AN ABSTRACT OF THE THESIS OF

John D. Jones for the degree of Master of Science in Chemistry presented on March 21, 1997. Title: Study of the Acid-Base Properties of Humic Acids.

Abstract approved: _____

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The acid-base chemistry of humic acids was investigated with a newly developed coulometric titration method and a discrete log K spectrum modeling approach.

The coulometric titration method was tested by titration of potassium hydrogen phthalate (KHP). Total phthalate was determined by inflection point location, a chemical equilibrium model with explicit nonlinear least squares parameter adjustment, and with the program FITEQL. The results found through each method agreed well with the known amount of KHP added to solution. A single FITEQL model of thirteen KHP titrations in 0.100 M KCl gave the optimized values of pK_{a1} = 2.783 ± 0.002, pK_{a2} = 4.940 ± 0.001, and pK_w = 13.800 ± 0.001. The coulometric titration method was found to be accurate and precise.

The discrete log K spectrum model was developed to describe proton and metal binding to two types of humic acid, leonardite humic acid (LHA) and peat humic acid (PHA). The model for binding of Co(II) to LHA was developed in several steps. First the values of acidity constants of the sites were set to span the pH range of the data (*e.g.*, log K_a = -4, -6, -8, -10). Then the total concentration and sodium binding constants for each of the sites was determined from acid-base titration data at two ionic strengths. Next Co(II) binding constants were determined from Co(II) binding data at pH ≈ 4.5 to pH ≈ 7, at two ionic

strengths, and total Co(II) concentration of 1 μM. Finally the model was extrapolated without further optimization to describe Co(II) binding by LHA from approximately 10 nM to 1 mM total Co(II) at pH ≈ 6.7 and two ionic strengths; agreement between the extrapolation of the model and experimental data was remarkably good.

The modeling strategy was applied to titrations of peat humic acid (PHA). The model showed that dialyzed and undialyzed PHA solutions were not significantly different. Titration hysteresis is unlikely to occur over the pH range 4-10 in a timeframe of a few hours. Titrations of LHA performed by different workers in different laboratories could be satisfactorily represented by the same model.

Although humic acids are heterogeneous, this work indicates their behavior is not unpredictable, showing both reproducible and generally reversible behavior.

Study of the Acid-Base Properties of Humic Acids

by

John D. Jones

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented March 21, 1997
Commencement June 1997

Master of Science thesis of John D. Jones presented on March 21, 1997

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John D. Jones, Author

Acknowledgments

There are a number of people who deserve credit in the preparation of this thesis. The first of these is Dr. John C. Westall who was instrumental in bringing this work about. His expertise and commentary throughout the process were invaluable. A second person I must thank is my good friend Armando Herbelin, whose insight and natural aptitudes provided welcome support. The third person who must be noted is my wife Lorna, whose support made all the difference.

Contribution of Authors

Dr. John C. Westall was involved in the analysis, organization, and writing of each manuscript. In addition, Gary D. Turner of Batelle Pacific Northwest Laboratories (PNL) was responsible for gathering the humate titration and cobalt complexation data in Chapter 3. Further, both Mr. Turner and PNL coworker Dr. John M. Zachara were involved in the preparation of the material in Chapter 3.

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Dedication

This thesis is dedicated to my parents, John and Barbra Jones, whose love, support, encouragement, and prayers made all of this possible. I can't thank them enough for their steadfast character and faithfulness in their service to God and teaching me that the greatest pursuit of all is in knowing Him.

Study of the Acid-Base Properties of Humic Acids

Chapter 1: Introduction

One of the first descriptive models of nature was put forth by Aristotle, who claimed that the elements of the universe were earth, air, fire, and water. On a large scale, this was not an unreasonable way of describing the directly observable world, especially if one describes an agrarian society. Scientists have certainly made much progress in producing more specific, and generally more accurate, models of natural phenomena since the third century B.C., but with those first simple descriptions Aristotle hit upon several important aspects of science.

One aspect demonstrated is empirical observation, the process of making appropriate measurements and gathering accurate information about some feature of the natural world. Another aspect learned from Aristotle's example is the utility of putting the various bits of information together into some type of framework, or model, that accurately describes what was observed. Further, the illustration suggests the importance of modeling in predicting the outcome of experiments, providing a way to think about a situation, and suggesting things to investigate to refine or reject the model. Finally, the example indicates that the model devised was sufficient for the purpose for which it was intended.

The work described herein is concerned with titration and modeling of the chemical equilibria of chemically heterogeneous materials termed humic substances, specifically, leonardite humic acid (LHA) and peat humic acid (PHA). Humic substances are products of the decay of organic material in the environment. They are environmentally important materials because they can affect the transport, availability, and fate

of other substances in environmental systems, both organic and inorganic, both natural and anthropogenic. The focus of this work is on the interactions of the selected humates with inorganic cations, particularly H^+, Na^+, and for LHA, Co^{2+}, and to use the gathered information to develop an effective model to describe the data.

Modeling of humic substances has been a focus of many researchers for several decades. Many models have been proposed; most of them do a reasonable job at describing the data. Indeed, two authors have noted for one-dimensional data sets that "Almost any function with several adjustable parameters will fit most or possibly all of the data points in a typical titration..." (Perdue and Lytle, 1983). However, it is apparent from the literature of the last few years that a consensus has formed that the most appropriate models for humic substances describe them with a distribution of binding energies. The distributions can either be discrete or continuous. Recent examples of discrete and continuous distribution models are Model V (Tipping and Hurley, 1992) and the nonideal competitive adsorption (NICA) model (Koopal *et. al.*, 1994; Benedetti *et. al.*, 1995; Kinniburgh *et. al.*, 1996; Benedetti *et. al.*, 1996), respectively. The common theme to these recent models is that the authors attempt to describe multidimensional data sets, covering a range of pH, ionic strengths, and metal concentrations. In the same vein, the work described in this thesis is directed toward the development of a discrete site model to describe humate titration data in which pH, ionic strength, and metal concentration are all variables. This model, reported by Westall *et. al.* (1995) termed the discrete log K spectrum, is described in detail in Chapter 3. A discrete site modeling strategy was chosen because it is conceptually easy to understand and is compatible with many readily available chemical equilibrium programs.

Prior to developing a model, one must first have reliable data. This is the focus of Chapter 2. In this chapter, a method for the coulometric titration of acids, humic substances included, is described and some of the concepts of chemical equilibrium modeling are introduced. The classical electroanalytical method of coulometric titration was chosen over volumetric titration for the titration work because of the greater accuracy and precision that it can produce and some of the problems that it avoids. The utility of chemical equilibrium modeling with the titration data obtained is also shown.

Chapter 3 introduces the heterogeneous substance leonardite humic acid (LHA) and describes work done with this material. The acid-base behavior of LHA is described and the semi-empirical chemical equilibrium model, termed the discrete log K spectrum model, developed to describe this behavior is expanded to include the association of LHA with Co(II) as a function of pH and ionic strength. The combining of multidimensional data sets will be shown to produce an effective model to describe, and to a certain extent predict, the behavior of LHA.

In Chapter 4, the titration method described in Chapter 2 and the modeling concept developed in Chapter 3 are applied to LHA and to a second material, peat humic acid (PHA). It will be demonstrated how the semi-empirical model developed for LHA can be used to resolve and reconcile apparent differences in LHA titrations produced by two different laboratories. The modeling framework is then applied to PHA in order to describe its behavior. Issues of reproducibility, reversibility, and hysteresis of PHA titrations are considered in order to evaluate this material for future investigations of its metal-complexing behavior.

The objective of the work is to describe a general method for the titration of heterogeneous substances and to put forth a framework to model their chemical behavior. It is hoped that Aristotle's example

will be seen through the chapter sequence. That is, the titration method was developed to produce the best quality data. The data were assembled together with a reasonable and intuitive explanation of the behavior to produce an internally self-consistent semi-empirical model to describe effectively what was observed. It is hoped that the approach taken here will be a useful tool in the study of environmental systems.

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Chapter 2: Development and Testing of a Coulometric Titrator

INTRODUCTION

Electrochemical methods have been used in analytical chemistry at least since the time of Faraday in the mid-nineteenth century and have proven to be a mainstay in the field. The endurance of such classical techniques of wet chemistry is attributable in large part to the great accuracy that can be obtained with them. With the advent of the personal computer, the utility of electrochemical methods has greatly improved through automation. This development allows great precision to augment the accuracy of electroanalytical techniques. The focus of the work described here is based upon the electrochemical method known as coulometry and coulometric titration.

The coulometric titration method was invented over fifty years ago by Szebelledy and Somogyi (Lingane, 1958). This technique was recognized as an excellent method of chemical analysis. As an analytical method, coulometric titration essentially employs the electron as a direct or indirect titrant for the analyte. In a direct, or primary, coulometric titration, the analyte being determined reacts immediately at the surface of the working electrode. For example, one might plate silver out of a solution onto an electrode and measure the amount of charge required to reach the endpoint. For an indirect, or secondary, coulometric titration, a titrant is generated *in situ* by electrochemical reaction at the surface of the working electrode. The titrant generated then reacts with the analyte; the endpoint of the titration is indicated by some other method, such as pH measurement.

Coulometric titrations have long been known to be some of the most precise and accurate methods for chemical analysis. Coulometric titrations eliminate or reduce difficulties associated with volumetric

titrations. Because the titrant is generated in the analyte solution, a coulometric titration eliminates the need for the preparation of primary standards for the determination of the concentration of the titrant, as required for volumetric titration. While the preparation of primary standards is not necessarily a problem, the coulometric titration has the potential of being a more efficient method, since the step of preparing a standard is not required to produce very accurate results. Once developed, a coulometric titration method requires a primary standard only from the standpoint of periodically verifying system accuracy, *i.e.*, for quality assurance and control.

If one is performing acid-base titrations, coulometric titrations also reduce "the CO_2 problem," the dissolution and reaction of atmospheric carbon dioxide in both analyte and titrant solutions. For example, when a weak acid is titrated with a strong base such as sodium hydroxide, accuracy is influenced by the reaction of atmospheric carbon dioxide with the titrant; NaOH concentration is changed throughout the analysis by reaction with atmospheric CO_2, adversely affecting the determination of acidity in the analyte. In addition to affecting the titrant concentration, CO_2 dissolved in the titrant induces error in the data, making location of the inflection point more difficult, which compounds the problem of changing the titrant concentration.

In the case of a coulometric titration of a weak acid, problems induced by CO_2 reaction with the titrant are clearly avoided. Error in the data from dissolved CO_2 in the analyte solution can be further reduced if the titration is carried out under N_2 atmosphere.

There are other advantages with the coulometric titration method. It eliminates dilution effects encountered in volumetric titrations, which can complicate data analysis. Further, the coulometric titrator can add very small amounts of acid or base to the titration cell more

precisely and accurately than volumetric titrators. In principle, accuracy and precision of charge additions is limited only by uncertainty in the measurement of current and time. In practice, current efficiency can pose a problem in the analysis and this problem must be dealt with on a case by case basis.

It makes sense to utilize the advantages of the coulometric titration method. Thus, the goal was set forth to develop and test a general coulometric titrator for the accurate and precise determination of acidity in both pure analytes and heterogeneous substances, *e.g.*, humic acids.

THEORY

There are two types of coulometry, constant potential coulometry and constant current coulometry. Both techniques are easily adapted to computer automation, allowing very precise titration control. If the electrochemical reaction proceeds with 100% efficiency, *i.e.*, no side reactions occur, every electron delivered goes only to the titration. In this case, coulometric techniques can produce extremely accurate results.

The coulometric titration method utilized in this work is based upon constant current coulometry. Constant current coulometry is well-suited for adaptation in the manner of traditional volumetric titrations. Constant current coulometry is based upon Faraday's Law

$$Q = N \cdot F \tag{2.1}$$

where Q is the charge in coulombs (C), N is the number of moles, and F is the Faraday, 96,486.56 C mol^{-1} (Diehl, 1979). In the coulometric titration method for acid-base analysis, when one faraday of charge has

been delivered, one mole of H^+ has been consumed or produced, depending on whether reduction or oxidation is occurring at the working electrode. Since the focus of this work is ultimately on the titration of humic acids, the reaction of most interest is the reduction of water at the working electrode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \qquad (2.2)$$

The amount of OH^- generated is determined by combining Equation 2.1 and Equation 2.2 with Ampère's Law

$$Q = i \cdot t \qquad (2.3)$$

where i is the current flow between the working and auxiliary electrodes in coulombs per second ($C\ s^{-1}$) or amperes (A), and t is the length of time in seconds that current flows. Thus, if 1 mA flows for 1 second, then 1 mC of charge will be delivered to the cell, and about 10 nmol of OH^- will be produced. Conversion to concentration units is achieved by simply dividing the number of moles of OH^- produced by the volume of liquid in the cell.

This coulometric titrator was developed to titrate humic substances in order to develop a chemical equilibrium model for the description of these substances. However, before work with heterogeneous substances could be performed, the coulometric titrator had to be verified for accuracy and precision by titrating a pure, homogeneous substance, such as the primary standard potassium hydrogen phthalate.

MATERIALS AND APPARATUS

Verification of the coulometric titration method is demonstrated by titrating solutions of the weak acid potassium hydrogen phthalate (KHP), Lot 84j from the National Institute of Standards and Technology. KHP solutions were prepared by first crushing the KHP crystals to a fine powder and then drying under vacuum at 115° C for 2-3 hours. The dry KHP (from 0.5 to 1.5 g) was weighed to 0.01 mg on a Mettler AE240 electronic analytical balance and then dissolved in a volumetric flask with de-ionized water (18 MΩ·cm) from a Millipore Milli-Q+ system. Potassium chloride (Mallinckrodt Analytical Reagent) or anhydrous sodium perchlorate (Mallinckrodt Analytical Reagent) served as the supporting electrolytes.

Apparatus for the titrations included a Keithley 617 electrometer with an Ingold glass electrode and an Orion double junction reference electrode for pH measurement; a Keithley 220 programmable current source for current delivery; a Corona PPC-400 computer for control of the Keithley instruments via a National PC-IIA GPIB; and a Haake G water circulator to maintain the temperature of the titration cell at 25 ± 0.2° C. Furthermore, titrations were performed under purified N_2 to exclude atmospheric CO_2.

Three configurations were tested for the cell. What proved to be the best configuration was a dual-chamber cell with a fritted salt bridge connecting the chambers, shown in Figure 2.1. In another setup, a Wilhelm bridge was used to complete the circuit between the working and auxiliary electrodes, shown in Figure 2.2. In a third configuration, the auxiliary electrode was placed directly in the analyte solution.

Figure 2.1. Coulometric Titration Cell. A is the auxiliary electrode compartment; B is the thermostatted compartment housing the working electrode, glass and reference electrodes, N_2 bubbler, thermometer, and stir bar (not shown); C are ceramic frits to prevent bulk solution flow; D is the bridge connecting the two half cells; E is a Teflon stopcock for emptying of the bridge; F is a 19/22 standard taper opening for filling the bridge with electrolyte; G is the water jacket where constant temperature water flows in the direction of the arrows. A representation of the electrode arrangement in B is shown in Figure 2.2.

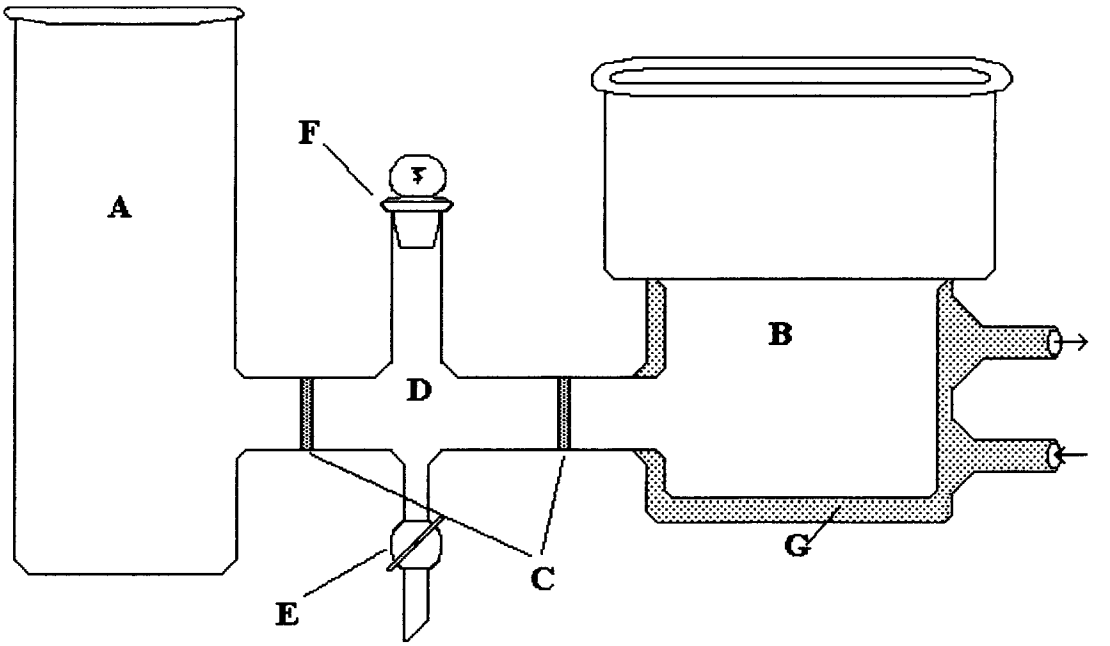
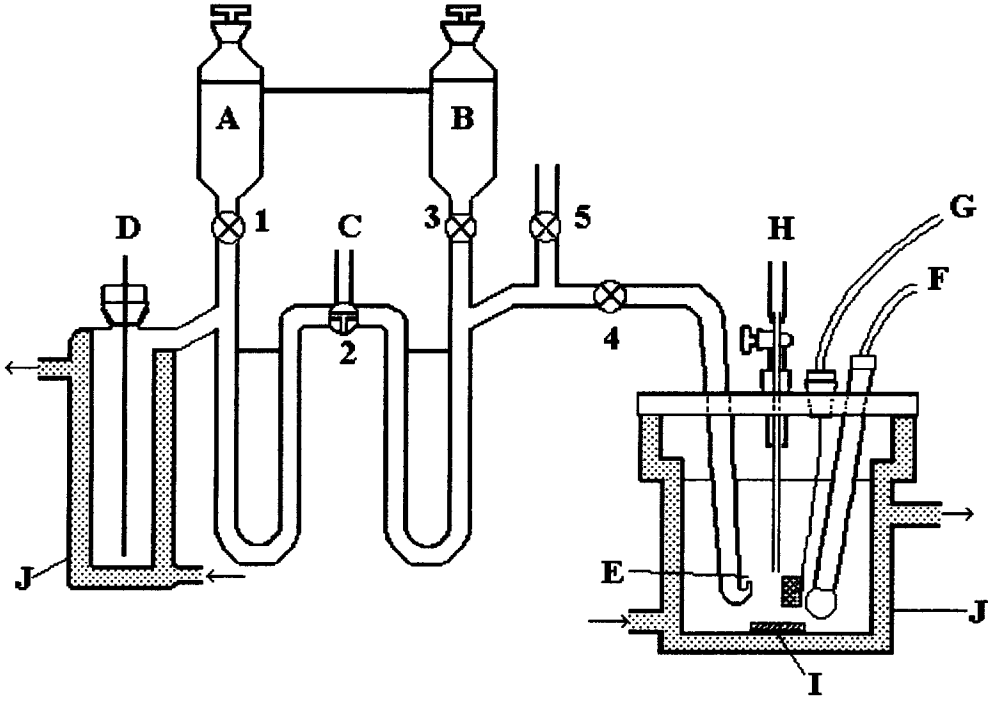


Figure 2.2. Coulometric Titrator with Wilhelm Bridge[a]. A and B contain supporting electrolyte to replenish the system; 1, 3, 4, and 5 are two-way stopcocks; 2 is a three-way stopcock; C is the drain point; D is the Ag auxiliary electrode; E is the liquid junction completing the circuit between the auxiliary and working electrodes; F is the glass electrode (reference electrode not shown); G is the Pt working electrode; H is the N_2 bubbler; I is the stir bar; J are the water jackets where constant temperature water flows in the direction of the arrows. The thermometer in the titration cell is not shown.



[a]After Shotts, 1987.

The coulometry circuit consisted of the Keithley 220 connected to a Pt gauze working electrode (40 mesh gauze, 1.5 cm long by 0.75 cm diameter cylinder) and a Ag auxiliary electrode (a 10-cm coil of 10 gauge Ag wire with the dual-chamber cell and direct placement configurations; a 5-cm coil of 18 gauge Ag wire with the Wilhelm bridge); the Ag electrode was isolated from the titration cell with a salt bridge. The whole apparatus, excluding the water circulator, was housed inside a grounded Faraday cage.

The dual-chamber cell (Figure 2.1) consisted of a main cell of 50-mL thermostatted volume with a lip to seal a clamp-on lid. A 180-mL electrolytic beaker served as the auxiliary cell. The two cells were connected by a bridge, 1 cm in diameter with a frit-to-frit length of about 4.5 cm and a total volume of approximately 9.4 mL, equipped with a stoppered opening and Teflon stopcock for easy filling and emptying. Fine frits on either end of the bridge prevented free flow of electrolyte solution. This configuration was most satisfactory and was used for most of the work.

The Wilhelm bridge (Figure 2.2) connected the working electrode in the analyte half cell to the auxiliary electrode through glass tubing about one meter in length and 5 mm in diameter. The end of the tubing in contact with the analyte solution was approximately two millimeters in diameter. This configuration was abandoned for several reasons. Firstly, the voltage required to drive 1 mA with 0.100 M KCl in the bridge was about 69 volts, not far from the maximum output of the Keithley 220. Secondly, titrations of millimolar concentrations of KHP produced results that were consistently +2.5% or greater in error, possibly from excess acidity in the 0.100 M KCl bridge electrolyte (pH of 0.100 M KCl solutions was typically about 5 to 5.5). Thirdly, because a tight seal could not be made between the bridge and the cell lid, this configuration seemed to allow atmospheric CO_2 to intrude into

the system, as evidenced by excessive error in the data near the inflection point of the titration curves. Finally, the Wilhelm bridge was, simply put, cumbersome to use.

Titration with direct placement of the Ag auxiliary electrode in the analyte solution initially produced better results than titrations with the Wilhelm bridge. Direct placement of the auxiliary electrode in the analyte solution is a feasible configuration if the product of the auxiliary electrode reaction is nearly insoluble. In this case, the auxiliary electrode is silver, and the supporting electrolyte is KCl. The auxiliary electrode reaction is

$$Ag^{\circ} + Cl^{-} \rightarrow AgCl(s) + e^{-} \qquad (2.4)$$

A few direct placement titrations worked well until a layer of AgCl built up on the electrode surface. When this happened, the concentration of Ag^{+} ion from the dissolution of AgCl apparently became high enough in the solution to plate out on the Pt working electrode, as evidenced by a grayish-brown coating on the Pt surface, assumed to be metallic silver. The coating was removed when the polarity on the Pt electrode was switched from negative to positive. The assumed side reaction of Ag^{+} plating the working electrode gave falsely high concentrations of KHP. Consequently, this setup was rejected.

EXPERIMENTAL METHODS

The general procedure for performing a coulometric titration is 1) calibrate the glass and reference electrodes for pH determination by volumetric addition of acid to an aliquot of the supporting electrolyte; 2) remove the calibration solution, add the supporting electrolyte for the titration, acidify, purge with N_2, and coulometrically neutralize to

pH 7; 3) add analyte solution and perform titration; and 4) re-calibrate the glass and reference electrodes to check for drift.

Calibration procedure

The electrodes were calibrated volumetrically in 25.00 mL of 0.100 M KCl or $NaClO_4$ with fixed additions of 0.0100 M HCl (standardized against *tris*(hydroxymethyl)aminomethane, or TRIS) dispensed by a Metrohm Dosimat 655 autoburet. The electrolyte solution was bubbled with N_2 gas for five minutes prior to acid addition. After each addition, voltage was polled by the computer every two seconds until ten consecutive readings showed less than 2.5 μV/s drift and less than 25 μV standard deviation of the mean of these data points. When these parameters were satisfied, the mean of the last ten voltage readings was taken to be the "equilibrium" voltage. The voltage *vs.* volume data were used in a nonlinear least squares optimization program to determine the parameters $E^{o'}$, k, and C_o as defined in the Nernst equation

$$E = E^{o'} + k \log[H^+] \tag{2.5}$$

and the concentration of acid in the cell, defined as

$$[H^+] = (C_oV_o + C_AV_A) \; / \; (V_o + V_A) \tag{2.6}$$

where C_o is the concentration of acid (M) in the electrolyte (assumed to be only strong acid), V_o is the initial volume (L) of electrolyte, C_A is the concentration of acid (M) added to the cell, and V_A (L) is the volume of acid added to the cell. Equations 2.5 and 2.6 are the definitive equations used by the fitting procedure. The fitting procedure minimizes the weighted sum of the squares of the differences

between $[H^+]$ in Equations 2.5 and 2.6 by adjusting the parameters $E^{o'}$, k, and C_o in a process very similar to the modeling routine used to compute total KHP, described later. The Nernst parameters determined were used later when fitting the coulometric titration curve.

Titration procedure

A 20-mL aliquot of 0.1500 M KCl or $NaClO_4$ was added to the cell; the cell lid was clamped on to obtain an airtight seal. Then 200 µL of 0.01 M HCl was added to the electrolyte and N_2 was bubbled through the acidified solution for 15 minutes to facilitate the removal of CO_2; N_2 pressure was equalized in the two cells via a short piece of flexible tubing. The electrolyte solution was then coulometrically neutralized to pH 7, indicated by the voltage reading on the electrometer and the calibrated pH electrode. At this point, a 10-mL aliquot of KHP solution was added to the cell for the titration. After KHP addition, experimental control was transferred to the computer.

After allowing five minutes for CO_2 to be swept out of the headspace of the cell after KHP addition, the controlling program made three small coulometric additions of OH^- (each was 1.0000 mA for 10 s, or 10 mC, equivalent to 3.43 µM additions of base). From the potential change produced by the first three additions, the number of coulombs required to change the potential by -0.010 V was calculated. The program then instructed the current source to operate at 1.0000 mA (or 10.000 mA for additions greater than 30 mC) either for the length of time to bring about the next -0.010 V change, or for a predetermined maximum length of time allowed for any one addition. Thus, a titration proceeded by fixed or variable length additions of charge, the amounts of which were computed from the potential change caused by the three previous additions. The parameters for voltage data acquisition in the

KHP titrations were the same as described for the electrode calibrations. The program terminated when a predetermined number of coulombs had been delivered or when the pH was 10 or greater as indicated by the potential reading at the electrometer.
After the titration, average values of the Nernst parameters $E^{o'}$ and k determined before and after the titrations were used to compute $[H^+]$ and subsequently total phthalate. Total phthalate added was determined by three methods: by inflection point estimation, by fitting the whole charge-voltage titration curve with a nonlinear least squares algorithm (a program listing is in the Appendix), and by modeling the data with the parameter optimization program FITEQL 3.1 (Herbelin and Westall, 1994).

RESULTS AND DISCUSSION

Initial Verification

Several different solutions of KHP were titrated in the dual-chamber cell to verify the accuracy and precision of the method. A summary of results of three titrations of an approximately 10 mM KHP solution are presented in Table 2.I as examples of system verification. These titrations are representative of a total of sixteen titrations of KHP used to ensure the quality of the data obtained over the course of titrating humic substances. Total KHP was determined initially by two methods: 1) inflection point location by numerical interpolation of the zero-crossing of the second derivative of the titration curves; and 2) by nonlinear least squares (NLLS) optimization, hereafter referred to as the NLLS model, which is described below. For the titrations summarized in Table 2.I, the concentration of KHP in the cell calculated from mass added and dilution was 3.3532 mM. Inflection point estimates gave a

Table 2.I. Summary of KHP Titration Results. A 10-mL aliquot of 0.010143 M KHP and a 20-mL aliquot of 0.1500 M KCl were added to the cell; [KHP] after dilution = 3.3532 mM in 0.100 M KCl; titrations represent cell calibrations 5, 6, and 7 in Table 2.III; values of pKa_1, pKa_2, and pK_w used in the model are from Smith and Martell, as described in text.

