible the direct, rigorous comparison of experimental results produced in different laboratories or with different fulvic acid samples. Although some examples may require computer techniques, a quick, simple calculation procedure can be demonstrated. (The only requirements are graph paper and a pocket calcu-



**Figure 5.** Calculation of  $K_4$ , the differential equilibrium function for Cu(II)-fulvic acid chelation. State function  $K_4 = K_4(x_c)$ , at  $x_{SH_2} \approx 0.37$  and  $T = 25.0^\circ\text{C}$

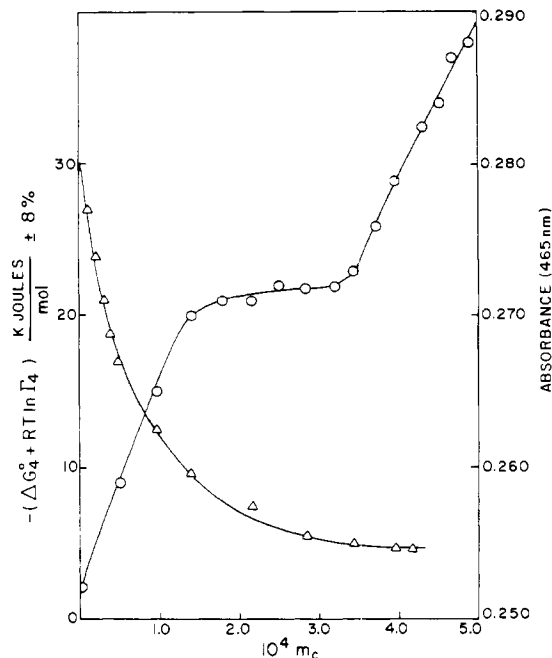
**Table III.** Calculation of  $K_4$ , the Differential Equilibrium  $x_{SH_2} \approx 0.37$ , Function for Cu(II)-Fulvic Acid Chelation<sup>a</sup>

$\bar{K}_4$	$K_4$	$-(\Delta G^\circ_4 + RT \ln \Gamma_4)$ (kJ/mol)	$x_c$
$1.53 \times 10^3$	$5.90 \times 10^4$	27.3	0.0181
$3.92 \times 10^2$	$1.39 \times 10^4$	23.6	0.0363
$1.97 \times 10^2$	$4.30 \times 10^3$	20.7	0.0540
97.8	$1.80 \times 10^3$	18.6	0.0717
67.5	$7.00 \times 10^2$	16.2	0.0896

<sup>a</sup>  $T = 25.0^\circ\text{C}$ .

lator.) Recalling that  $x_{SH} = (1 - x_c - x_{SH_2})$ , one simply plots the product  $x_{SH}\bar{K}_4$  against  $x_c$ , as in Figure 5. Graphical differentiation directly gives  $-K_4$  as a function of  $x_c$ , for a given constant  $x_{SH_2}$ . For example, it is seen in Figure 3 that in the first part of the Cu(II) titration, up to 0.5 (mmol/g fulvic acid) of total added Cu(II),  $x_{SH_2}$  is approximately constant at  $x_{SH_2} \approx 0.37$ . This is the parameter for the curve in Figure 5. The resulting state functions  $\bar{K}_4(x_c, 0.37)$  and  $K_4(x_c, 0.37)$  are compared in Table III.  $K_4$  is found in this case to be 10 to 40 times greater than  $\bar{K}_4$ . Qualitatively, this result is theoretically anticipated for low Cu(II) loadings. It also emphasizes that the theoretical distinction between  $K_4$  and  $\bar{K}_4$  is not a trivial one. The difference is practical as well as fundamental. Only  $K_4$  may properly be used for the calculation of thermodynamic functions or for comparison with the stability constants of chelates having monomeric ligands.

The second type of  $K_4$  calculation does not produce a state function for the direct comparison of different samples. Instead, it uses Equations 17, 19, and 20 for the calculation of  $K_4$  along the path followed by a particular experiment. This permits  $K_4(x_{SH})$  or  $\Delta G^\circ_4(x_{SH})$  to be compared or correlated with measurements of the same experiment with a different probe. In this case, a quick calculation of  $K_4$  may be made by graphical differentiation of a simple plot of  $x_{SH}\bar{K}_4$  against  $x_{SH}$ . Neither  $x_c$  nor  $x_{SH_2}$  is held constant. Figure 6 demonstrates the use of this calculation, for the comparison of



**Figure 6.** Dependence of Gibbs free energy for complexation and absorbance at 465 nm on the molarity of complexed Cu(II)

$-(\Delta G^\circ_4(x_{SH}) + RT \ln \Gamma_4)$  with photometric absorbance readings at 465 nm.

The standard Gibbs energy and photometric absorbance curves in Figure 6 are plotted against the molality of bound Cu(II). The  $-\Delta G^\circ_4$  curve is quite featureless, except for its substantial decrease with increasing Cu(II) loading. This should be expected, simply because in a mixture, the strongest chelate or complexes will form first. Otherwise, the sort of curve fine structure that has been observed for  $H^+$  dissociation is not observed here for Cu(II)- $2H^+$  competition (2, 7-9). In this respect, the contrast between the absorbance and standard Gibbs energy curves is quite striking.

The usefulness of photometric absorbance for Cu(II)-fulvic acid complexing had previously escaped notice, partly because of the lack of spectral peaks and isobestic points but also because of the relatively small absorbance changes. The whole photometric curve from 0 to  $5.0 \times 10^{-4} m$  Cu(II) complex has an absorbance range of less than 0.04 absorbance unit. In spite of this, the curve is readily reproduced on a spectrophotometer with high absorbance intensity and shows some very distinctive features.

