

AN EQUILIBRIUM DISTRIBUTION OF
TRACE ELEMENTS IN A NATURAL STREAM EMBIRONMENT,
THE RED RIVER NEAR
QUESTA, NEW MEXICO

by
Stuart E. Faith

Submitted in Partial Fulfillment
of the Requirements for the Degree of
Master of Science in Geochemistry

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY

Socorro, New Mexico

November, 1974

This thesis is accepted on behalf of the faculty of the

Institute by the following committee:

Thomas H. Gray

Richard C. Beane

Carl J. Papp

Date 12/16/74

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the members of his thesis committee: Doctors Thomas Plouf, Richard Beane and Carl Popp for their assistance and encouragement during the course of this study.

A special thanks is extended to the New Mexico Bureau of Mines and Mineral Resources for their financial support and use of laboratory and office facilities.

Lastly, my most sincere gratitude is given to my wife Connie, whose many hours of assistance in all phases of this thesis study may have been unrewarded, but never unappreciated.

ABSTRACT

Various reports concerning the toxicity of metals to aquatic life, livestock, agricultural, and human populations show large variabilities in their reported toxic limits. The variability is largely dependent upon the metal compound used in the toxicity test, the chemical characteristics of the water used in the toxicity test, and the type of aquatic, animal, or plant species exposed to the metal.

A quantitative characterization of the stable aqueous metal species in a given natural stream environment would be of benefit in evaluating the effect of metals on the ecology of a stream or river. Such an analysis would facilitate accurate description of the chemical quality of natural waters and the subsequent implementation of water quality standards for trace metal concentrations.

The Red River in northern New Mexico, in the vicinity of Molybdenum Corporation of America's open pit molybdenum mine was selected for this study because the stream is perennial, has recreational and domestic uses, and may be receiving metal contaminant inputs from other than natural weathering processes.

After analyzing the metal and ligand components, a computer program was utilized to accomplish distribution of metals among various aqueous species at two locations in the Red River near Questa, New Mexico. The concentration of the stable metal species was then compared to available toxicity data to see if toxic limits were being exceeded. The stable aqueous metal

species concentrations did not exceed toxic levels. However, the concentration of calcium at one of the sampling locations was found to exceed the recommended limit of concentration for domestic use.

TABLE OF CONTENTS

I. Introduction.....	1.
A. Statement of Problem.....	1.
B. Objective.....	1.
C. Study Location.....	2.
II. Sampling and Experimental Considerations.....	7.
A. Sampling Schedule.....	7.
B. Sampling Procedure.....	7.
C. Analytical Techniques.....	8.
D. Equilibrium Model.....	12.
III. Results.....	22.
IV. Discussion.....	30.
A. Analytical Work.....	30.
B. Analysis of Error.....	31.
C. Anomalous Fe and Cu Concentrations.....	32.
D. Trace Metal Concentrations.....	34.
E. Other Work in the Red River Area.....	35.
F. Equilibrium Distribution.....	37.
G. Comparison of Equilibrium Concentrations to Toxicity Data.....	37.
V. Conclusions.....	39.
A. Trace Metal Concentrations.....	39.
B. Equilibrium Concentration of Aqueous Metal Species.....	39.
C. Sampling Considerations.....	41.
D. Utility of This Study.....	42.

References.....	43.
Appendix A.....	45.
Appendix B.....	47.
Appendix C.....	50.

LIST OF TABLES

Table 1	Toxicity Values for Various Metal Compounds.....	4.
Table 2	Analytical Techniques.....	9.
Table 3	Ion Size Parameters Used in This Study for the Various Charged Ions and Complexes.....	17.
Table 4	Lateral Concentration Averages (ppm.) of the Five Samples Collected Every Three Hours for 24 Hours At Sample Site A and Their Standard Deviations Appearing Just Below the Concentration Values.....	24.
Table 5	Lateral Concentration Averages (ppm.) of the Five Samples Collected Every Three Hours for 24 Hours At Sample Site B and Their Standard Deviations Appearing Just Below the Concentration Values.....	25.
Table 6	24 Hour Concentration Averages of Metals (in ppm. with Standard Deviations Below) from the Two Sampling Points.....	26.
Table 7	Equilibrium Distribution of Aqueous Species From Sample Site A.....	27.
Table 8	Equilibrium Distribution of Aqueous Species From Sample Site B.....	28.
Table 9	Equilibrium Distribution of Aqueous Species From Samples Collected At 5 P.M. At Sample Site B...	29.

LIST OF FIGURES

Figure 1 Sampling Area.....3.

Figure 2 Flow Chart of Computer Program
to Calculate Equilibrium Distribution.....21.

Figure 3. Lateral Concentration Profile for Fe, Cu,
and Mo During the B-5PM Sampling Sequence.....33.

Figure 4 Comparison of Concentrations Reported
by the Environmental Protection Agency
to Those Values Determined in This Study.....36.

I. INTRODUCTION

A. Statement of Problem

Toxicologists and government agencies concerned with establishing water quality criteria have, in the past, studied the effects of metal contamination in natural water on the basis of total metal concentration. Data concerning the toxicities of metals (McKee and Wolf, 1971) indicates that a certain metal may have an extremely varied toxic effect depending upon:

(1) which metal compound was used in the toxicity test (ie. as a chloride, sulfate, nitrate, etc.), (2) the type of water used for the test (ie. highly alkaline water, distilled water, acidic water, etc.), and (3) the aquatic animal or plant species exposed to the metal. Evaluation of these extremely varied reports on toxic levels of metals in order to establish water quality standards in terms of trace metal concentrations is tenuous. In order to illustrate this variability in reported toxic limits, a compilation of toxic limits for a variety of metals (McKee and Wolf, op cit) is presented in Table 1.

B. Objective

The purpose of this thesis is to characterize the equilibrium distribution of aqueous Na, K, Ca, Mg, Fe, Mn, Al, Cu, Ni, Sn, Mo, SiO_2 , OH, CO_3 , HCO_3 , SO_4 and Cl in a natural stream environment which may be receiving metal contaminant inputs from other than natural weathering processes. When the distribution of aqueous metal species are quantitatively evaluated, their concentration will be compared with the toxic limits

shown in Table 1, in order to determine whether or not toxic limits are being exceeded.

C. Study Location

The Red River in northern New Mexico, in the vicinity of Molybdenum Corporation of America's (hereafter referred to as MCA in the text) open pit molybdenum mine was selected for this study because the stream is perennial, has recreational and domestic uses, and may be receiving metal contaminant inputs from other than natural weathering processes. Presented in Figure 1 is the sampling area that was studied on the Red River, with the location of sampling sites, molybdenum mine, and the molybdenum mine tailings pond.

Figure 1
Sampling Area

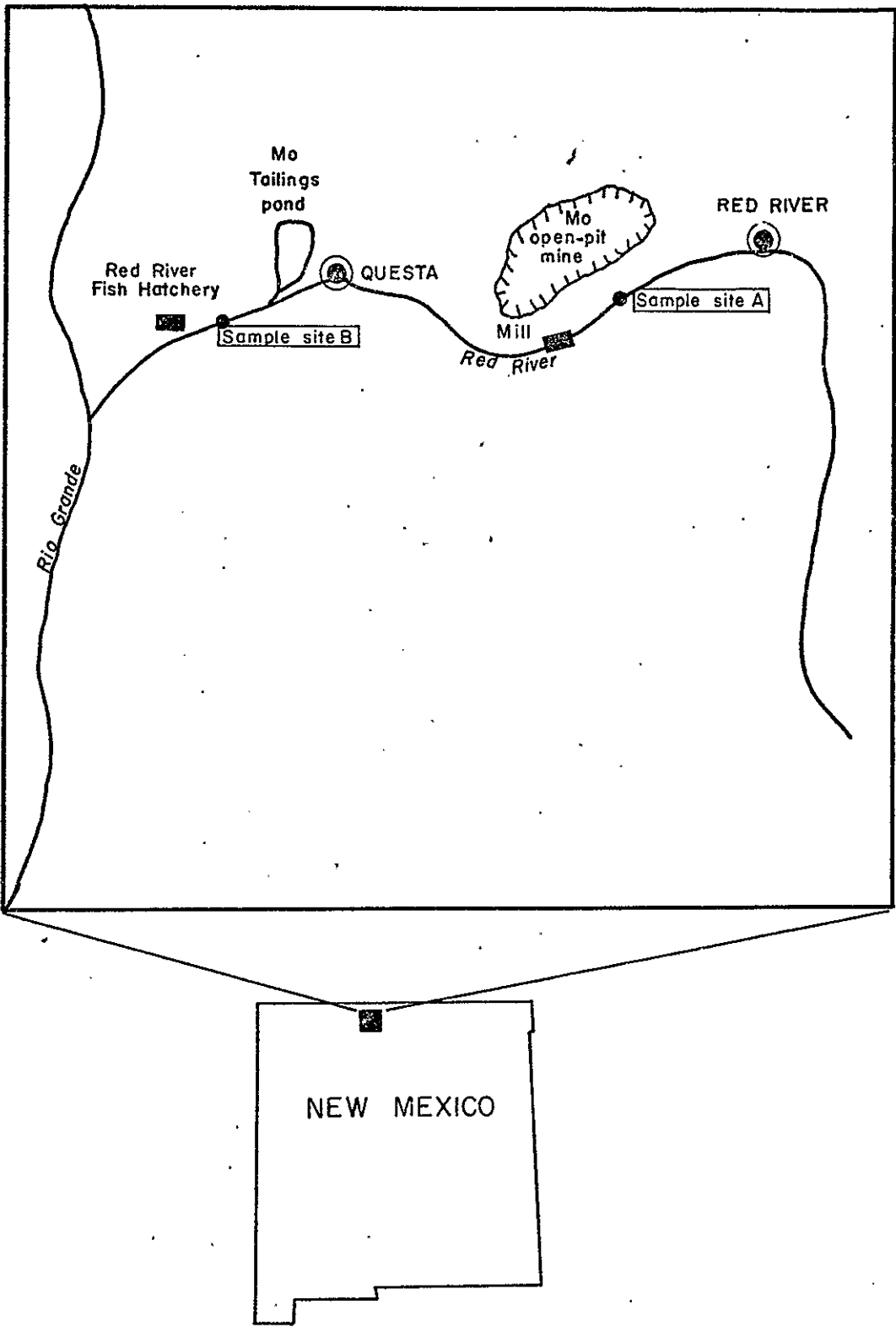


Table 1.

