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I hereby recommend that the thesis prepared under my supervision by Kenneth E. Paulsen

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be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Harry B. Mark

William R. Heineman

Darl H. McDaniel

Form 668—Grad. School—IM—12–69

CHARACTERIZATION OF GLASS IMMOBILIZED 8-HYDROXYQUINOLINE FOR *IN SITU* PRECONCENTRATION OF TRACE METALS FROM AQUEOUS MEDIA

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BY

Kenneth E. Paulsen

A.B. Hope College, 1970
M.S. University of Cincinnati, 1972

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DEDICATION

This dissertation is dedicated to my parents, whose continuing love, support, and encouragement are so helpful and appreciated.

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ABSTRACT

The use of controlled pore glass immobilized 8-hydroxyquinoline (CPG-8HOQ) for preconcentration of trace metals in aqueous media has been examined with in situ sampling as the objective. Quantities of the immobilized chelate were synthesized for the subsequent characterization which included determining capacities, batch kinetics, and kinetics in a flow system.

Capacities were determined by analyzing the CPG-8HOQ by X-ray fluorescence spectrometry and by polarography. For x-ray fluorescence, samples of the immobilized chelate were equilibrated with an aliquot of copper (II) solution, filtered, rinsed with distilled/deionized water, and analyzed directly by non-dispersive x-ray fluorescence. In the polarographic method, a sample of CPG-8HOQ was equilibrated in a pH 6.70 buffer solution with an excess of copper (II). The amount of copper (II) remaining in solution after equilibrium was determined polarographically.

A semi-continuous limited bath method using polarographic measurement of copper (II) and nickel (II) was used to determine the kinetics of exchange. By examining the affects of particle size, temperature, and exchanging cation, in solutions 25 to 10 ppm in metal ion, it was determined that diffusion through a surface gradient film was the rate controlling process. Air entrapped in the porous glass was found to interfere significantly with the kinetics so was removed by vacuum degassing.

Affects of column configuration, particle size, and flow rate were examined in a flow system providing information useful for _in situ_ use of the CPG-8HOQ for preconcentration. Samples of 100 mg of CPG-8HOQ (212 to 150 microns) removed Cu (II) ions when used with flow rates of 2 to 5 ml/min. Columns narrower than 3.6 mmID resulted in columns with back pressures too high to achieve useful flow rates. Effluent of the extraction columns was monitored with a copper ion specific electrode. Use of CPG-8HOQ appears to be attractive for _in situ_ preconcentrations where information about both the quantity and speciation of metal ions can be obtained.

CHAPTER I

INTRODUCTION

A. Chemistry of Trace Metals

Trace metal concentrations of marine samples are of use to a number of scientific disciplines. Biochemists interested in the availability and metabolism of trace metals need reliable data concerning the sources and concentrations of these trace metals. Oceanographers use trace metal concentrations to characterize and identify water masses and marine geochemists are interested in the incorporation and redissolution of minerals in ocean water. More recently, as our interest in the quality of our environment has increased, the effects of modern industrialization and agriculture on our environment have been measured by monitoring the increased concentrations of marine trace metals near highly developed population centers.

B. Trace Metal Analysis

Trace metal analysis, especially in environmental samples and specifically in marine samples is the source of many difficulties and errors. This fact is demonstrated by two intercalibration studies in which carefully prepared samples were distributed to and analyzed by a variety of different laboratories.

Rottschaffer, Jones, and Mark (1971) conducted an inter-lab analysis for mercury in homogenized fish tissue using results of their own ion exchange/neutron activation procedure (Jones, Rottschaffer, Mark, Paulsen, and Patriarch (1971)) and those of LaFleur (1970) of the National Bureau of Standards as a baseline for the comparison. The results of 15 different laboratories (industrial, government, and academic) showed deviations up to 5%--clearly unacceptably high.

A more comprehensive inter-lab study was coordinated by Brewer and Spencer (1970) using large samples of sea water which were carefully handled to assure homogeneity and minimize sources of error in the sample. Sources of error were limited to subsampling by the participating laboratory, sample storage, and the analysis itself. Subsampling was shown not to be a source of error and no clear conclusion could be reached about the effects of sample storage. Still, coefficients of error ranged from 2.5% for strontium to >30% for nickel (II) from the 20 participating labs.

Studies have shown that chemical changes occurring in the sample during storage result from biological activity and interaction with container surfaces. One group of samples in Brewer and Spencer's study was discounted because of continued biological activity in the sample during storage, which resulted from an improperly "fixed" sample. There are a variety of methods for controlling biological activity but problems arise when some treatments interfere with subsequent analyses, and, as in Brewer and Spencer's case, are not adequately effective.

Adsorption and contamination of the sample by the storage container have led to ambiguous results. One group of workers found contamination of trace mercury samples stored in polyethylene containers to be a problem (Bothner and Robertson (1975)) while others have found adsorption to decrease the mercury concentrations of similar samples stored under similar conditions (Bate (1971); Feldman (1974)). Robertson (1968a,b) has determined potential contaminants in common laboratory equipment and storage containers and suggests procedures for minimizing contamination of stored samples. Chemical properties such as pH and salinity have been shown to change in stored samples (K. Parks (1968)). Such changes clearly affect trace metal concentrations through their coupled equilibria.

It becomes clear, then, that the initial problem in studying the effects of changing trace metal concentrations is one of analytical chemistry. Of the various trace techniques available in analytical chemistry, several well defined methods such as emission spectroscopy, anodic stripping voltammerty, neutron activation analysis, atomic absorption spectroscopy, electron microprobe spectroscopy, etc., and some mass spectrometry are sufficiently sensitive to carry out trace analysis of metal ions in natural water systems. But while the sensitivities may be adequate, these methods still require some form of preconcentration to remove interferences.

Neutron activation, for example, has a sensitivity of one part per billion (Leddicotte and Reynolds (1953); Yule (1965)) but direct analysis of sea water or serum samples is impossible because of interferences arising from the activation of the ever-present sodium chloride.

C. Preconcentration Methods

Commonly used methods for preconcentrating samples include evaporation, solvent extraction, precipitation, electrochemical deposition, and ion exchange. The most common methods are discussed in detail elsewhere (Riley and Skirrow (1965); Rottschafer, Boczkowski and Mark (1972); Cendelman and Caruso (1971)). These methods are possible sources of error in that they involve sample transfers and addition of reagents, steps that can be eliminated by doing the preconcentrating _in situ_. Methods such as solvent extraction and precipitation are not adaptable to _in situ_ use. However, electrochemical and ion exchange methods can be adapted for in situ use.