Total KHP determinations by inflection point		
Titration	[KHP] mM	% error[a]
5	3.3435	-0.29
6	3.3553	0.06
7	3.3466	-0.20
Mean	3.348	
S.D. of mean	0.006	
R.S.D. of mean	0.18%	
Total KHP determinations by NLLS model		
Titration	[KHP] mM	% error[a]
5	3.342	-0.33
6	3.354	0.02
7	3.345	-0.24
Mean	3.347	
S.D. of mean	0.006	
R.S.D. of mean	0.19%	

[a] %error = 100*(value - "true")/ "true" , where "true" equals the mass-dilution concentration of KHP.

mean of 3.348 ± 0.006 mM. Estimates of total phthalate from the NLLS model gave a mean concentration of 3.347 ± 0.006 mM. The excellent agreement between the two methods is evidence that the coulometric titration system works well with very good accuracy and precision.

The nonlinear least squares model

The fitting routine minimizes the weighted sum of the squares of the differences between two terms: total H potentiometric (T_H^P) and total H coulometric (T_H^C), as defined in Equations 2.7.13 and 2.7.16, in Table 2.II, respectively. Equation 2.7.16 in Table 2.II expresses T_H^P in terms of experimentally determined values of $[H^+]$, the dissociation constants K_W, K_{a1}, K_{a2}, and the adjustable parameter total phthalate (T_P). The literature values 13.78 (Smith and Martell, 1976), 2.75, and 4.93 (Martell and Smith, 1977) were used for pK_W, pK_{a1}, and pK_{a2}, respectively, in the NLLS model. T_H^C is the concentration of OH^- added, calculated from Faraday's Law (Table 2.II, Equation 2.7.14), the number of coulombs delivered to the cell, and the volume of liquid in the cell. From Reaction 2.2 it is seen that for every Faraday of electrons delivered, one mole of OH^- is produced. Thus, T_H^P is the value of total H "found" potentiometrically in the cell, while T_H^C is the known value of total H "added" coulometrically to the cell. The derivation of each of the terms used in the fitting algorithm is listed in Table 2.II.

The difference, $T_H^P - T_H^C$, is defined as the objective function, Y_H, of the algorithm, where T_H^P is computed from the measured potential at each titration point, Equation 2.5, and Equation 2.7.13 in Table 2.II, and T_H^C is the experimental value of T_H added to the system calculated from Equation 2.7.16 in Table 2.II. The uncertainty in Y_H is computed by propagation of error from the two parameters in the

Table 2.II. Equations for Weighted Nonlinear Least Squares Determination of Total Phthalate.

Objective Function

$$Y_H = T_H^P - T_H^C \tag{2.7.1}$$

Mass Action

$$K_{a1} = \frac{[H^+][HP^-]}{[H_2P]} \tag{2.7.2}$$

$$K_{a2} = \frac{[H^+][P^{2-}]}{[HP^-]} \tag{2.7.3}$$

$$K_W = [H^+][OH^-] \tag{2.7.4}$$

Mass Balance

$$T_P = [H_2P] + [HP^-] + [P^{2-}] \tag{2.7.5}$$

Mole Balance

$$T_H^P = [H^+] - [OH^-] + [H_2P] - [P^{2-}] \tag{2.7.6}$$

$$T_P = [H_2P] + \frac{K_{a1}[H_2P]}{[H^+]} + \frac{K_{a1}K_{a2}[H_2P]}{[H^+]^2} \tag{2.7.7}$$

$$T_P = [H_2P]\ (1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\ ) \tag{2.7.8}$$

$$[H_2P] = T_P\ (1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\ )^{-1} \tag{2.7.9}$$

$$T_P = [P^{2-}] + \frac{[H^+][P^{2-}]}{K_{a2}} + \frac{[H^+]^2[P^{2-}]}{K_{a1}K_{a2}} \tag{2.7.10}$$

$$T_P = [P^{2-}]\ (1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}}) \tag{2.7.11}$$

$$[P^{2-}] = T_P\ (1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}})^{-1} \tag{2.7.12}$$

$$T_H^P = [H^+] - \frac{K_W}{[H^+]} + T_P\ (\frac{[H^+]^2 - K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}) \tag{2.7.13}$$

Coulometric H^+

$$Q = N \cdot F \quad \text{(Faraday's Law)} \tag{2.7.14}$$

$$N = \frac{Q}{F} \tag{2.7.15}$$

$$T_H^C = -\frac{Q}{FV_o} \tag{2.7.16}$$

objective function through the equation $s_Y^2 = (\partial Y/\partial T_H^P)^2 s_{THP}^2 + (\partial Y/\partial T_H^C)^2 s_{THC}^2$, where s_{THP} is derived from the estimated uncertainty in the measured potential, 0.0005 V, and s_{THC} is derived from the estimated uncertainty of coulombs delivered to the cell, 0.0005 C. The program minimizes Y_H by minimizing the function $\Sigma(Y_H^2/s_Y^2)$ with respect to the adjustable parameters, subject to the constraints imposed by Equations 2.7.5 - 2.7.16 in Table 2.II, with the summation taken over all data points.

Model analysis

In the absence of error, T_H^P and T_H^C will have the same value at each data point, and the objective function would be zero at each point. However, systematic and random errors usually prevent Y_H from having a value of zero. A difference plot of Y_H *vs.* log H can reveal both systematic and random errors in the model and data.

The difference plots for the three titrations under consideration are shown in Figure 2.3. Immediately noticeable from these are a small dip at log H = -5, and a substantial deviation beginning at about where log H = -10. The large error at pH 10 and above corresponds to the knee on the titration curve where the values of K_W and $[OH^-]$ become significant. Thus, the sharp deviation on the difference plot is possibly a result of error in K_W. Another possibility, but somewhat unlikely, is electrode nonlinearity due to cation interference, a phenomenon encountered in strongly basic solution. Fortunately, the region of interest for the work planned for this titrator, the titration of humic substances, is at pH values less than pH 10. An expansion of the curve of greatest deviation (Titration 6) below pH 10 is shown in Figure 2.4.

Figure 2.3. Difference Plots for KHP Titrations Summarized in Table 2.I.

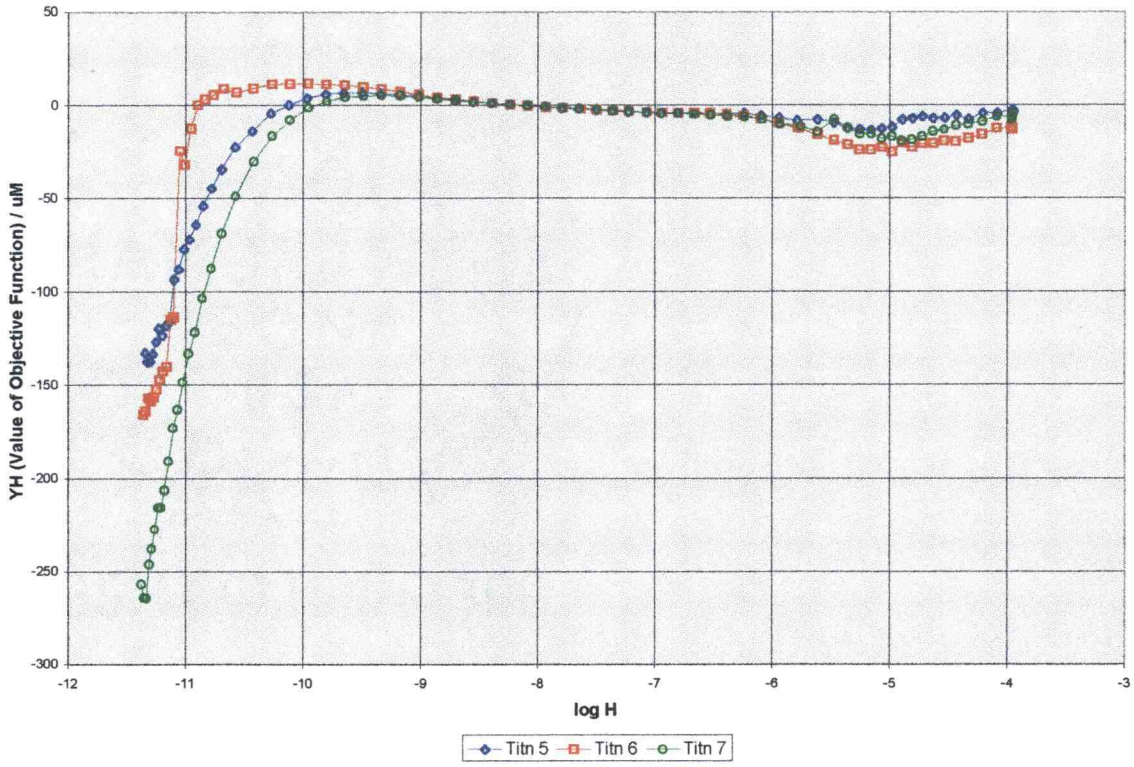
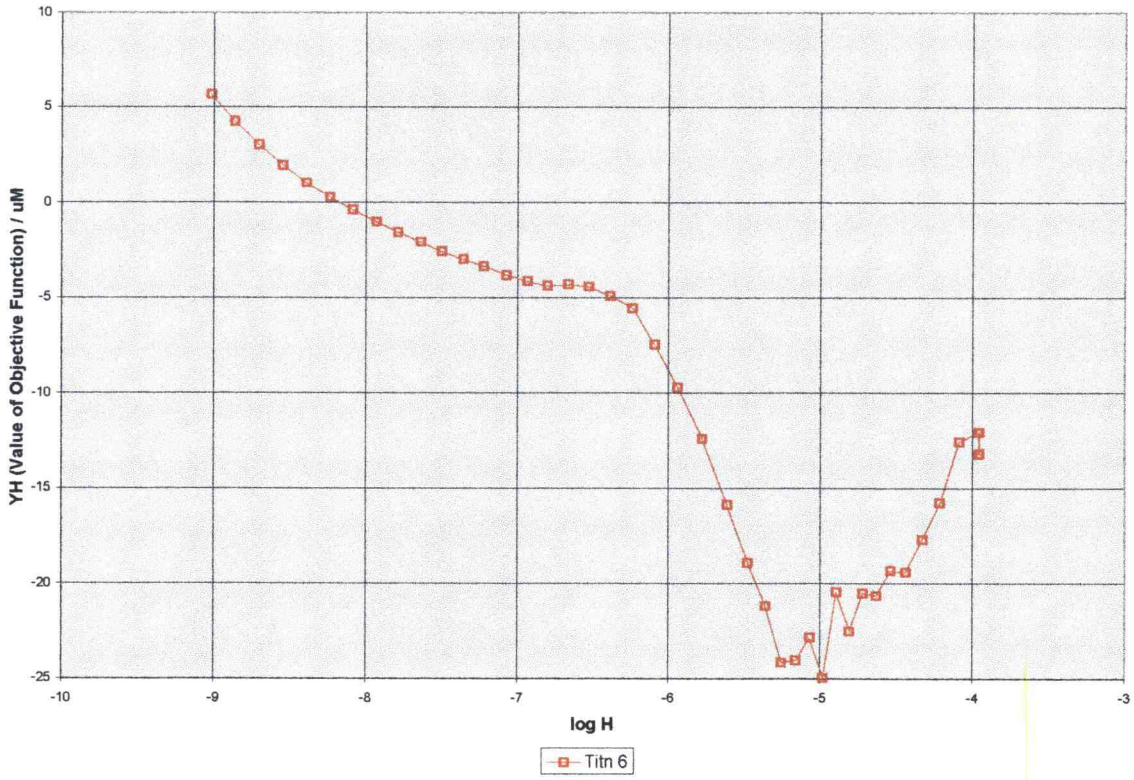


Figure 2.4. Expansion of KHP Titration 6 Difference Plot.



The dip at pH 5 is very pronounced on this scale, reaching a maximum of about -25 micromolar. It is very likely that this feature is due to error in pK_{a2} of KHP. The literature value of 4.93 was chosen for modeling the data, and the largest absolute values of Y_H are found in this pH region. Outside this region, it appears that a negative 5-13 micromolar systematic deviation persists where pH is less than 7, and improves to about pH 9. The systematic deviation may be the result of a small error in the calculated volume of solution in the cell, or a small amount of excess acid that was not neutralized after the CO_2 purge, or loss of a small amount of the phthalate anion due to diffusion/migration into the salt bridge.

Part of the negative systematic deviation was found to be due to biasing as a result of having taken literature values for the equilibrium constants. A similar effect occurred, shown in Figure 2.5, when the data were modeled with FITEQL 3.1 (Herbelin and Westall, 1994) under the conditions of total KHP as the only adjustable parameter and fixed literature values for the equilibrium constants. Rounding errors introduced in preparation of the data for FITEQL are responsible for the oscillatory errors seen in Figure 2.5, as discussed below. This consistently negative error disappeared, illustrated by Figure 2.6, and was reversed when the equilibrium constants were simultaneously adjusted during the optimization. The values determined by the FITEQL optimization were 2.756, 4.945, and 13.79, and 2.71, 4.96, and 13.76 by the NLLS optimization, for pK_{a1}, pK_{a2}, and pK_w, respectively. The difference in the values was later determined to be caused by the difference in the way the titration data are input to the two programs. The NLLS program takes in charge and potential serial data and computes T_H and log H internally; FITEQL receives the serial titration data as T_H and log H after these values have been computed externally. Rounding

Figure 2.5. Comparison of NLLS and FITEQL Difference Plots for KHP Titration 6.

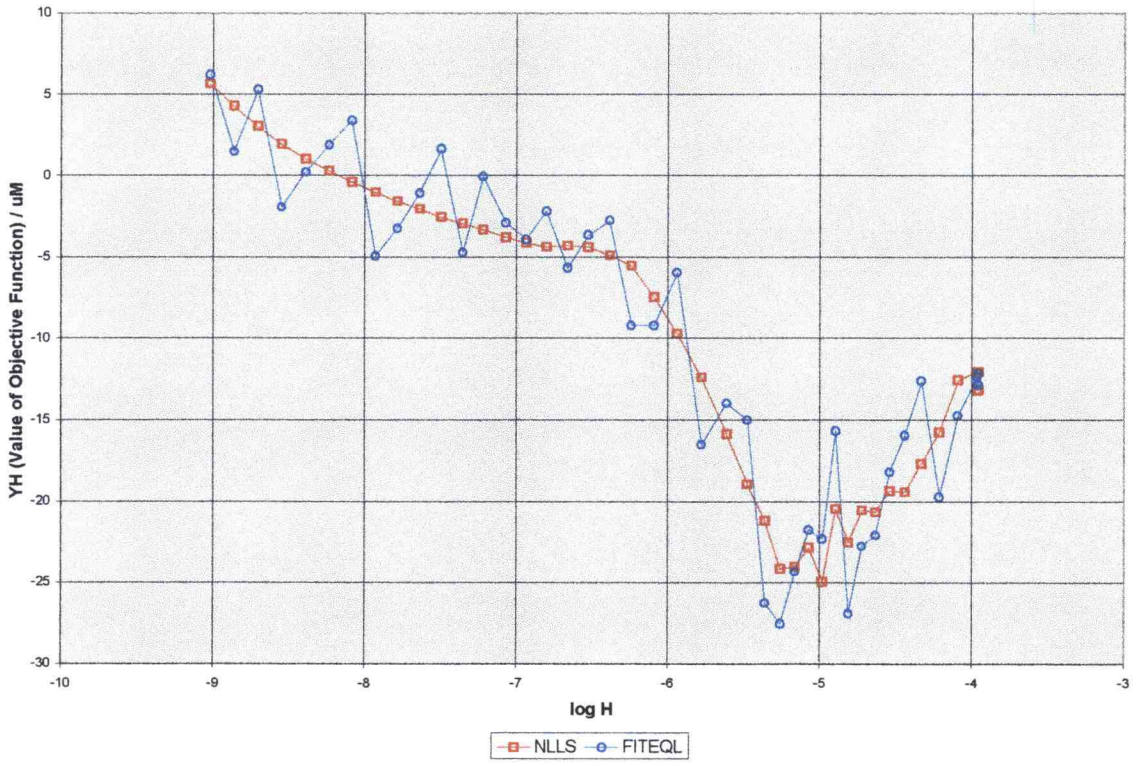
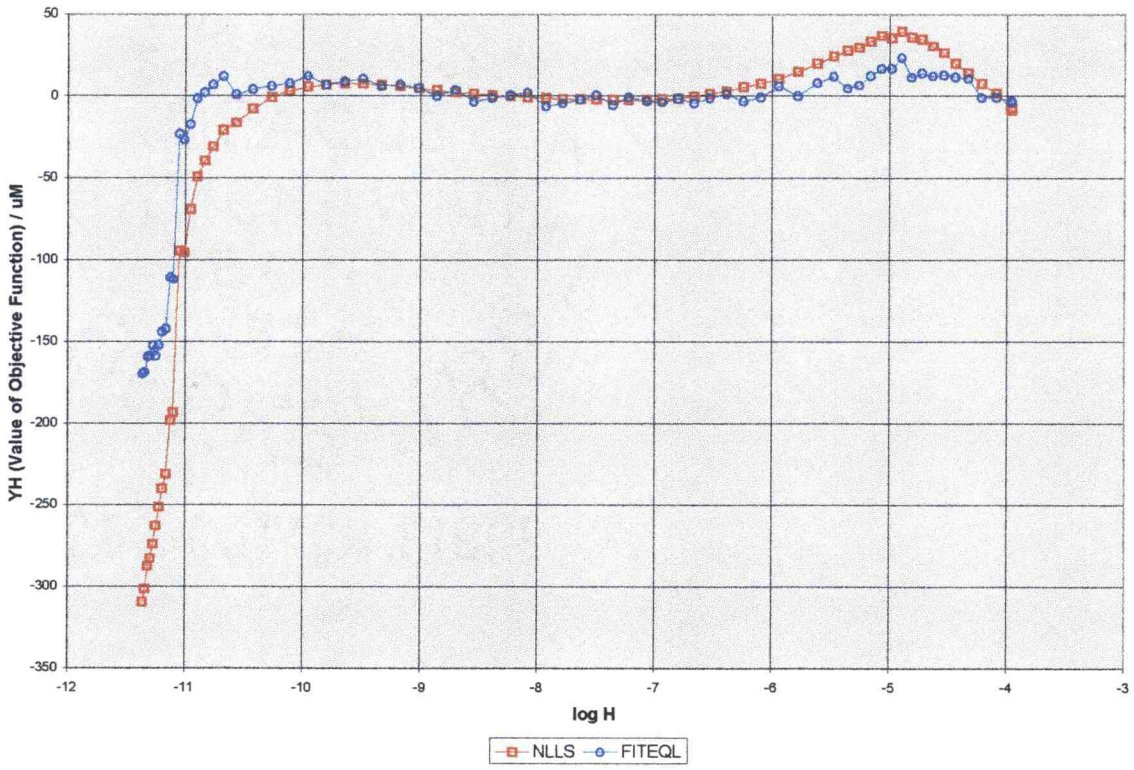


Figure 2.6. NLLS and FITEQL Difference Plots Produced from Four Adjustable Parameter Models for KHP Titration 6.



errors in the serial data and slightly different weighting of the data points by the two different computer programs apparently is responsible for the differences in the log K values computed by the two programs; it also turns out to be the source of the differences between the two curves shown in Figure 2.5.

The value of the objective function alone does not fully indicate the appropriateness of the NLLS model. If one plots the ratio of the objective function to the estimated error in the data (Y/sY) *vs.* $\log_{10} H$, the data should be centered about zero and deviate randomly from about 1 to -1, if the model is appropriate and the error estimates of the data are chosen correctly. Such a plot is shown in Figure 2.7. In Figure 2.7, the value of Y/sY begins to diverge away from its approximate value of -1 about 1.5 log units away from the endpoint (about pH 8), and then returns nearly to zero at about pH 10. This shape indicates that the greatest proportion of error in the model was assigned to the data points closest to the inflection point in the estimation of total phthalate (as one would expect), and that the use of literature values for dissociation constants did not greatly affect the estimation of total phthalate. Rather, one would suspect that residual acidity in the KCl or the loss of a small amount of KHP through the frit into the bridge probably had the most significant effect in the estimation of total phthalate by the NLLS model. Thus, the shape of the plot in Figure 2.7 is supportive of the approach used in establishing the NLLS model to estimate total phthalate.

A final check of the NLLS model and the titration data is to overlay the model calculation on the data, demonstrated in Figure 2.8. On the X-axis are the values of T_H^C (the experimental data) and T_H^P (optimized data). The fitted curve overlays the experimental curve almost exactly, and so it seems safe to conclude that the system will

Figure 2.7. NLLS Objective Function Values Relative to Error.

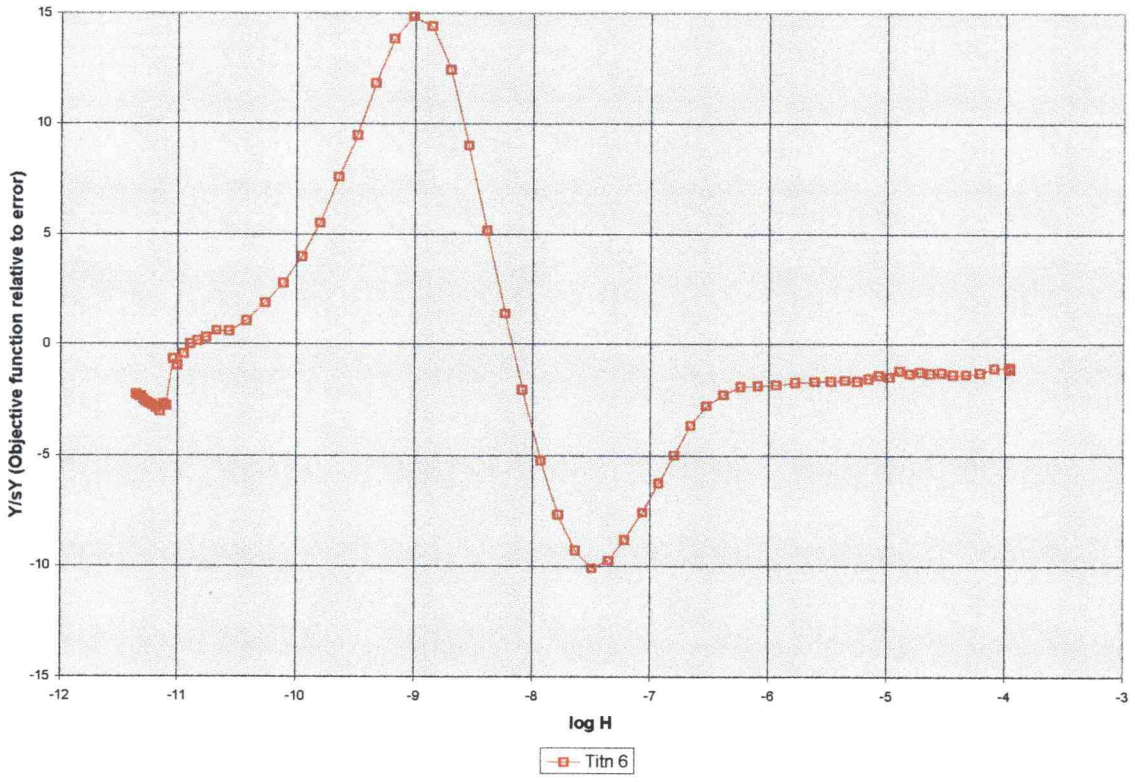
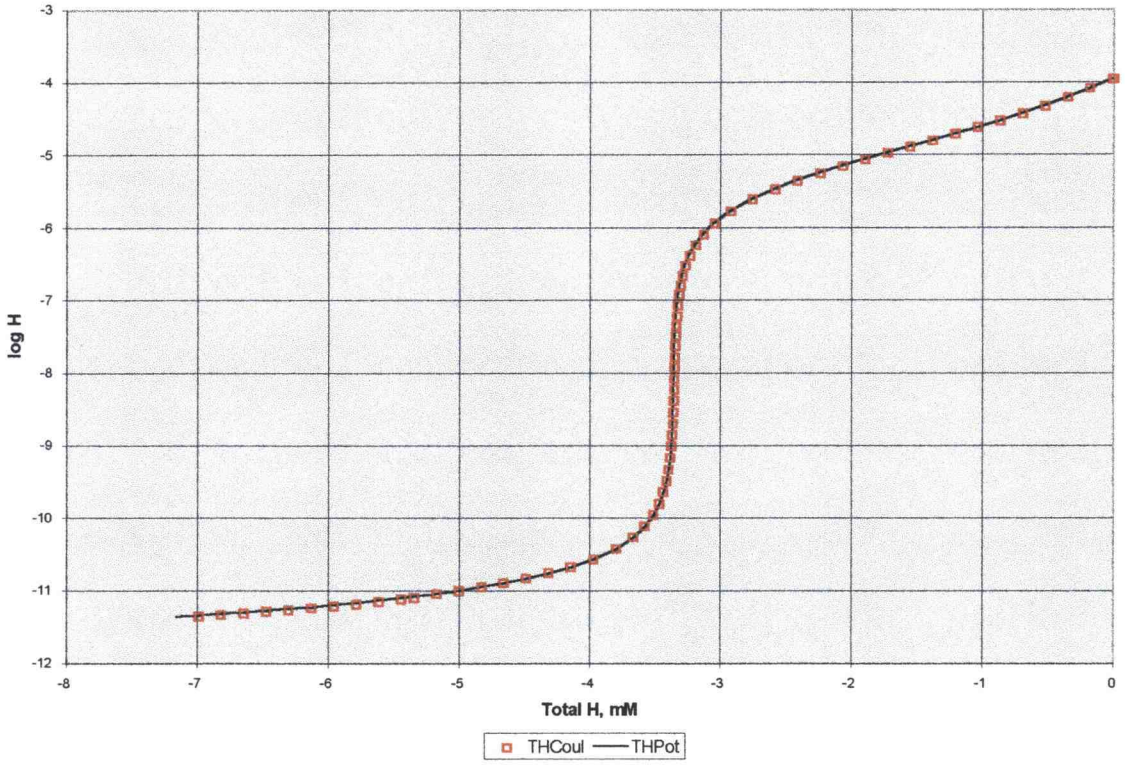


Figure 2.8. KHP Titration 6, Experimental Data and NLLS Model. On X-axis are coulometric (experimental) and potentiometric (model output) T_H values; on Y-axis is $\log_{10}$ H calculated from Nernst parameters determined from electrode calibrations.



produce accurate and precise results within about 0.2%, as shown at the bottom of Table 2.III.

Long-term verification

Over the course of the work of titrating humic substances, the titrator system was periodically checked by titrating KHP and modeling with FITEQL to ensure the quality of the humic acid titrations. The results of these "cell calibrations" are displayed in Table 2.III. These results are further evidence of the reliability of this simple coulometric titrator. Relative error in a typical titration was usually no more than 0.3 percent with reproducibility on the order of 0.2%. In addition, the good agreement between the "true" concentration of KHP (known by preparation), the concentration of KHP determined by inflection point location, and total KHP determined by FITEQL supports the use of FITEQL in the determination of total KHP.

A side benefit of the titrations is the verification of pK_{a2} of KHP. On the basis of sixteen titrations of KHP in 0.100 M KCl or $NaClO_4$, each modeled with FITEQL, the average $-\log_{10}$ of the second dissociation constant of KHP was found to be 4.94 ± 0.02, very close to the literature value 4.93 ± 0.01 (Martell and Smith, 1977). In a further test of model and data, titrations 1 through 10 and 12 through 14 (Table 2.III, all in 0.100 M KCl, 866 data points) were combined into a single model with pK_{a1}, pK_{a2}, and pK_W as adjustable parameters. The relative error estimates of the serial data in this "superfit" were adjusted to the values of 0.2%, 0.5%, and 0.5%, for total phthalate, T_H, and log H, respectively. These estimates of uncertainty were chosen so that the value computed by FITEQL for $\Sigma(Y_H^2/s_Y^2)$ relative to the degrees of freedom in the model (SOS/DF) with the optimized log K values was approximately equal to one, indicating both an appropriate model and

Table 2.III. Results of KHP Titrations in 0.100 M Electrolyte[a].