Toxicity Values for Various
Metal Compounds

Metal	Toxicity ¹	Effect	Susceptible species
Al	1.0 - 5.0	injury to roots, reduced growth	corn
AlCl ₃	6.7	immobilization	<u>Daphnia magna</u>
AlCl ₃	0.5	lethal	stickleback
Al ₂ (SO ₄) ₃	25.0	reduced growth	oats
Al ₂ (SO ₄) ₃	250.0	lethal	bass, minnow, goldfish
Ca	30.0	recommended limit	for domestic use
CaCl ₂	10,000.	loss of appetite	cows
CaCl ₂	10,000.	lethal	fish
Ca(OH) ₂	100.0	lethal	bass, carp, trout
CaSO ₄	non-toxic at saturation levels for fish and cattle		
Cu	1.0	U.S.P.H.S. limit for domestic use	
Cu	0.17 - 0.20	lethal	barley, sugar beet
Cu	reciprocally anatagonistic with Mo		
Cu	0.02	threshold for beneficial growth of aquatic life	
CuCl ₂	0.009	lethal	goldfish
CuCl ₂	1.25	96 hr. TLm	sunfish

¹ all concentrations reported as ppm.

Metal	Toxicity	Effect	Susceptible species
CuO	56,000.	96 hr. TLm	sunfish
CuSO ₄	0.14	harmful	trout
FeCl ₃	1.0 - 100.	lethal	goldfish
Fe ₂ (SO ₄) ₃	0.72	lethal	carp
FeCl ₂	40.0	immobilization	<u>Daphnia magna</u>
FeO	10,000.	96 hr. TLm	mosquito fish
FeSO ₄	152.	immobilization	<u>Daphnia magna</u>
MgCl ₂	2,000.	inhibited growth	beans
MgCl ₂	500.	lethal	minnows
MgSO ₄	1,000.	purgative	human
Mn	1.0 - 10.0	harmful	legumes
Mn	5.0 - 10.0	harmful	tomatoes
Mn	150. - 500.	harmful	oats
MnCl ₂	12.0	lethal	minnows
MnSO ₄	150. - 200.	chlorosis	oats
MnSO ₄	1,000.	lethal	fish
NiCl ₂	1.0 - 10.0	lethal	fish
NiSO ₄	2.5 - 5.0	reduced growth	oats
NiSO ₄	16.0	tolerance level	eels
KHCO ₃	2,000.	lethal	minnows
K ₂ SO ₄	1,000.	lethal	bluegills
Na ₂ SO ₄	3,600.	100 hr. TLm	<u>Daphnia magna</u>
Na ₂ CO ₃	524.	100 hr. TLm	<u>Daphnia magna</u>

Metal	Toxicity	Effect	Susceptible species
SnCl_4	146.	lethal	<u>Daphnia magna</u>
SnCl_2	25.	lethal	<u>Daphnia magna</u>
$\text{MoO}_4^{=}$	40.	injurious	sugar beets
Mo	5.0 (forage)	molybdenosis (scour)	cattle
Mo	Cu/Mo < 2	molybdenosis	cattle

II. SAMPLING AND EXPERIMENTAL CONSIDERATIONS

A. Sampling Schedule

Shown in Figure 1 is the area on the Red River that was studied. Water samples were collected from two positions along the river: location A is one-half mile upstream from the MCA mill, location B is located one-half mile downstream from the MCA tailings pond discharge point and immediately upstream from the Red River Fish Hatchery.

At 8:00 A.M. on June 4, 1974, sampling commenced at sample site A. Five samples were collected at evenly spaced locations laterally across the stream. Five samples were collected at these locations within a ten minute interval every three hours for twenty-four hours. The same sampling schedule was utilized at sample site B commencing at 8:00 A.M. on June 6, 1974.

B. Sampling Procedure

Each sample was collected in a one liter polyethylene bottle. Previously the bottles had been rinsed with dilute nitric acid followed by three rinsings with distilled and deionized water. This washing procedure was repeated three times for each bottle. Prior to sample collection, the bottle was rinsed several times with stream water. Samples were then collected by submerging the bottle to approximately half of the stream depth and allowing the water to fill the bottle.

Immediately after sample collection, an aliquot of the sample was removed to determine the bicarbonate concentration

by acid titration, using a field test kit. The remainder of the sample was then placed in a PVC and lucite positive pressure filtration apparatus, which utilizes a 0.45 micron filter to remove all suspended matter from the sample. After placing the sample in the filtration apparatus, the sample bottle was placed beneath the device to collect the sample. Filter residues and filters were placed in small polyethylene bags and sealed. Following filtration, the water samples were acidified using three to four milliliters of concentrated nitric acid. Sample numbers indicate location, time, and position as follows: sample number A-11AM-3 indicates that the sample was collected at sample site A, during the 11 A.M. sampling sequence, and was collected in the third or middle stream position.

During each three hour sampling sequence, the stream hydrogen ion activity (pH) and electrode potential (Eh) were measured using a portable Orion pH meter. At both sampling locations, stream width and depth profiles were recorded. At both locations, a stream velocity measurement was made by timing floating objects through a measured section of the stream in order to obtain an approximation of the stream discharge rate.

C. Analytical Techniques

The analytical techniques used for the different chemical components that were analyzed in this study are listed in Table 2.

As can be seen from Table 2, standard wet chemical

Table 2

Analytical Techniques

Chemical Component	Technique
HCO ₃	acid titration
SO ₄	gravimetric
Cl	mercuric nitrate titration
Na	A.A. spectroscopy (flame)
K	A.A. spectroscopy (flame)
Ca	EDTA titration
Mg	A.A. spectroscopy (flame)
Fe	A.A. spectroscopy (graphite furnace)
Mn	A.A. spectroscopy (graphite furnace)
Al	A.A. spectroscopy (graphite furnace)
Cu	A.A. spectroscopy (graphite furnace)
Ni	A.A. spectroscopy (graphite furnace)
Sn	A.A. spectroscopy (graphite furnace)
Mo	thiocyanate complexation (colorimetric)
SiO ₂	molybdate complexation (colorimetric)

techniques were used for the analysis of anionic or ligand components, and atomic absorption spectrophotometry was utilized for the majority of the metals. Appendices A and B describe the instrumental parameters utilized for the atomic absorption spectrophotometer in determining metal concentrations in the water samples.

Prior to doing work on the atomic absorption spectrophotometer, filter residues were treated by a procedure described by the Environmental Protection Agency (E.P.A., 1971). Residues remaining after filtration through a 0.45 micron filter are digested in warm concentrated nitric acid, and then diluted with distilled water to 100. milliliters. These samples were then analyzed by atomic absorption spectrophotometry. The E.P.A. has defined such metal concentrations as "suspended metals" (E.P.A., on cit). The procedure does not dissolve any of the solids, but rather dissolves adsorbed metal phases from the surface of the solids and puts them in solution. By quantitatively diluting the acid residue solution and determining the metal concentrations in it, the appropriate stream or river concentration may be determined by knowing the original sample volume.

For all chemical components that were determined by spectrophotometry or colorimetry, standards in the appropriate concentration range had to be determined. The appropriate concentration range of the standards for each metal were determined by measuring absorbance values for various metal

concentrations. That portion of a plot of concentration versus absorbance yielding a straight line is the appropriate concentration range for the standards. Standards in such a concentration range are said to be obeying the Beer-Lambert Law (Fischer, 1968). Once absorbance values were determined for the metal standards, a least squares linear regression computer program was utilized to find the best line or equation to describe absorbance in the concentration range of the standards. This equation was then utilized to convert absorbance values of the samples to concentration values. Listed in Appendices A and B, along with the instrumental parameters for each metal, are the equations used to describe the standard curves, the multiple correlation coefficient, and the standard error of the estimate. A value of unity for the multiple correlation coefficient indicates that the regressed equation is a perfect fit for the data used. Lower values of the multiple correlation coefficient indicates that there is more scatter in the data used to make the standard curve. The standard error of the estimate is the parameter that describes how much error one may attribute to the concentration values derived from the standard curve equation.

Because of the large number of samples that were analyzed, standards were run three to four times in the course of analyzing all the samples for each metal. Each of these sets of standards was used to recalibrate the absorbance curve which was then applied to that set of standards; ie. a new equation

was determined for each new set of standards and samples. For the samples that were run on the graphite furnace, a chart recorder was utilized that amplifies the signal from the photomultiplier, and records a peak that is proportional to absorbance. It was peak heights instead of absorbance values that were recorded for these metals in order to determine standard curves and sample concentrations.

D. Equilibrium Model

The use of the term "equilibrium" as it is used in this study requires certain assumptions. Equilibrium does not imply that the aquatic system studied is static or at steady state within a closed system. Instead, the concept of homogeneous aqueous equilibrium as applied in this study assumes that the reaction rates of the aqueous species involved are sufficiently rapid to warrant their characterization by strictly thermodynamic equilibrium relations. Also, the quantitative characterization of the stable aqueous species assumes equilibrium in discrete units of time and space; ie. the equilibrium distribution applies only to when and where the samples were collected. In addition, the assumption was made that the equilibrium distribution could be made at 25° C instead of the true temperature of the Red River, which ranged between 8° and 15° C when the samples were collected, without having significant effect upon the results of the equilibrium distribution of the various aqueous metal species.

After determining the total analytical concentration of

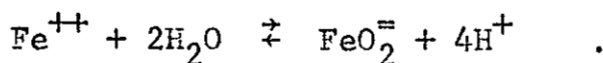
metals and ligands, a computer program was utilized to determine the equilibrium distribution of metals among various aqueous species. The system essentially consists of an eleven metal-six ligand matrix, each one added at a fixed total analytical concentration. Within the eleven metal-six ligand matrix, approximately 120 mass action equations and seventeen mass balance equations have to be solved simultaneously. The unknowns in each of these equations are the activities of free ions and aqueous species. The independent variables consist of the total analytical concentrations of metals and ligands, equilibrium constants describing the activity product of free ions and aqueous species, the hydrogen ion activity (pH), and electron activity (pE).

The literature describing the computation of chemical equilibria is extensive. A list of references describing the various techniques is provided by Morel and Morgan (1972) and Stumm and Morgan (1970). The technique of using the so-called equilibrium constant approach is described in great detail by Morel and Morgan (op cit); however, a description of the methodology employed in this study using the equilibrium constant approach will be discussed.