D. In Situ Preconcentration

The requisite characteristics of in situ preconcentration are only slightly more demanding than for laboratory preconcentration. The ideal characteristics include:

1. The system is sampled in a manner which is chemically and physically inert upon removal from its environment.
2. The sample is in a form which can be analyzed by a direct, nondestructive method (no additional preparative steps).
3. The preconcentrated sample is quantitative and representative with respect to the concentration of the original sample.

It should also be inexpensive and result in a small sample for convenient storage. Techniques involving the electrochemical plating of the trace metals onto a graphite electrode have been reported (Vassos, Hirsch and Letterman (1973); Rottschaffer, Boczkowski, and Mark (1972)). Modifications in their original design are results of different approaches to adapting the electrochemical instrumentation to in situ use.

Ion exchange techniques have also been adapted for in situ sampling. Ion exchange membranes have been used for in situ preconcentration of metals, but the long equilibration times (30 hours) were found to be unsatisfactory

(Mark, Eisner, Rottschaffer, Berlandi, and Mattson (1969)). Others have used the long equilibration times to advantage to obtain "integrated" samples where high frequency variations in estuaries were averaged out over the sampling period of 2 to 3 days (Lochmüller, Galbraith, Walter and Joyce (1972)).

General use of weak and strong cation exchange resins has found little application in the preconcentration of sea water trace metals because of their affinity for monovalent alkali metals at the high concentrations present in marine samples. However, chelating ion exchange resins with imidodiacetic acid functional groups have been used to preconcentrate metals from sea water samples, but not for in situ work. These resins have a very high specificity for divalent transition metals and a reasonably high capacity (0.6 mmole $Cu(NH_3)_6^{++}$/gm, Dow Chemical Co.) Riley and Taylor (1968a, 1968b, 1972) have successfully preconcentrated Bi, Cd, Co, Cu, In, Mn, Mo, Ni, Pb, Re, Sc, Th, W, V, Y, Zn and the rare earth elements from sea water. The elements were analyzed by atomic absorption in the acid effluent. The work of Riley and Taylor was applied to the determination of indium (Matthews and Riley (1970)) and vanadium (Kireyama and Kuroda (1972)) in sea water and to traces of copper, lead, zinc, cadmium, nickel and iron in industrial effluents (Biechler (1965)). Callahan, Pascural and Lai (1966) found Chelax 100 useful for concentrating cobalt (II). They were concerned with concentrating radionucleides (principally cobalt), and found that while cobalt (II) could be quantitatively concentrated, cobalt (III) was not removed from solution. Chelating resins like Dowex A-1 and Chelex 100 have not been used for in situ applications for several reasons. One, the kinetics have been shown to be relatively fast but still not adequate enough to make it attractive for in situ preconcentration (Eger, Anspach, and Marinsky (1968)). Two, organic polymer based resins like Dowex and Chelex swell and contract as ion exchange proceeds and with changes in ionic strength. This, in turn, alters the flow characteristics of a column or cartridge configuration and makes the calibration and measurements required for in situ work difficult to maintain. Finally, it is possible that the organic substrate would be biologically degraded during storage. These problems, both real and potential, were reasons enough to look at another substrate to be used as a sampling matrix for in situ preconcentration.

E. Glass Immobilized Chelates

Recently, a material has been developed which consists of an organic chelating ligand covalently immobilized on the surface of controlled pore glass (Sugawara, Weetall, and Schucker (1972, 1973, 1974)). This material has several attractive properties as a matrix for in situ preconcentration of trace metals. Of these ion exchangers, the most successful in terms of synthetic yield, capacity, and general applicability was immobilized 8-hydroxyquinoline (8-HOQ). At neutral pH, the control pore glass immobilized 8-HOQ (CPG-8HOQ) was found to quantitatively remove nickel (II), copper (II), cobalt (III) and vanadium (II) from solution. Further, it has been shown that the immobilized chelate will remove these and other transition metals from sodium chloride matrices (Fasching, Buono, Karin (1974)) and from electrolytes used in anodic stripping vottammetry (Moorehead and Davis (1974)).

The control pore glass product, when compared to organic polymer chelating ion exchangers with the 8-hydroxyquinoline functional group (Vernon and Eccles (1973); Parrish and Stevenson (1974)), clearly has several advantages. Most importantly, equilibration rates will be expected to be much greater for the CPG 8-HOQ because of its more open macroporous nature compared to a highly cross-linked polymer. The kinetics of the CPG 8-HOQ will be examined as part of this work. At the same time the glass substrate gives the immobilized chelate material the rigid structure needed to prevent expansion or contraction coincident with ion exchange as is the case with organic polymer based ion exchangers. Also the inorganic glass substrate is inert to most solutions. The silane will hydrolyze under ammonical alkaline conditions and the glass will dissolve with hydro-fluoric acid, but both will remain unchanged under the conditions used sea water analysis.

F. Analysis of the CPG-8HOQ

There are several methods of analysis available for determining the amount of metals contained on the CPG-8HOQ which fall into two general categories. One group requires the metals to be eluted from the immobilized chelate with acid. This is a necessary step for most methods from gravimetry to mass spectrometry. However, elimination of this additional manipulatory and chemical step would be advantageous. First, it presents the possible introduction of errors through contamination or incomplete recovery from the immobilized chelating agent. Second, the elution step would extend the analysis time. Most solution methods require sequential analysis if more than one element were of interest, and this would extend the analysis time even further. Elution does make additional preconcentration possible, but, as mentioned previously, methods of analysis are available which are sensitive enough to analyze the immobilized chelated metals without additional preconcentration.

Methods which can be used to analyze directly the metals on the CPG-8HOQ include non-flame atomic absorption spectroscopy, neutron activation analysis and x-ray fluorescence spectrometry. Non-flame atomic absorption using a graphite rod or tantalum atomizer could be used with direct atomization of a small sample of CPG-8HOQ. Atomic absorption has a fairly high sensitivity but would require separate analysis for each element of interest and is a destructive type of analysis. Possible sources of difficulty include incomplete atomization and the imprecise delivery of small samples of the granular solid. Neutron activation analysis has very high sensitivity for most elements, has the inherent capability of analyzing a wide variety of elements simultaneously and is nondestructive. However, neutron activation analysis is not generally available nor is it readily adaptable to on-site use. X-ray fluorescence (XRF) spectrometry has the capability of simultaneous analysis, is adaptable to on-site use but suffers from limited sensitivity. XRF has been shown to be useful for analysis of ion exchange material, mainly for ion exchange resin loaded papers and membranes (Campbell, Green and Law (1970)) where limits of detection are generally <.5 mg for most transition metals (Campbell, Spano, Green (1966)). XRF has been used in the direct analysis of trace metals in geological samples preconcentrated on Chelex 100 (Blount, Leyden, Thomas, and Guill (1973)). The 100 to 200 mg samples of ion exchange resin were made into pellets using pressure (30,000 psi) and heat (150°C), but still retained their characteristics of swelling and shrinking with changes in water content making storage and duplication difficult.