Titr'n.	[KHP][b,d], true	[KHP][b], inflect.	% error[c]	[KHP][b], FITEQL	% error[c]	pKa_2, FITEQL
1	9.9407	9.9241	-0.17	9.919	-0.22	4.948
2	9.9407	9.9165	-0.24	9.909	-0.32	4.945
3	0.99408	0.99621	0.20	0.9976	0.35	4.956
4	0.99408	0.99423	0.02	0.9948	0.07	4.945
5	3.3532	3.3435	-0.29	3.346	-0.21	4.938
6	3.3532	3.3553	0.06	3.358	0.14	4.945
7	3.3532	3.3466	-0.20	3.349	-0.12	4.941
8	3.3416	3.3354	-0.19	3.336	-0.17	4.937
9	3.3416	3.3375	-0.12	3.338	-0.11	4.938
10	3.3416	3.3334	-0.24	3.335	-0.20	4.930
11[a]	3.3218	3.3211	-0.02	3.320	-0.05	4.971
12	3.3690	3.3748	0.17	3.382	0.39	4.930
13	3.3527	3.3442	-0.25	3.347	-0.17	4.928
14	3.3527	3.3420	-0.32	3.358	0.16	4.900
15[a]	0.49765	0.49938	0.35	0.4995	0.37	4.968
16[a]	0.49765	0.50095	0.66	0.5013	0.73	4.962
average[e]			0.22		0.24	4.94
S.D.			0.2		0.2	0.02

[a] Titrations 11, 15, and 16 in $NaClO_4$, all others in KCl.

[b] KHP concentration has units of millimoles per liter.

[c] % error = (result - true)/true x 100, where "result" is KHP concentration determined from inflection point, or the optimized value returned by FITEQL.

[d] "True" KHP concentration determined from mass and dilution.

[e] Average percent error computed from absolute values of individual errors.

error estimation. This "superfit" produced the following results: pK_{a1} = 2.783 ± 0.002, pK_{a2} = 4.940 ± 0.001, and pK_W = 13.800 ± 0.001. Such close agreement of the optimized values with published values is evidence of the reliability of the method developed here.

SUMMARY

A simple coulometric titration method was developed for the accurate and precise determination of total acidity. Three configurations of working and auxiliary electrodes were tested; a dual-chamber cell with a fritted salt bridge was found to work well. In tests of the system with the primary standard potassium hydrogen phthalate (KHP), total phthalate was determined by inflection point location, a nonlinear least squares model, and FITEQL, and each method used to determine KHP concentration agreed well with the known concentration of KHP in the titration cell. From sixteen FITEQL models of titrations of KHP, an average value of pK_{a2} of KHP was determined to be 4.94 ± 0.02. Thirteen titrations of KHP in 0.100 M KCl were combined into a single FITEQL model which produced the values of pK_{a1} = 2.783 ± 0.002, pK_{a2} = 4.940 ± 0.001, and pK_W = 13.800 ± 0.001. The coulometric titration method was found to be reliable, accurate, and precise.

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Chapter 3: Association of Co(II) with Leonardite Humic Acid as a Function of pH and Electrolyte Concentration

INTRODUCTION

Humic substances (humic and fulvic acids) are the decay products of organic matter in the environment. It is widely known that they can influence the mobility and availability of both organic and inorganic materials in natural systems. Further, if the inorganic substance happens to be a transition metal, humics can also affect the speciation of the metal, and consequently, its toxicity. As environmental protection and remediation became national priorities, the need for numerical models to describe natural chemical systems became more apparent.

The goal of developing a numerical description of the behavior of humic substances as well as other heterogeneous materials has been pursued for decades. It seems that models run the gamut of simple non-linear least squares curve fits to theory-laden descriptions of chemical interactions. Such a plethora of models arises from the heterogeneity of humic substances. Because it is virtually impossible to know the structure, charge, size, and molecular weight of these materials, a unique, definitive model of the chemistry of humic substances is non-existent. In fact, it has been demonstrated that several models with contradictory assumptions can acceptably model the same data set (Cabaniss *et. al.*, 1984). However, there are several reasonable approaches to modeling humic substances. In general, the methods for modeling humic substances fall into two categories: 1) discrete site models; and 2) continuum models.

Discrete site models have the advantage of being conceptually easy to visualize. In the simplest case for proton-metal exchange, one can

envision a single binding site having 1:1 stoichiometry, with a single pK_a for proton dissociation, and another constant for the binding of a metal cation to the site. Further, discrete site models are compatible with common chemical equilibrium speciation programs, *e.g.*, MINTEQ (Allison *et. al.*, 1990) and MICROQL (Westall, 1986). If electrostatics are incorporated into the model, discrete site models can account for ionic strength effects and the "smeared" appearance of proton and metal binding isotherms.

A discrete site oligoelectrolyte (intermediate between a true polyelectrolyte and simple ions) model has been proposed by Bartschat *et. al.* (1992). The approach here was to develop a model for Cu(II)-binding to a fulvic acid based upon a model developed from acid-base titration data. Along with the incorporation of electrostatic theory, this model also allows for size heterogeneity in the fulvic acid. These authors conclude that size heterogeneity is not significant in describing pH titrations of fulvic acid, but is significant in describing copper binding titrations. From this observation, the authors point out the following caveat: that electrostatic information derived from pH titrations is meaningless if the binding of metals is dominated by different size fractions in the fulvic acid.

Another discrete site model, termed Model V, has recently been introduced (Tipping and Hurley, 1992). With eight proton donating sites, yielding eight monodentate and 12 bidentate binding sites, and Donnan-type electrostatics, this model was applied to published data sets of proton binding (eight data sets) and metal binding (26 sets, 11 metals). Model V correctly reproduced trends of binding strength for the metals considered. This model was further applied to describe the competition of Ca^{2+} and Mg^{2+} with trace metals for binding to humic

substances (Tipping, 1993). Thus, the utility of the discrete site approach is demonstrated.

The second major strategy in the modeling of humic substances is to treat them as though they are composed of a continuous distribution of sites. This concept dates back more than 50 years (Pauling *et. al.*, 1944). This approach has the advantage of describing whole titration curves with only a few adjustable parameters. Unfortunately, the derived parameters are not immediately compatible with many chemical equilibrium speciation programs.

Perdue and Lytle (1983) successfully treated fulvic acid and aquatic humus pH and Cu(II) titration data with a continuous multiligand distribution, in which the relative concentration of each discrete ligand was normally distributed relative to the log K of the ligand, *i.e.*, a Gaussian distribution. Unfortunately, the proton and metal titration models were created separately and the competition between Cu(II) and H^+ was not described. Inability to model competition is often a problem with continuous distribution models.

Progress has been made by Susetyo *et. al.* (1990) in modeling competition and ionic strength effects with a Gaussian model. These authors assume that the distribution width for binding is the same for protons and metal cations. Ionic strength considerations are also considered, and this model does a good job of reproducing the experimental data.

It may be objectionable to some to assume a Gaussian distribution of binding sites. Other workers (DeWit *et. al.*, 1990) make no assumptions of the shape of the distribution of the ligands. With what they call the LOGA-1 method, these authors were able to determine what they describe as an intrinsic affinity distribution for humate proton

binding. Thus, it is apparent that a Gaussian function is not necessary for continuous distribution models.

In the light of so many different ways to describe humate titration data, it seems that many of them overstate the problem (or the solution). Certainly humic substances are complex, but are not composed of an infinite number of ligands, as implied by continuous distribution models. On the other hand, it is questionable whether discrete site models should rely so heavily on electrostatic information to produce their results. The heterogeneity of these substances renders most electrostatic parameters as nothing more than empirical fitting parameters.

The goal of this work is to develop a simple discrete log K spectrum model to describe both acid-base titrations and metal complexation by humic acids, based on representative data for leonardite humic acid (LHA) obtained at Battelle Pacific Northwest Laboratories (PNL) and reported by Westall *et. al.* (1995). It is asserted that there is no need to treat acid dissociation constants as adjustable parameters, or to arbitrarily select representative values from the literature, because neither of these approaches can produce a unique set of values, anyway. The preferred strategy described herein is to fix a set of log K's that cover the range of pH of acid-base titrations of the LHA, and adjust for the total amount of ligand corresponding to each log K. Further, ionic strength effects will be considered via activity coefficients calculated with the Davies equation (Davies, 1962). The acid-base model will be extended to include interactions with Co(II). In this way, it is hoped to develop an internally self-consistent model of LHA that is straightforward and compatible with chemical equilibrium speciation programs.

EXPERIMENTAL METHODS

Materials

Leonardite humic acid (LHA) was obtained from the International Humic Substances Society (IHSS). The elemental composition of this material is reported by the IHSS as 64.1% C, 3.51% H, 29.82% O, 1.43% N, 0.78% S, 0.30% P by weight, on an ash-free and moisture-free basis. The ash content is 2.38% by weight.

Reagents were $HClO_4$ (Baker ULTREX), NaOH (Baker CO_2-free Dilut-it ampules), and $NaClO_4 \cdot H_2O$ (EM-Science). $HClO_4$ was standardized against Fisher primary standard *tris*(hydroxymethyl)aminomethane, NaOH was standardized against Aldrich primary standard potassium hydrogen phthalate, and the concentrations of $NaClO_4$ stock solutions were determined by direct analysis.

Apparatus

Titrations at PNL were performed with a Metrohm Model DL-40 programmable titrator. A Beckman Model 39423 saturated calomel reference electrode (SCE) with ceramic frit and a Beckman Model 39321 glass electrode were used in the cell:

SCE | $NaClO_4$ (x M), agar | $NaClO_4$ (x M), LHA | glass electrode

The cell was thermostatted at 25.0° ± 0.2° C. All operations (transfers, dialysis, and titrations) were carried out in a N_2-filled glove box.

Acid-base titrations

The LHA was pretreated by dialysis to replace all strong-acid anions with ClO_4^- and all strong-base cations with Na^+, establishing well

defined starting conditions for subsequent acid-base balances. LHA was added to 0.001 M $NaClO_4$ to make a solution of approximately 2000 mg_{LHA}/L (1200 mg_C/L) and pH value in the range 3.7-3.8. This solution was adjusted to pH ≈ 7.2 and maintained at this value for 1 week. The LHA appears to dissolve readily under these conditions. This LHA solution was then transferred to dialysis tubing (Spectrum Spectra/Por, 3500 molecular-weight-cutoff) and dialyzed for 1 week against 0.001 M $NaClO_4$, with daily replacement of $NaClO_4$. The dissolved organic carbon (DOC) concentration determined for this dialyzed LHA solution was 861 mg_C/L. The difference between carbon added and found was attributed to loss of DOC through the dialysis membrane and dilution during dialysis.

The titration procedure consisted of three cycles in pH, each at a different $NaClO_4$ concentration. An aliquot of the dialyzed stock solution of LHA was added to the titration vessel and the concentrations of LHA and $NaClO_4$ adjusted. The solution was then titrated from the initial pH ≈ 7 to pH ≈ 4 to pH ≈ 10 and back to pH ≈ 7, with $HClO_4$ or NaOH. The $NaClO_4$ concentration was then adjusted, and the titration cycle repeated. Thus, the data available from these experiments are solution pH over the range pH ≈ 4-10 and corresponding total concentrations of strong acid and strong base added, at three nominal $NaClO_4$ concentrations: 1.37 mM, 10.1 mM, and 88.3 mM. For determination of the acidity constants of LHA, only the data at the two higher ionic strengths, between pH 4.5 and 9.5, were used.

Additional experiments investigating effect of DOC concentration and hysteresis in the titration cycles were conducted, but the results are not discussed in detail here. In summary, effects are detectable, but not large enough to affect the general conclusions presented here.

Association of Co(II) with LHA

Methods and data are described in detail by Zachara *et al.* (1993). Solutions of LHA in 0.1 M or 0.01 M $NaClO_4$ were added to Spectrum Spectra/Por 1000 molecular-weight-cutoff dialysis tubing immersed in 0.1 M or 0.01 M $NaClO_4$ solution. Co(II) was added to the external solution. After a four-day equilibration period, the DOC concentration and total concentration of Co(II) were determined inside and outside the dialysis tubing. The average concentration of LHA was 50 mg_C/L inside the tubing. The data available from these experiments are Co(II) concentrations inside and outside the dialysis bag under two sets of conditions: (i) varying total Co(II) concentration at constant pH ≈ 6.7 at 0.1 M and 0.01 M $NaClO_4$; and (ii) varying pH, at constant total Co(II) concentration (10^{-6} M) at 0.1 M and 0.01 M $NaClO_4$.

RESULTS

Proton balance for acid-base chemistry of LHA in $NaClO_4$

The objective of a model for the acid-base chemistry of a humic substance is to relate the observed hydrogen ion activity (pH) to the amount of strong acid or base added to the system. This relation is defined by the proton balance equation (Morel, 1983):

$$T_H = C_a - C_b = [H^+] - [OH^-] - \Sigma [L_i^-] - \Sigma [NaL_i] \qquad (3.1)$$

where T_H is a convenient abbreviation for $C_a - C_b$, C_a and C_b represent the total concentrations of strong acid and strong base added to the system (mol/L), [*X*] represents the concentration of species *X* (mol/L),

and the summation is taken over all types of acidic functional groups *i*, each of which is said to react according to

$$HL_i = L_i^- + H^+ \qquad K_a(i) \qquad (3.2)$$

$$HL_i + Na^+ = NaL_i + H^+ \qquad {}^*K_{Na}(i) \qquad (3.3)$$

and to be constrained by the material balance condition

$$T_{HL}(i) = [HL_i] + [L_i^-] + [NaL_i] \qquad (3.4)$$

Implicit in the formulation of Equation 3.1 is the understanding that the species HL_i is the *de facto* reference state for the ligand with respect to proton balance, that is, if only pure HL is added to a pure strong electrolyte solution, $T_H = 0$ for that solution.

Development of the model amounts to determining values of $K_a(i)$, ${}^*K_{Na}(i)$, and $T_{HL}(i)$ that relate experimentally determined values of pH to T_H. Although this problem statement appears to be straightforward, a fundamental problem exists in characterizing the proton balance. The quantity T_H can be separated into two components,

$$T_H = T_H^0 + \Delta T_H \qquad (3.5)$$

where T_H^0 accounts for the amount of residual acid or base that is in the humic substance as it is received or that is added during pretreatment, and ΔT_H represents the amount of acid or base added to the solution during a titration. Although ΔT_H can be determined with ease, it is very difficult to determine unambiguously the value of T_H^0. Thus,

despite the fact that the value of ΔT_H is easily known, the *actual value* of T_H is not known with such certainty.

There are several partially satisfactory approaches to solving this problem. Method 1: before titration of the humic substance, dialyze it exhaustively against deionized water, or pass it through a mixed bed ion-exchanger until all traces of strong acid anions and strong base cations are removed from the system; Method 2: before titration of the humic substance, adjust the pH of the solution to a predetermined low value, (*e.g.*, pH 3), at which it is assumed that $[L_i^-]$, $[NaL_i]$, and $[OH^-]$ contribute negligibly to Equation 3.1, and set $T_H = [H^+]$ at this point; Method 3: before titration of the humic substance, adjust the pH of the solution to a predetermined moderately low pH value (*e.g.*, pH 4), at which point it is assumed that Equation 3.1 reduces to

$$[H^+] \approx \Sigma [L_i^-] + \Sigma [NaL_i] \qquad (3.6)$$

and set $T_H = 0.0$ at this pH; and Method 4: carry out the titration without any special pretreatment of the humic substance as described above, and simply treat the initial value of T_H at the outset of the titration, T_H^0, as an adjustable parameter.

In this study, both the third and fourth methods were applied to titrations of LHA and produced essentially the same results. For the third method, the initial cycle of the titration curve was extrapolated-interpolated to estimate the value of ΔT_H required to adjust the LHA solution from its initial pH ≈ 7.2 to exactly pH 4.00, at which point T_H was set to 0.0 M. All other T_H values were calculated relative to this reference point (pH 4.00, 1.37 mM $NaClO_4$).

For the fourth method, the raw ΔT_H data was used, for which ΔT_H = 0 when the LHA solution was initially added to the titration vessel (pH ≈ 7.2, 1.37 mM $NaClO_4$), and let T_H^0 be an adjustable parameter. In this case, T_H^0 effectively is the amount of base added to dissolve and then pH-stat the initial LHA solution at pH 7.2. As will be discussed, the absolute value that was returned by the model for T_H^0 was 302 μM, a little more than the amount of acid estimated in the third method that was required to adjust the solution from pH 7.2 back to the reference pH 4.00, namely 238 μM. The values of the other adjustable parameters were virtually the same in both approaches; only $T_{HL}(1)$, with pK_a = 4, covaries slightly with T_H^0, as might be expected. Thus, it appears that methods 3 and 4 agree reasonably well, except that the model of method 4 indicates that the pH of a solution of pure LHA in the fully protonated form, is slightly less than pH 4.00, the declared reference value in method 3. This is encouraging, because the initial LHA solution, before any pretreatment, does have a pH less than 4.00, and that is pH 3.8.

Method 4 can be tested experimentally by titration and model of undialyzed LHA. One factor affecting the knowledge of T_H is the loss of H^+ or LHA during the dialysis step. Thus, titration and model of undialyzed LHA should indicate the validity of the determination of T_H^0 by the discrete log K spectrum model.

In a check of method 4, a batch of LHA was prepared by dissolution and pH-stat at pH 7. After a four day dissolution period, the solution was stored under N_2 for one week. A portion of the stock solution was diluted and then titrated in 0.100 M and 0.0100 M $NaClO_4$. The data were modeled as described above, and the absolute value that was returned for T_H^0 was 227.4 μM; accounting for dilution, the amount of base in the LHA solution when added to the titration cell was 224.3 μM. The excellent

agreement between these two values is evidence of the correct estimation of T_H^0 by the discrete log K spectrum model.

Model for acid-base chemistry of LHA

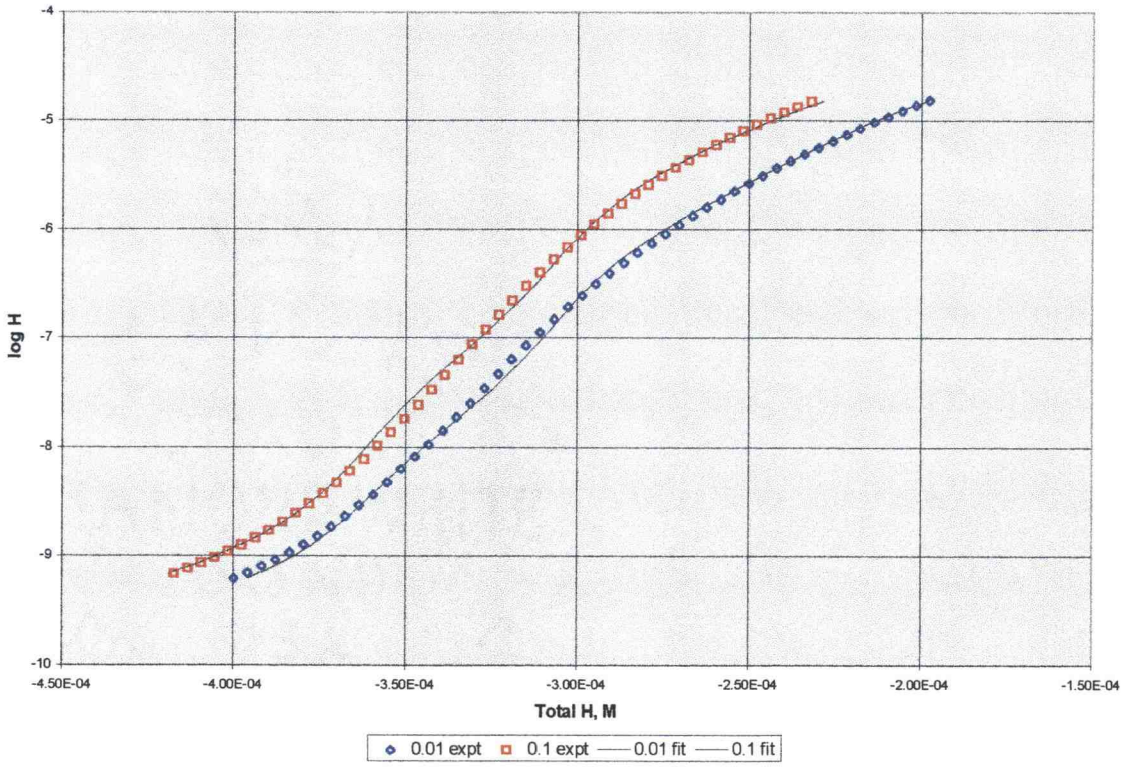
The experimental data for the titration of LHA in 0.01 M and 0.1 M $NaClO_4$ are shown in Figure 3.1. These curves show no distinct inflection points and are generally featureless, as is typical for humic acid titrations.

The model is based on Equations 3.1-3.5, with four acid sites HL_i. In principle, this model for LHA could involve 13 adjustable parameters--four $T_{HL}(i)$, T_H^0, four $K_a(i)$, and four $^*K_{Na}(i)$--which is how the modeling initially began. However, it was quickly realized that so many adjustable parameters produced an intractable problem. To reduce the number of adjustable parameters, the four $K_a(i)$ were fixed as a discrete pK_a spectrum and assigned values of 4, 6 ,8, and 10 to cover the pH range of the experiment; the four $T_{HL}(i)$ remain adjustable parameters. With this modification, the values determined for the four $K_{Na}(i)$ were approximately equal. Furthermore, because the shift of the curves with sodium concentration is relatively independent of pH, it was felt that a single constant for sodium exchange could replace the four individual constants. Thus, the association of Na^+ with LHA (Reaction 3.3) was re-expressed by the reaction

$$L_i^- + Na^+ = NaL_i \qquad K_{Na}(i) \qquad (3.7)$$

and one value of K_{Na} was used for all four of the acid groups. Hence, the six adjustable parameters that remain are the four values of $T_{HL}(i)$, T_H^0, and K_{Na}.

Figure 3.1. Titrations of LHA in 0.01 M and 0.1 M $NaClO_4$, with LHA Concentration of 41.2 mg_C/L. Modeled with four-discrete-site pK_a spectrum: pK_a = 4, 6, 8, and 10 with one constant for the exchange of sodium for hydrogen; constants listed in Table 3.II. Symbols represent experimental data; lines were calculated from model defined in Tables 3.I and 3.II.



The values of these adjustable parameters have been determined by the parameter optimization program FITEQL 3.1 (Herbelin and Westall 1994; Westall, 1982a,b). Since some aspects of this study involve unconventional applications of FITEQL, the procedure will be described briefly.

In the preparation of a problem for FITEQL, components are sorted into three formal categories: Type I are those for which *only* total concentration is known or to be determined (*i.e.*, HL_i and Na^+); Type II are those for which *both* total concentration and free concentration are known (*i.e.*, H^+); and Type III are those for which *only* "free concentration" is known or to be determined (*i.e.*, y and K_{Na}).

The Type III components in this problem, y and K_{Na} as shown in Tables 3.I and 3.II, are unconventional. Component y is part of the mathematical formalism through which ionic strength and activity coefficient calculations are made in FITEQL (Westall 1982b); values of activity coefficients were calculated with the Davies equation (Davies, 1962). By treating K_{Na} as a Type III component, a single value for K_{Na} that applies simultaneously for all four acid groups can be determined. The FITEQL stoichiometry matrix (A-matrix) that was used for this problem is shown in Table 3.I (with only two of the four acid groups shown for economy).

The values of total concentrations $T_{HL}(i)$ and T_H^0, and log K_{Na} from the parameter adjustment procedure are listed in Table 3.II, and the titration curves calculated from the model are represented by the lines in Figure 3.1. The agreement between the experimental data and the calculations is very satisfactory. This model was used as a starting point to describe the interaction of Co(II) with LHA.

Table 3.I. FITEQL Stoichiometry Matrix for Acid-base Chemistry. For simplicity, LHA has been represented here by two acid groups; in the actual model, four acid groups were used, as shown in Table 3.II.

Name	log K	HL_1	HL_2	Na^+	H^+	y[a]	K_{Na}
HL_1	0.000	1	0	0	0	0	0
HL_2	0.000	0	1	0	0	0	0
Na^+	0.000	0	0	1	0	0	0
H^+	0.000	0	0	0	1	0	0
L_1^-	-4.000	1	0	0	-1	-2	0
L_2^-	-6.000	0	1	0	-1	-2	0
NaL_1	-4.000	1	0	1	-1	0	1
NaL_2	-6.000	0	1	1	-1	0	1
OH^-	-14.00	0	0	0	-1	-2	0

[a] Used to incorporate activity coefficient in mass action equations; the value of y is the $\log_{10}$ of the activity coefficient for a singly charged ion. See Westall (1982b) for details.

Table 3.II. Parameter Values for Model of LHA Acid-base Chemistry. Parameters derived from data in Figure 3.1, for titrations of 41.2 mg_c/L LHA in 0.01 M and 0.10 M $NaClO_4$ and four site discrete log K spectrum model illustrated in Table 3.I.

Components ID	Type	Species ID	log K	T (M)	Adjustable Parameters	Serial Data
HL_1	I	L_1	-4.000	HL_1 2.215E-4	T HL_1	Total Na
HL_2	I	L_2	-6.000	HL_2 8.400E-5	T HL_2	Total H
HL_3	I	L_3	-8.000	HL_3 5.725E-5	T HL_3	Free H
HL_4	I	L_4	-10.000	HL_4 6.465E-5	T HL_4	"Free" y
Na	I	NaL_1	1.791	H^0 -3.021E-4	T_H^0	
H	II	NaL_2	1.791		log K_{Na}	
y	III	NaL_3	1.791			
K_{Na}	III	NaL_4	1.791			
		OH	-14.000			

Model for interaction of Co(II) with LHA

Data are available for two sets of conditions: (i) continuously varying pH at constant total Co(II) concentration and two concentrations of $NaClO_4$, as shown in Figure 3.2; and (ii) continuously varying concentrations of Co(II) at constant pH and two concentrations of $NaClO_4$, as shown in Figure 3.3. The data in Figure 3.2 are presented as the distribution ratio as a function of pH. The distribution ratio (K_d) is defined by:

$$K_d = \frac{\Sigma\ [CoL_i]}{DOC(g_C/L)\quad [Co^{2+}]} \qquad L/g_C \qquad (3.8)$$

where $\Sigma\ [CoL_i]$ is the concentration of Co(II) bound to LHA (mol/L), $DOC(g_C/L)$ is the concentration of LHA in g_C/L, and $[Co^{2+}]$ is the concentration of free Co^{2+} (mol/L). K_d has the units L/g_C. Co^{2+} is assumed to react with LHA formally by the reaction

$$HL_i + Co^{2+} = CoL_i^{+} + H^{+} \qquad {}^{*}K_{Co}(i) \qquad (3.9)$$

Equations 3.8 and 3.9 are re-expressed in the FITEQL stoichiometry matrix for the Co-LHA interaction as illustrated in Table 3.III (with only two of the four sites shown for simplicity). In the model, components HL_i and Na^+ are Type I, component $\overline{Co^{2+}}$ (where the overbar designates material balance for species in the dialysis bag) is Type II, and components Co^{2+}, H^+, y, K_{Na}, and $K_{Co}(i)$ are Type III. Two unconventional features of FITEQL warrant further explanation.