The equilibrium constants used in this study were almost entirely those reported by Sillen (1964), at 25° C, one atmosphere pressure, and zero ionic strength (and shown in Appendix C). Some of the aqueous species that were originally considered in this study had equilibrium constants reported at high ionic

strengths. After reviewing the literature from which Sillen reported the equilibrium constants, it could not be substantiated whether the reported values were true equilibrium constants, representing activity products of free ions and aqueous species; or that the values were molar ratios requiring extrapolation to zero ionic strength. The aqueous species for which this doubt exists were not of significant concentration in the equilibrium distribution relative to the other species that were involved. For these reasons, the equilibrium distribution among the various metal aqueous species does not include the aqueous species that have questionable equilibrium constants.

Some of the chemical reactions of interest in the equilibrium model have equilibrium constants derived from free energies of formation of the species of interest and the free ions. For example: $\text{FeO}_2^=$ (aq.) has a free energy of formation (ΔG_f°) of -128.0 kcal. (Parker, et al, 1971). Now, writing the reaction with the ferrous ion, water, and hydrogen ion:



The Gibbs free energy of reaction at 25° C may be calculated from the free energies of formation of the reactants and products according to the following relation:

$$\Delta G_r^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

Thus,

$$\Delta G_r^\circ = \Delta G_{f_{\text{FeO}_2^=}}^\circ + 4\Delta G_{f_{\text{H}^+}}^\circ - \Delta G_{f_{\text{Fe}^{++}}}^\circ - 2\Delta G_{f_{\text{H}_2\text{O}}}^\circ$$

where: $\Delta G_{f_{H^+}}^\circ = 0.0$ kcal.

$\Delta G_{f_{Fe^{++}}}^\circ = -20.3$ kcal.

$\Delta G_{f_{H_2O}}^\circ = -56.7$ kcal. (Parker, et al, op cit).

Thus,

$$\begin{aligned}\Delta G_r^\circ &= (-128.0) + (0.0) - (-20.3) - 2(-56.7) \\ &= 5.7 \text{ kcal.}\end{aligned}$$

Using the free energy of reaction, the equilibrium constant, which is defined in terms of ion activities, may be calculated for 25° C according to the following relation:

$$\log K = \frac{-\Delta G_r^\circ}{1.364}$$

For the reaction just considered, at 25° C

$$\begin{aligned}\log K &= \frac{(-5.7)}{1.364} \\ &= -4.2\end{aligned}$$

Figure 2 is a flow chart representation of the methodology employed in the computer based equilibrium calculations. After reading in the total concentrations of metals and ligands, the appropriate equilibrium constants, hydrogen ion activity (pH), and electrode potential (Eh), which were measured in the field; the total metal and ligand concentrations are set equal to the concentration of the predominant species of that metal or ligand. A first approximation of the ionic strength is then

made according to the following equation:

$$I = 0.5 \sum C_i Z_i^2$$

where: I = ionic strength

C_i = true molality of the i^{th} charged species

Z_i = the charge on the i^{th} charged species

After calculating the ionic strength, the individual ion activity coefficients are calculated using the extended Debye-Hückel equation:

$$\log \gamma_i = \frac{-A\sqrt{I} Z_i^2}{1 + Ba\sqrt{I}}$$

where: $A = 0.5085$ for water at 25°C

$B = 0.328 \times 10^8$ for water at 25°C

a = ion size parameter dependent upon charge and size of ion

Z_i = charge on the i^{th} charged species

Butler (1964) lists the various ion size parameters for free ion and some aqueous metal species. The ion size parameters used in this study are presented in Table 3. For those species not listed by Butler, the ion size parameter was estimated on the basis of charge and structural similarity to the species for which data are available. The error introduced by selecting the wrong ion size parameter (for example 3×10^{-8} instead of 4×10^{-8}) at the ionic strength used in this model would be negligible in the calculation of activity coefficients.

Table 3

Ion Size Parameters Used in This Study
for the Various Charged Ions and Complexes

Ion	a° ($\times 10^{-8}$)	Ion	a° ($\times 10^{-8}$)
CO_3^-	5.0	MgOH^+	4.0
HCO_3^-	4.0	MgHCO_3^+	4.0
Cl^-	3.0	MgCl^+	4.0
SO_4^-	4.0	CaOH^+	4.0
MoO_4^-	5.0	CaHCO_3^+	4.0
Na^+	4.0	MnOH^+	4.0
K^+	3.0	Mn(OH)_3^-	4.0
Ca^{++}	6.0	MnHCO_3^+	4.0
Mg^{++}	8.0	MnCl^+	4.0
Fe^{++}	6.0	MnCl_3^-	4.0
Fe^{+3}	9.0	MnCl^{++}	5.0
Mn^{++}	6.0	MnO_4^-	5.0
Mn^{+3}	9.0	MnO_4^-	3.0
Al^{+3}	9.0	FeOH^+	4.0
Cu^+	3.0	Fe(OH)_3^-	3.0
Cu^{++}	6.0	FeOH^{++}	4.0
Ni^{++}	6.0	Fe(OH)_2^+	4.0
Sn^{++}	6.0	$\text{Fe}_2(\text{OH})_2^{+4}$	5.0
Sn^{+4}	11.0	FeSO_4^+	4.0
NaCO_3^-	4.0	$\text{Fe(SO}_4)_2^-$	3.0
KSO_4^-	4.0	FeCl^+	4.0
HSO_4^-	4.0	FeCl^{++}	5.0

Ion	$a^{\circ} (x10^{-8})$
$FeCl_2^+$	3.0
$FeCl_4^-$	4.0
$NiOH^+$	4.0
$Ni(OH)_3^-$	3.0
$NiCl^+$	4.0
$CuOH^+$	4.0
$Cu(OH)_4^=$	4.0
$Cu(OH)_3^-$	3.0
$CuCl_2^-$	4.0
$CuCl_3^=$	5.0
$CuCl^+$	4.0
$CuCl_3^-$	3.0
$CuCl_4^=$	4.0
Cu_2Cl^{+3}	4.0
$AlOH^{++}$	5.0
$Al(OH)_2^+$	3.0
$Al(OH)_4^-$	3.0
$Al_2(OH)_2^{+4}$	5.0
$AlSO_4^+$	4.0
$Al(SO_4)_2^-$	3.0
$SnOH^+$	4.0
$Sn(OH)_3^-$	3.0
$Sn_2(OH)_2^{+2}$	5.0

Ion	$a^{\circ} (x10^{-8})$
$Sn_3(OH)_4^{+2}$	4.0
$SnCl^+$	4.0
$SnCl_3^-$	3.0
$SnCl_4^=$	5.0
$SnCl_6^=$	4.0
$HMoO_4^-$	3.0
MoO_2^+	3.0
Mo^{+3}	9.0
$FeMoO_4^+$	3.0
$Fe(MoO_4)_3^{-3}$	4.0
$SiO(OH)_3^-$	3.0
$SiO_2(OH)_2^=$	4.0
$Si_4O_6(OH)^=$	4.0
$NaSO_4^-$	4.0
$CuO_2^=$	4.0
$HCuO_2^-$	3.0
$FeO_2^=$	4.0
$HFeO_2^-$	3.0
$Fe(OH)_4^=$	4.0
$SnO(OH)^+$	3.0
$SnSO_4^{++}$	5.0
AlO_2^-	4.0
ClO^-	3.0

For uncharged species, the activity coefficients were assigned values of unity. For non-symmetrical species the activity coefficients are greater than unity at high ionic strengths, because of dipole-dipole interaction. However, the departure of the activity coefficients from unity for the neutral species is not significant at low ionic strengths.

According to Garrels and Christ (1965, p.102):

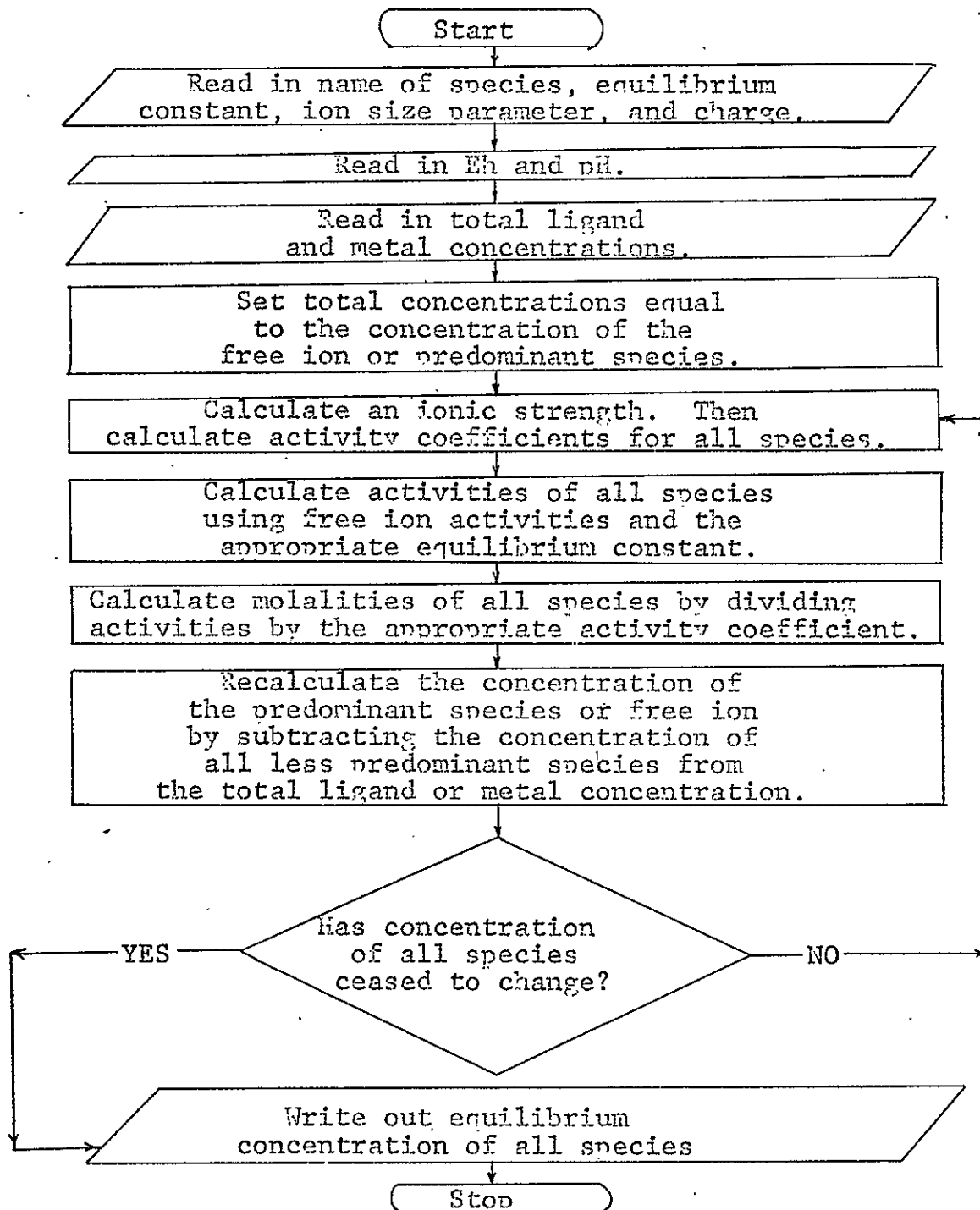
"Information on the activity coefficients of neutral ion pairs such as CaSO_4 , MgSO_4 , CaCO_3 , MgCO_3 , and NaHCO_3 is not available. It does not seem likely that these species will behave in aqueous electrolyte solution in the way that dissolved gases do, for example, so that no analogy readily presents itself. At present it seems best to assume activity coefficients of unity for these species."