Using XRF for analysis of metals in CPG-8HOQ presents no special problems. Interelement effects will be minimal by using copper (II) and nickel (II) solutions for "model" studies. Matrix absorption will be somewhat higher than found for the organic resins (Blount, Leyden, Thomas, and Guill (1973)) because of the higher absorption coefficient of Si compared to C, but will not be excessive.

G. Research Objective

This work examines some of the characteristics of the glass immobilized 8-hydroxyquinoline to evaluate its usefulness for in situ preconcentration and its applicability to simple, direct analysis by x-ray fluorescence (XRF) spectroscopy. Included are experiments characterizing its analysis by XRF, capacities, kinetics and optimum column configuration and flow conditions.

CHAPTER II

PREPARATION AND CAPACITIES OF CONTROLLED PORE GLASS IMMOBILIZED 8-HYDROXYQUINOLINE (CPG-8-HOQ)

A. Introduction

The CPG-8HOQ was synthesised and the capacity measured by XRF. Several 10 gram batches of CPG-8HOQ were blended together to give a supply of material with a consistant capacity. XRF analysis was used to determine the capacities which agreed well with results obtained by K. F. Sugawara (1973a) and which was more convenient for use in our laboratory.

B. Experimental

1. Formation of the arylamine glass: Controlled pore glass (177 to 125 microns, 550 Å pore dia., supplied by Pierce Chemical Co., Rockford, Ill.) was refluxed in 5% HNO_3 for one hour, filtered in a fritted glass funnel and washed twice with boiling distilled water. The glass was allowed to dry overnight at 95°C. Twenty grams of the activated glass was then refluxed overnight in 10% γ-aminopropyltriethoxysilane (A1100, Union Carbide Corp.) in toluene. The sample was filtered, washed with toluene,

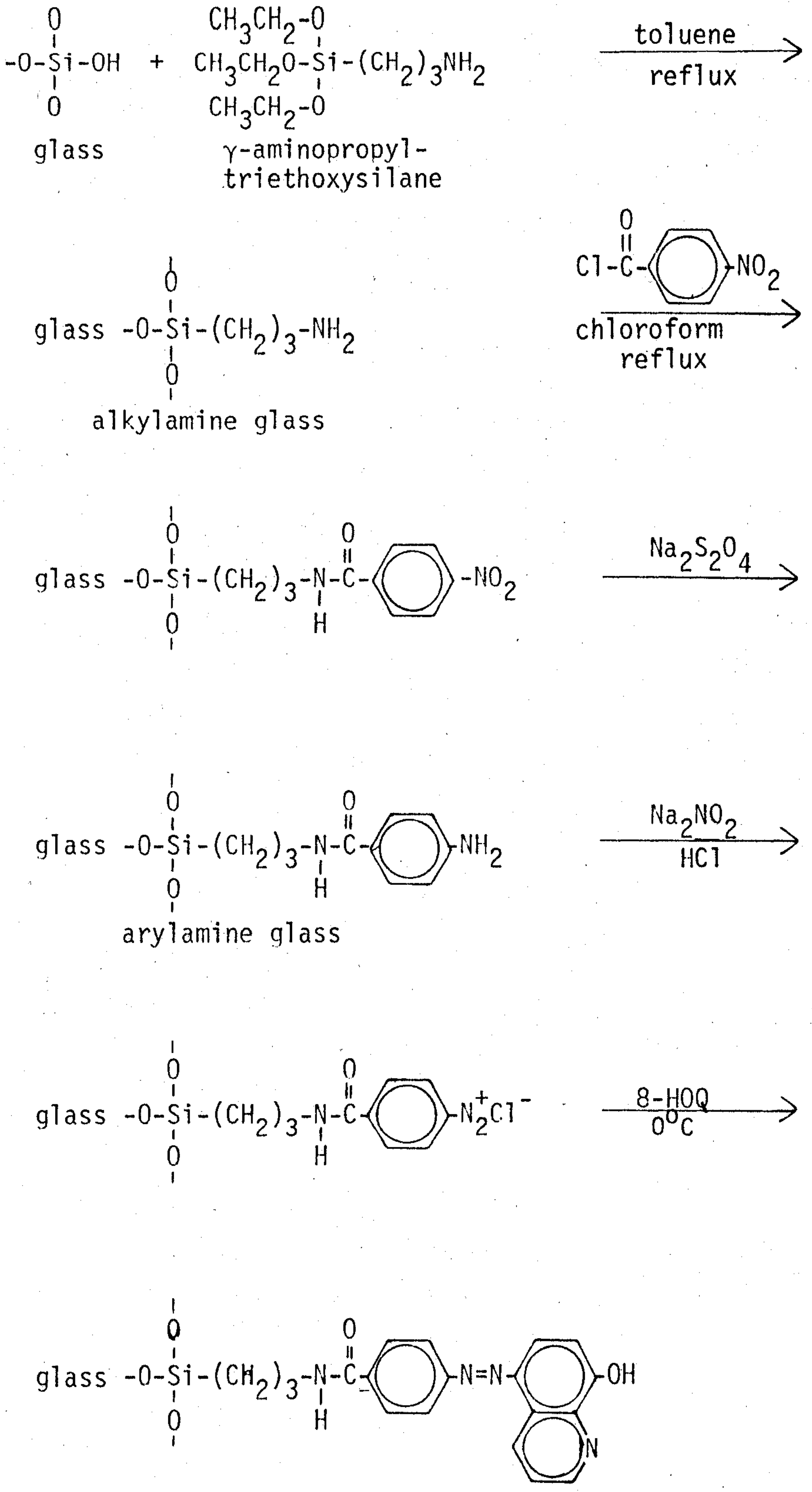
and allowed to air dry.

The dried sample of alkylamine glass was refluxed overnight in chloroform containing 10% triethylamine and 0.6 gram para-nitrobenzoyl chloride. The sample was then filtered, washed with chloroform, and allowed to air dry. The nitro group was reduced by heating the sample in freshly prepared 10% sodium dithionite after which the sample was again filtered, washed with distilled water, and air dried. The resulting product is the arylamine glass.

2. Coupling the 8-Hydroxyquinoline: In an ice bath, 10 grams of arylamine glass and 100 ml of 2N HCl were allowed to cool before transferring to a vacuum dessicator also containing ice. Sodium nitrite (2.5 grams) was then added to the reaction mixture. A water aspirator was used to remove entrapped air from the porous glass and excess NO_2 from the dessicator. After 30 minutes, the sample was filtered and washed with ice cold 1% sulfamic acid solution. The diazotized glass was quickly transferred to a 0.05 M $NaCO_3$ solution saturated with 8-hydroxyquinoline. After 30 minutes the sample was filtered, washed with distilled/deionized water and air dried.