The important observations about Figure 6 are as follows: (a) The absorbance curve has sharply characteristic features not reflected in the standard Gibbs energy plot. These include two distinct steep regions with a plateau between. (b) The absorbance curve has a sharp break just under  $3.4 \times 10^{-4} m$  Cu(II) complex. This is reasonably close to the expected concentration of salicylic acid type Cu(II) chelate. Another absorbance curve at 650 nm has the same features, including the sharp break just before  $2.4 \times 10^{-4} m$  chelated Cu(II). It seems that chromophores absorbing over a relatively wide range of wavelengths are a much more differentially sensitive

**Table IV.** Mole Fraction Derivatives for Fulvic Acid-Cu(II) Complexing<sup>a</sup>

$x_{SH_2}$	$\frac{dx_c}{dx_{SH_2}}$	$\frac{dx_{SH}}{dx_{SH_2}}$	$\frac{dx_c}{dx_{SH_2}} + \frac{dx_{SH}}{dx_{SH_2}}$	error, %
0.080	-2.30	1.32	-0.98	+2.
0.210	-2.47	1.45	-1.02	-2.
0.330	-2.95	1.93	-1.02	-2.

<sup>a</sup> See Equations 30-32.



indicator of Cu(II) complexing and/or chelation than is  $\Delta G^\circ_4$ .

Equations 30 to 32 form the basis of another simple calculation procedure having considerable diagnostic value. Values of  $d\chi_c/d\chi_{SH_2}$  and  $d\chi_{SH}/d\chi_{SH_2}$  calculated by graphical differentiation are listed in Table IV. Three conclusions are drawn from this table about the experimental data and the complexing or chelation reaction: (a) The mole fraction data are internally self-consistent to  $\pm 2\%$ . (b)  $Cu^{2+}$  has reacted with the bidentate sites SH and  $SH_2$  in the SH to  $SH_2$  mole ratio range  $2 \leq a \leq 3$ .  $a$  gives the reaction stoichiometry in Equations 30. (c) As the degree of protonation increases from 0.08 to 0.33, the increasing  $a$  indicates an increasing preference of the  $Cu^{2+}$  for reaction with sites in the SH form. As  $Cu^{2+}$  complexing displaces protons, the decreases in electrostatic charge on the fulvic acid is

$$2a - (a + 1) = (a - 1) \equiv \frac{d\chi_{SH}}{d\chi_{SH_2}} \quad (47)$$

This measures the effectiveness with which the  $Cu^{2+}$  displaces the protons. It is found in Table IV that the protons are less effectively displaced as  $\chi_{SH_2}$  increases.

Since this last point is contrary to expectation, this raises questions about changes in conformation and aggregation. Because of this and because there is some suspicion that light scattering may exist in the absorbance curve in Figure 6 beyond  $3.4 \times 10^{-4} M$  chelate, it is believed that light scattering measurements will be required in the future for this system.

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# Combustion-Ion Chromatographic Determination of Chlorine in Silicate Rocks

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**A method is described for the analysis of chlorine in silicate rock standards. The proposed combustion-ion chromatographic method is compared with previous methods of analysis and optimum working conditions are investigated. Detection limits are presently 0.8  $\mu g$  absolute and precision is commonly  $\pm 5\%$  relative standard deviation. The method is rapid and compares favorably with neutron activation analysis and X-ray fluorescence techniques. Chlorine values are listed for 28 silicate rock standards.**

The determination of chlorine in rock samples is important because of the significant role that chlorides play in the geochemical para-genesis of geologic sequences. Mason (1) states that "chlorides are the most important form in which metals are removed from a magma". Numerous workers have commented on the role of chlorides in ore deposition (1-7), rock weathering (8, 9), and the metamorphism (10, 11). Thus, the need for a rapid, accurate method of chlorine determination, which is capable of handling large numbers of rock samples easily and relatively inexpensively, is well documented.

Previous methods of analysis for chlorine in geochemical samples include spectrophotometry (12), neutron activation (NAA) (13), and X-ray fluorescence (XRF) (14, 15). Extensive sample preparation makes chlorine contamination a serious problem in the spectrophotometric method, which also suffers from a lack of precision. While neutron activation techniques have been shown to be highly accurate, precise, and avoid many of the contamination problems of other methods, the

technique is rather expensive and the post-irradiation separation procedures can be time consuming and laborious. The X-ray fluorescence method is rapid and yields values which are in good agreement with neutron activation analysis values. However, it is a secondary method of analysis and fresh standard pellets must be prepared and run with each lot of samples, because of Cl adsorption from the atmosphere upon regassing of the pellets after analysis under vacuum conditions. High and inconsistent Cl content of the pellet binding material can also be a problem in the XRF method (14).

Ion chromatographic techniques (16) offer certain advantages over other methods. The proposed combustion-ion chromatographic method (CIC) eliminates many of the above mentioned problems usually encountered in Cl analysis of rock samples. Sample preparation is minimized and so most problems due to lab contamination are avoided. Once sample solutions have been obtained, they may be stored, if necessary, before final IC determination and standards may be saved for subsequent analyses. The technique is rapid, precise, capable of handling large numbers of samples with ease, and does not require a large number of geochemical standards for the preparation of a working curve. In the present study, up to 60 samples a day including blanks were run with the induction furnace and up to 40 sample solutions a day were analyzed with the IC.

## EXPERIMENTAL

**Apparatus.** A DIONEX model 10 Ion Chromatograph equipped with a  $3 \times 150$  mm anion precolumn, a  $3 \times 500$  mm anion separator column, and a  $9 \times 250$  mm anion suppressor