After the activities of the free ions and predominant species are calculated, the activities of the various associated species are calculated using the appropriate equilibrium constants. The activities of the free metal ions of different oxidation states are calculated using equilibrium constants describing the reduction of the oxidized metal ion with a single electron to the reduced oxidation state. The electron activity used in the mass action equation is obtained (Sillen, op cit) by dividing the electrode potential (Eh) by -0.059 (valid only for 25° C) to obtain the negative base ten logarithm of the electron activity (pE), which is analogous to the hydrogen ion or proton activity (pH). The molalities are then calculated by dividing the activities by the activity coefficients of the different species. After making the initial calculation

of the concentrations of all species, a new estimate of the predominant species concentration is made by subtracting the concentration of all other species of that particular metal or ligand from the total analytical concentration of that metal or ligand. The iteration sequence then begins again by calculating a new ionic strength and new activity coefficients. The equilibrium calculation generally requires about thirty to forty iteration cycles before the concentration of the various species ceases to change from the previous step, and the true equilibrium concentrations are represented.

Figure 2

Flow Chart of Computer Program to
Calculate Equilibrium Distributions
(Stumm and Morgan, 1970)



III. RESULTS

The chemical analyses for samples are shown in Tables 4 and 5, which list concentration averages of the five samples that were collected every three hours at sample points A and B respectively. The values appearing just under the concentration values are the values of standard deviation of the five sample concentrations averaged. The values shown in the average column are the twenty-four hour concentration values; again, with the standard deviation shown just below the concentration value.

An illustration of the differences in the twenty-four hour concentration averages between the two sample locations is shown in Table 6. The twenty-four hour concentration averages were used as the total analytical concentrations of metals and ligands used in the equilibrium calculations.

The distributed or equilibrium concentrations for metals from sample site A are shown in Table 7. Those for sample site B are shown in Table 8. Samples taken during the 5 P.M. sampling sequence, below the tailings pond, have anomalously high Fe and Cu concentrations. A statistical t-test (Volk, 1958) was performed on this data, and indicates that the 5 P.M. concentrations of these two metals is significantly higher (ie. not of the same population at the 90% confidence level) concentration than the concentration values for these metals obtained during the other sampling sequences at sample site B. These high Fe and Cu concentrations were not included in the twenty-four hour concentration values or the B-series

distribution. Instead, the metal and ligand concentrations for the 5 P.M. sequence, below the tailings pond, were treated seperately, and the equilibrium distribution for the 5 P.M. sequence is shown in Table 9.

Table 4

Lateral Concentration Averages (ppm.) of the Five Samples Collected Every Three Hours for 24 Hours At Sample Site A, and Their Standard Deviation Shown Just Below the Concentration Values

	8AM	11AM	2PM	5PM	8PM	11PM	2AM	5AM	avg.
HCO ₃	67. 4.	73. 0.	73. 0.	71. 4.	76. 2.	75. 2.	67. 2.	66. 2.	71. 4.
SO ₄	31. 2.	29. 4.	37. 4.	37. 2.	37. 3.	36. 2.	37. 1.	37. 1.	35. 3.
Cl	1.6 .1	1.7 .0	2.0 .1	2.3 .3	2.4 .2	2.4 .1	2.1 .1	1.9 .1	2.0 .3
Na	2.8 .1	2.7 .2	2.8 .2	2.9 .0	2.9 .0	3.0 .2	2.9 .0	2.9 .0	2.9 .1
K	.33 .10	.29 .02	.32 .04	.38 .07	.42 .01	.44 .02	.48 .04	.44 .02	.39 .07
Ca	26. 1.	27. 1.	27. 1.	28. 1.	28. 1.	28. 0.	28. 0.	28. 0.	27. 1.
Mg	4.4 .2	4.4 .2	4.5 .1	4.8 .1	4.6 .9	4.9 .8	4.2 .8	5.0 .3	4.6 .3
Fe	.29 .05	.39 .02	.44 .08	.51 .04	.55 .05	.55 .06	.42 .03	.43 .02	.45 .09
Mn	.079 .008	.087 .011	.082 .002	.088 .003	.093 .006	.095 .006	.094 .006	.094 .002	.089 .006
Al	.144 .023	.135 .010	.150 .014	.152 .010	.167 .012	.154 .006	.167 .007	.141 .004	.148 .010
Cu	.005 .002	.005 .003	.005 .002	.003 .000	.003 .001	.004 .002	.003 .001	.002 .001	.004 .001
Ni	.008 .001	.009 .002	.009 .001	.011 .003	.008 .001	.009 .001	.008 .002	.008 .001	.009 .001
Sn	.030 .003	.028 .005	.026 .002	.026 .006	.019 .009	.014 .009	.019 .005	.016 .006	.022 .006
Mo	.011 -	⁻¹ -	⁻¹ -	⁻¹ -	⁻¹ -	⁻¹ -	.011 -	.012 -	.007 .003
SiO ₂	8.7 .5	7.0 .1	8.0 .5	8.3 .2	8.3 .2	7.8 -	7.8 -	7.3 -	7.9 .5

¹Below detection limits of 0.005 ppm.

Table 5

Lateral Concentration Averages (ppm.) of the Five Samples Collected Every Three Hours for 24 Hours At Sample Site B, and Their Standard Deviation Shown Just Below the Concentration Value

	8AM	11AM	2PM	5PM	8PM	11PM	2AM	5AM	avg.
HCO ₃	93. 2.	90. 0.	92. 2.	91. 2.	93. 2.	100. 2.	98. 2.	98. 0.	98. 4.
SO ₄	165. 4.	152. 3.	139. 1.	127. 2.	115. 3.	109. 2.	107. 1.	101. 1.	127. 23.
Cl	2.2 .0	2.2 .0	2.5 .2	2.5 .1	2.9 .1	3.3 .4	2.8 .1	2.6 .2	2.6 .4
Na	12.5 .5	10.9 .4	11.5 1.1	11.7 .3	12.0 .3	11.0 .4	10.1 .5	9.9 .6	11.2 .8
K	3.2 .1	2.8 .1	2.5 .2	3.1 .0	2.4 .8	1.7 .1	1.6 .1	1.6 .0	2.3 .6
Ca	75. 1.	70. 1.	64. 1.	60. 1.	57. 1.	54. 1.	57. 1.	58. 1.	60. 9.
Mg	7.8 1.1	7.7 .2	8.6 1.5	6.5 .7	6.7 1.0	6.6 .7	6.3 .2	6.6 1.7	7.0 .8
Fe	.30 .06	.25 .07	.22 .03	1.38 1.41	.24 .03	.27 .03	.30 .03	.31 .04	.27 ¹ .03
Mn	.111 .011	.085 .018	.078 .013	.084 .008	.085 .010	.069 .006	.080 .005	.074 .007	.083 .012
Al	.052 .003	.062 .010	.082 .019	.079 .010	.088 .011	.088 .003	.080 .007	.084 .005	.077 .013
Cu	.002 .001	.002 .001	.005 .002	.318 .233	.003 .001	.001 .000	.001 .001	.001 .001	.002 ¹ .002
Ni	.029 .002	.024 .001	.024 .001	.022 .002	.026 .004	.023 .001	.024 .005	.021 .003	.024 .003
Sn	.047 .006	.040 .003	.042 .010	.033 .005	.034 .003	.025 .003	.020 .003	.020 .004	.033 .010
Mo	.155 -	.164 -	.130 -	.128 .018	.100 -	.100 -	.103 -	.115 -	.124 .024
SiO ₂	8.5 -	10.9 -	8.7 -	11.4 0.7	11.1 -	9.6 -	10.7 -	8.7 -	9.9 1.2

¹does not include 5PM value

Table 6

24 Hour Concentration Averages of Metals (in ppm. with Standard Deviations Below) from the Two Sampling Points

Metal	Above Mill	Below Tailings Pond
Na	2.9 .1	11.2 .8
K	.39 .07	2.3 .6
Ca	27. 1.	60. 9.
Mg	4.6 .3	7.0 .8
Fe	.45 .09	.27 ¹ .03
Mn	.089 .006	.083 .012
Al	.148 .010	.077 .013
Cu	.004 .001	.002 ¹ .002
Ni	.009 .001	.024 .003
Sn	.022 .006	.033 .010
Mo	.007 .003	.124 .024
SiO ₂	7.9 0.5	9.9 1.2
pH	7.62 .09	7.92 .16
Eh (volts)	.405 .043	.385 .032
temp. (C)	11.5 3.0	12.4 3.8

¹does not include 5 P.M. value

Table 7

Equilibrium Distribution of Aqueous Species

From Samples Collected At Sample Site A

All Values as negative base ten logarithms of molality
(concentration(moles/liter) = $10^{-\text{table value}}$). Numbers in
the metal-ligand matrix indicate the concentration of all
metal-ligand complexes for that ligand.