3. Capacity measurements: Solutions were made using distilled/deionized (D/D) water that was stored in high density polyethylene carboys (Nalgene).

Figure 1: Synthisis of controlled pore glass 8-hydroxyquinoline


glass
γ-aminopropyl-triethoxysilane
toluene
reflux
chloroform
reflux
alkylamine glass
$Na_2S_2O_4$
arylamine glass
Na_2NO_2
HCl
8-HOQ
0°C

A stock solution of copper was prepared by dissolving a 0.5013 gram piece of acid cleaned copper foil in a minimum amount of reagent grade nitric acid and bringing the solution volume to 500 ml. The final concentration was 1,003 μg/ml (0.0158 M).

Two procedures were used in determing the capacities.

Method I: A measured volume of copper (II) solution was equilibrated with 200 mg. CPG-8HOQ and 10 ml D/D water in acid washed (8 M HNO_3) polyethylene bottles for 4 hours on a reciprocating shaker. The samples were filtered and washed with two 15 ml aliquots of D/D water, air dried, and analyzed by x-ray fluorescence spectroscopy (XRF).

Method II: A set of standards was first prepared by measuring out 100 mg. of CPG-8HOQ, two to five ml. of D/D water, and a measured aliquot of copper (II) stock solution into a plastic x-ray analysis cell (Spex Industries, Metuchen, N. J.) and allowed to evaporate. The air dried sample was analyzed by XRF. Then a single 100 mg. sample of CPG-8HOQ of unknown capacity was prepared by equlibrating the sample with an excess of copper (II) (1.5 ml stock solution), filtering, rinsing with two 15 ml aliquots of D/D water, and analyzing by XRF.

For both methods, samples were analyzed by non-dispersive XRF (EDAX, International, Chicago, Ill.) for 100 seconds using a gold x-ray tube for x-ray excitation

Figure 2: Capacities determined
by XRF, Method I.

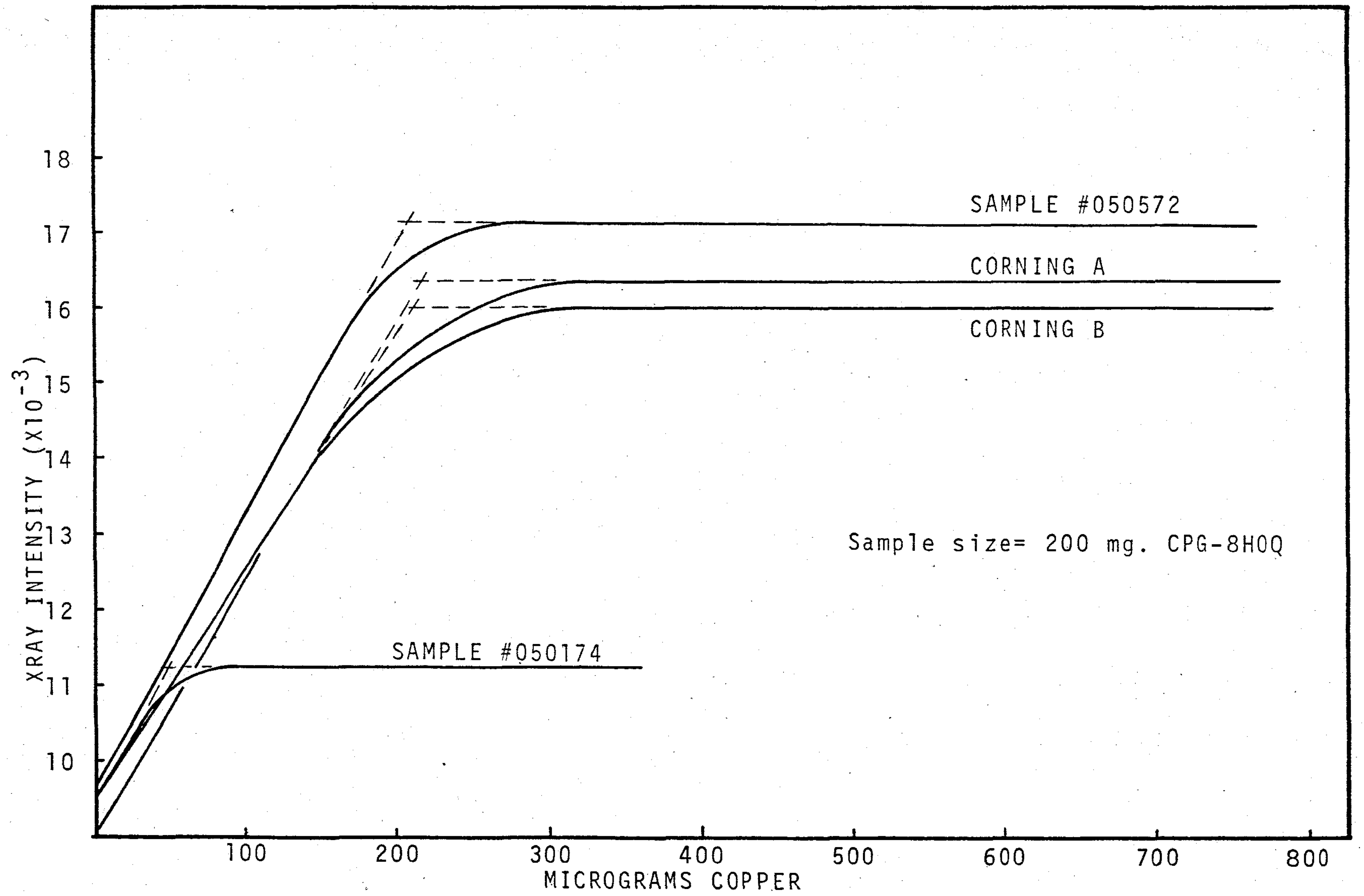
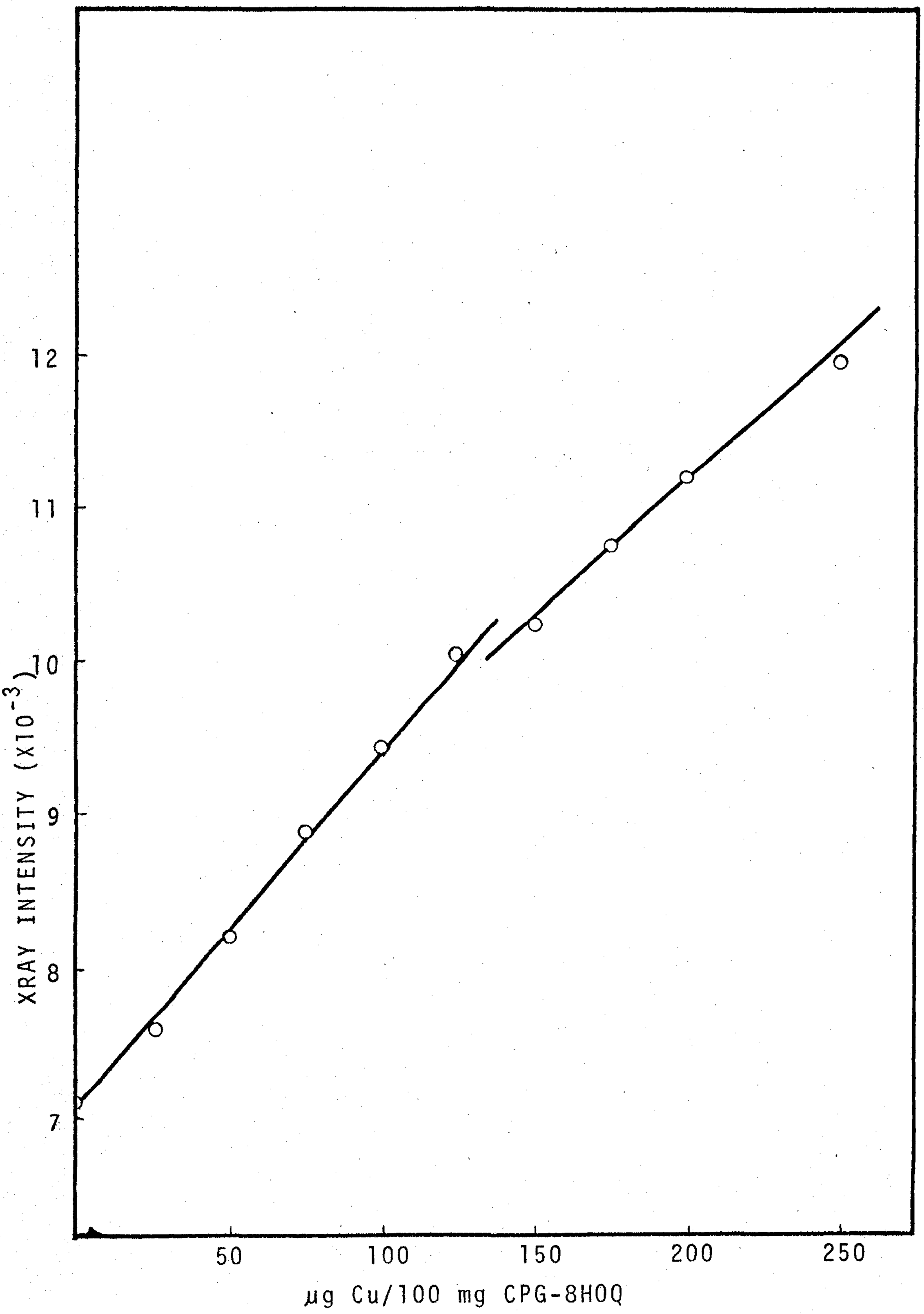