The key to this optimization problem is the use of $\overline{Co^{2+}}$ as a Type II "dummy" component. The value of $\overline{T_{Co}}$ is the total concentration of Co(II) determined for the solution in the dialysis bag. FITEQL's

optimization procedure is based on adjusting parameters to minimize the weighted difference between *experimental* and *calculated* total concentrations of Type II components. In this case, the optimization procedure adjusts the log K's of $\overline{CoL_i}$ to minimize the difference between the *experimental* value for Co(II) in the dialysis bag (*i.e.*, $\overline{T_{Co}}$) and the *calculated* value for Co(II) in the dialysis bag (*i.e.*, $\overline{[Co^{2+}]} + \Sigma\ \overline{[CoL_i]}$). This procedure can be restated: minimize the weighted sum of squares of the values of $\overline{Y_{Co}}$ calculated at each serial data point, where

$$\overline{Y_{Co}} = \overline{[Co^{2+}]} + \Sigma\ \overline{[CoL_i]} - \overline{T_{Co}} \qquad (3.10)$$

This concept is incorporated in the FITEQL stoichiometry matrix for this problem, shown in Table 3.III.

The formation constants for CoL_i were set up as Type III components (similar to K_{Na} in the acid-base model) to represent the binding constants of Co^{2+} to the deprotonated sites:

$$Co^{2+} + L_i^- = CoL_i^+ \qquad K_{Co}(i) \qquad (3.11)$$

This formulation with $K_{Co}(i)$ as a Type III component allows the Co(II) binding constant to be uncoupled from the acidity constant of the LHA, as shown in Table 3.III.

Thus, the model for the Co-LHA interaction is the acid-base model for LHA with four additional reactions for the formation of CoL_i^+. (The values of $T_{HL}(i)$ for the Co-LHA model are of course scaled to correspond to the DOC concentrations of the Co-LHA experiments.)

Values of log $K_{Co}(i)$ were determined from the pH-dependent data in Figure 3.2 and the model in Table 3.III. The values of log $K_{Co}(i)$ that

Figure 3.2. Distribution Ratio (K_d) of Co^{2+} Bound to LHA as a Function of pH and $NaClO_4$ Concentration. Average LHA concentration was 50.3 mg_C/L isolated in dialysis bag. Modeled with the four-discrete-site spectrum model; constants listed in Table 3.IV. Symbols represent experimental data; lines were calculated from model defined in Tables 3.III and 3.IV. Data from Zachara *et. al.* (1993).

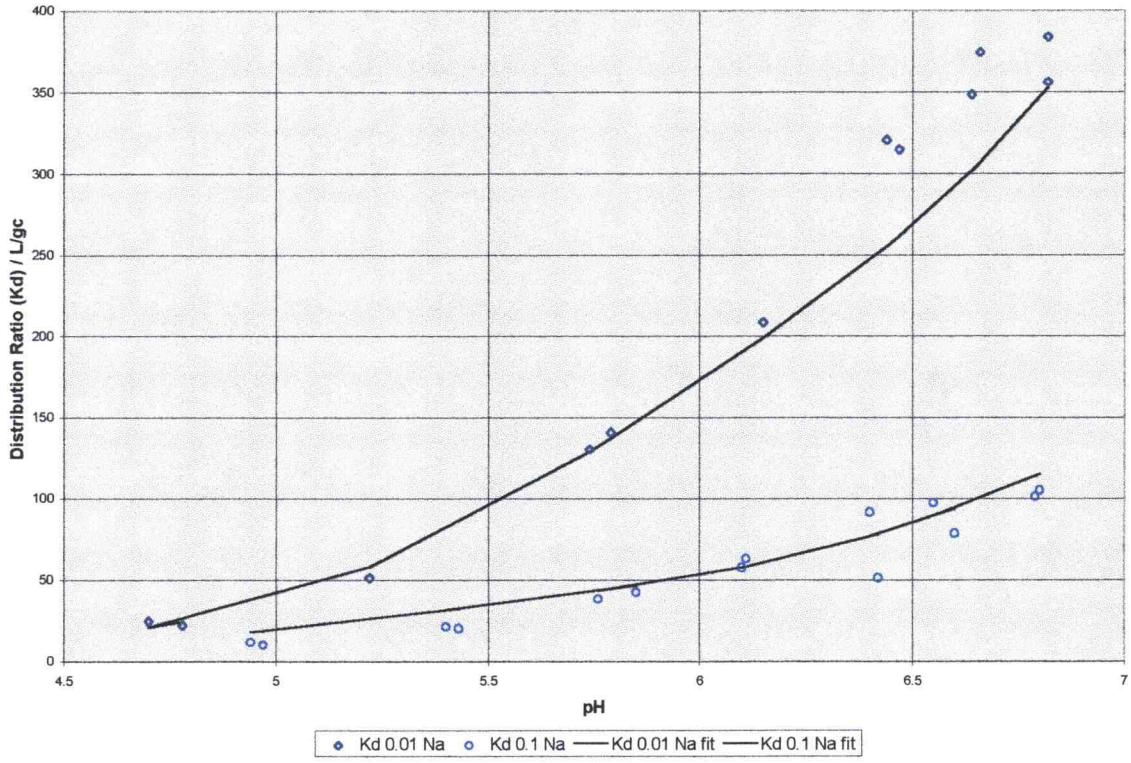


Figure 3.3. Co^{2+} Binding to LHA at Constant pH ≈ 6.7 at Two $NaClO_4$ Concentrations. Average LHA concentration was 50.3 mg_C/L isolated in dialysis bag. Modeled with the four-discrete-site spectrum model; constants listed in Table 3.IV. Symbols represent experimental data; lines were calculated from model defined in Tables 3.III and 3.IV. Data from Zachara *et. al.* (1993).

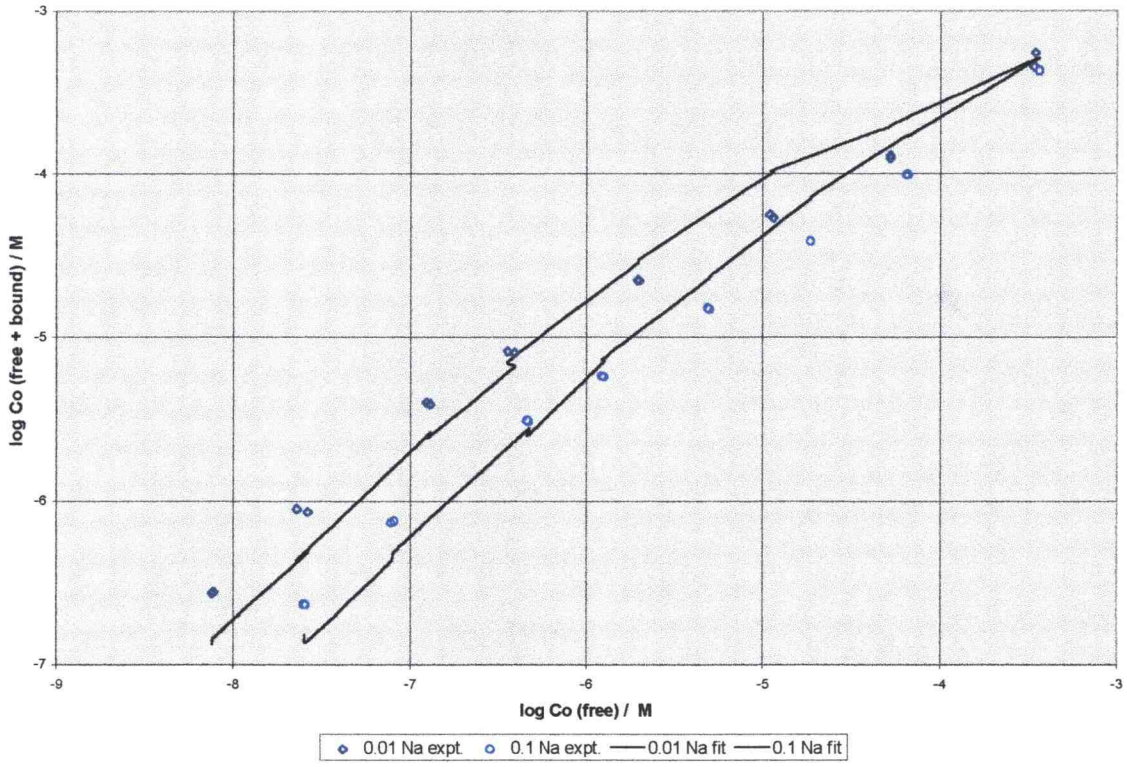


Table 3.III. FITEQL Stoichiometry Matrix for Co(II)-LHA Interaction. For simplicity, the LHA has been represented by a two-site system. The actual model was a four-site system as shown in Table 3.IV.

Name	log K	HL_1	HL_2	Na^+	$\overline{Co^{2+}}$	Co^{2+}	H^+	y[a]	K_{Na}	$K_{Co}1$	$K_{Co}2$
HL_1	0.00	1	0	0	0	0	0	0	0	0	0
HL_2	0.00	0	1	0	0	0	0	0	0	0	0
Na^+	0.00	0	0	1	0	0	0	0	0	0	0
$\overline{Co^{2+}}$	0.00	0	0	0	1	1	0	0	0	0	0
Co^{2+}	0.00	0	0	0	0	1	0	0	0	0	0
H^+	0.00	0	0	0	0	0	1	0	0	0	0
L_1^-	-4.00	1	0	0	0	0	-1	-2	0	0	0
L_2^-	-6.00	0	1	0	0	0	-1	-2	0	0	0
NaL_1	-4.00	1	0	1	0	0	-1	0	1	0	0
NaL_2	-6.00	0	1	1	0	0	-1	0	1	0	0
$\overline{CoL_1^+}$	-4.00	1	0	0	1	1	-1	2	0	1	0
$\overline{CoL_2^+}$	-6.00	0	1	0	1	1	-1	2	0	0	1
OH^-	-14.0	0	0	0	0	0	-1	-2	0	0	0

[a] Used to incorporate activity coefficient in mass action equations; the value of y is the $\log_{10}$ of the activity coefficient for a singly charged ion. See Westall (1982b) for details.

were determined are listed in Table 3.IV, and values of K_d calculated from the model are shown as the lines in Figure 3.2. As seen in the figure, agreement is best below pH 6. As the pH increases, the influence of sodium on cobalt binding is not represented well by the model, but overall agreement is good.

These values of log $K_{Co}(i)$ were then applied to the fixed-pH, varying-T_{Co} data (Figure 3.3) without further adjustment. The calculated distributions of Co(II) are represented by the lines in Figure 3.3. Attempts at improving the fit, within the constraints of the model described so far, were unsuccessful.

As one might expect, agreement in Figure 3.3 is best in the region where Co(II) concentration is about 1 μM, the concentration of Co(II) in the experiment from which the adjustable parameters were determined. The model underestimates the competition between sodium and cobalt, particularly as Co(II) concentration increases. Sodium concentration has a large effect on the cobalt binding but does not have such a pronounced effect on the proton binding. This competition between sodium and cobalt cannot be explicitly represented in the simple model of LHA presented here. It is possible to adapt the model into a Stern representation, treating H^+ as an inner-sphere cation and Na^+ and Co^{2+} as outer-sphere cations, but this modification has not been attempted, for reasons to be discussed.

DISCUSSION

This work presents a scheme to represent humate titration data in the framework of a discrete site pK_a spectrum model. While it is recognized that humic substances are not actually composed of a few

Table 3.IV. Parameter Values for Model of Co(II)-LHA Interaction. $T_{HL}(i)$ and K_{Na} from acid-base model of LHA; average concentration of LHA in Co-LHA data sets was 50.3 mg_C/L.

Components ID	Type	Species ID	log K	T^a (M)	Adjustable Parameters	Serial Data
HL_1	I	L_1	-4.000	HL_1 2.706E-4	log $K_{Co}(2)$	Total Na^+
HL_2	I	L_2	-6.000	HL_2 1.026E-4	log $K_{Co}(3)$	Total Co^{2+}
HL_3	I	L_3	-8.000	HL_3 6.995E-5		Free Co^{2+}
HL_4	I	L_4	-10.000	HL_4 7.899E-5		Free H^+
Na^+	I	NaL_1	1.791			"Free" y
$\overrightarrow{Co^{2+}}$	II	NaL_2	1.791			
Co^{2+}	III	NaL_3	1.791			
H^+	III	NaL_4	1.791			
y	III	CoL_1[b]	-12.00			
K_{Na}	III	CoL_2	5.415			
$K_{Co}(1)$	III	CoL_3	6.329			
$K_{Co}(2)$	III	CoL_4[b]	-12.00			
$K_{Co}(3)$	III	OH^-	-14.00			
$K_{Co}(4)$	III					

[a] $T_{HL}(i)$ values in Table 3.II scaled for [DOC] by the factor 50.325/41.19.

[b] During fitting procedure, contributions of CoL_1 and CoL_4 were found to be negligible. Thus, log $K_{Co}(1)$ and log $K_{Co}(4)$ were set to -12.00 to eliminate these species from consideration.

distinct functional groups, it is clear from Figure 3.1 that titrations of these materials can be described in this manner.

To describe the titration curves of LHA, it was first necessary to choose an appropriate spectrum of log K_a. The spectrum should correspond to the pH range of the data and should contain pK_a values representative of functional groups that one would expect to find in a humic acid. The spectrum of pK_a's chosen here (4, 6, 8, and 10) fills both of these requirements: i) the pH of the LHA titrations runs from about 4 to 10; and ii) pK_a's 4 and 6 approximately correspond to carboxylic acids, pK_a 8 to amino acids, and pK_a 10 to phenols.

The appropriateness of the values of $T_{HL}(i)$ determined in this study can be supported by comparing them to literature values for other humic substances. It is important at this point to note that the carboxylic, amino, and phenolic content of LHA has not yet been determined, and the following comparisons are made only as a check to see if the model makes physical sense, and should not be construed as deriving structural information from the titration data, as others have done (Ephraim *et. al.*, 1986).

If the sum of $T_{HL}(1)$ and $T_{HL}(2)$ (see Table 3.II) is taken to indicate carboxylic acid content in LHA and normalized to the mass of LHA present, one obtains 4.8 $mmol/g_{LHA}$. This compares well to values published for other humic substances: Perdue and others (1980) report 4.4 - 6.3 mmol/g carboxylic acid content for Satilla River humic substance (SRHS); Malcolm and MacCarthy (1986) give 4.6 mmol/g for Sanhedron A1 soil humic acid (SSHA). Similarly, if $T_{HL}(4)$ represents the phenolic content of LHA, one calculates 1.0 $mmol/g_{LHA}$, which is close to the published value of 1.7 mmol/g for SSHA (Malcolm and MacCarthy, 1986). $T_{HL}(3)$, the "amino acid" contribution in the model, gives 0.89 $mmol/g_{LHA}$, possibly a little high for this type of group, but not

unreasonable compared to Thurman's (1989) values of 0.478 - 0.707 mmol/g for soil humic acids. The "total acidity" found in the LHA, the sum of $T_{HL}(i)$, is 6.6 mmol/g_{LHA}, comparable to other humic substances, *e.g.*, 5.0 mmol/g for SRHS (Perdue *et. al.*, 1980).

The value determined for T_H^0, 302 μM, is a little more than the 238 μM value estimated to change the LHA solution from pH ≈ 7.2 to pH = 4.00, but is consistent with the initial pH value of the LHA suspension of about 3.8. Application of the model to titration data of undialyzed LHA produced an estimate of T_H^0 of 227.4 μM, a nearly exact calculation of the 224.3 μM concentration of base known to be in the system. The success in estimating T_H^0 supports the validity of the definitions and assumptions underlying the parameters of the model.

Finally, the small value of K_{Na} indicates that sodium is weakly bound by LHA, and that a change in Na^+ concentration will have a small effect on acid-base titrations of LHA. This observation is also reported by other authors (Bartschat *et. al*, 1992). The agreement between model, data, and the physical values reported for other humic substances fully supports the discrete log K spectrum model for LHA.

Consider now the issue of the model applied to the interaction of Co(II) and LHA. It can be seen in Figure 3.2 that the model accounts fairly well for the amount of Co(II) bound to LHA, particularly in 0.1 M $NaClO_4$. The values of log $K_{Co}(i)$ (see Table 3.IV) are in the range of log K's determined for the 1:1 complexes (ML) of Co(II) with salicylic acid (6.72 @ 20° C, 0.15 I), citric acid (5.00 @ 20° C, 0.1 I) (Martell and Smith, 1977), N,N-*bis*(2-hydroxypropyl) glycine (5.16 @ 30° C, 0.1 I) and L-histidine (6.90 @ 25° C, 0.1 I) (Martell and Smith, 1974). Thus, the model is consistent with types of molecules that one might expect to find in LHA, and this consistency supports the approach used here.

There is room for improvement for the fit in Figure 3.3, and one might expect improvement by the addition of an electrostatic parameter to the model. At pH 6.8, the charge on the LHA is likely to be substantial, and so have an important influence on the shape of the isotherm. However, before the electrostatic modification can be done satisfactorily, certain information needs to be obtained, namely, the size of LHA molecules and the molecular weight of LHA. At the time of this writing, these parameters are unknown to have been determined. On the other hand, if size heterogeneity in LHA molecules is as significant as has been reported for other humic substances (Bartschat *et. al.*, 1992), addition of electrostatic parameters to the current model is of questionable value. They would amount to just another set of empirical adjustable parameters. One may as well just include more binding sites for Co(II), or devise an empirical electrostatic relationship (*e.g.*, Tipping and Hurley, 1992) to account for ionic strength effects and the influence of charging of the humate molecule on metal binding.

To its favor, the simple model of Co-LHA interaction reasonably describes the shape of the isotherm in Figure 3.3. This seems quite remarkable since the model was developed from pH-dependent data at *constant* total Co(II) concentration. Furthermore, this agreement affirms the plausibility of the approach in developing the model. That is, from "multidimensional" data sets, an internally self-consistent model was produced that accounts for the small effect of ionic strength on acid-base titrations and the larger effect of ionic strength on metal binding. This strategy is followed to some degree in the development of other discrete site models (Bartschat *et. al.*, 1992; Tipping and Hurley, 1992; Ephraim and Marinsky, 1986), and in at least one continuous distribution model (Susetyo *et. al.*, 1990). In each case, the model reasonably represented the data, illustrating the fact that there is no

unique solution to modeling heterogeneous substances. What seems to be most important in the numerical modeling of humic substances is to develop and maintain a consistent approach to solving the problem.

SUMMARY

In this work, a discrete log K spectrum model was developed to describe proton and metal binding by leonardite humic acid (LHA). By fixing a set of log $K_a(i)$ corresponding to the pH range of acid-base titrations, and adjusting for $T_{HL}(i)$ and a common sodium exchange constant for each site, it was found that the acid-base titrations could be described very well without the addition of complex electrostatic parameters. The model of LHA was extended to model the Co(II) interaction with LHA as a function of pH and a cobalt concentration of 1 μM. With only two active binding sites for Co(II), the model accounted well for the large effect of ionic strength on the Co-LHA interaction and correctly reproduced the distribution of bound and free cobalt between pH ≈ 4.5 and pH ≈ 7. The model was extrapolated to describe the isotherm of Co-LHA interaction from approximately 10^{-8} to 10^{-3} M Co(II) at pH ≈ 6.7. The discrete log K spectrum model did a reasonable job of predicting the shape of the isotherm, even better than one might expect. Such good agreement between model and data is supportive of the strategy of incorporating several different data sets to produce an internally self-consistent model of a humic substance.

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Chapter 4: On Variations in Humate Titrations

INTRODUCTION

It has been noted elsewhere (Chapter 3) that studies of heterogeneous materials are plagued by many problems that are inherent to the heterogeneity of the material itself. Among the properties that can cause difficulties in data analysis are heterogeneity in size, shape, and chemical composition. Each of these contributes to less than ideal observations of say, adsorption, electrostatic interactions, and chemical reactivity, complicating any model developed to explain or predict them.

In the study of humic acids, many models and approaches have been proposed to account for the known or assumed heterogeneity of the material being studied. These range from completely empirical models that describe the data with a minimum of adjustable parameters, to very detailed models extrapolated from theoretical calculations and experiments performed on pure, homogeneous substances. In the first approach, the fit to the data is usually quite good, however, the model is sufficient only for interpolation within the data set that produced the model. In the second approach, the fit to the data may also be very good, but it seems questionable to assume that one can effectively translate chemical theory meant for homogeneous materials to a heterogeneous and only partially characterized material like a humic acid. There is merit for both approaches in the modeling of heterogeneous substances, but it would seem that the most effective approach lies somewhere in the middle, *i.e.*, a semi-empirical approach.

One merit of the semi-empirical approach is basically that of the purely empirical approach: to produce a model that fits the data with a

minimal number of adjustable parameters. A second strength of the semi-empirical approach is that it is based upon fundamental mass action and mass balance equations defined by a logical set of chemical reactions that are expected to take place within the substance being studied.

The usefulness of the semi-empirical framework for modeling the chemical equilibria of a humic substance has recently been demonstrated (Westall *et. al.*, 1995). These authors developed an internally self consistent model to describe the acid-base and metal complexation equilibrium of leonardite humic acid (LHA) which they describe as a discrete log K spectrum model. Briefly, this model describes a humic acid by specifying a discrete distribution of values of log K_a that are typical of organic acids and cover the range of pH of the data, and adjusts the total amount of acidic functionality for each log K_a to account for the shape of the titration curves. The model is described in a bit more detail below.

It is the purpose of this paper to further demonstrate the usefulness of the discrete log K spectrum model by applying it to variations and variants of the authors' original data. Specifically, the modeling framework will be applied to sets of LHA titration data obtained by two different laboratories (Battelle Pacific Northwest Laboratories (PNL) and Oregon State University (OSU)) and used to reconcile apparent differences in the data. It will then be shown that the discrete log K spectrum model can be applied to another humic substance, furthering our understanding of its behavior.

THEORY

The discrete log K spectrum model is described in detail by Westall *et. al.* (1995) to which the reader should refer for a lengthier

treatment of the development of the model. A summary of the model is described here. The model consists of a set of acidic functional groups, HL_i, said to react according to

$$HL_i = H^+ + L_i^- \qquad K_a(i) \qquad (4.1)$$

$$HL_i + M^+ = ML_i + H^+ \qquad {}^*K_M(i) \qquad (4.2)$$

and to be constrained by the material balance condition

$$T_{HL}(i) = [HL_i] + [L_i^-] + [ML_i] \qquad (4.3)$$

In the case of the acid-base chemistry for LHA (and later for peat humic acid, PHA) the metal denoted in Equations 4.2 and 4.3 is sodium.

The objective of the model is to relate the measured hydrogen ion activity to the amount of strong acid or base added to the system, defined by Morel (1983) as

$$T_H = C_a - C_b = [H^+] - [OH^-] - \Sigma\,[L_i^-] - \Sigma\,[NaL_i] \qquad (4.4)$$

where C_a and C_b represent the total concentrations (mol/L) of strong acid or base added to the system and $[X]$ represents the concentration (mol/L) of species X. The value of T_H can be further defined during a titration as

$$T_H = T_H^0 + \Delta T_H \qquad (4.5)$$

where T_H^0 represents the total amount of strong acid or base present in the system at the outset of the titration, added during pretreatment, or

already present in the material as received, and ΔT_H is the amount of acid or base added incrementally to the solution during the titration. Establishing the model amounts to determining values of $T_{HL}(i)$, ${}^*K_{Na}(i)$, and T_H^0 that relate the experimentally determined values of pH to T_H within the constraints of material balance and the log K spectrum, which is described below.

Defining the log K spectrum is straightforward. One chooses a set of acid dissociation constants as defined by Reaction 4.1 that bracket the pH range of the titrations to be modeled and that are typical of acidic functional groups expected to be present. For example, the pH range of interest in the LHA titrations is from pH 4 to pH 10. Thus, the pK_a values chosen for the spectrum, 4, 6, 8, and 10, bracket this pH range. Further, these values are representative of acidic functional groups that one would expect to find in LHA molecules, namely, carboxylic acids, amines, and phenols.

EXPERIMENTAL METHODS

The procedure for pretreatment and titration of LHA at PNL is described in detail by Westall *et. al.* (1995). Essentially the pretreatment of LHA is to dissolve it by pH-stat at pH $\approx$ 7 for a period of one week. After dissolution, the LHA solution is transferred to a dialysis bag and equilibrated with 1 mM $NaClO_4$ for another week, with daily changing of the external solution. The intent of the dialysis is to reduce the amount of impurities in the LHA solution that could complicate T_H calculations. After dialysis, the LHA solution is ready for titration.

The pretreatment of the LHA was kept as consistent as possible between PNL and OSU researchers. The procedure for titration of the

material did differ, however. For details of the PNL titration procedure, one should again refer to Westall *et. al.* (1995). The titration of LHA at PNL followed the basic procedure of adjusting the pH of the LHA solution from pH 7 to pH 4, titrating the solution to pH 10, then re-adjusting the solution back to pH 7. At this point, the ionic strength was adjusted by addition of a small volume of concentrated $NaClO_4$, and the cycle of titrations was repeated. This procedure was performed for LHA titrations in $NaClO_4$ concentrations of 0.001 M, 0.01 M, and 0.1 M.

The titration of dialyzed LHA at OSU was performed coulometrically. This method has been demonstrated to produce very accurate and precise results in the titration of primary standards and is expected to work well in the titration of LHA.

Coulometric titration of LHA at OSU was done according to the following general procedure: 1) calibrate the electrodes; 2) perform the humate titration; and 3) recalibrate the electrodes to check for drift. The procedures in the titration process are explained in greater detail below.

Calibration procedure

The electrodes were calibrated volumetrically in 25.00 mL of 0.100 M $NaClO_4$ with fixed additions of 0.0100 M HCl dispensed from a Metrohm Dosimat 655 autoburet. The electrolyte solution was bubbled with N_2 gas for five minutes prior to acid addition. Voltage was polled by the computer every two seconds until ten consecutive readings showed less than 2.5 μV/s drift and less than 25 μV standard deviation of the mean of the ten data points. When these parameters were satisfied, the mean of the last ten voltage readings was taken to be the "equilibrium"

voltage. The voltage *vs.* volume data were used in a non-linear least squares optimization program to determine the parameters $E^{o'}$, k, and C_o as defined in the Nernst equation

$$E = E^{o'} + k \cdot \log[H^+] \tag{4.6}$$

and the concentration of acid in the cell, defined as

$$[H^+] = (C_o V_o + C_A V_A) \; / \; (V_o + V_A) \tag{4.7}$$

where C_o is the concentration of acid in the electrolyte (assumed to be only strong acid), V_o is the initial volume of electrolyte, C_A is the concentration of acid added to the cell, and V_A is the volume of acid added to the cell. Equations 4.6 and 4.7 are the definitive equations used by the fitting procedure. The fitting procedure minimizes the weighted sum of the squares of the differences between $[H^+]$ in Equation 4.6 and Equation 4.7 by adjusting the parameters $E^{o'}$, k, and C_o. The Nernst parameters determined were used later when interpreting the coulometric titration curves.

Titration procedure

A 20-mL aliquot of 0.1500 M or 0.0150 M $NaClO_4$ was added to the cell and the cell lid was clamped on to obtain an airtight seal. Next, 200 µL of 0.01 M HCl was added to the electrolyte and N_2 was bubbled through the acidified solution for 15 minutes to facilitate the removal of CO_2. Nitrogen pressure was equalized in the two cells via a short piece of flexible tubing. The electrolyte solution was then coulometrically neutralized to pH 7, indicated by the potential reading on the electrometer and the calibrated pH electrode. At this point, a 10-mL aliquot of humate solution was added to the cell for the

titration. After humate addition, experimental control was transferred to the computer.