Metal		Ligand						Free Metal
		OH ⁻	CO ₃ ⁼	HCO ₃ ⁻	SO ₄ ⁼	Cl ⁻	MoO ₄ ⁼	
	Total	6.38	5.50	2.93	3.44	4.23	7.36	
Na	3.97	11.09	8.33	7.28	6.89	-	-	3.97
K	5.00	-	-	-	7.62	-	-	5.00
Ca	3.17	8.63	5.79	4.97	4.65	11.67	14.24	3.19
Mg	3.72	7.62	6.13	5.62	5.29	6.41	-	3.74
Fe II	5.09	5.09	-	-	32.84	-	-	31.38
Fe III	24.69	24.69	-	-	37.24	40.28	-	37.36
Mn II	5.78	5.78	-	37.62	37.80	40.71	-	36.34
Al III	5.26	5.26	-	-	13.05	24.87	-	12.87
Cu I	14.23	-	-	-	-	17.27	-	14.23
Cu II	7.20	7.75	7.46	-	9.33	12.29	-	7.97
Ni II	6.81	6.93	-	-	8.90	16.55	-	7.44
Sn II	30.02	30.02	-	-	-	41.29	-	38.42
Sn IV	6.73	6.73	-	-	36.11	47.00	-	29.53
SiO ₂	3.76	-	-	-	-	-	-	3.76
Free Ligand		6.38	5.51	2.94	3.47	4.23	7.36	
LH		-	-	4.20	9.30	12.94	9.09	

Table 8

Equilibrium Distribution of Aqueous Species

From Samples Collected At Sample Site B

All values as negative base ten logarithms of molality (concentration(moles/liter) = $10^{-\text{table value}}$). Numbers in the metal-ligand matrix indicate the concentration of all metal-ligand complexes for that ligand.

Metal		Ligand						Free Metal
	Total	OH ⁻	CO ₃ ⁼	HCO ₃ ⁻	SO ₄ ⁼	Cl ⁻	MoO ₄ ⁼	
Na	3.38	10.21	7.34	6.61	5.82	-	-	3.38
K	4.23	-	-	-	6.37	-	-	4.23
Ca	2.82	7.79	5.12	4.59	3.90	11.25	12.90	2.87
Mg	3.54	7.19	5.62	5.39	4.70	6.21	-	3.53
Fe II	5.27	5.27	-	-	33.79	-	-	32.76
Fe III	25.69	25.69	-	-	38.52	41.92	-	39.03
Mn II	5.84	5.84	-	38.47	38.28	41.59	-	37.25
Al III	5.54	5.54	-	-	13.99	26.07	-	13.07
Cu I	14.52	-	-	-	-	17.40	-	14.52
Cu II	7.50	8.07	7.70	-	9.48	12.84	-	8.55
Ni II	6.47	6.51	-	-	8.58	16.57	-	7.55
Sn II	29.52	29.52	-	-	-	41.30	-	38.47
Sn IV	6.60	6.60	-	-	36.35	47.48	-	30.14
SiO ₂	3.66	-	-	-	-	-	-	3.66
Free Ligand		6.08	5.05	2.82	2.93	4.14	6.24	
LH		-	-	4.93	9.11	13.16	8.30	

Table 9

Equilibrium Distribution of Aqueous Species
 From Samples Collected At 5 P.M. At Sample Site B
 All values as negative base ten logarithms of molality
 (concentration(moles/liter) = $10^{-\text{table value}}$). Numbers in
 the metal-ligand matrix indicate the concentration of all
 metal-ligand complexes for that ligand.

Metal		Ligand						Free Metal
	Total	OH ⁻	CO ₃ ⁼	HCO ₃ ⁻	SO ₄ ⁼	Cl ⁻	MoO ₄ ⁼	
	Total	5.92	4.89	2.81	2.88	4.15	6.10	
Na	3.36	10.04	7.17	6.60	5.80	-	-	3.36
K	4.23	-	-	-	6.37	-	-	4.23
Ca	2.82	7.63	4.97	4.60	3.90	11.28	12.77	2.87
Mg	3.57	7.07	5.51	5.44	4.74	6.26	-	3.62
Fe II	4.61	4.61	-	-	33.77	-	-	32.74
Fe III	25.36	25.36	-	-	38.51	41.93	-	39.03
Mn II	5.78	5.78	-	38.91	38.71	42.03	-	37.68
Al III	5.48	5.48	-	-	14.55	26.69	-	14.26
Cu I	12.44	-	-	-	-	15.35	-	12.44
Cu II	5.30	5.85	5.49	-	7.42	10.79	-	6.49
Ni II	6.47	6.49	-	-	8.88	16.84	-	7.85
Sn II	29.65	29.65	-	-	-	41.76	-	38.91
Sn IV	6.60	6.60	-	-	36.82	48.02	-	30.62
SiO ₂	3.67	-	-	-	-	-	-	3.67
Free Ligand		5.92	4.91	2.83	2.93	4.15	6.10	
LH		-	-	4.57	9.26	13.34	8.33	

IV. DISCUSSION

A. Analytical Work

Because the study was conducted in the vicinity of a molybdenum mine, the molybdenum concentrations in the Red River were of great interest. As noted on Table 2, molybdenum was not determined by atomic absorption spectroscopy. Analytical techniques for determining molybdenum by A.A. methods indicate that molybdenum is subject to chemical and ionization interferences by a variety of other metals (Ramakrishna, 1969). Furthermore, the detection of molybdenum utilizing the graphite furnace is hampered by the fact that molybdenum forms refractory carbides in the graphite tube, with the result that concentrations are not reproducible (Meglin, 1973). For these reasons, a colorimetric procedure was utilized for the determination of molybdenum that, while slower and more tedious than A.A. techniques, gave reproducible results with good sensitivity.

Originally, it was intended to determine zinc concentrations in the samples; however, two problems were encountered. First, the detection limit for zinc by conventional flame spectroscopy is approximately 0.1 ppm., and all samples contained zinc concentrations at appreciably lower concentrations, which necessitated determination in the graphite furnace. A second problem was encountered when trying to prepare a standard curve for zinc in the graphite furnace. Because of the extreme sensitivity of zinc in the graphite furnace, standards had to be prepared in the concentration range below parts per billion.

The doubly distilled and deionized water that was used for standard preparation had zinc concentrations that were higher than those required for the standards. For these reasons, the determination of zinc was abandoned for this study.

B. Analysis of Error

As can be seen from Tables 4 and 5, the majority of chemical components showed very little deviation at intermediate times over the twenty-four hour period from the twenty-four hour concentration averages. For the metals determined spectrophotometrically, a comparison of the standard deviation of the five sample concentrations that were averaged to the standard error of the estimate reveals that either there is significant variation among the five samples, or that the variation is due only to experimental error. For those standard deviation values which are greater than the standard error of the estimate, some variance other than experimental is responsible for the within-sample variance. Examining the reported standard deviations in Tables 4 and 5, one may determine whether or not there is significant variation of the eight individual concentrations of an element from the reported twenty-four hour concentration average. If the standard deviation of the twenty-four hour concentration average is less than or equal to the standard deviations of the eight values of standard deviation shown to the left, then there is no significant difference between the twenty-four hour concentration average and the concentration values shown to the left. For example, from Appendix B, the

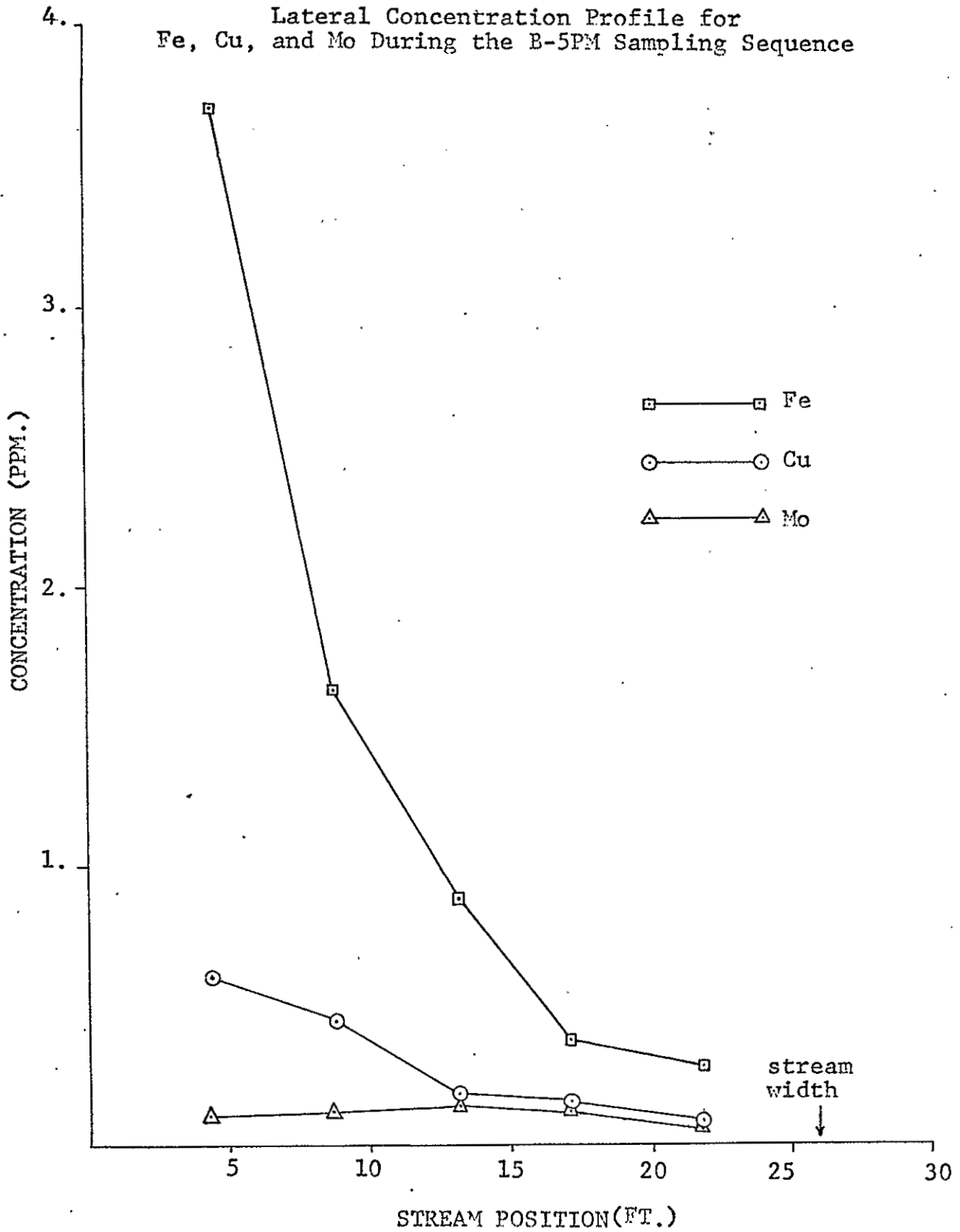
standard error of the estimate for nickel analyses for the sample numbers A-8AM through A-5PM is $\pm 2.7 \times 10^{-3}$ ppm. The standard deviation for the eight-three hour concentration averages are all less than or equal to the standard error of the estimate. Therefore, there is no significant variation within the five sample concentrations that were averaged to obtain the three hour average, (i.e. there is more variance in analyses than can be attributed to natural variance within the five sample concentrations). Now, comparing the standard deviation of the twenty-four hour concentration average to the standard deviations of the eight-three hour concentration averages, it can be seen that the deviation from the twenty-four hour average is less than or equal to the standard deviations of the three hour averages. Therefore, there is no significant difference between the twenty-four hour concentration average to the three hour averages shown to the left, (i.e. the within-sample variance is just as significant as the among-sample variance).