18
17
16
15
14
13
12
11
10
XRAY INTENSITY (X10^{-3})
100
200
300
400
500
600
700
800
MICROGRAMS COPPER
SAMPLE #050572
CORNING A
CORNING B
SAMPLE #050174
Sample size= 200 mg. CPG-8HOQ

Figure 3: Calibration curve for determining capacities by XRF, Method II.



12
11
10
9
8
7
XRAY INTENSITY (X10^{-3})
50
100
150
200
250
µg Cu/100 mg CPG-8HOQ

operated at 32 microamps and 30 kev. The intensity of emitted x-ray at 8.040 kev was measured by integrating the area at full width at half the maximum (FWHM) and subtracting the background. The background was obtained from a sample treated identically as the other samples but without the addition of copper (II).

C. Results

The conditions necessary to optimize surface activation of silylic groups were studied by Aue and Hastings (1968). The procedure used here is a modified version based on their conclusions. The remaining procedures were as described by Sugawara, Weetall and Schucker (1972, 1973) and more recently by the same authors (1974).*

A fairly large range of product yields was encountered as indicated by the varied intensity of the red color resulting from the azo chromophore. The color intensity correlated well with subsequently determined metal capacities and so served as a convenient indication of yield. The primary reason for poor yield was found to be incomplete reduction of the p-nitro group caused by the use of degraded dithionite solution. It is important therefore that the

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*Corning Glass (Corning, N. Y.) now manufactures CPG-8HOQ which is commercially available through Pierce Chemical Co., (Rockford, Ill.).

dithionite reducing solution be prepared fresh as it is needed. Small variations in yields were undoubtedly also caused by variations in surface coverage by the organosilane.

Capacities determined by Method I involved plotting the intensity measured by XRF versus the mg of copper (II) added. The amount of copper (II) taken up by the CPG-8HOQ increases linearly up to the level where the number of equivalents of copper (II) is equal to the number of equivalents of 8HOQ. Figure 2 shows some typical results for 4 samples. Two samples, 050572 and 050172, were prepared in the lab and show the variation in yield, and hence capacity, encountered. The other two samples were provided by Sugawara at Corning for comparison. Both Corning samples were from the same lot and so indicate the repeatability of the method for capacity measurements. A disadvantage of Method I is that it requires several samples and measurements for each capacity determination.

In Method II the capacity is calculated by determining the maximum amount of copper (II) which will react with a single sample of CPG-8HOQ. The amount of copper present is determined by comparing the XRF results with those of a set of standards using the calibration curve in Figure 3. Table I summarizes the capacities of various batches of CPG-8HOQ determined by XRF using Cu (II).

Table II shows the capacities determined by Sugawara (1973a) using Fe at a pH = 5. For this work the XRF method was preferred because of its convenience and the XRF results are in reasonable agreement with those by Sugawara.

Analyzing the metal uptake by XRF has several distinct advantages over other, more frequently used methods. First, it measures the amount of elements contained directly in the CPG-8HOQ without depending upon elution of the metals from the material prior to analysis. Errors which may be introduced in the elution step are incomplete elution resulting in capacities lower than expected and/or the loss or contamination of the sample during elution resulting in lower or higher capacities, respectively. The accuracy of either approach is further dependent upon careful instrument calibration.

Second, XRF is well suited to direct analysis of metals in the CPG-8HOQ because of the low absorption by the silica matrix of both the excitation and emitted x-rays. This results in a low background and allows quantitative determination of 10 mg. Cu or less in a 0.1 to 1.0 gm. sample of CPG-8HOQ.