After allowing five minutes for CO_2 to be swept out of the headspace of the cell after humate addition and equilibration of the solution (starting pH was ≈ 6), the controlling program made three small coulometric additions of OH^- (each was 1.0000 mA for 10 s, or 10 mC, equivalent to 3.43 μM additions of base). From the potential change produced by the first three additions, the amount of charge required to change the voltage by -0.010 V was calculated. The program then instructed the current source to operate at 1.0000 mA (or 10.000 mA for additions greater than 30 mC) for the appropriate length of time. The magnitude of each new addition was calculated from the potential change produced by the three previous additions. The parameters for voltage data acquisition were the same as those described for the electrode calibrations. The program terminated when a predetermined number of coulombs was delivered or when the solution pH was computed to be 10 or greater.

After titration of the humate solution, the information in the charge-potential curve was converted to a total H *vs.* log H curve. The converted data was then fit to the discrete log K spectrum model with FITEQL 3.1 (Herbelin and Westall, 1994).

RESULTS AND DISCUSSION

The data from PNL and OSU were modeled with the parameter optimization program FITEQL 3.1 (Herbelin and Westall, 1994) in accordance with the matrix of components and species shown in Table 4.I. The component denoted "y" in the matrix is part of the mathematical formalism for the correction for ionic strength. The equilibrium

Table 4.I. FITEQL Matrix for Model of Leonardite Humic Acid.

	Components								
Species	HL_1	HL_2	HL_3	HL_4	Na	H	y	K_{Na}	log K
HL_1	1								0
HL_2		1							0
HL_3			1						0
HL_4				1					0
Na^+					1		-1		0
H^+						1			0
L_1^-	1					-1	-1		-4
L_2^-		1				-1	-1		-6
L_3^-			1			-1	-1		-8
L_4^-				1		-1	-1		-10
NaL_1	1				1	-1		1	-4
NaL_2		1			1	-1		1	-6
NaL_3			1		1	-1		1	-8
NaL_4				1	1	-1		1	-10
OH^-						-1	-1		-14

constant K_{Na} is represented in the matrix as a component so that a single constant can be used for formation of the species NaL_i at each ligand site. The serial data input to FITEQL for the parameter optimization was total sodium, ΔT_H, log H, and log "y". The parameters optimized were the total concentrations of HL_1, HL_2, HL_3, HL_4, T_H^0, and log K_{Na}.

A set of titrations from PNL (Westall *et. al.*, 1995) and a set of titrations from OSU were modeled with FITEQL; the results obtained are listed in Table 4.II, individually represented in Figures 4.1 and 4.2, and are shown on the same scale in Figure 4.3. Comparing the parameter values in Table 4.II for the two sets of titrations, one sees both similarities and apparent disparities. The similarities are that values for the total concentrations for the groups HL_2, HL_3, and HL_4 were determined to be about the same for both the PNL and OSU data sets. The values of log K_{Na} are also similar. This is encouraging, considering that both laboratories used the same material. However, the values of HL_1 and T_H^0 are significantly different. It will be shown that the internally self-consistent model can be used to resolve apparent differences in the two models of the same substance.

As a first step in resolving the differences between the PNL and OSU models of LHA, consider the overall appearance of the different titration curves in Figure 4.3. The titration curves are similar, except that the pH ranges of the two sets of data are different and are shifted apart along the T_H axis; implications from both of these characteristics will be addressed in turn.

The PNL data run from about pH 4.8 to 9 and the OSU titrations run from pH 4 to 10. Thus, for the model derived from the PNL data, the value for $T(HL_1)$, a species with a defined log K of -4, is based upon an extrapolation outside of the pH range of the data. It is therefore

Table 4.II. FITEQL-Optimized Parameters for LHA Titrations.

Parameter optimized	PNL Result	OSU Result
Total HL_1 (M)	2.215E-04	1.055E-04
Total HL_2 (M)	8.400E-05	8.565E-05
Total HL_3 (M)	5.724E-05	5.435E-05
Total HL_4 (M)	6.466E-05	4.379E-05
Total H^0 (M)	-3.021E-04	-1.392E-04
log K_{Na}	1.791	1.601

Figure 4.1. PNL Titrations of LHA, Data and FITEQL Model.

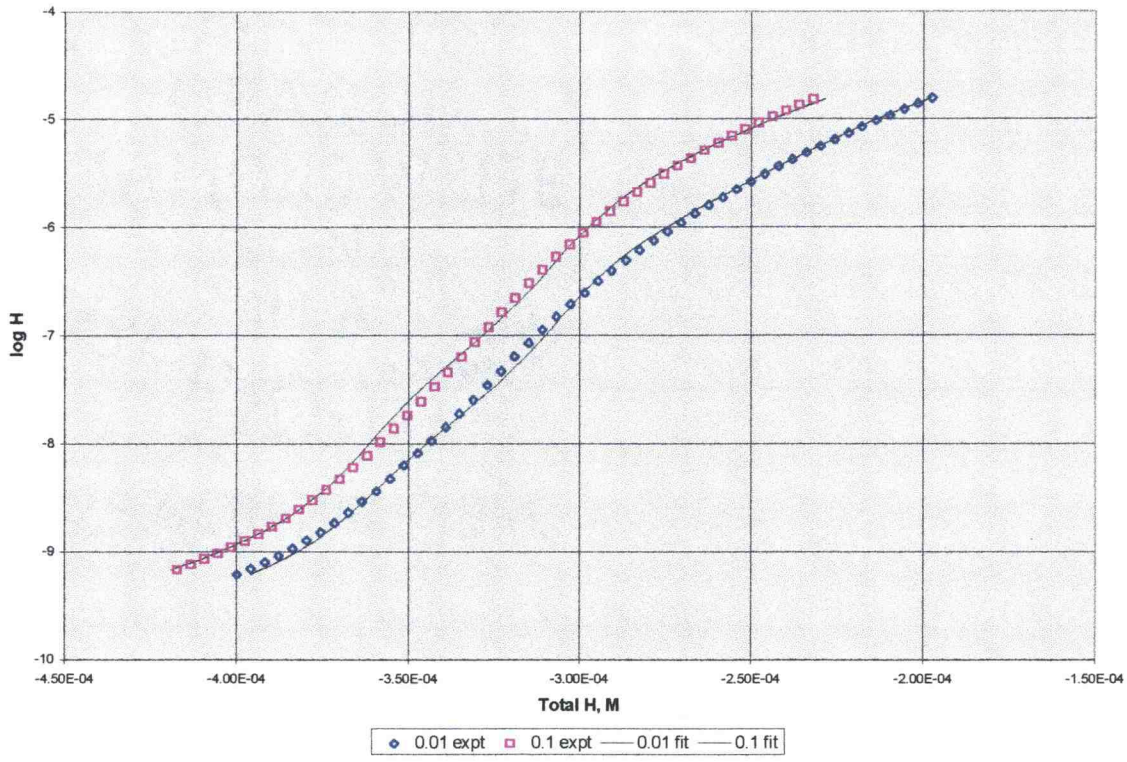


Figure 4.2. OSU Titrations of LHA, Data and FITEQL Model.

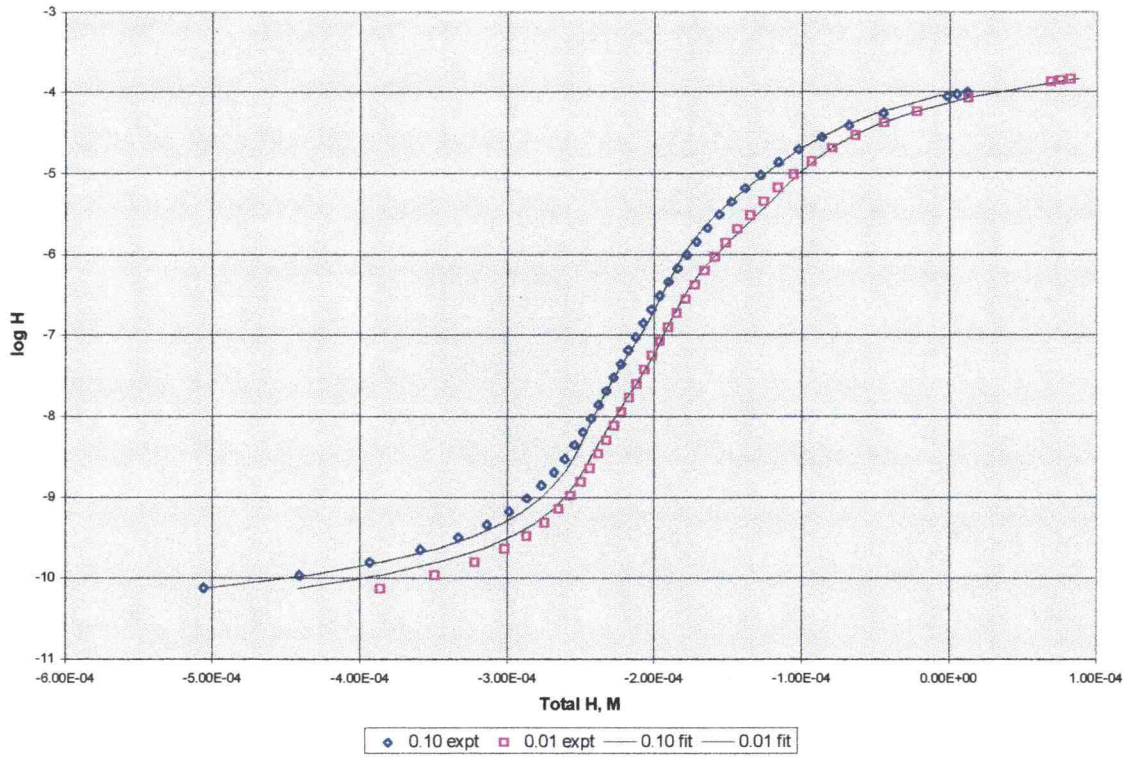
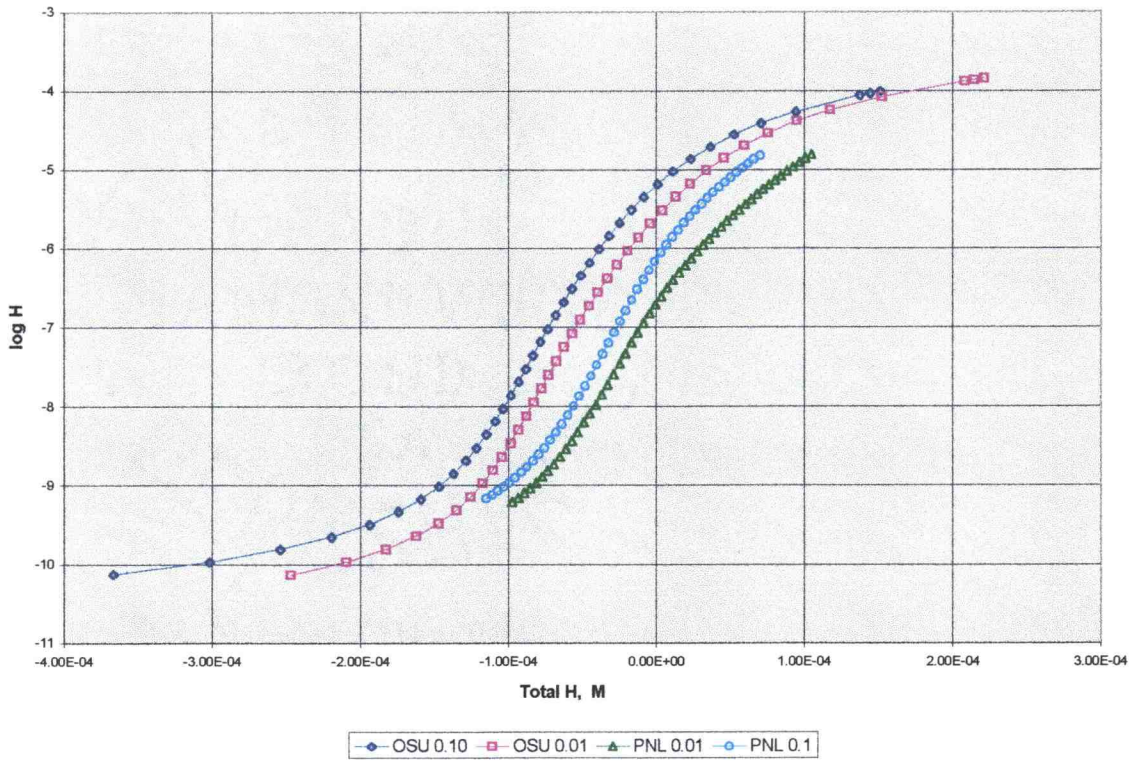


Figure 4.3. OSU and PNL LHA Titrations.



possible that the difference in the models is the result of covariance in the optimization of $T(HL_1)$ and T_H^0. If the modeling strategy is sensitive to the pH range of the data, it should be possible to change the model of the OSU data to be like the PNL model simply by reducing the pH range of the OSU data and refitting the model to the reduced data set. This exercise was performed and the results are listed in Table 4.III. Note that the model produced with the reduced OSU data set is not much different than the model produced by the full data set. The values of $T(HL_1)$ and T_H^0 did not change significantly, and not in the direction that was expected if covariance between these parameters is the cause of the difference between the PNL and OSU models.

Since it is apparent that the difference is not just a mathematical artifact of the model, some other explanation is needed to describe it. Differences in concentration can be ruled out by judicious use of the models obtained. Both the PNL and OSU models of LHA were adapted for use in the program MICROQL (Westall, 1986). Each model of LHA was used to compute the value of ΔT_H to change the pH of the LHA solution from pH 5 to pH 8 for both 0.01 and 0.1 M $NaClO_4$ concentrations. For the PNL model the computed values of ΔT_H for this pH change was 132.1 μM and 117.6 μM for 0.01 and 0.1 M $NaClO_4$ concentrations, respectively. For the OSU model, ΔT_H values of 124.9 μM and 117.7 μM were determined to effect the desired pH change at 0.01 and 0.1 M $NaClO_4$ concentrations, respectively. Because the values of ΔT_H required to bring about a pH increase from 5 to 8 is nearly the same for both models, the LHA solutions titrated at PNL and OSU must have been nearly the same concentration. Thus, differences in LHA concentration cannot account for the observed differences between the PNL and OSU models of LHA. It should be noted that an attempt was made to determine

Table 4.III. Comparison of Models of LHA Titrations.

Parameter optimized	PNL Data Result	OSU full data set result	OSU reduced data set result[a]
Total HL_1 (M)	2.215E-04	1.055E-04	9.592E-05
Total HL_2 (M)	8.400E-05	8.565E-05	8.129E-05
Total HL_3 (M)	5.724E-05	5.435E-05	5.427E-05
Total HL_4 (M)	6.466E-05	4.374E-05	6.421E-05
Total H^0 (M)	-3.021E-04	-1.392E-04	-1.269E-04
log K_{Na}	1.791	1.601	1.631

[a] pH range for model was 4.5 to 9.5.

the carbon concentration of the OSU LHA solution by direct measurement. Unfortunately, the determination was found to be in error and there was not enough material left for a second attempt.

Since the solutions of LHA in the PNL and OSU models apparently have nearly the same concentration of LHA, then the models derived for the LHA from the two data sets should be "interchangeable." The models should only vary primarily in the value of T_H^0 if both laboratories followed the same procedure. To test "interchangeability" between the models, each model was applied to the other data set and only T_H^0 was adjusted to account for possible differences in the amount of acidity that was changed during the dialysis step of the pretreatment. The results of this test are shown in Figures 4.4 and 4.5.

Examination of Figures 4.4 and 4.5 reveals very quickly that the model of LHA derived from the OSU data set is more appropriate to the PNL data than is the converse case. However, the reasonable approximations of both models to a different data set supports the assumption that the data sets are very similar. It makes sense then to attempt to reconcile the two data sets into a single model.

Because the model of LHA derived from the OSU data set is more appropriate to both data sets, it is convenient for the PNL data to be reconciled to the OSU data. Attention is focused once again on Figure 4.3. Visual examination of Figure 4.3 suggests that the PNL titration curves can be overlaid onto the OSU titration curves simply by shifting them in the negative T_H direction. To determine how much to shift the titration curves, MICROQL is applied once again to the models to estimate the value of ΔT_H required to reconcile the PNL titrations of LHA to the OSU titrations of LHA.

Figure 4.4. PNL Model of LHA on OSU LHA Titrations.

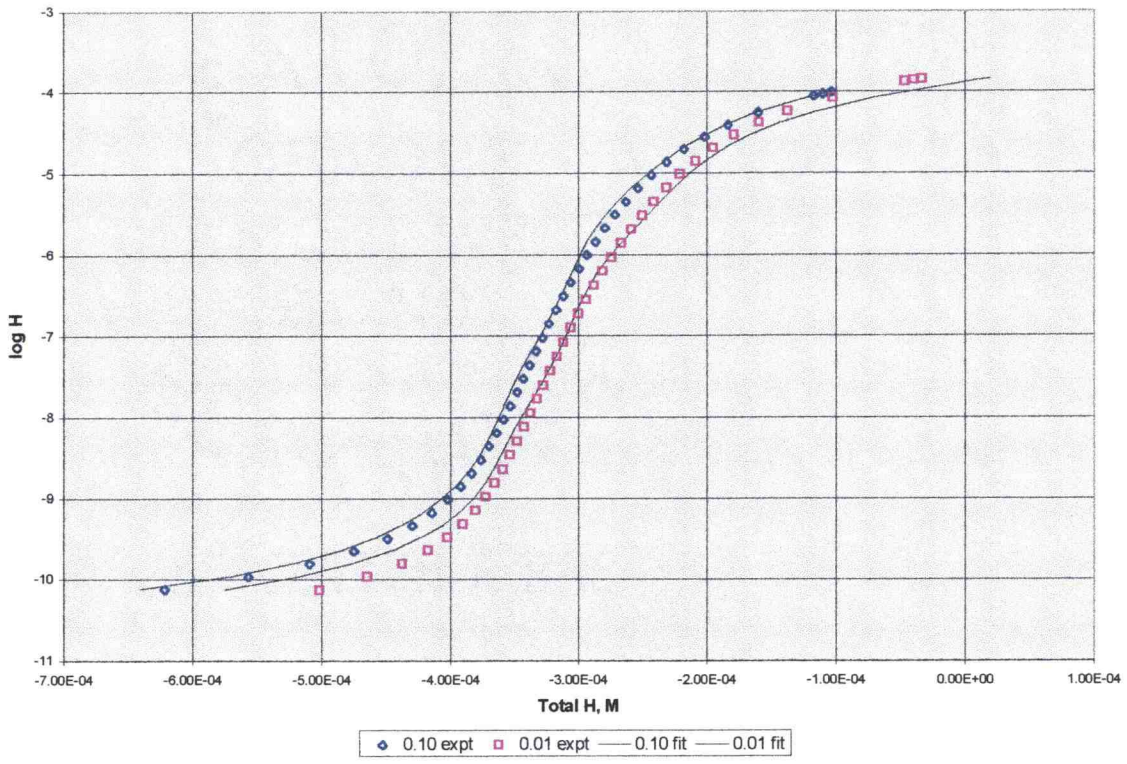
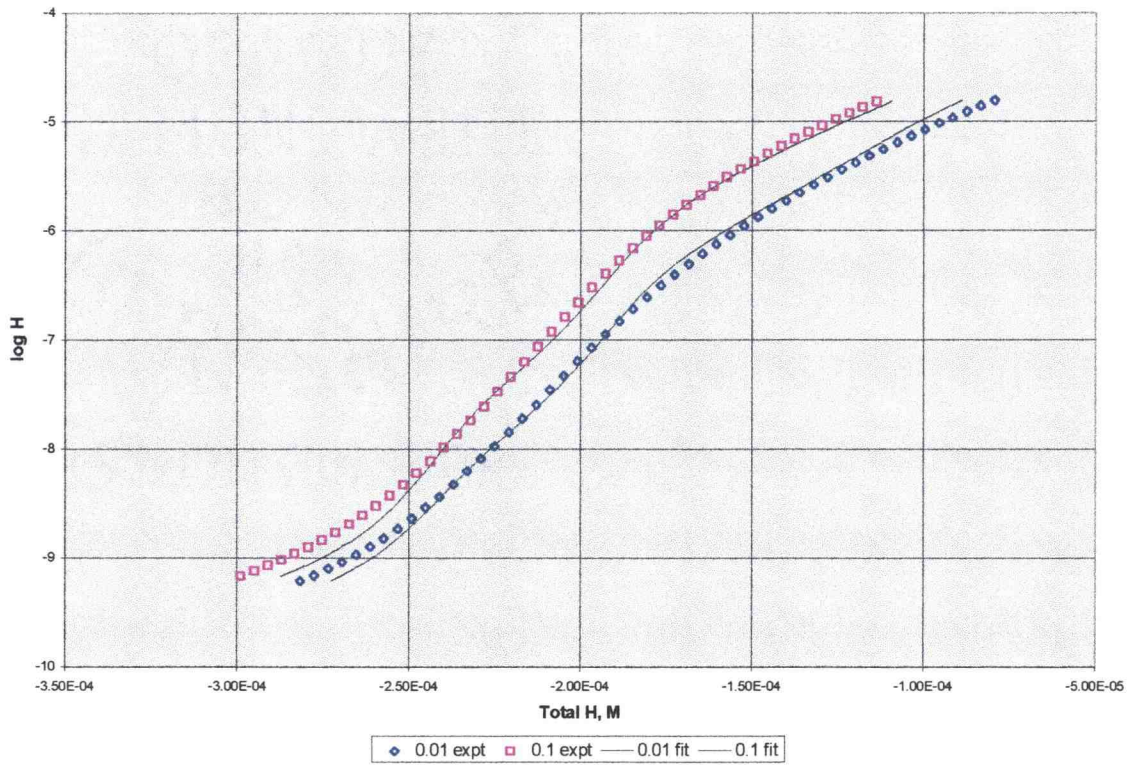


Figure 4.5. OSU Model of LHA on PNL LHA Titrations.



Each model of LHA was used in MICROQL to determine the value of T_H required to adjust the pH of the LHA solution to pH 5, 6, 7, and 8 in both concentrations of sodium perchlorate (0.01 and 0.1 M). For each pH value, a value of ΔT_H was computed by subtracting $T_{H,PNL}$ from $T_{H,OSU}$. The difference, ΔT_H^0, between the optimized values of T_H^0 computed by FITEQL for the two models was then subtracted from each value of ΔT_H to compute the shift required to overlay the PNL titration onto the OSU titration at the specified pH. The results of each computation are listed in Table 4.IV. It was observed that the computed values of ΔT_H are all very similar. Because of this observation, it was decided that an average value of ΔT_H computed from the eight values of ΔT_H could be used to reconcile the titration data. The average value of ΔT_H, δT_H, was found to be 44.46 μM, and was subtracted from each value of T_H in the PNL data set to shift the curves so that they would overlay the OSU titration curves. The reconciled data sets are illustrated in Figure 4.6.

The close overlay of the reconciled data sets clearly indicates that the LHA material used in the two laboratories behaves similarly, in spite of any differences in treatment and titration methods. Up to this point, the two data sets have been treated independently. Careful use of the two separate models of LHA has made it possible to merge the independently determined data sets into a single model of LHA. The result of the FITEQL optimization on the combined data sets is shown in Table 4.V and illustrated in Figure 4.7. If one compares the results shown in Table 4.II to those in Table 4.V it can be seen that the model of LHA produced by the combined OSU and PNL titrations is most like the model of LHA determined with the OSU data. This similarity makes

Table 4.IV. Computed Values of ΔT_H for Data Reconciliation.

	0.01 M $NaClO_4$			
pH	$T_{H,OSU}$ (M)	$T_{H,PNL}$ (M)	ΔT_H (M)	$\Delta T_H - \Delta T_H^0$ (M)[a]
5	-9.904e-5	-2.103e-4	1.113e-4	-5.16e-5
6	-1.544e-4	-2.719e-4	1.175e-4	-4.54e-5
7	-1.921e-4	-3.085e-4	1.164e-4	-4.65e-5
8	-2.239e-4	-3.424e-4	1.185e-4	-4.44e-5
	0.1 M $NaClO_4$			
pH	$T_{H,OSU}$ (M)	$T_{H,PNL}$ (M)	ΔT_H (M)	$\Delta T_H - \Delta T_H^0$ (M)[a]
5	-1.222e-4	-2.439e-4	1.217e-4	-4.12e-5
6	-1.782e-4	-2.978e-4	1.196e-4	-4.33e-5
7	-2.078e-4	-3.287e-4	1.209e-4	-4.20e-5
8	-2.399e-4	-3.615e-4	1.216e-4	-4.13e-5
	Average shift in ΔT_H, δT_H			-4.45e-5

[a] ΔT_H^0 = difference in T_H^0 values in FITEQL models developed on OSU and PNL data sets = 1.629e-4 M.

Figure 4.6. PNL and OSU Titrations Overlaid.

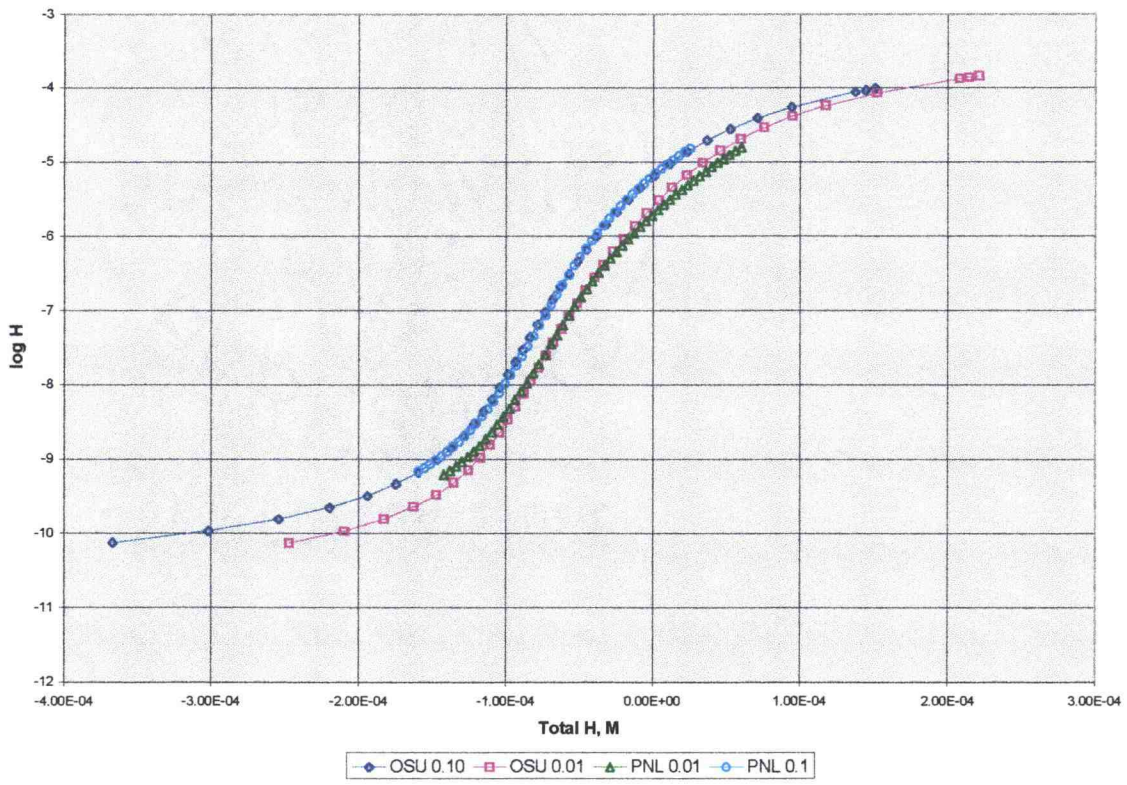
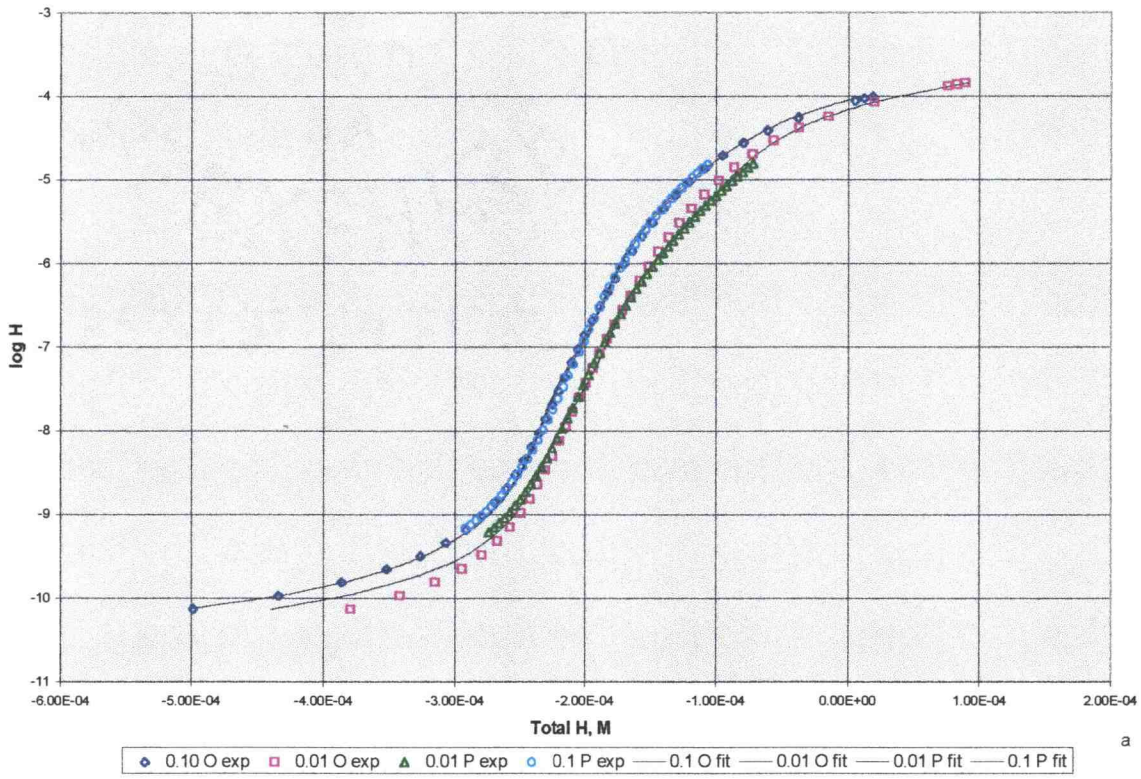


Table 4.V. FITEQL Model of Combined PNL and OSU LHA Titrations.