C. Anomalous Fe and Cu Concentrations

The samples that were collected below the tailings pond during the 5 P.M. sampling sequence show anomalously high concentrations of Fe and Cu. Both of these metals show similar lateral concentration profiles within the stream, as can be seen in Figure 3. When these anomalously high concentrations were first noted it was thought that some type of overflow or discharge had occurred in the tailings pond upstream, which

Figure 3.

Lateral Concentration Profile for
Fe, Cu, and Mo During the B-5PM Sampling Sequence



may possibly be indicated by anomalously high Mo concentrations in the same sample sequence. However, as can be seen from Figure 3, there is no concomitant increase in Mo concentrations in the same sequence, and the data is insufficient to speculate on the source of the anomalously high Fe and Cu concentrations.

D. Trace Metal Concentrations

As can be seen from Table 6, the concentrations of Na, K, Ca, Mg, Sn and Mo were significantly higher at the sample location below the tailings pond than the location upstream. The increased levels of Na, K and Ca may possibly be attributed to the milling operations of Molybdenum Corporation of America, because use of lime (Fuersteneau, 1962) and Nokes¹ reagent (Sutulov, 1974) in the floatation of molybdenum ore is commonly practiced. The increased pH levels resulting from the addition of lime may also be responsible for the decreased concentrations of Fe and Al at the sampling location below the tailings pond as a result of the precipitation of Fe and Al hydroxides. Dilution by tributary or groundwater discharge may also be responsible for the decreased levels of Fe and Al.

Other possibilities for the increased concentrations of the above mentioned metals may be one or a combination of the following: (1) weathering of minerals associated with the

¹Reagent obtained by the reaction of potassium pentasulfide with sodium hydroxide, and used for the depression of copper and iron sulfides in molybdenite floatation.

geology of the Red River drainage area, (2) leaching of waste materials associated with the mining activities in the Red River drainage area, (3) discharge from MCA's tailings pond, and (4) discharge from domestic activities in the Red River drainage area.

E. Other Work in the Red River Area

The metals investigated and analysed in this study were selected on the basis of a report compiled by the Environmental Protection Agency (Kerr, 1971). In this particular report, the analyses of metal concentrations in the water being discharged by the MCA tailings pond for various metals are listed. The metals Fe, Mn, Sn, Ni, Mo, and Cu were highest in concentration in the decant water, according to the above mentioned report.

This same report also lists the results of analyses for Cl, SO₄, Ca, and Mg in various locations on the Red River. Shown in Figure 4 are the comparisons of the twenty-four hour concentration averages and standard deviations found in this study to the results of the E.P.A.'s analyses for the above mentioned components in the two locations that were closest to sample sites A and B. The results of the E.P.A.'s analyses show good agreement with the results of this study. The concentration of Ca and SO₄ below the tailings pond is significantly higher than the Ca and SO₄ concentrations reported by the E.P.A. This may be the result of the fact that the E.P.A. sampling station number 3 is located upstream from the point where the MCA tailings pond discharges into

Figure 4.

Comparison of Concentrations Reported by Environmental Protection Agency to Those Values Determined in this Study (Kerr, 1971)

Chemical component	Sample site A	Station 7 (E.P.A.)	Sample site B	Station 3 (E.P.A.)
Cl	2.0 ¹	0.4 ²	2.6	1.5
	0.3	0.5	0.4	2.0
SO ₄	35.	41.	127.	69.
	3.	3.	23.	9.
Ca	27.	34.	60.	36.
	1.	1.	9.	2.
Mg	4.6	5.1	7.0	7.1
	.3	.9	.8	1.4

¹all concentrations reported as ppm.

²E.P.A. concentrations are six day averages of samples collected 11/70

the Red River, or because of different sampling times of this study and the E.P.A.'s study.

F. Equilibrium Distribution

The distributed species concentrations for sample site A are shown in Table 7, for sample site B in Table 8, and for the B-5PM sequence in Table 9. Because the molalities are expressed as negative base ten logarithms, the smallest or least negative value represents the predominant species of a particular metal or ligand.

All three distributions (A-series, B-series and B-5PM sequence) have the same predominant species, differing only in the concentration of the predominant species. The classification of predominant species falls into ^{two} categories for the metals. For the major cations, Na, K, Ca and Mg the free ion is the predominant form. For the metals Fe, Mn, Cu, Ni, Sn and Al the hydroxide complex is the predominant species. There is no distinction made in Tables 7, 8 and 9 as to how many OH⁻ radicals are present on the predominant species, only that the hydroxide form is stable.

For the ligand components CO₃, HCO₃, SO₄, Cl and MoO₄ the uncomplexed ion is the predominant form. With the exception of the carbonate ion, all protonated ligand components are of lower concentration than the unprotonated forms.

G. Comparison of Equilibrium Concentrations to Toxicity Data

As mentioned above, Table 1 is a compilation of toxic

limits for a variety of metal compounds. It is difficult to speculate on the stable metal species of the various metals used in the toxicity tests without more specific information on the chemical characteristics (pH, alkalinity etc.) of the water used in the toxicity tests. However, Figure 2 does serve as a good index of the toxic limits of the various metals studied in this thesis work.

A comparison of Tables 7, 8 and 9 to Table 1 indicates that the concentration of stable metal species at the two sampling points do not exceed the toxic limits for these metals. At sample site B, however, the concentration of calcium does exceed the recommended limit for domestic use.

V. CONCLUSIONS

A. Trace Metal Concentrations

The increased concentrations of Na, K and Ca in the samples collected downstream from the point where Molybdenum Corporation of America discharges water from their tailings pond, compared to samples collected upstream from their mill, may be the result of the addition of Nokes reagent and lime for the floatation of molybdenum ore. The addition of lime to the process or waste waters may cause precipitation of the metals Fe and Al as insoluble hydroxides. This may account for the fact that Fe and Al concentrations were lower at the sampling location below the tailings pond, compared to the sampling location upstream.

The metals Mg, Sn, Ni and Mo showed higher concentrations in samples collected below the tailings pond, compared to those collected upstream. The increased concentrations may be the result of one or a combination of the following: (1) weathering of minerals associated with the natural geology of the Red River drainage area, (2) leaching of waste materials and tailings associated with the mining activity in the Red River drainage area, (3) discharge from MCA's tailings pond and (4) discharge associated with domestic activities in the Red River drainage area.

B. Equilibrium Concentration of Aqueous Metal Species

Although there were higher total concentrations of some

metal and ligand components in samples collected downstream from the tailings pond, compared with concentrations in samples collected upstream, at both locations the predominant aqueous metal species were the same. For the metals Na, K, Ca and Mg the unassociated free ion is the predominant aqueous species. For the metals Fe, Mn, Al, Cu, Ni and Sn the hydroxide aqueous species is the predominant form. With the exception of the carbonate ion, for all ligand components the unprotonated ion is the predominant form.

Calcium was the only cation that had significant sulfate complexing. Divalent metal-sulfate ion pairs have approximately the same equilibrium constants; therefore, had other divalent metal cations been on the order of the concentration of calcium their equilibrium concentrations of sulfate-metal ion pairs would have been higher.

Because of the somewhat alkaline conditions of the Red River, the hydroxide forms of Fe, Mn, Al, Cu, Ni and Sn were the predominant aqueous species for those metals. Had lower pH values been encountered, the metal hydroxides would have been of lower concentration with consequent increases in free ion concentration.

Although the concentration of calcium exceeds the proposed limit of concentration for domestic use at the sample location below the tailings pond, it does not exceed toxic levels. The concentration of the other predominant aqueous metal species Na^+ , K^+ , Mg^{++} , $\text{Fe}(\text{OH})_x^{2-x}$, $\text{Al}(\text{OH})_x^{3-x}$, $\text{Mn}(\text{OH})_x^{2-x}$, $\text{Cu}(\text{OH})_x^{2-x}$, $\text{Ni}(\text{OH})_x^{2-x}$ and $\text{Sn}(\text{OH})_x^{4-x}$, where x is an integer > 0

do not exceed the toxic levels for these metals in samples collected in this study.

C. Sampling Considerations

Noting the concentration fluctuations at both sampling locations, it is apparent that there is more significant variation in concentration levels between sampling locations than there is at one location over a twenty-four hour interval. Although this conclusion may be disputed because of the anomalous Fe and Al concentrations found in some samples collected below the tailings pond, it would be advantageous, while planning a sampling program, to collect fewer samples at a single location and collect more samples along the length of a stream or river to be sampled. This fact becomes apparent when one considers the fact that locating contaminant sources and sinks would be easier if samples were collected over the entire reach of a stream over a shorter time interval, rather than collecting samples at two widely separated locations. This conclusion is contingent upon the fact that it be shown that there is insignificant variation in concentration at a single location over the entire sampling time interval. This may be accomplished by continuously sampling one location, while having samples collected elsewhere on the stream at the same time. It is possible that concentrations could vary significantly at a single location, as it did in this study, because of such things as storm runoff and/or sudden or accidental discharges from point sources on the river or stream.

D. Utility of This Study

As mentioned previously, the extremely varied reports concerning the toxicities of various metals to aquatic, livestock, and human populations make it difficult to establish realistic or justifiable water quality standards in terms of trace metal concentrations. However, if more effort is made by toxicologists to define the specific chemical parameters (hydrogen ion activity, electron activity, and total cationic and anionic concentrations) under which the toxicity tests are conducted, then it might be possible to describe accurately and quickly the stable aqueous metal that is causing the apparent toxic effect.