Because of the variation between batches of synthesized CPG-8HOQ, a number of batches were combined

TABLE I

Capacities determined by x-ray fluorescence spectroscopy

Sample: CPG-8HOQ	Capacity (pH7)
050572	1.05 mg Cu (II) gm^{-1}
Corning a	1.10
Corning b	1.05
050172	0.25

TABLE II

Capacities determined by the method of
K. F. Sugawara, et al. (1974)

Sample: CPG-8HOQ	Capacity (pH5)
050572	1.7 mg Fe gm^{-1}
Corning	1.4

and the capacity determined to be 1.05 mg Cu (II)/gm. This is the material which was used for most of the subsequent work. Commercial CPG-8HOQ was used where noted.

CHAPTER III

KINETICS: BATCH

A. Introduction

1. General: In field tests conducted in and around the Straits of Florida, samples of CPG-8HOQ were evaluated for *in situ* preconcentration sampling. Samples of sea water were pumped through 15 cm x 0.36 cm glass columns containing the immobilized chelate or were equilibrated in a 5 l. carboy containing the immobilized chelate. Some samples were prefiltered using a .45μ Millipore filter, others were not. XRF analysis indicated no detectable amounts of any transition metals except in two samples. These two samples were equilibrated with sea water which was made 0.05 ppm in Cu (II) by spiking it with standard solutions. Still, the CPG-8HOQ contained only trace quantities (<20 mg) of copper instead of the expected quantities (250 mg).

These results suggested several possible sources of difficulty. Either there were no metals in the samples taken, the metals were not available for complexation with the immobilized CPG-8HOQ, or there were operational difficulties which prevented complexation. Florida waters, like all ocean waters do contain trace metals of average concentrations (Brewer and Spencer (1970)). Stability constants for metal complexes of unattached 8-hydroxyquinoline presented in Table III indicate the thermodynamic favorability of complex formation for a number of metal ions and similar values can be expected for immobilized 8HOQ. Therefore the possibility of operational difficulties indicated a need for a more detailed study of the complexation kinetics of copper (II) and nickel (II) with the CPG-8HOQ.

TABLE III

Complexes of 8-hydroxyquinoline

$pk_{1a} = 3.76$

$pk_{2a} = 11.90$

M	log K_1	log K_2
Cu (II)	12.2	11.2
Ni (II)	9.9	8.8
Co (II)	9.1	8.1
Fe (II)	8.0	7.0

Sillén and Martell (1964)

2. Ion Exchange Kinetics: There are four generally accepted rate-controlling mechanisms which may predominate under various conditions in the exchange of ions in both chelating and non-chelating ion exchange resins. One mechanism is that of a second order reversible chemical reaction. This mechanism has been found to be rate determining for large and/or tetravalent cations like UO_2^+ and Th^{+4} on a chelating resin containing phosphonic acid functional groups (Heitner-Wirguin and Urbach (1965); Heitner-Wirguin and Kendler (1971)). Other authors have, erroneously, concluded that the rate of exchange of non-chelating alkali earth ion pairs on Chelex 100 was controlled by second order chemical kinetics (Turse and Reiman (1961)). Their conclusion was based on data where capacities were incorrectly calculated as a result of the resin-bed volume changes accompanying ion exchange in the polymer-based resin. The work was later repeated and correctly reported as being diffusion controlled (Varon and Reiman (1964)).

The other three mechanisms involve diffusion as rate limiting but only two are important. Rate limitations by slow bulk diffusion are rarely encountered in stirred batch or column systems so are of little consequence.

The two important diffusion mechanisms are particle diffusion, where diffusion through the pores of the matrix is rate limiting, and film diffusion, where diffusion through a Nernstian-type film is rate limiting. Generally, it has been shown by two experimental approaches that particle diffusion predominates at higher concentrations (>0.1M) and low valence while film diffusion predominates at low concentrations (Boyd, Adamson and Myer (1947); Reichenberg (1953); Heitner-Wriguin and Kendler (1971); Heitner-Wirguin and Markowitz (1963)).

Factors which determine which rate-limiting mechanism predominates are: 1) particle size, 2) degree of agitation of solution, 3) diffusion coefficients of the exchanging ions in the solution and within the resin particle, 4) temperature, 5) equilibrium distribution coefficients, and 6) solution concentration. The influence of these factors in determining the rate-limiting mechanism can be evaluated using either the infinite bath technique or the limited bath method.

Boyd, et al. (1947) utilized an infinite bath technique and developed equations to describe the rate limiting mechanism for the existing boundary conditions. This method uses a column in which the concentration of the incoming cation remains constant because a large volume and high flow rate through a shallow resin bed are used. The outgoing ion is measured to monitor the extent of exchange with time.

Kressman and Kitchener (1949) used a limited bath method to study exchange kinetics. This is a non-continuous batch method where the decreasing concentration of the ingoing ion is monitored to follow the exchange kinetics. An important result of the limited bath method is that the ion exchange reaches an equilibrium level and is not forced to completion as in the infinite bath method. This necessitates the derivation of a different set of equations for the two diffusion mechanisms (Kressman and Kitchener (1949)) and for second order chemical reaction mechanism (Turse and Reiman (1961)) which are summarized below:

Film Diffusion

$$\log (1-5) = \frac{-Rt}{2.303}$$

where $F = \frac{Qt}{Q\infty}$, R is a function of the diffusion coefficient and film thickness, and the equation is found to apply up to $F = 0.9$.

Particle Diffusion

$$F = \frac{6}{r} \; \frac{Q}{Q_0 - Q_\infty} \sqrt{\frac{Dt}{\Pi}}$$

where D is the observed diffusion coefficient and an approximation in the derivation causes deviations in the equation when $F>0.6$

Second Order chemical reaction

$$\ln Z = 2kQ_o\ (Q_o - Q_\infty)\ t/Q_\infty$$

where

$$Z = \frac{Q_t\ (Q_o - 2Q_\infty) + Q_o Q_\infty}{Q_o\ (Q_\infty - Q_t)}$$

k is the effective rate constant

Application of these equations to the kinetic data taken under limited bath conditions should indicate the rate-limiting mechanism.

Very useful information for identifying the slow step of an ion exchange process can be determined on a qualitative basis. In two experiments conducted under identical conditions except for changes in particle size, a diffusion controlled exchange will be accelerated by a decrease in particle size while a chemically controlled exchange will be unaffected by particle size changes.

Another indication of the rate limiting mechanism can be determined by changing only the concentration. As long as the change in concentration is not so great as to exceed the limits where diffusion in the resin is the slow step, the change should have no affect on the diffusion controlled process. However, an exchange controlled by a slow second order chemical reaction should be significantly changed by a change in concentration.

Still another experiment useful in identifying the slow step in an exchange is to change only the exchanging cation. Copper (II) complexes are generally labile while those of nickel (II) are generally inert. There should be a marked increase in the rates of exchange by using Ni (II) compared to Cu (II) if the chemical reaction is rate-limiting. Both would be expected to have similar diffusion coefficients so that there would be little difference in the exchange rates if the rate-controlling mechanism is diffusion controlled.