Parameter Optimized	Result
Total HL_1	9.090e-5 M
Total HL_2	8.954e-5 M
Total HL_3	5.681e-05 M
Total HL_4	5.046e-5 M
Total H^0	-1.320e-4 M
log K_{Na}	1.796

Figure 4.7. PNL and OSU Combined Model and Titration Curves.



[a] O denotes OSU data, P denotes PNL data; 0.10 and 0.01 indicate 0.10 or 0.01 M $NaClO_4$, respectively.

intuitive sense since both models cover the same pH range and the OSU data was the frame of reference in reconciling the data.

The important point to note in comparing the results in Table 4.II and Table 4.V is that the two data sets were reconciled by taking a consistent approach in application of the discrete log K spectrum to each data set. This strategy in modeling revealed that the only major difference in the two data sets was in the definition of T_H. In the PNL data T_H was originally defined to be zero at pH = 4.00 in 1 mM $NaClO_4$. The data was later mathematically adjusted so that T_H was set equal to zero at pH 7.00, near the pH at which the titration cycles actually began. As it turns out, the discrete log K spectrum model can accommodate different definitions of T_H so long as one maintains a consistent approach in modeling the data.

Application to a different humic substance

It has been fully demonstrated that the discrete log K spectrum model can be used to describe the behavior of leonardite humic acid. Attention now is turned to applying the model to a different material, peat humic acid (PHA) another humic substance available from the IHSS. The objective here is to determine how different treatments of the material itself affect the quality of the data obtained from titration and the influence of treatment variability on models based on the titration data. The focus will be on the effects of dialysis on the PHA and on whether or not changes to the material during the titration, hydrolysis, for example, affect the quality of the data.

Effects of Dialysis

The effects of dialysis are examined in two ways: 1) in regard to reproducibility, *i.e.*, do two batches of PHA dialyzed at two different times produce the same or nearly the same titration curve and model; and 2) in regard to lability, *i.e.*, does the dialysis itself change the nature of the PHA such that comparison of "native," undialyzed PHA to dialyzed PHA may not be meaningful?

With respect to the issue of reproducibility, two batches of PHA were dissolved and dialyzed at two different times of the year. The first batch was prepared during the winter and the second batch was prepared during the spring. Although both batches spent about the same amount of time at the same temperature (25° C) during dissolution, the dialysis time for the first batch was almost two days shorter than the second batch (nine days *vs.* eleven days). Another factor is that the nitrogen-filled glove box where the dialysis was performed was not temperature controlled, so that the second (spring) batch of PHA experienced significantly warmer temperatures during the dialysis than did the first (winter) batch. However, when titrated and modeled with the discrete log K spectrum, they produce very similar results. The titration curves are illustrated in Figure 4.8 and the results of the model are listed in Table 4.VI.

Note in Figure 4.8 that the curves nearly overlay each other and that there are only minor differences between them. The differences in the titration curves are consistent with the individual treatment of each batch of PHA. The "spring" batch which experienced higher temperatures and a longer dialysis time required a greater amount of base to go from pH 4 to pH 7 than did the "winter" batch. If the PHA undergoes hydrolysis during dialysis, then one would expect the "spring"

Figure 4.8. Reproducibility in Titrations of Different PHA Batches.

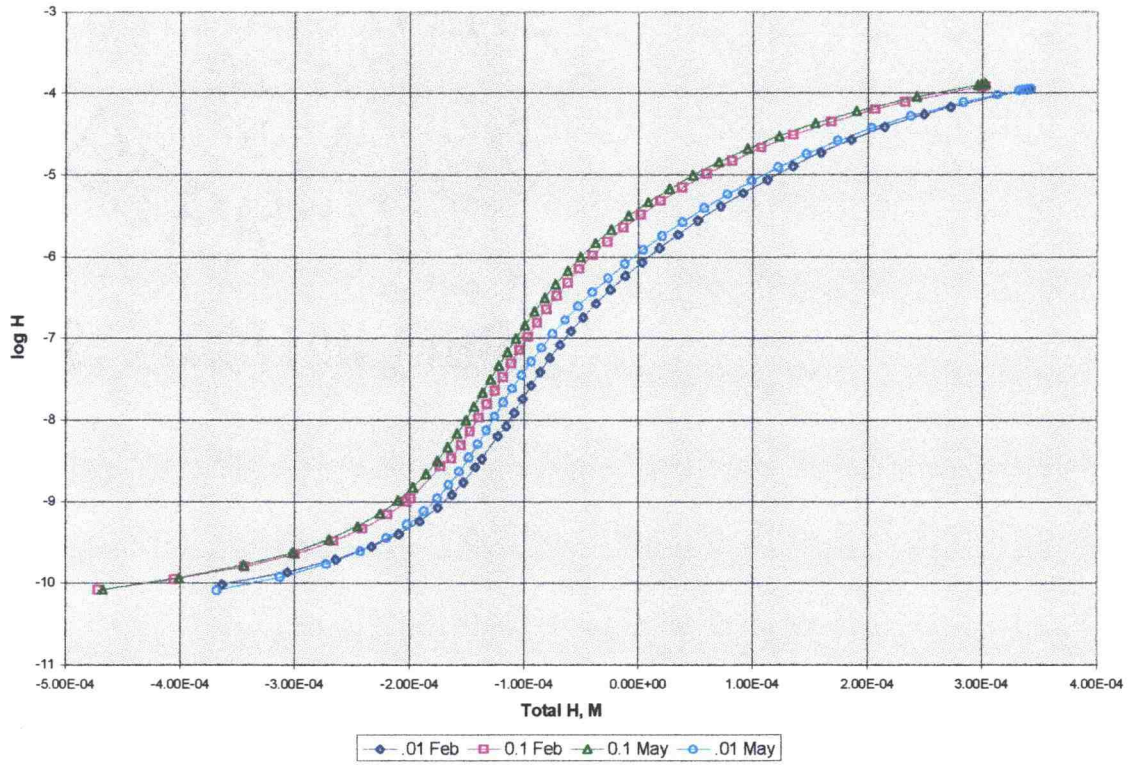


Table 4.VI. Models of Dialyzed PHA.

Model Parameter	"Winter" PHA Batch	"Spring" PHA Batch
HL_1 (M)	2.924 e-04	3.129 e-04
HL_2 (M)	1.930 e-04	1.902 e-04
HL_3 (M)	7.383 e-05	7.436 e-05
HL_4 (M)	1.270 e-04	1.123 e-04
H_0 (M)	-4.167 e-04	-4.223 e-04
log K_{Na}	1.616	1.597

PHA to be more hydrolyzed than the "winter" PHA by virtue of a longer dialysis time at higher temperature. However, the differences in T_H between the titrations are small and it seems apparent that small variations in the dissolution and pretreatment of PHA batches have only minor effects on the analysis of the material.

Since the PHA seems to be affected somewhat by dialysis, the extent of the change brought about by the dialysis becomes an issue. This type of variation was investigated in the following way. A batch of PHA was dissolved over a four day period as before and then divided into two portions. The first portion was dialyzed against 1 mM $NaClO_4$ while the second portion was put into a glass bottle and stored in the glove box with the first portion. After a 10-day dialysis, both solutions were then titrated and modeled as before. Each titrated solution was removed from the titration cell and saved in order to determine carbon concentration. The results of modeling the titrations are shown in Table 4.VII and the titrations of the dialyzed and undialyzed material are shown in Figures 4.9 and 4.10, respectively.

Note from Table 4.VII that the titrations produce significantly different models. There are at least two possibilities for the differences: 1) the PHA, either dialyzed or undialyzed, was altered during the dialysis time period by hydrolysis reactions or some other unknown reaction; and 2) the differences are due largely to a dilution effect produced in the dialyzed PHA by osmosis during the dialysis. In order to determine which of these two possibilities could account for the difference observed in the titrations, an approach similar to the way two different LHA titrations were reconciled will be taken.

The first step in comparing the PHA solutions is to normalize the values of T_H to the concentration of PHA in the cell, in order to adjust for dilution. At this point it can be determined if one of the

Table 4.VII. Models of Dialyzed and Undialyzed PHA.

Parameter Optimized	Dialyzed PHA	Undialyzed PHA
HL_1 (M)	3.129 e-04	3.063 e-04
HL_2 (M)	1.902 e-04	2.363 e-04
HL_3 (M)	7.438 e-05	8.720 e-05
HL_4 (M)	1.123 e-04	1.485 e-04
H_0 (M)	-4.223 e-04	-5.336 e-04
log K_{Na}	1.597	1.908

Figure 4.9. Titrations and Model of Dialyzed PHA.

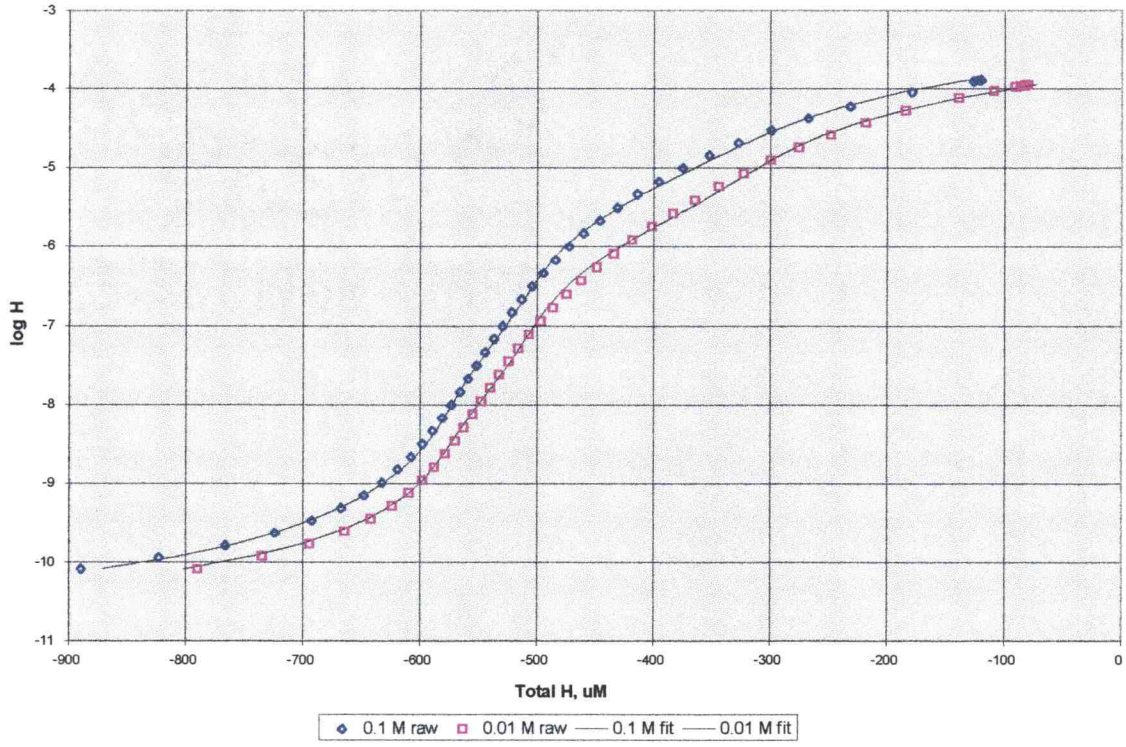
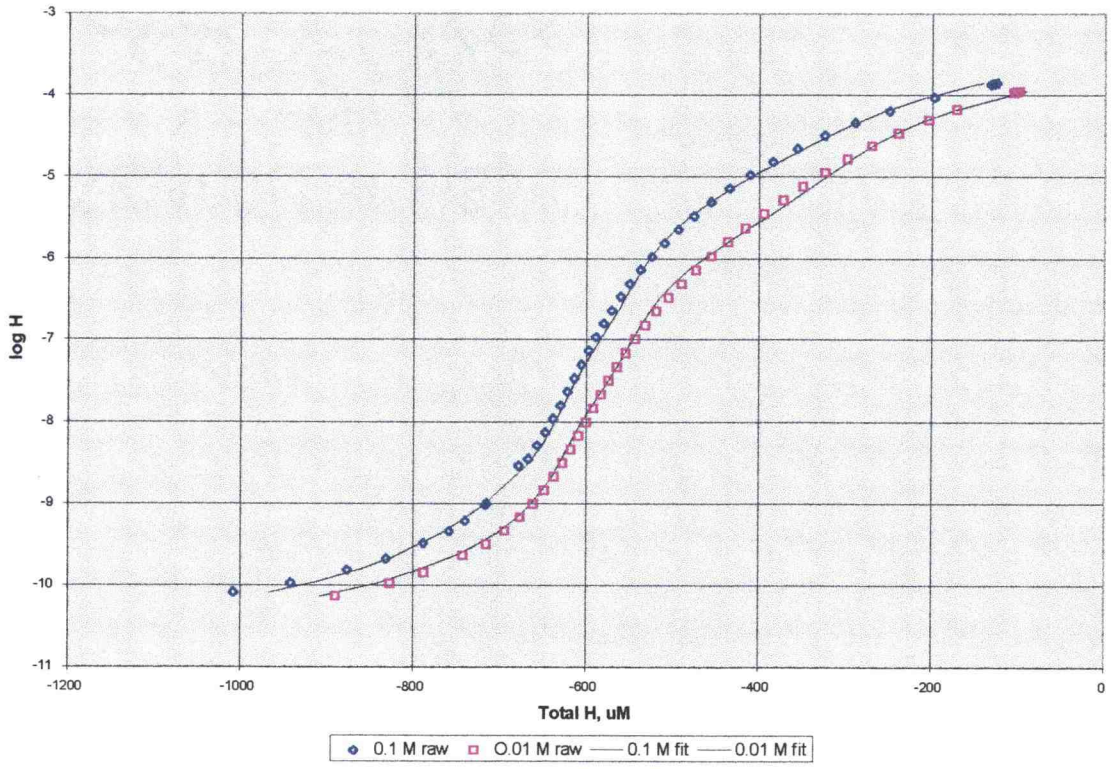


Figure 4.10. Titrations and Model of Undialyzed PHA.

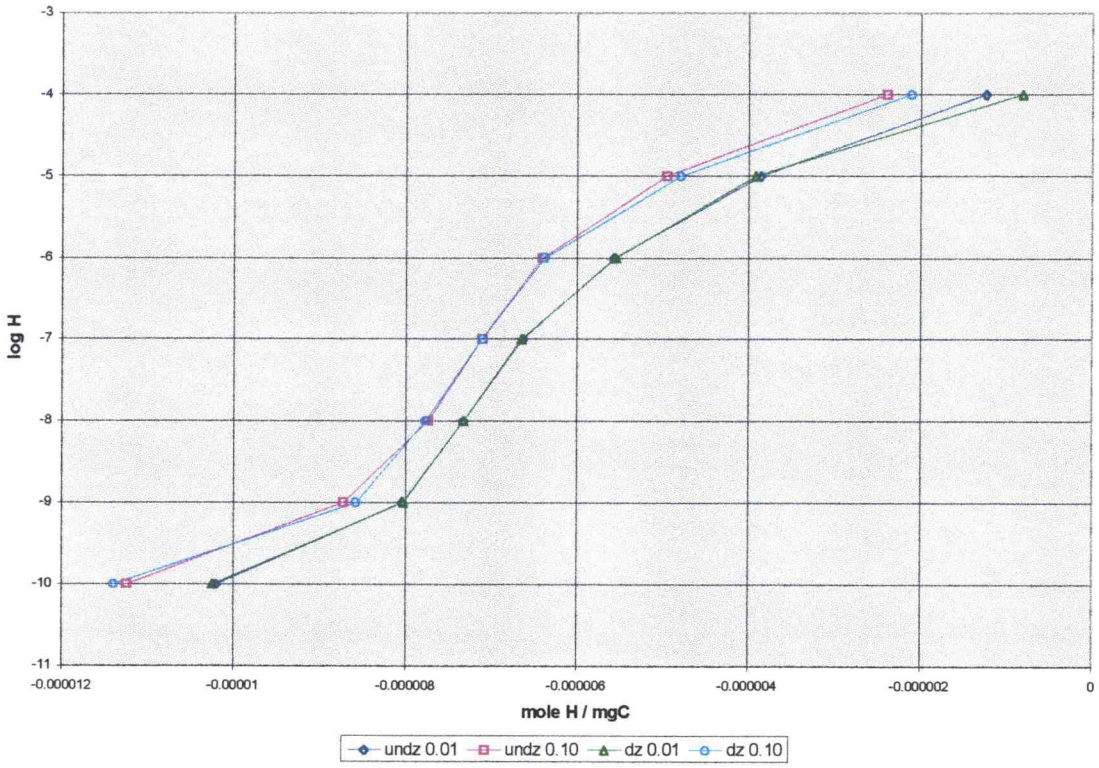


titration curves can be overlaid on the other by translating it along the T_H axis. If this is possible, then it is likely that the major difference in the titration curves is just a dilution effect. A further check on the similarity of the undialyzed and dialyzed PHA can be made by calculating T_H consumed per pH unit. If the dialyzed and undialyzed material produce similar values, then it may be concluded that dialysis has only a minor effect on the material.

MICROQL was applied to the models of dialyzed and undialyzed PHA to compute the values of T_H that would be required to adjust PHA solutions in 0.1 M and 0.01 M $NaClO_4$ electrolyte from pH 4 to 10 in 1 pH unit increments to create "titration" curves. These computed values of T_H were normalized by the concentrations of PHA in the titrations that the model was derived from, 80.6 mg_C/L and 71.0 mg_C/L for undialyzed PHA and dialyzed PHA, respectively. Next, the normalized model titrations in each $NaClO_4$ concentration were compared to compute the shift from the undialyzed curve to the dialyzed curve in mol_H/mg_C at pH values of 6, 7, and 8. The average value of the shifts at these points, -3.85×10^{-7} mol_H/mg_C and -2.82×10^{-7} mol_H/mg_C for 0.01 and 0.1 M $NaClO_4$ solutions, respectively, was subtracted from the normalized model titration of dialyzed PHA at each point. Treating the data in this manner very effectively overlaid the titration curves of dialyzed PHA on the titration curves of undialyzed PHA, as illustrated in Figure 4.11. The close point to point overlay of the normalized model titration curves indicates that the dialysis step has little effect on the PHA material.

To check further on the effects of dialyzing PHA, one can compare the amount of base consumed (normalized to PHA carbon concentration) in a set pH range in each titration in the two sodium concentrations. In this case the range of pH considered will be the same as that used to overlay the titration curves, namely pH 6 to pH 8. From the titration

Figure 4.11. Normalized and Overlaid PHA Model Titrations.



data of PHA in 0.01 M $NaClO_4$, about -1.7222×10^{-6} mol_H/mg_C is consumed by the dialyzed PHA while about -1.6881×10^{-6} mol_H/mg_C is consumed by the undialyzed PHA in the same pH range, which represents a 2% decrease with respect to the dialyzed material. From the model titration curves, between pH 6 and pH 8, -1.7775×10^{-6} mol_H/mg_C is consumed by the dialyzed PHA and -1.7561×10^{-6} mol_H/mg_C is consumed by the undialyzed PHA, indicating a 1.2% decrease with respect to the dialyzed material.

Similarly, from the titration data of PHA in 0.1 M $NaClO_4$, about -1.4025×10^{-6} mol_H/mg_C is taken up by the dialyzed PHA, while -1.3813×10^{-6} mol_H/mg_C is consumed by the undialyzed PHA, a 1.5% decrease with respect to the dialyzed PHA. From the model, -1.386×10^{-6} mol_H/mg_C is computed to be taken up by the dialyzed material while -1.337×10^{-6} mol_H/mg_C is taken up by the undialyzed material, a 3.5% decrease with respect to the dialyzed PHA.

Two things are notable from this comparison: 1) there does appear to be some change to the PHA during dialysis, indicated by a greater consumption of base per mg_C of dialyzed PHA relative to undialyzed PHA, however, this increase is small, only about 2 to 3%; and 2) the models of PHA do a good job of estimating the behavior of PHA, at least in the pH range examined. Such a small change in the PHA material during dialysis and the fact that the PHA model is able to reflect this small difference should serve to lessen any concerns about the pretreatment of the PHA material.

Effects of titration

In many experiments involving humic substances, uncertainties brought about by titration hysteresis can cause problems in predicting the behavior of the substance under investigation. Hysteresis in

titrations was noted and put forth as a potential problem to the model developed for leonardite humic acid in a previous chapter (Chapter 3), but was not believed to affect the overall conclusions drawn. In the case of peat humic acid, potential problems brought about by changing the material during the titration could occur. Therefore, some investigation into the issue of hysteresis and the effects of titrating the PHA material are warranted.

The titration method in checking the PHA solutions for hysteresis is to adjust the pH of the solution from its initial point to pH 6, then to pH 8, to pH 5, to pH 9, to pH 4, to pH 10, and then back to pH 4 again, adding base coulometrically and acid volumetrically to achieve the desired changes in pH. In this way, it is hoped that any pH-dependent changes to the PHA that can occur during the course and timeframe of a titration (about five hours) will be revealed.

As a check on the method's robustness to effects that could be interpreted as hysteresis, the primary standard potassium hydrogen phthalate (KHP) was titrated by the volumetric-coulometric cycles described above. An approximately 1.5 mM solution of KHP was prepared for the titration. This concentration of KHP produced approximately the same concentration of titratable acidity as undialyzed PHA after addition to the supporting electrolyte in the coulometric titrator. Just prior to commencing the cycle titration, the pH of the KHP solution was increased to 6.2 by manual coulometric additions (to mimic a PHA solution), and then titration control was given to the computer.

The result of the cycle titration of KHP is shown in Figure 4.12, and the forward titrations are displayed in Figure 4.13 for clarity. Examining Figure 4.13, one observes a shift in the curves toward positive T_H from C1 to C3. Further, an unexplained slight negative shift of C2 with respect to C1 is also visible; this small deviation

Figure 4.12. Titration Cycles of 1.5 mM KHP.

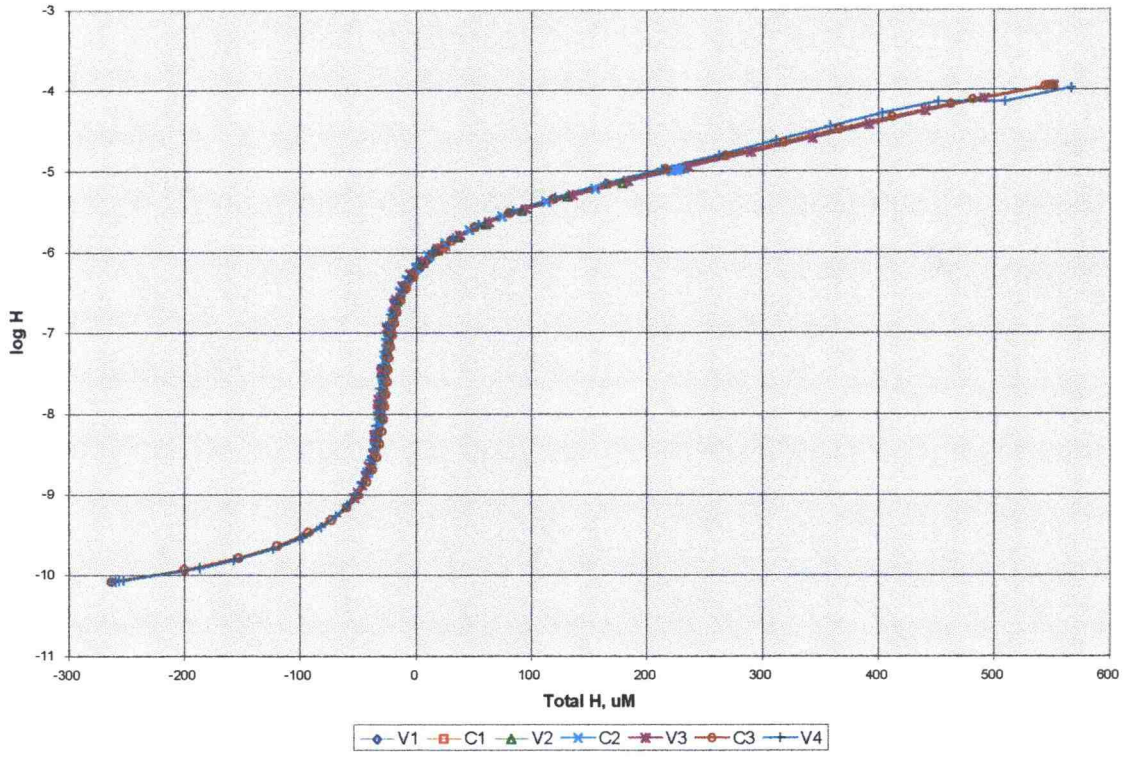
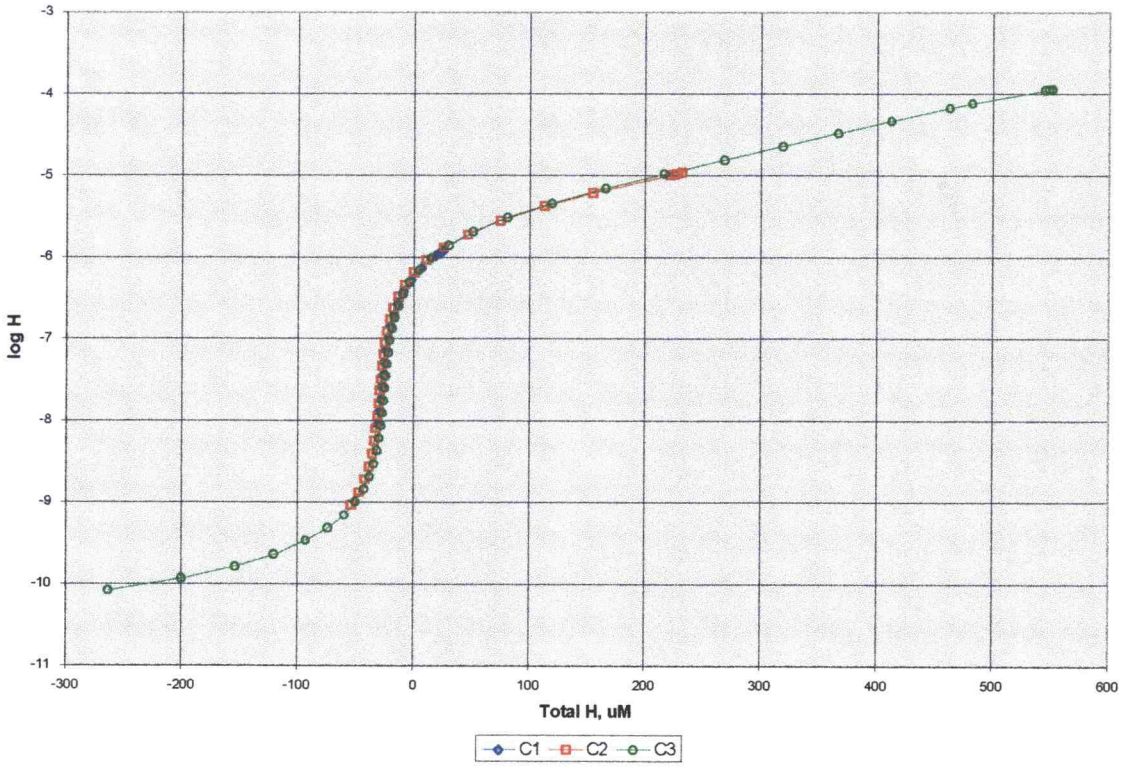


Figure 4.13. Coulometric Titration Cycles of 1.5 mM KHP.



suggests a possible, but probably insignificant, systematic error in the method.