In addition to the above mentioned application, environmentalists, State and Federal agencies, and concerned individuals and communities which are responsible for establishing environmental impact statements or baseline studies on aquatic systems will find the description of stable aqueous metal species advantageous. Once the existing or baseline conditions are established, in terms of stable aqueous metal species, one may predict accurately what effect new or added sources of chemical inputs will have on the aquatic system being studied.

REFERENCES

- Butler, J.N., Ionic Equilibria-A Mathematical Approach, Addison Wesley Publishing Company: Reading, Massachuttes, 1964, p. 434.
- Fischer, R.B. and D.G. Peters, Quantitative Chemical Analysis, W.B. Saunders Company: Philadelphia, 1968, pp. 624-25.
- Fuersteneau, D.W., Froth Floatation, A.I.M.E.: New York, 1962, p. 395.
- Garrels, R.M. and C.L. Christ, Solutions, Minerals and Equilibria, Harper and Row: New York, 1965, p. 102.
- Kerr, R.S., Water Quality Survey of the Red River of the Rio Grande, New Mexico, Environmental Protection Agency Water Research Center: Ada, Oklahoma, 1972.
- McKee, J.E. and H.W. Wolf, Water Quality Criteria, Publication Number 3-A, California State Water Resources Control Board, 1971.
- Meglin, R.R. and M.L. Glaze, Analytical Methods, The Molybdenum Project- University of Colorado: Boulder, Colorado, 1973.

Parker, V.B., et al, Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards Technical Note 270-4, Washington, D.C., 1971.

Ramakrishna, T.V., "The Determination of Molybdenum by Atomic Absorption," Analyt. Chem. Acta., (48), 1969, pp. 437-39.

Sillen, L.G. and Martell, A.E., Stability Constants of Metal-Ion Complexes, Special Publication Number 17, The Chemical Society: London, 1964.

Stumm, W. and J.J. Morgan, Aquatic Chemistry-An Introduction Emphasizing Chemical Equilibria in Natural Waters, Wiley Interscience: New York, 1970.

Sutulov, A., Copper Porphyries, University of Utah Printing: Salt Lake City, 1974, p. 149.

Perkin Elmer Corporation, Analytical Methods for Atomic Absorption Spectroscopy Using the Graphite Furnace, 1973.

Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Analytical Quality Control Laboratory: Cincinnati, Ohio, 1971.

APPENDIX A

Instrumental Parameters for Atomic Absorption
Spectrophotometer (Flame) and
Standard Curve Equations

Element: Na

Wavelength: 589. nm.

Slit band width: 1.4 nm.

Flame: air-acetylene (oxidizing)

Standard Curve	r^2	s^3	Sample numbers
$y = 9.56x - 0.29^1$	0.988	0.175	A-8AM - A-2PM
$y = 9.59x - 0.32$	0.988	0.126	A-5PM - A-11PM
$y = 9.35x - 0.33$	0.991	0.111	A-2AM - A-5AM
$y = 8.56x - 0.45$	0.988	0.177	B-8AM - B-2PM
$y = 9.74x - 0.49$	0.993	0.135	B-5PM - B-11PM
$y = 8.89x - 0.52$	0.988	0.177	B-2AM - B-5AM

Element: K

Wavelength: 766.5 nm.

Slit band width: 2.0 nm.

Flame: air-acetylene (oxidizing)

Standard Curve	r	s	Sample numbers
$y = 25.59x - 0.27$	0.995	0.166	A-8AM - A-2PM
$y = 24.40x - 0.24$	0.995	0.173	A-5PM - A-11PM

¹Where: y = concentration in ppm. and x = absorbance²multiple correlation coefficient³standard error of the estimate

$y = 24.47x - 0.28$	0.994	0.195	A-2AM - B-8AM
$y = 25.19x - 0.47$	0.996	0.161	B-11AM - B-2PM
$y = 26.68x - 0.36$	0.995	0.180	B-5PM - B-5AM

Element: Mg

Wavelength: 285.2 nm.

Slit band width: 0.7 nm.

Flame: air-acetylene (oxidizing)

Standard Curve	r	s	Sample numbers
$y = 4.87x - 0.07$	0.999	0.039	A-8AM - A-2PM
$y = 5.68x - 0.13$	0.998	0.076	A-5PM - A-11PM
$y = 5.16x - 0.12$	0.999	0.059	A-2AM - B-8AM
$y = 5.62x - 0.20$	0.999	0.059	B-11AM - B-5PM
$y = 7.94x - 0.17$	0.996	0.098	B-8PM - B-5AM

(standard curves for residue samples not included)

Element: Fe (residue samples)

Wavelength: 248.3 nm.

Slit band width: 0.2 nm.

Flame: air acetylene (oxidizing)

Standard Curve	r	s	Sample numbers
$y = 72.1x - 1.2$	0.996	0.60	A-8AM - A-11PM
$y = 61.8x - 1.2$	0.998	0.36	A-2AM - B-5PM
$y = 63.6x - 0.7$	0.998	0.42	B-8PM - B-5AM

APPENDIX B

Instrumental Parameters for Atomic Absorption
Spectrophotometer (Graphite Furnace)
and Standard Curve Equations

Element: Fe (filtered samples)

Wavelength: 248.3 nm.

Slit band width: 0.2 nm.

Atomizing temp.: 2500 C

Standard Curve ¹	r ²	s ³	Sample numbers
$Y = 7.3 \times 10^{-4}X - 3.1 \times 10^{-3}$	0.998	7.8×10^{-4}	A-8AM - A-11PM
$Y = 7.4 \times 10^{-4}X - 1.3 \times 10^{-3}$	0.993	1.5×10^{-3}	A-2AM - B-5PM
$Y = 6.7 \times 10^{-4}X - 1.6 \times 10^{-3}$	0.986	1.8×10^{-3}	B-8PM - B-5AM

Element: Mn (filtered samples)

Wavelength: 279.5 nm.

Slit band width: 0.2 nm.

Atomizing temp.: 2400 C

Standard Curve	r	s	Sample numbers
$Y = 1.2 \times 10^{-4}X - 5.2 \times 10^{-4}$	0.998	2.4×10^{-4}	A-8AM - A-5PM
$Y = 1.2 \times 10^{-4}X - 4.2 \times 10^{-4}$	0.998	2.5×10^{-4}	A-8PM - A-5AM
$Y = 1.3 \times 10^{-4}X - 4.2 \times 10^{-4}$	0.997	2.9×10^{-4}	B-8AM - B-8PM
$Y = 1.2 \times 10^{-4}X - 5.8 \times 10^{-4}$	0.997	3.1×10^{-4}	B-11PM - B-5AM

(residue samples not included)

¹Where: Y = concentration in ppm. and X = peak height

²multiple correlation coefficient

³standard error of the estimate

Element: Al (filtered samples)

Wavelength: 309.2 nm.

Slit band width: 0.7 nm.

Atomizing temp.: 2600° C

Standard Curve	r	s	Sample numbers
$Y = 3.5 \times 10^{-3}X - 1.7 \times 10^{-3}$	0.995	3.8×10^{-3}	A-8AM - A-11PM
$Y = 3.3 \times 10^{-3}X - 2.5 \times 10^{-3}$	0.998	4.3×10^{-3}	A-2AM - B-5PM
$Y = 3.0 \times 10^{-3}X - 3.1 \times 10^{-3}$	0.999	3.4×10^{-3}	B-8PM - B-5AM

(residue samples not included)

Element: Cu

Wavelength: 324.7 nm.

Slit band width: 0.7 nm.

Atomizing temp.: 2500° C

Standard Curve	r	s	Sample numbers
$Y = 3.3 \times 10^{-4}X - 7.7 \times 10^{-4}$	0.969	9.0×10^{-4}	A-8AM - A-5PM
$Y = 3.3 \times 10^{-4}X - 7.0 \times 10^{-4}$	0.974	8.2×10^{-4}	A-8PM - B-11AM
$Y = 2.9 \times 10^{-4}X - 3.2 \times 10^{-4}$	0.952	1.1×10^{-3}	B-2PM - B-5AM

(no Cu detected on residue samples)

Element: Ni (filtered samples)

Wavelength: 232.0 nm.

Slit band width: 0.2 nm.

Atomizing temp.: 2500° C

Standard Curve	r	s	Sample numbers
$Y = 9.1 \times 10^{-4}X + 6.3 \times 10^{-4}$	0.998	2.7×10^{-3}	A-8AM - A-5PM
$Y = 1.0 \times 10^{-3}X - 1.2 \times 10^{-3}$	0.997	3.1×10^{-3}	A-8PM - A-5AM
$Y = 9.0 \times 10^{-4}X + 3.1 \times 10^{-3}$	0.994	4.5×10^{-3}	B-8AM - B-5PM
$Y = 9.4 \times 10^{-4}X + 8.0 \times 10^{-4}$	0.999	1.6×10^{-3}	B-8PM - B-5AM

(residue samples not included)

Element: Sn

Wavelength: 286.3 nm.

Slit band width: 0.2 nm.