B. Experimental

1. General: In this experiment, the limited bath method has been modified slightly to use semi-continuous polarographic monitoring of the metal ion concentration. Such a method requires the ion exchange reaction to be not too fast ($t_{1/2} > 1$ min.) because of the necessity to interrupt the solution agitation to measure the diffusion current. This semi-continuous method was compared to the discontinuous method of Kressman and Kitchener (1949) and agreed within 1 to 3% (Kendler and Heitner-Wirguin (1970)) and so has been adapted for use here.

2. Instrumentation: A Sargent Model VII polarographic analyser was used with a dropping mercury electrode and a saturated calomel reference electrode (SCE). The

latter was connected to the sample cell via a double junction saturated KCl salt bridge using porous Vycor (Corning Glass, Corning, N. Y.) in polyethylene tubing. For copper (II) solutions, a reduction potential of -0.40V (vs. SCE) was used and for nickel (II), -1.20V (vs. SCE) (Figure 4). Current sensitivities used were 0.001, 0.002, or 0.004 microamp/mm. depending on the metal ion concentration.

The temperature was controlled by equilibrating the polarographic cell in a 500 ml thermostated water bath. The controller (H. B. Instrument Co., Phila., Pa.) used mercury thermometer probes and maintained the temperature to within 0.1°C. of the designated temperature.

3. Reagents and solutions: The copper (II) stock solution used was the same as described in Chapter II.

A nickel (II) stock solution was prepared by dissolving 0.5002 grams of high purity nickel metal in minimum volume of nitric acid and diluting to 500 ml with D/D water. The final concentration of the stock solution was 1000.1 μg/l (0.0170 M). Volumes of metal solution were delivered using a Gilmont micrometer pipet which measures to 0.001 ml (Cole Parmer, Chicago, Ill.).

A single volume of pH 6.70 phosphate buffer was prepared from reagent grade K_2HPO_4 and KH_2PO_4 and D/D water. The buffer was prepared with an ionic strength of 0.1 moles/liter.

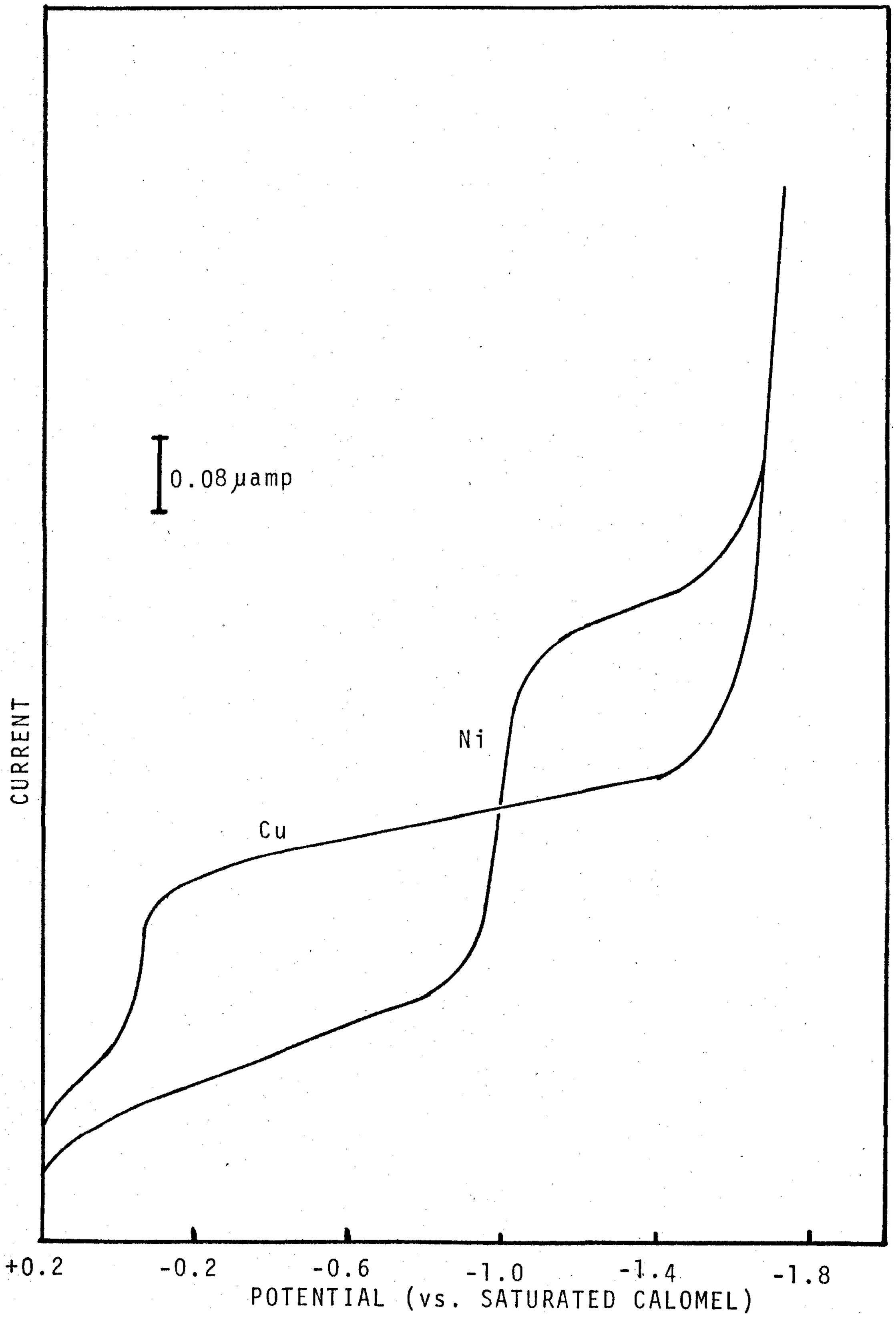
Figure 4: Polarograms for

Ni (II) and Cu (II)

[Ni] = 4.98 μg/ml

[Cu] = 4.98 μg/ml

pH = 6.7


0.08 µamp
CURRENT
Ni
Cu
+0.2
-0.2
-0.6
-1.0
-1.4
-1.8
POTENTIAL (vs. SATURATED CALOMEL)

The CPG-8HOQ used was from two sources. Several lots of synthesized CPG-8HOQ were combined. This material had an average particle size of 177 to 125 microns and a capacity of 1.05 mg $Cu/_{gm}$. Several bottles of commercially available CPG-8HOQ were also combined in a separate batch. This material was ground with an agate mortar and pestle and seived to an assorted range of particle sizes. All samples of CPG-8HOQ were stored in a dessicator over $CaCl_2$.