Since there should be no hysteresis due to hydrolysis in the KHP titration, it is reasonable to believe that the offset in the coulometric titration cycles is due to dilution during the volumetric cycles. The respective volumes for legs C1, C2, and C3 are 30.271 mL, 31.033 mL, and 32.889 mL. The increases in volume translate to dilution factors of 1.0252 for C2 and 1.0865 for C3, with respect to the volume of C1. Applying the dilution factors to legs C2 and C3 causes them to be virtually indistinguishable from C1 as well as each other, as shown in Figure 4.14. Such excellent agreement of the forward cycles in the KHP titration supports the validity of the method in attempts to determine what effects are due to hysteresis in the PHA and what effects are due to other factors such as dilution.

Having established a method to check for hysteresis, solutions of both dialyzed and undialyzed PHA in 0.10 M $NaClO_4$ were cycle-titrated. The cycle titrations of dialyzed and undialyzed PHA are shown in Figures 4.15 and 4.16, respectively. It is apparent from both figures that there is hysteresis to some degree in both the dialyzed and undialyzed PHA solutions, but it does not appear to be a major problem. In fact, at the extremes of pH, the titration curves are nearly convergent. It turns out that there is greater deviation from the last coulometric cycle to the last volumetric cycle in the undialyzed solution than in the dialyzed solution. For the sake of brevity, attention will be focused on the titrations of the undialyzed material because it shows an apparently greater degree of variation than the dialyzed material.

In examining Figure 4.16, it is difficult to distinguish one titration cycle from another. For clarity, the coulometric (base-addition) cycles and the volumetric (acid-addition) cycles are separated

Figure 4.14. Coulometric Cycles of KHP Titration Corrected for Dilution.

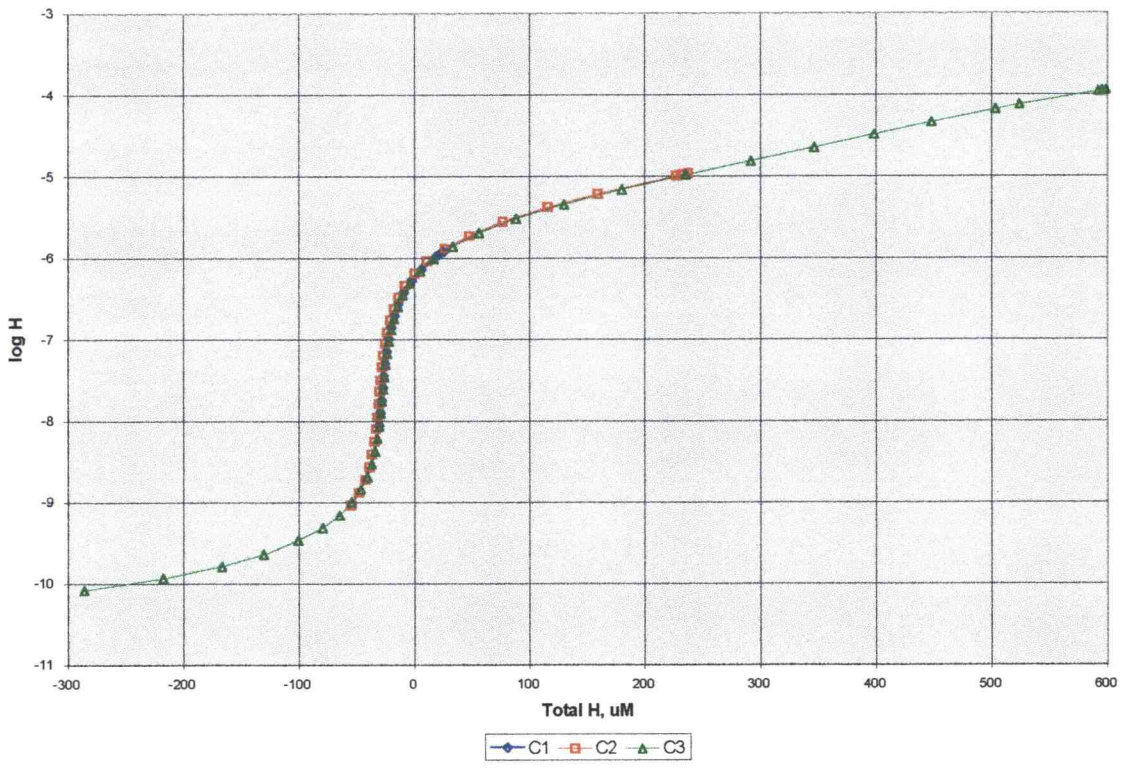


Figure 4.15. Titration Cycles of Dialyzed PHA.

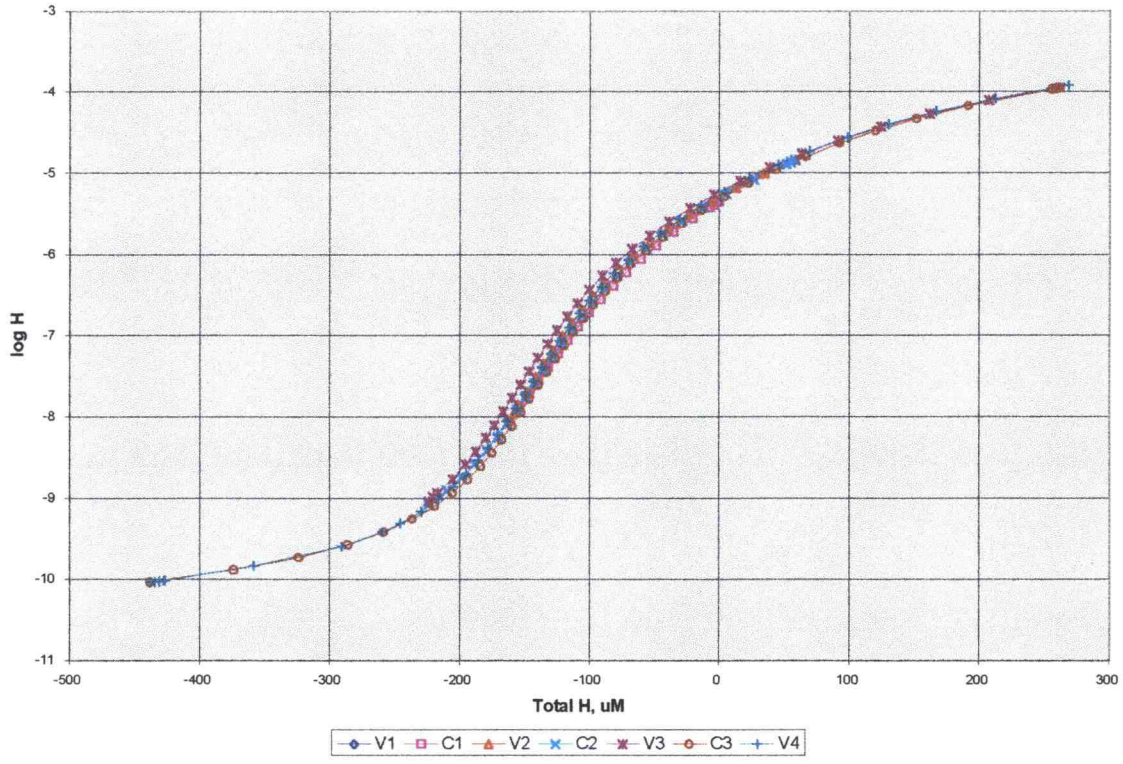
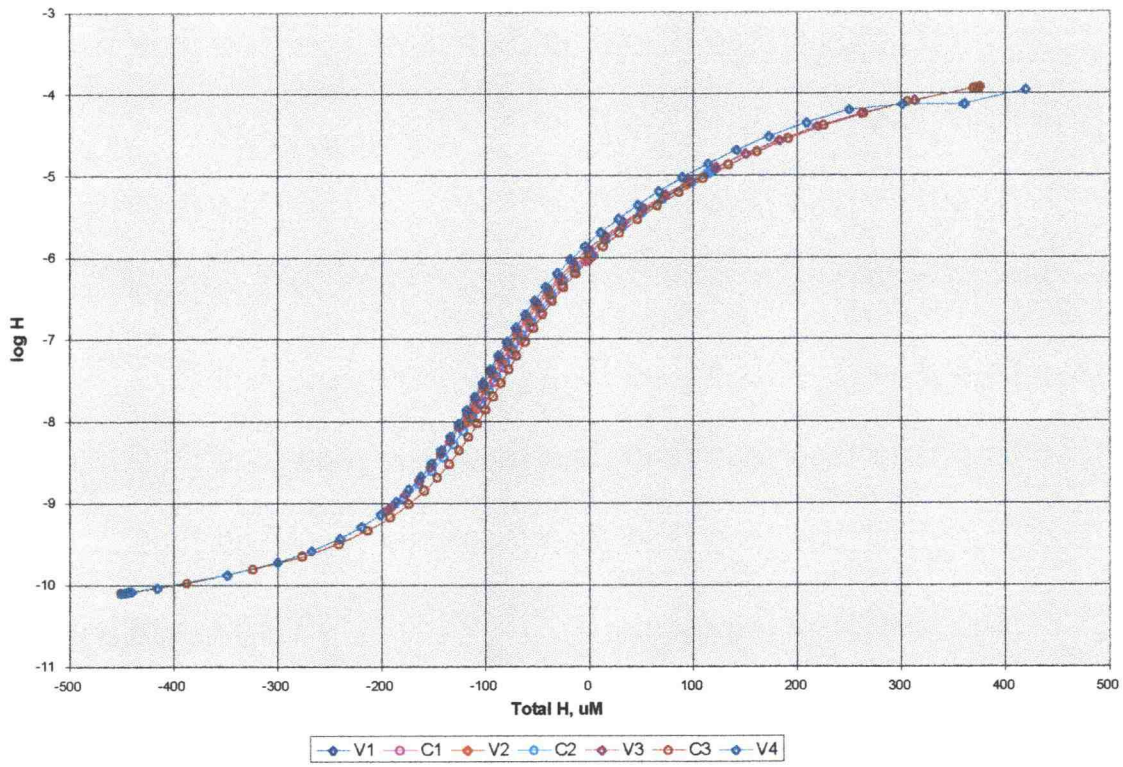


Figure 4.16. Titration Cycles of Undialyzed PHA.



out into Figures 4.17 and 4.18, respectively. Examination of the coulometric cycles of this titration reveals a small positive shift along the T_H axis from leg C1 to leg C3. The volumetric cycles (Figure 4.18) are similar with a negative shift along the T_H axis from V1 to V4. In separating the halves of this titration one thing that is revealed is that there is little hysteresis in the titration of PHA if the titration direction is constant. That is, there is good agreement between any two coulometric titrations or volumetric titrations, but there is less agreement among coulometric-volumetric legs of the cycles.

In regard to the coulometric cycles shown in Figure 4.17, it is apparent that the positive shift along the T_H axis is also largely due to a dilution effect from the volumetric cycles, as was true for the KHP cycle titration. From legs C1 to C2 to C3 in Figure 4.17, the volume of the solution in the cell increased from 30.210 mL to 30.891 mL to 32.609 mL, producing dilution factors of 1.0225 and 1.0794 for C2 and C3 with respect to the volume of C1. Applying the dilution factors to the titration data effectively overlays the three titration curves as shown in Figure 4.19. Some hysteresis is apparent in Figure 4.19, particularly when comparing C2 to C3 from pH 5 to about pH 7. However, the difference in T_H between the two curves at pH $\approx$ 5 is only about 5 μM, and this difference decreases to less than 1 μM at pH $\approx$ 7. By comparison, the small positive shift apparent in the corresponding KHP titration cycles has a value of about 8 μM at pH $\approx$ 5, decreasing to about 2 μM at pH $\approx$ 8.2, indicating that this deviation is inherent to the system, and not necessarily attributable to the PHA itself. Thus, it would seem that hysteresis in PHA titrations does not present a significant problem, and PHA would make a good material for further study in regard to its metal-complexing behavior.

Figure 4.17. Coulometric Titration Cycles of Undialyzed PHA.

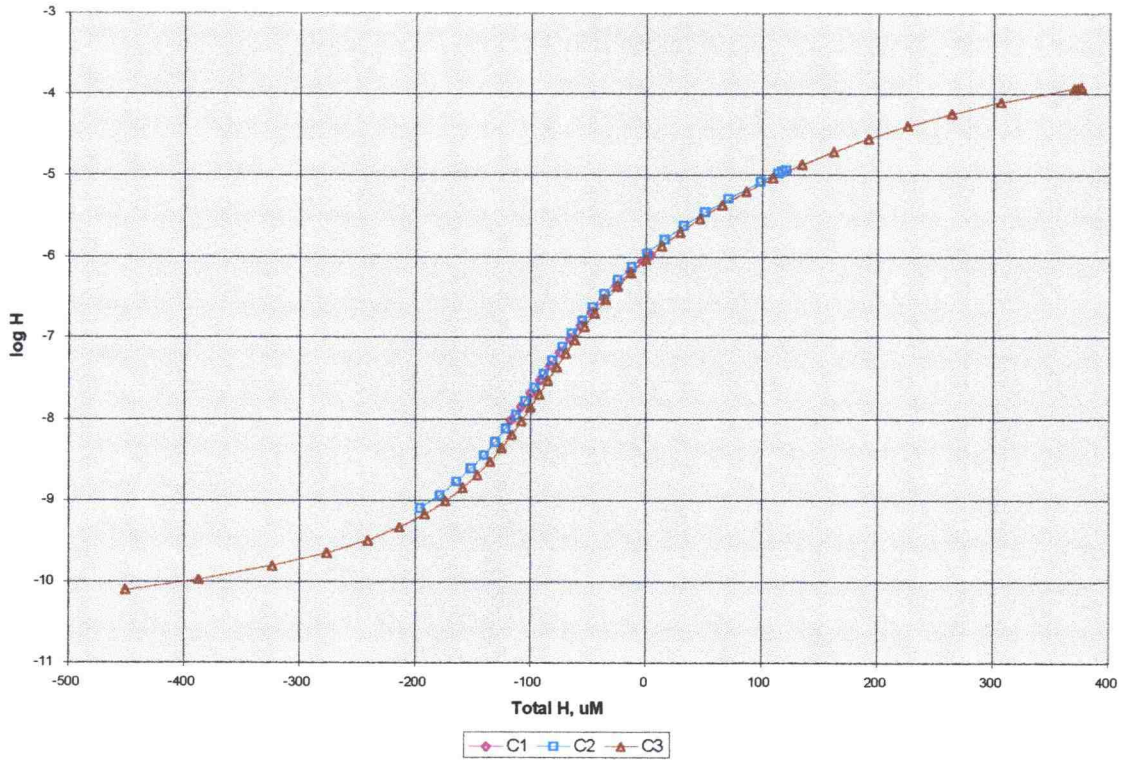


Figure 4.18. Volumetric Titration Cycles of Undialyzed PHA.

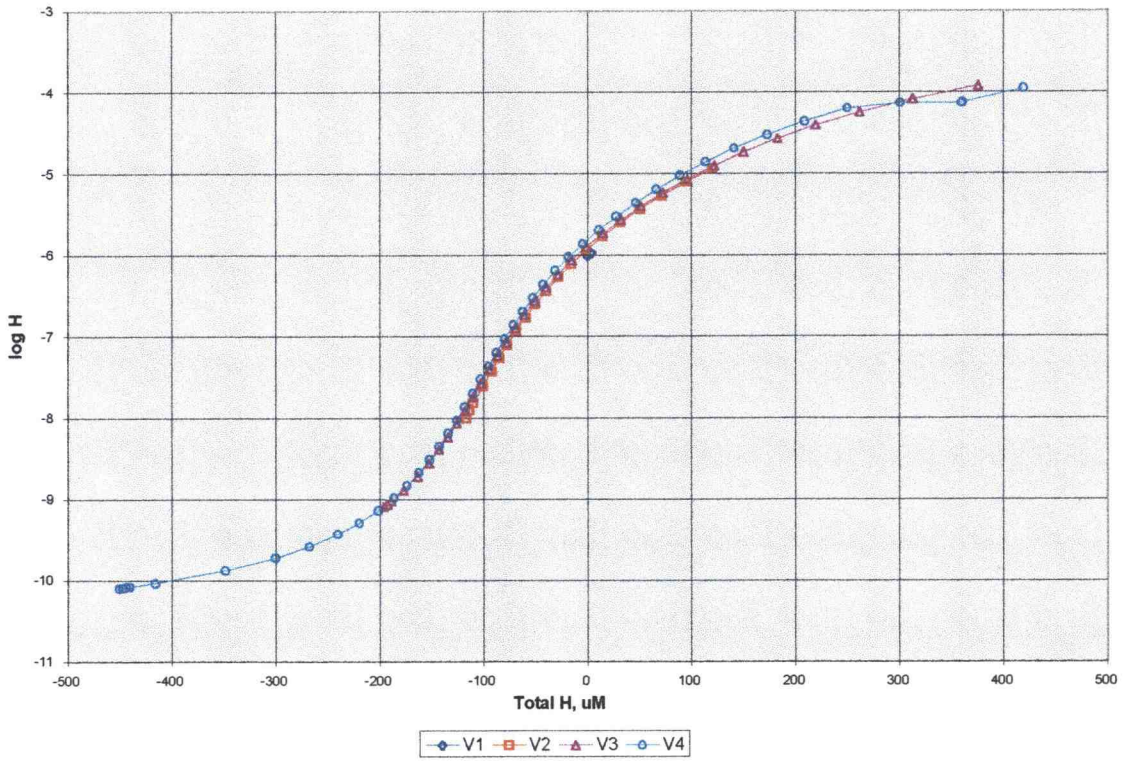
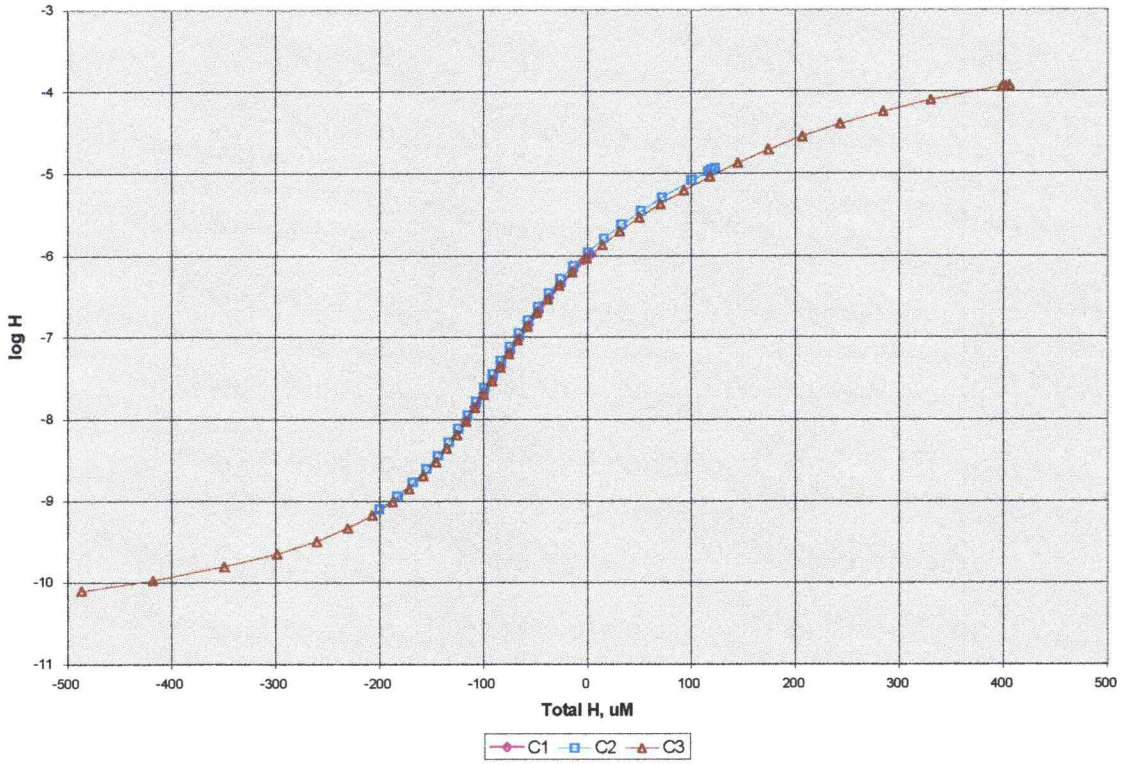


Figure 4.19. Coulometric Cycles of PHA Titration Corrected for Dilution.



SUMMARY

From the data presented here of titrations of leonardite humic acid and peat humic acid (LHA and PHA) it is apparent that these materials, although heterogeneous, are not unpredictable, exhibiting reproducible and reversible behavior.

For both materials, a semi-empirical model of their acid-base behavior was developed. For the case of LHA, the model was used to evaluate the differences between titrations produced in two different laboratories. It was possible to produce a single model of this heterogeneous material with the discrete log K spectrum model and judicious analysis of the titration data.

For PHA, the discrete log K spectrum model was used to demonstrate that the humic acid in dialyzed and undialyzed PHA solutions was not significantly different and that "titrations" recalculated from each model could be overlaid. However, the model did reflect small differences between dialyzed and undialyzed PHA solutions that were revealed in the individual data points. Additionally, cycle titrations of PHA indicated that titration hysteresis is unlikely to be a problem for this material over the range of pH from 4-10 in a timeframe of a few hours.

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Chapter 5: Summary

At the outset of this work two goals were put forth: 1) to develop a precise and accurate method for the titration of heterogeneous substances; and 2) to develop a modeling strategy to describe the behavior of heterogeneous substances.

A simple coulometric titration method utilizing a dual-chamber cell with a fritted salt bridge was found to give very accurate and precise results in the titration of weak acids. In tests of the system with the primary standard potassium hydrogen phthalate (KHP), total phthalate was determined by three methods: 1) by inflection point location; 2) with a nonlinear least squares model; and 3) with the program FITEQL. Each method used to determine KHP concentration agreed very well with the concentration of KHP in the titration cell, known by mass and dilution. From sixteen FITEQL models of titrations of KHP, an average value of pK_{a2} of KHP was determined to be 4.94 ± 0.02. Thirteen titrations of KHP in 0.100 M KCl were combined into a single FITEQL model which produced the optimized values of pK_{a1} = 2.783 ± 0.002, pK_{a2} = 4.940 ± 0.001, and pK_W = 13.800 ± 0.001. The coulometric titration method was found to be reliable, accurate, and precise.

After development of the coulometric titrator, a discrete log K spectrum model was developed to describe proton and metal binding by leonardite humic acid (LHA). By fixing a set of log $K_a(i)$ corresponding to the pH range of acid-base titrations, and adjusting for $T_{HL}(i)$ and a common sodium exchange constant for each site, it was found that the acid-base titrations could be described well with no addition of complex electrostatic parameters. The model of LHA was extended to model the Co(II) interaction with LHA as a function of pH and a cobalt concentration of 1 μM. With only two apparent active binding sites for

Co(II), the model accounted well for the large effect of ionic strength on the Co-LHA interaction and correctly reproduced the distribution of bound and free cobalt between pH ≈ 4.5 and pH ≈ 7. The model was extrapolated without further parameter optimization to describe the isotherm of Co-LHA interaction from approximately 10^{-8} to 10^{-3} M Co(II) at pH ≈ 6.7. The discrete log K spectrum model did a reasonable job of predicting the shape of the isotherm, even better than one might expect. Such good agreement between model and data is supportive of the strategy of using multidimensional data to produce an internally self-consistent model of a humic substance.

The discrete log K spectrum model was shown to be quite useful in comparing and reconciling different humate titration data sets. From the data presented here of titrations of leonardite humic acid and peat humic acid (LHA and PHA) it is apparent that these materials, although heterogeneous, are not unpredictable, exhibiting reproducible and, to a certain extent, reversible behavior.

A semi-empirical model of the acid-base behavior of both LHA and PHA was developed. For the case of LHA, the model was used to evaluate the differences between titrations produced in two different laboratories, Battelle Pacific Northwest Laboratories (PNL) and an Oregon State University laboratory (OSU). Although at first glance the titration data produced by the two laboratories appeared to be different, it was possible to produce a single model of LHA from the combined PNL and OSU titrations with the discrete log K spectrum model. This data reconciliation further attests to the usefulness of this modeling framework.

For PHA, use of the discrete log K spectrum model showed that the material in dialyzed and undialyzed PHA solutions was not significantly different and that "titrations" normalized for concentration differences

and computed from each model could be overlaid. However, the model did reflect small differences between dialyzed and undialyzed PHA solutions that were revealed in the individual data points.

Further analysis of PHA by cycle titration indicated that titration hysteresis is unlikely to be a problem for this material over the range of pH from 4-10 in a timeframe of a few hours. It was found that "forward" titration cycles of PHA (from acidic to basic pH) overlaid no worse than the corresponding cycles of a KHP titration. From this study two things are apparent. One is that the coulometric titrator worked quite well with humic acids, producing very reproducible results. The second is that PHA is apparently fairly robust with respect to hysteresis and would likely be a good material for future investigation.