Atomizing temp.: 2500° C

Standard Curve	r	s	Sample numbers
$Y = 2.2 \times 10^{-3}X + 3.7 \times 10^{-3}$	0.999	1.0×10^{-3}	A-8AM - A-5PM
$Y = 3.0 \times 10^{-3}X - 1.2 \times 10^{-4}$	0.999	2.0×10^{-3}	A-8PM - A-5AM
$Y = 2.4 \times 10^{-3}X - 7.6 \times 10^{-4}$	0.998	2.2×10^{-3}	B-8AM - B-5PM
$Y = 2.4 \times 10^{-3}X - 7.9 \times 10^{-4}$	0.999	1.6×10^{-3}	B-8PM - B-5AM

(no Sn detected in residue samples)

APPENDIX C

Chemical Reactions and Their
Log K @ 25 C

(from Sillen, except where noted)

<u>Reaction</u>	<u>Log K @ 25 C</u>
$H^+ + OH^- \rightleftharpoons H_2O$	14.0
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$	10.3
$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$	6.4
$Na^+ + OH^- \rightleftharpoons NaOH$	-0.7
$Na^+ + HCO_3^- \rightleftharpoons NaHCO_3$	-0.3
$Na^+ + CO_3^{2-} \rightleftharpoons NaCO_3$	1.3
$Na^+ + SO_4^{2-} \rightleftharpoons NaSO_4$	0.7
$K^+ + SO_4^{2-} \rightleftharpoons KSO_4$	1.0
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	1.9
$2H^+ + SO_4^{2-} \rightleftharpoons H_2SO_4$	-8.3
$Mg^{++} + H_2O \rightleftharpoons MgOH^+ + H^+$	-11.4
$Mg^{++} + HCO_3^- \rightleftharpoons MgHCO_3^+$	1.2
$Mg^{++} + CO_3^{2-} \rightleftharpoons MgCO_3$	3.4
$Mg^{++} + SO_4^{2-} \rightleftharpoons MgSO_4$	2.2
$Mg^{++} + Cl^- \rightleftharpoons MgCl^+$	1.7
$Ca^{++} + H_2O \rightleftharpoons CaOH^+ + H^+$	-12.7
$Ca^{++} + HCO_3^- \rightleftharpoons CaHCO_3^+$	1.3
$Ca^{++} + CO_3^{2-} \rightleftharpoons CaCO_3$	3.2
$Ca^{++} + SO_4^{2-} \rightleftharpoons CaSO_4$	2.3
$Ca^{++} + MoO_4^{2-} \rightleftharpoons CaMoO_4$	-3.4
$Mn^{++} + H_2O \rightleftharpoons MnOH^+ + H^+$	-10.6

<u>Reaction</u>	<u>Log K @ 25 C</u>
$\text{Mn}^{++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Mn}(\text{OH})_3^- + 3\text{H}^+$	7.8
$\text{Mn}^{++} + \text{HCO}_3^- \rightleftharpoons \text{MnHCO}_3^+$	1.8
$\text{Mn}^{++} + \text{SO}_4^{=} \rightleftharpoons \text{MnSO}_4$	2.3
$\text{Mn}^{++} + \text{Cl}^- \rightleftharpoons \text{MnCl}^+$	0.0
$\text{Mn}^{++} + 3\text{Cl}^- \rightleftharpoons \text{MnCl}_3^-$	-0.4
$\text{Mn}^{+++} + e^- \rightleftharpoons \text{Mn}^{++}$	25.2
$\text{Mn}^{+++} + \text{Cl}^- \rightleftharpoons \text{MnCl}^{++}$	0.5
$\text{Mn}^{++} + 4\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^{=} + 8\text{H}^+ + 4e^-$	-117.3
$\text{Mn}^{++} + 4\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^- + 3\text{H}^+ + 5e^-$	-127.0
$\text{Fe}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^+ + \text{H}^+$	-8.3
$\text{Fe}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{H}^+$	-18.8
$\text{Fe}^{++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3^- + 3\text{H}^+$	-31.8 ¹
$\text{Fe}^{++} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_4^{=} + 4\text{H}^+$	-38.0 ¹
$\text{Fe}^{++} + \text{SO}_4^{=} \rightleftharpoons \text{FeSO}_4$	2.3
$\text{Fe}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{FeO}_2^{=} + 4\text{H}^+$	-4.2 ¹
$\text{Fe}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{HFeO}_2^- + 3\text{H}^+$	-31.8 ¹
$\text{Fe}^{+++} + e^- \rightleftharpoons \text{Fe}^{++}$	13.0
$\text{Fe}^{+++} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{++} + \text{H}^+$	-2.2
$\text{Fe}^{+++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})^+ + 2\text{H}^+$	-20.9
$\text{Fe}^{+++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{H}^+$	-9.9
$2\text{Fe}^{+++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{+4} + 2\text{H}^+$	-2.9
$\text{Fe}^{+++} + \text{SO}_4^{=} \rightleftharpoons \text{FeSO}_4^+$	4.0
$\text{Fe}^{+++} + 2\text{SO}_4^{=} \rightleftharpoons \text{Fe}(\text{SO}_4)_2^-$	5.3

¹derived from free energy of formation (Parker, et al, 1971)

<u>Reaction</u>	<u>Log K @ 25 C</u>
$\text{Fe}^{+++} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{++}$	1.5
$\text{Fe}^{+++} + 2\text{Cl}^- \rightleftharpoons \text{FeCl}_2^+$	2.2
$\text{Fe}^{+++} + 3\text{Cl}^- \rightleftharpoons \text{FeCl}_3$	1.2
$\text{Fe}^{+++} + 4\text{Cl}^- \rightleftharpoons \text{FeCl}_4^-$	-0.7
$\text{Fe}^{+++} + 4\text{Cl}^- + \text{H}^+ \rightleftharpoons \text{HFeCl}_4$	-2.7
$\text{Ni}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$	-10.6
$\text{Ni}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_2 + 2\text{H}^+$	-14.6
$\text{Ni}^{++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{OH})_3^- + 3\text{H}^+$	-32.8
$\text{Ni}^{++} + \text{SO}_4^{=} \rightleftharpoons \text{NiSO}_4$	2.3
$\text{Ni}^{++} + \text{Cl}^- \rightleftharpoons \text{NiCl}^+$	0.4
$\text{Cu}^{++} + e^- \rightleftharpoons \text{Cu}^+$	0.7
$\text{Cu}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-7.3
$\text{Cu}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2 + 2\text{H}^+$	-13.3
$\text{Cu}^{++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_3^- + 3\text{H}^+$	-26.8
$\text{Cu}^{++} + 4\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_4^{=} + 4\text{H}^+$	-39.8
$\text{Cu}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{CuO}_2^{=} + 4\text{H}^+$	-39.5 ¹
$\text{Cu}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{HCuO}_2^- + 3\text{H}^+$	-26.4 ¹
$\text{Cu}^{++} + \text{CO}_3^{=} \rightleftharpoons \text{CuCO}_3$	6.3
$\text{Cu}^{++} + \text{SO}_4^{=} \rightleftharpoons \text{CuSO}_4$	2.4
$\text{Cu}^{++} + \text{Cl}^- \rightleftharpoons \text{CuCl}^+$	0.05
$\text{Cu}^{++} + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_2$	-0.5
$\text{Cu}^{++} + 3\text{Cl}^- \rightleftharpoons \text{CuCl}_3^-$	-1.9
$\text{Cu}^{++} + 4\text{Cl}^- \rightleftharpoons \text{CuCl}_4^{=}$	-4.2
$2\text{Cu}^{++} + \text{Cl}^- \rightleftharpoons \text{Cu}_2\text{Cl}^{+++}$	-0.5

<u>Reaction</u>	<u>Log K @ 25 C</u>
$\text{Cu}^+ + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_2^-$	5.5
$\text{Cu}^+ + 3\text{Cl}^- \rightleftharpoons \text{CuCl}_3^-$	4.2
$\text{Al}^{+++} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{++} + \text{H}^+$	-4.8
$\text{Al}^{+++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	-8.6
$\text{Al}^{+++} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + 4\text{H}^+$	-27.7
$\text{Al}^{+++} + 2\text{H}_2\text{O} \rightleftharpoons \text{AlO}_2^- + 4\text{H}^+$	-23.2
$2\text{Al}^{+++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}_2(\text{OH})_2^{+4} + 2\text{H}^+$	-7.5
$\text{Al}^{+++} + \text{SO}_4^- \rightleftharpoons \text{AlSO}_4^+$	3.2
$\text{Al}^{+++} + 2\text{SO}_4^- \rightleftharpoons \text{Al}(\text{SO}_4)_2^-$	5.1
$2\text{Al}^{+++} + 3\text{SO}_4^- \rightleftharpoons \text{Al}_2(\text{SO}_4)_3$	2.8
$\text{Sn}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{SnOH}^+ + \text{H}^+$	-1.7
$\text{Sn}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Sn}(\text{OH})_2 + 2\text{H}^+$	-6.7
$\text{Sn}^{++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Sn}(\text{OH})_3^- + 3\text{H}^+$	-16.2
$2\text{Sn}^{++} + 2\text{H}_2\text{O} \rightleftharpoons \text{Sn}_2(\text{OH})_2^{++} + 4\text{H}^+$	-11.1
$\text{Sn}^{++} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+$	1.5
$\text{Sn}^{++} + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_2$	2.2
$\text{Sn}^{++} + 3\text{Cl}^- \rightleftharpoons \text{SnCl}_3^-$	2.0
$\text{Sn}^{++} + 4\text{Cl}^- \rightleftharpoons \text{SnCl}_4^-$	1.5
$\text{Sn}^{+4} + 2e^- \rightleftharpoons \text{Sn}^{++}$	5.2
$\text{Sn}^{+4} + 2\text{H}_2\text{O} \rightleftharpoons \text{SnO}(\text{OH})^+ + 3\text{H}^+$	0.4
$\text{Sn}^{+4} + 6\text{Cl}^- \rightleftharpoons \text{SnCl}_6^-$	0.8
$\text{Sn}^{+4} + \text{SO}_4^- \rightleftharpoons \text{SnSO}_4^{++}$	-2.6
$\text{H}^+ + \text{MoO}_4^- \rightleftharpoons \text{HMoO}_4^-$	6.0
$2\text{H}^+ + \text{MoO}_4^- \rightleftharpoons \text{H}_2\text{MoO}_4$	2.2

<u>Reaction</u>	<u>Log K @ 25 C</u>
$4\text{H}^+ + \text{MoO}_4^{=2} + \text{e}^- \rightleftharpoons \text{MoO}_2^+ + 2\text{H}_2\text{O}$	2.9
$4\text{H}^+ + \text{MoO}_4^{=2} + \text{Cl}^- + \text{e}^- \rightleftharpoons \text{MoOCl} + 2\text{H}_2\text{O}$	-0.4
$\text{Si}(\text{OH})_4 \rightleftharpoons \text{SiO}(\text{OH})_3^- + \text{H}^+$	-9.7
$\text{Si}(\text{OH})_4 \rightleftharpoons \text{SiO}_2(\text{OH})_2^{=2} + 2\text{H}^+$	-22.0
$4\text{Si}(\text{OH})_4 \rightleftharpoons \text{Si}_4\text{O}_6(\text{OH})_6 + 2\text{H}^+ + 4\text{H}_2\text{O}$	-12.6
$2\text{Cl}^- \rightleftharpoons \text{Cl}_2 + 2\text{e}^-$	-44.8
$\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{H}^+ + 2\text{e}^-$	-49.3
$\text{Cl}^- + \text{H}_2\text{O} \rightleftharpoons \text{ClO}^- + 2\text{H}^+ + 2\text{e}^-$	-57.6
$\text{H}^+ + \text{Cl}^- \rightleftharpoons \text{HCl}$	-1.05