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Appendix: Program listing of NLLSKHP.BAS used for determining total phthalate concentration.

```
DEFDBL A-Z
DECLARE FUNCTION QRule# (You#, DYouDx#, Vee#, DVeeDx#)
DECLARE SUB ErrDump ()
DECLARE SUB SUBMAIN ()
DECLARE SUB OUTPLT (N%)
DECLARE SUB ADJUST ()
DECLARE SUB BILDNM ()
DECLARE SUB GAUSSL ()
DECLARE SUB MATINV ()
DECLARE SUB CNVCHK ()
DECLARE SUB INITNM ()
DECLARE SUB OUTFNL (N%)
DECLARE SUB INFIT ()
DECLARE SUB OUTRUN (N%, K%)
DECLARE SUB OBJECT (I%)
'

'   General nonlinear least squares optimization with extensive output:
'      Values, variances, deviations
'      Plot of function and data
'      Derivatives, sources of error, terms in sum of squares
REM Input from data file:
'   TITLE$
'   NPARM#
'     PARMID$(j), PARM(j)
'   NUK%%
'     UID$(j),    U(j)
'   NDAX%, NDAP%
'     XID$(j)
'       XDA(i,j), SDAX(i,j)
REM Modify program at the following lines:
' OBJECT  Object function
' OBJECT  Derivatives
' OBJECT  Dimensions of plot
' OBJECT  Data for plot
' OBJECT  Function for plot
' MAIN    Program name
' MAIN    Program description
'
'
REM initialize ***********************************************************
DIM SHARED UID$(5), XID$(5), U(5), FU(5), FX(5), DAX(130, 5), DAXC(130, 5), DELTAX(130,
5), SDAX(130, 5), PARMID$(10), PARM(10)
DIM SHARED q(5, 5), P(5), R(5, 5), D(5), Z(5, 6)

ScreenMode% = 11

PROG$ = "NLLSKHP.BAS": '    Program NLLSX  04/18/88        jcw
'Modified by jdj 1992 through 1996
'Set Constants for Object Function

Faraday# = 96486.56#  'Faraday constant (NBS/ Diehl, 1979)
V0# = .0302#    'volume in cell
Kw# = 10# ^ (-13.78#)  'water dissoc. const. (Smith & Martell)
Ka1 = 10# ^ (-2.75#)
Ka2 = 10# ^ (-4.93#)

TP = .003361#
CALL INFIT
'
CALL SUBMAIN
'
CALL ErrDump: STOP
PRINT : PRINT "Press F5 for output on screen plot": STOP
SCREEN ScreenMode%
CALL OUTPLT(1)
'
'PRINT : PRINT "Press F5 to send plot to LaserJet": STOP
'CALL ScrnDump(11, 0)

'PRINT : PRINT "Press F5 for output of data on printer": STOP
'CALL OUTFNL(2)
CALL OUTFNL(6)
CLOSE #6
SHELL "QE " + Hardfile$
```

```
'
END

DEFSNG A-Z
SUB ADJUST
DEFDBL A-Z
SHARED NUK%, ITER%

FOR I% = 1 TO NUK%
'  U(I%) = U(I%) - D(I%)                                    'allow negative
 IF D(I%) < U(I%) THEN U(I%) = U(I%) - D(I%) ELSE U(I%) = U(I%) / 2#'avoid negative
NEXT I%
ITER% = ITER% + 1

END SUB

DEFSNG A-Z
SUB BILDNM
DEFDBL A-Z
SHARED NUK%, VF, FF, SOS

REM build normal matrix
FOR J% = 1 TO NUK%
P(J%) = P(J%) + FF * FU(J%) / VF
FOR K% = 1 TO NUK%: q(J%, K%) = q(J%, K%) + FU(J%) * FU(K%) / VF: NEXT K%
NEXT J%
SOS = SOS + FF * FF / VF

END SUB

DEFSNG A-Z
SUB CNVCHK
DEFDBL A-Z
SHARED ITFLAG%, EPS, NUK%

REM convergence check
ITFLAG% = 0
FOR I% = 1 TO NUK%
    IF ABS(D(I%)) > ABS(U(I%)) * EPS THEN ITFLAG% = 1
NEXT

END SUB

SUB ErrDump
SHARED NDAP%, Ka1, Ka2, Kw#, Faraday#, V0#, E0prime, Slope
q$ = CHR$(34)
s1$ = q$ + "Point" + q$
s2$ = q$ + "log H" + q$
s3$ = q$ + "YH" + q$
s4$ = q$ + "THPot" + q$
s5$ = q$ + "THCoul" + q$
PRINT #7, USING "\     \, \     \, \  \, \     \, \      \"; s1$; s2$; s3$; s4$; s5$

FOR IDAP% = 1 TO NDAP%
   REM recover data for point IDAP%*****************************************
    XEXP = DAX(IDAP%, 1)
    YEXP = DAX(IDAP%, 2)
   REM set fundamental constants for use in object function*****************
    REM recover values for adjustable parameters*****************************
    Hpot = 10# ^ ((YEXP - E0prime) / Slope)
    LogH! = LOG(Hpot) / LOG(10#)
    TP = U(1)
    'Kw# = U(1)
    'TAM = U(2)
    'KaM1 = U(3)
    'KaM2 = U(4)
    'TH0 = U(3)
    'KaM2 = U(2)
    'Ka2 = U(2)

    KHP = (TP * (Hpot * Hpot - Ka1 * Ka2)) / (Hpot ^ 2# + Hpot * Ka1 + Ka1 * Ka2)
    'HAM = (TAM * Hpot) / (Hpot + KaM1)
    'HAM = (TAM * (Hpot * Hpot - KaM1 * KaM2)) / (Hpot ^ 2# + Hpot * KaM1 + KaM1 * KaM2)

    THPot! = Hpot - (Kw# / Hpot) + KHP '+ HAM
```

```
    THCoul! = -XEXP / (Faraday# * V0#)
    REM use recovered data to calculate object function for point IDAP%*******
    FF! = THPot! - THCoul!
    PRINT #7, USING "### ###.#### ##.####^^^^ ##.####^^^^ ##.####^^^^"; IDAP%; LogH!; FF!;
THPot!; THCoul!

NEXT IDAP%
CLOSE #7
END SUB

DEFSNG A-Z
SUB GAUSSL
DEFDBL A-Z
SHARED NUK%
REM GAUSSIAN ELIMINATION
FOR J% = 1 TO NUK%: FOR K% = 1 TO NUK%: Z(J%, K%) = q(J%, K%): NEXT: Z(J%, NUK% + 1) =
P(J%): NEXT
FOR I% = 1 TO NUK% - 1: ZII = Z(I%, I%)
FOR J% = I% + 1 TO NUK%: ZJI = Z(J%, I%) / ZII
FOR K% = I% TO NUK% + 1: Z(J%, K%) = Z(J%, K%) - Z(I%, K%) * ZJI
NEXT: NEXT: NEXT
REM BACK SUBSTITUTION
FOR I% = NUK% TO 1 STEP -1
DI = Z(I%, NUK% + 1): FOR J% = I% + 1 TO NUK%: DI = DI - Z(I%, J%) * D(J%): NEXT: D(I%) =
DI / Z(I%, I%)
NEXT
END SUB

DEFSNG A-Z
SUB INFIT
DEFDBL A-Z
SHARED infile$, Hardfile$, TTitle$, NPARM#, NUK%, NDAX%, NDAP%, E0prime, Slope
    GOSUB 10000: REM initialize output
    GOSUB 15000: REM read data
    GOSUB 20000: REM output of input
EXIT SUB
'
10000 : REM open output files
    OPEN "scrn:" FOR OUTPUT AS #1
    OPEN "lpt1:" FOR OUTPUT AS #2
RETURN
'
15000 : REM get data that defines problem
'get filename
  CLS
  CHDIR "\qb45\khpexamp"


  FileType$ = "*.DAT"
  FILES FileType$
  INPUT "Enter name of file with data: ", infile$
'open file
  editin$ = "QE " + infile$
  SHELL editin$
  OPEN infile$ FOR INPUT AS #3
  Hardfile$ = LEFT$(infile$, 8) + ".OUT"
  ErrFile$ = LEFT$(infile$, 8) + ".ERR"
  OPEN Hardfile$ FOR OUTPUT AS #6
  OPEN ErrFile$ FOR OUTPUT AS #7

'get data
  INPUT #3, TTitle$
  INPUT #3, E0prime, Slope
  INPUT #3, NPARM#
  FOR I% = 1 TO NPARM#: INPUT #3, PARMID$(I%), PARM(I%): NEXT
  INPUT #3, NUK%
  FOR I% = 1 TO NUK%: INPUT #3, UID$(I%), U(I%): NEXT
  INPUT #3, NDAX%, NDAP%
  FOR IDAX% = 1 TO NDAX%
        INPUT #3, XID$(IDAX%), dummy$
        FOR IDAP% = 1 TO NDAP%
              INPUT #3, DAX(IDAP%, IDAX%), SDAX(IDAP%, IDAX%)
        NEXT
  NEXT
  CLOSE #3
```

```
RETURN

20000 : REM output of input data for verification ******************************
    NOUT% = 1'output to screen (nout=1); output to lpt1:(nout=2)
    F2$ = "\          \"
    F1$ = "  ##.###^^^^"
'
    PRINT #NOUT%, "INPUT DATA FOR VERIFICATION "
    PRINT #NOUT%, "Number of adjustable parameters       (NUK%): "; NUK%
    PRINT #NOUT%, "Number of experimental data points   (NDAP%): "; NDAP%
    PRINT #NOUT%, "Number of variables with serial data (NDAX%): "; NDAX%
    PRINT #NOUT%, USING "E0' = ##.####^^^^"; E0prime
    PRINT #NOUT%, USING "Nernst slope = ##.####^^^^"; Slope
'
    PRINT #NOUT%, "Initial estimate for adjustable parameters "
    FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F2$; UID$(J%); : NEXT: PRINT #NOUT%,
    FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F1$; U(J%); : NEXT: PRINT #NOUT%,
'
    PRINT #NOUT%, "Experimental Data"
    PRINT #NOUT%, USING "\   \"; "  N";
    FOR J% = 1 TO NDAX%: PRINT #NOUT%, USING F2$; XID$(J%); : NEXT: PRINT #NOUT%,
    FOR I% = 1 TO NDAP%: PRINT #NOUT%, USING "###"; I%;
        FOR J% = 1 TO NDAX%: PRINT #NOUT%, USING F1$; DAX(I%, J%); : NEXT: PRINT #NOUT%,
    NEXT
'
    PRINT #NOUT%, "Estimates of Error in Experimental Data"
    PRINT #NOUT%, USING "\   \"; "  N";
    FOR J% = 1 TO NDAX%: PRINT #NOUT%, USING F2$; XID$(J%); : NEXT: PRINT #NOUT%,
    FOR I% = 1 TO NDAP%: PRINT #NOUT%, USING "###"; I%;
        FOR J% = 1 TO NDAX%: PRINT #NOUT%, USING F1$; SDAX(I%, J%); : NEXT: PRINT #NOUT%,
    NEXT
RETURN
END SUB

DEFSNG A-Z
SUB INITNM
DEFDBL A-Z
SHARED NUK%, SOS
    REM initialize normal matrix
    FOR I% = 1 TO NUK%: FOR J% = 1 TO NUK%: q(I%, J%) = 0#: NEXT: P(I%) = 0#: NEXT: SOS =
0#
END SUB

DEFSNG A-Z
SUB MATINV
DEFDBL A-Z

SHARED NUK%
    REM matrix inversion
    FOR ICOL% = 1 TO NUK%
    FOR I% = 1 TO NUK%: P(I%) = 0#: NEXT: P(ICOL%) = 1#
        CALL GAUSSL: FOR I% = 1 TO NUK%: R(I%, ICOL%) = D(I%): NEXT
    NEXT
END SUB

DEFSNG A-Z
SUB OBJECT (NENTRY%)
DEFDBL A-Z
SHARED FF, VF, FUNC$, NDAX%, IDAP%, E0prime, Slope, Faraday#, V0#, Kw#, Ka1, Ka2, KaM1,
KaM2, TP
SHARED XPLOT, YPLOT, SXPLOT, SYPLOT
SHARED XMin, XMax, XTic, YMin, YMax, YTic
IF NENTRY% = 1 THEN GOSUB 10' calculate object function and derivatives
IF NENTRY% = 2 THEN GOSUB 30' get dimensions for plot
IF NENTRY% = 3 THEN GOSUB 40' get experimental data for plot
IF NENTRY% = 4 THEN GOSUB 50' get calculated data for plot
EXIT SUB
'
10 :   REM recover data for point IDAP%*****************************************
    XEXP = DAX(IDAP%, 1)
    YEXP = DAX(IDAP%, 2)

20 :   REM set fundamental constants for use in object function*****************
    REM recover values for adjustable parameters*****************************
```

```
TP = U(1)
Ka1 = U(2)
Ka2 = U(3)
Kw# = U(4)

REM use recovered data to calculate object function for point IDAP%*******

Hpot = 10# ^ ((YEXP - E0prime) / Slope)
KHP = TP * ((Hpot * Hpot - Ka1 * Ka2) / (Hpot * Hpot + Hpot * Ka1 + Ka1 * Ka2))
THPot = Hpot - (Kw# / Hpot) + KHP
THCoul = -XEXP / (Faraday# * V0#)

'THPot is determined from the voltage at each point with the Nernst
'slope and E0 value from the electrode calibration
'THCoul is determined from the coulombs delivered to the cell

FUNC$ = "THPot - THCoulometric"
FF = THPot - THCoul

REM calculate derivatives ******************************
REM plug in object function & derivatives for point IDAP%*****************

dHdE = Hpot * LOG(10#) / Slope
DYDEOH = -Kw# * LOG(10#) * 10# ^ (-(YEXP - E0prime) / Slope) / Slope

  KHP1 = TP * Hpot ^ 2
  dKHP1 = 2 * TP * Hpot * dHdE
  Denom = Hpot ^ 2# + Hpot * Ka1 + Ka1 * Ka2
  dDenom = 2 * Hpot * dHdE + Ka1 * dHdE
  DYDKHP1 = QRule#(KHP1, dKHP1, Denom, dDenom)

  KHP2 = TP * Ka1 * Ka2
  dKHP2 = 0#
  DYDKHP2 = QRule#(KHP2, dKHP2, Denom, dDenom)

DYDKHP = DYDKHP1 - DYDKHP2

DYDTP = (Hpot * Hpot - Ka1 * Ka2) / (Hpot ^ 2# + Hpot * Ka1 + Ka1 * Ka2)

  Ka11 = TP * Hpot ^ 2
  dKa11 = 0#
  dDenom = Hpot + Ka2
  DYDKa11 = QRule#(Ka11, dKa11, Denom, dDenom)

  Ka12 = TP * Ka1 * Ka2
  dKa12 = TP * Ka2
  DYDKa12 = QRule#(Ka12, dKa12, Denom, dDenom)

DYDKa1 = DYDKa11 - DYDKa12

  Ka21 = TP * Hpot ^ 2
  dKa21 = 0#
  dDenom = Ka1
  DYDKa21 = QRule#(Ka21, dKa21, Denom, dDenom)

  Ka22 = TP * Ka1 * Ka2
  dKa22 = TP * Ka1
  DYDKa22 = QRule#(Ka22, dKa22, Denom, dDenom)

DYDKa2 = DYDKa21 - DYDKa22

DYDKw = -1# / Hpot

DYDE = dHdE - DYDEOH + DYDKHP
DYDQ = 1# / (Faraday# * V0#)

FU(1) = DYDTP
FU(2) = DYDKa1
FU(3) = DYDKa2
FU(4) = DYDKw

FX(1) = DYDQ
FX(2) = DYDE

REM calculate expected variance in ff=y**********************************
```

```
    VF = 0#: FOR I% = 1 TO NDAX%: VF = VF + FX(I%) * FX(I%) * SDAX(IDAP%, I%) *
SDAX(IDAP%, I%): NEXT
    REM VF=1# : REM override the normal expression to give equal weights
RETURN
'
30 : REM get dimensions of plot*********************************************
    XMin = 0: XMax = 45: XTic = 5
    YMin = -.3: YMax = .2: YTic = .1
RETURN
'
40 : REM get experimental data for plot ************************************
    XPLOT = DAX(IDAP%, 1): SXPLOT = SDAX(IDAP%, 1)
    YPLOT = DAX(IDAP%, 2): SYPLOT = SDAX(IDAP%, 2)
RETURN
'
50 : REM get calculated data for plot
    XEXP = XPLOT
    GOSUB 20
    YPLOT = THPot
RETURN
'
END SUB

DEFSNG A-Z
SUB OUTFNL (NOUT%)
DEFDBL A-Z
SHARED PROG$, infile$, TTitle$, FUNC$, E0prime, Slope
SHARED NPARM#, NUK%, NDAX%, NDAP%, IDAP%
SHARED VF, FF, SOS
    GOSUB 52000: GOSUB 59000: GOSUB 54000'output of big picture
    GOSUB 56000: GOSUB 57000: GOSUB 58000'output of details
    IF NOUT% = 2 THEN PRINT #NOUT%, CHR$(12)
EXIT SUB
'
52000 : REM report results *****************************************************
PRINT #NOUT%, DATE$, TIME$, "Program: "; PROG$
PRINT #NOUT%,
PRINT #NOUT%, "Dataset: "; infile$
PRINT #NOUT%,
PRINT #NOUT%, "Title: "; TTitle$
PRINT #NOUT%,
PRINT #NOUT%, "Function: "; FUNC$
PRINT #NOUT%,
PRINT #NOUT%, USING "Eo' = ##.#####^^^^ Slope = ##.#####^^^^"; E0prime; Slope
CALL OUTRUN(NOUT%, 4)       'output of adjustable paramters
PRINT #NOUT%,
RETURN
'
54000 : REM calculate corrected values of experimental data
F1$ = "     ##.#####^^^^   ##.#####^^^^   ##.###^^^^   ##.###^^^^"
F2$ = " N   Raw          Optimized    Delta        SD (data) "
FOR IDAP% = 1 TO NDAP%
  CALL OBJECT(1): REM get data, calculate functions and derivatives
  FOR IDAX% = 1 TO NDAX%
    DELTAX(IDAP%, IDAX%) = SDAX(IDAP%, IDAX%) ^ 2 * FX(IDAX%) * FF / VF
    DAXC(IDAP%, IDAX%) = DAX(IDAP%, IDAX%) - DELTAX(IDAP%, IDAX%)
  NEXT
NEXT
FOR J% = 1 TO NDAX%
   PRINT #NOUT%, "Optimized values for "; XID$(J%): PRINT #NOUT%, F2$
   FOR I% = 1 TO NDAP%
     PRINT #NOUT%, USING "###"; I%;
     PRINT #NOUT%, USING F1$; DAX(I%, J%); DAXC(I%, J%); DELTAX(I%, J%); SDAX(I%, J%)
   NEXT: PRINT #NOUT%,
NEXT
REM check sos ***********
WSOSY = 0#: WSOSX = 0#
FOR IDAP% = 1 TO NDAP%
  CALL OBJECT(1)
  FOR J% = 1 TO NDAX%
    IF SDAX(IDAP%, J%) > 0# THEN WSOSX = WSOSX + DELTAX(IDAP%, J%) ^ 2 / SDAX(IDAP%, J%) ^
2
  NEXT
  WSOSY = WSOSY + FF ^ 2 / VF
NEXT
```

```
PRINT #NOUT%, "  wsosy       wsosx   "
PRINT #NOUT%, USING "##.###^^^^  ##.###^^^^"; WSOSY; WSOSX
PRINT #NOUT%,
RETURN
'
56000 : REM Importance of data in determining K
F1$ = "Importance of data in determining K: fU^2/sY^2/Q"
F2$ = "\        \"
F3$ = "  ###.##  "
CALL INITNM: FOR IDAP% = 1 TO NDAP%: CALL OBJECT(1): CALL BILDNM: NEXT
PRINT #NOUT%, F1$
PRINT #NOUT%, "   ";
FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F2$; UID$(J%); : NEXT: PRINT #NOUT%,
FOR IDAP% = 1 TO NDAP%
  CALL OBJECT(1)
  PRINT #NOUT%, USING "###"; IDAP%;
  FOR IUK = 1 TO NUK%
    PRINT #NOUT%, USING F3$; FU(IUK) ^ 2 / q(IUK, IUK) / VF;
  NEXT
  PRINT #NOUT%,
NEXT
PRINT #NOUT%,
RETURN
'
57000 : REM Importance of error in raw data
F1$ = "Importance of error in raw data: (fX*sX)^2/sY^2"
F2$ = "\        \"
F3$ = "###.##    "
PRINT #NOUT%, F1$
PRINT #NOUT%, "   ";
FOR J% = 1 TO NDAX%: PRINT #NOUT%, USING F2$; XID$(J%); : NEXT: PRINT #NOUT%,
FOR IDAP% = 1 TO NDAP%
  CALL OBJECT(1)
  PRINT #NOUT%, USING "###"; IDAP%;
  FOR IDAX% = 1 TO NDAX%
    PRINT #NOUT%, USING F3$; FX(IDAX%) ^ 2 * SDAX(IDAP%, IDAX%) ^ 2 / VF;
  NEXT
  PRINT #NOUT%,
NEXT
PRINT #NOUT%,
RETURN
'
58000 : REM Importance of error in object function
F1$ = "Importance of error in object function"
F2$ = "           Y/sY      Y^2/SOS"
F3$ = "###     ###.######  ###.##  "
PRINT #NOUT%, F1$
PRINT #NOUT%, F2$
FOR IDAP% = 1 TO NDAP%
CALL OBJECT(1)
PRINT #NOUT%, USING F3$; IDAP%; FF / SQR(VF); FF * FF / VF / SOS
NEXT
PRINT #NOUT%,
RETURN
'
59000 : REM variance
F1$ = "Standard deviation in adjustable parameters"
F2$ = "Covariance matrix"
F3$ = "Normalized covariance matrix"
F4$ = "##.###^^^^  "
F5$ = "\          \"
CALL MATINV 'invert Q matrix
PRINT #NOUT%, F1$
FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F5$; UID$(J%); : NEXT: PRINT #NOUT%,
FOR I% = 1 TO NUK%: PRINT #NOUT%, USING F4$; SQR(R(I%, I%)); : NEXT: PRINT #NOUT%,
PRINT #NOUT%,
PRINT #NOUT%, F2$
FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F5$; UID$(J%); : NEXT: PRINT #NOUT%,
FOR I% = 1 TO NUK%: FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F4$; R(I%, J%); : NEXT: PRINT
#NOUT%, : NEXT
PRINT #NOUT%,
PRINT #NOUT%, F3$
FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F5$; UID$(J%); : NEXT: PRINT #NOUT%,
FOR I% = 1 TO NUK%: FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F4$; R(I%, J%) / SQR(R(I%, I%)
* R(J%, J%)); : NEXT: PRINT #NOUT%, : NEXT
```

```
PRINT #NOUT%,
RETURN
'
END SUB

DEFSNG A-Z
SUB OUTPLT (NENTRY%)
DEFDBL A-Z
SHARED IDAP%, NDAP%, TTitle$
SHARED XPLOT, YPLOT, SXPLOT, SYPLOT
SHARED XMin, XMax, XTic, YMin, YMax, YTic
    IF NENTRY% = 1 THEN GOSUB DIMPLOT
    IF NENTRY% = 2 THEN GOSUB INITSCR
    IF NENTRY% = 3 THEN GOSUB PLTDATA
EXIT SUB
'
DIMPLOT: 'get dimensions of plot
    CALL OBJECT(2)
INITSCR: 'initialize screen
    SCREEN 11
    CLS
PLTDATA: 'set scale
    XDEL = (XMax - XMin) / 640: YDEL = (YMax - YMin) / 480
    XMINW = XMin: YMINW = YMin: XMAXW = XMax: YMAXW = YMax
    WINDOW (XMINW, YMINW)-(XMAXW, YMAXW)'set scale
    LINE (XMin, YMin)-(XMax, YMax), , B'outline area
'draw box and tics (grids)
   FOR X = XMin TO XMax STEP XTic
       LINE (X, YMin)-(X, YMin + 10 * YDEL)
       LINE (X, YMax)-(X, YMax - 10 * YDEL)
      'LINE(X,YMIN)-(X,YMAX)
   NEXT
   FOR Y = YMin TO YMax STEP YTic
       LINE (XMin, Y)-(XMin + 10 * XDEL, Y)
       LINE (XMax, Y)-(XMax - 10 * XDEL, Y)
      'LINE(XMIN,Y)-(XMAX,Y)
   NEXT
'plot data and error bars
   FOR IDAP% = 1 TO NDAP%
       CALL OBJECT(3)
       X = XPLOT: Y = YPLOT: SX = SXPLOT: SY = SYPLOT
       LINE (X - XDEL * 5, Y - YDEL * 5)-(X + XDEL * 5, Y + YDEL * 5), , B
       LINE (X, Y - SY)-(X, Y + SY): LINE (X - SX, Y)-(X + SX, Y)
   NEXT
'plot function
   FOR X = XMin + XDEL TO XMax STEP XDEL
       XPLOT = X: CALL OBJECT(4): Y = YPLOT
       IF X = XMin + XDEL THEN PSET (X, Y) ELSE LINE -(X, Y)
   NEXT
'additional information
  CLOSE #11
  LOCATE 20, 20
'  CALL ScrnDump(11, 0)
  PRINT
  PRINT " "; TTitle$
  PRINT " "; DATE$, TIME$
  PRINT " "; "XMAX = "; XMax; ":XMIN = "; XMin; ":XTIC = "; XTic
  PRINT " "; "YMAX = "; YMax; ":YMIN = "; YMin; ":YTIC = "; YTic
RETURN
'
61900 : 'information for screen plot dump
LPRINT : LPRINT : LPRINT : LPRINT
LPRINT : LPRINT TTitle$
LPRINT : LPRINT "Data file: "; infile$
LPRINT : LPRINT "XMAX = "; XMax; ":XMIN = "; XMin; ":XTIC = "; XTic
LPRINT : LPRINT "YMAX = "; YMax; ":YMIN = "; YMin; ":YTIC = "; YTic
LPRINT CHR$(12)
RETURN
'
END SUB

DEFSNG A-Z
SUB OUTRUN (NOUT%, NENTRY%)
DEFDBL A-Z
SHARED PROG$, FUNC$, infile$, TTitle$, NPARM#, NUK%, NDAX%, NDAP%
```

```
SHARED ITER%, ITMAX, EPS, SOS
    F1$ = "  ##.###^^^^"
    F2$ = "\          \"
        IF NENTRY% = 1 THEN GOSUB 22000
        IF NENTRY% = 2 THEN GOSUB 22200
        IF NENTRY% = 3 THEN GOSUB 22400
        IF NENTRY% = 4 THEN GOSUB 22600
EXIT SUB
'
22000 : 'heading for interim output
   PRINT #NOUT%, "ITERATING ON ADJUSTABLE PARAMETERS ..."
   PRINT #NOUT%, USING F2$; "Iteration";
   FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F2$; UID$(J%); : NEXT
   PRINT #NOUT%, USING F2$; "SOS/DF"
   RETURN
'
22200 : 'interim output, adjustable parameters
   PRINT #NOUT%, USING "###"; ITER%;
   FOR J% = 1 TO NUK%: PRINT #NOUT%, USING F1$; U(J%); : NEXT
   RETURN
'
22400 : 'interim output, sos/df
   PRINT #NOUT%, USING F1$; SOS / (NDAP% - NUK%)
   RETURN
'
22600 : 'output of all data
   GOSUB 22000: GOSUB 22200:  GOSUB 22400
   RETURN
'
END SUB

FUNCTION QRule# (You#, DYouDx#, Vee#, DVeeDx#)

   QRule# = (Vee# * DYouDx# - You# * DVeeDx#) / (Vee# * Vee#)

END FUNCTION

DEFSNG A-Z
SUB SUBMAIN
DEFDBL A-Z
SHARED EPS, ITER%, ITFLAG%, NDAP%, IDAP%
NOUT% = 1' Output to screen (nout=1); Output to lpt1: (nout=2)
    CALL OUTRUN(NOUT%, 1): REM heading for interim output
    EPS = .0001#: ITER% = 0: ITFLAG% = 1
    WHILE ITFLAG% > 0: REM loop
        CALL INITNM: REM initialize normal matrix
        CALL ADJUST: REM adjust u
        CALL OUTRUN(NOUT%, 2): REM output for adjustable parameters
        FOR IDAP% = 1 TO NDAP%: REM step through data points
            CALL OBJECT(1): REM function and derivatives
            CALL BILDNM: REM build normal matrix
        NEXT
        CALL GAUSSL: REM solve normal equations
        CALL CNVCHK: REM convergence check, set ITFLAG%
        CALL OUTRUN(NOUT%, 3): REM interim output of sos/df
    WEND: REM end of loop
END SUB
```