The high purity nitrogen used to deoxygenate polrographic samples was further purified by passing it through copper turnings heated in a tube furnace (150°C.) and then bubbled through buffer solution to saturate the nitrogen stream with water vapor. Samples were deoxygenated with purified nitrogen for 30 minutes prior to the first polarographic measurement and maintained under a blanket of nitrogen during the kinetic experiment.

4. Procedure: a) Calibration: A twenty ml. sample of buffer solution was deoxygenated and the diffusion current measured prior to the addition of a measured volume of stock metal ion solution. The diffusion current was then measured after the addition of each aliquot of metal ion solution using the initial measurement for the deoxygenated buffer solution as the blank.

b) Kinetics: A measured sample (100 mg) of dry

CPG-8HOQ was added to 20 ml of buffer solution and degassed under vacuum. Degassing was accomplished by placing the sample in a vacuum dessicator and drawing a partial vacuum with a water aspirator for 30 minutes or until no air bubbles were observed from the porous glass. The sample was then deoxygenated with purified nitrogen for 30 minutes. A measured volume of metal ion solution was added to the mixture and the magnetic stirrer and clock started. The magnetic stirrer was stopped 15 seconds prior to and restarted immediately following each polarographic measurement.

c) Capacity measurement: The sample of 100 mg. of CPG-8HOQ was added to 20 ml of buffer, degassed, and deoxygenated as described above. A 1.50 ml aliquot of the copper (II) stock solution was allowed to equilibrate for 60 to 90 minutes. The amount of copper (II) remaining in solution was then measured polarographically.

C. Results

1. Degassing: Early experiments indicated the importance of removing air entrapped in the porous glass. Samples took excessively long times to equilibrate (>10 hours) as the solution slowly displaced the air, making diffusion of Cu(II) ions to the 8HOQ sites possible. Each CPG-8HOQ sample was therefore degassed in buffer solution. The resulting equilibration rates in subsequent experiments

are representative of the ion exchange and not air displacement.

2. Calibration: The diffusion current was plotted *vs*. calculated metal ion concentration giving a linear calibration plot like the one shown in Figure 5. Calibration curves were run frequently because of small changes in the characteristics of the mercury capillary. All of the calibrations were linear but had slightly different slopes. A least squares analysis was done on each calibration to calculate the slope and intercept and are presented in Appendix I with an example plotted in Figure 5. These data were then used to calculate the metal ion concentrations from the experimentally determined current measurements.

3. Effect of initial metal ion concentration: The rate curves of the metal ion concentration versus time for different initial metal ion concentrations are shown in Figure 6. Initial concentrations ranged from 2.5 to 8.75 mg/ml and the rates, which are measured by the time required to reach 50% of the equilibrium concentration ($t_{1/2}$), are essentially the same. These rates are sufficiently equal to indicate the absence of a chemically controlled exchange mechanism. If the chemical reaction was rate-limiting, there would be a strong dependence on changes in the initial concentration.

Figure 5: Polarographic calibration curve
for copper (II)
E = -0.40 volts (vs. SCE)
Experiment No. 03037505
(see Appendix I)

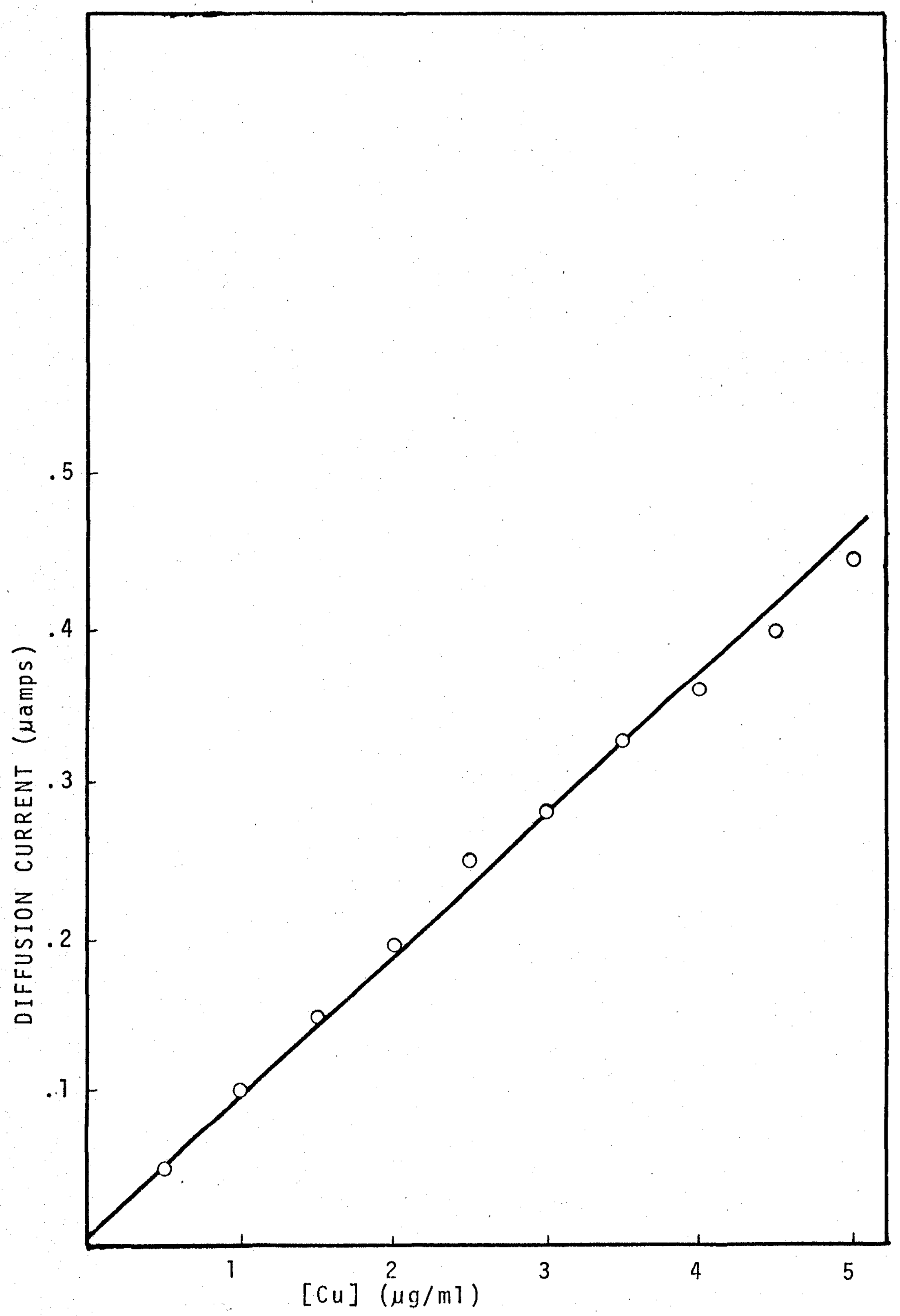
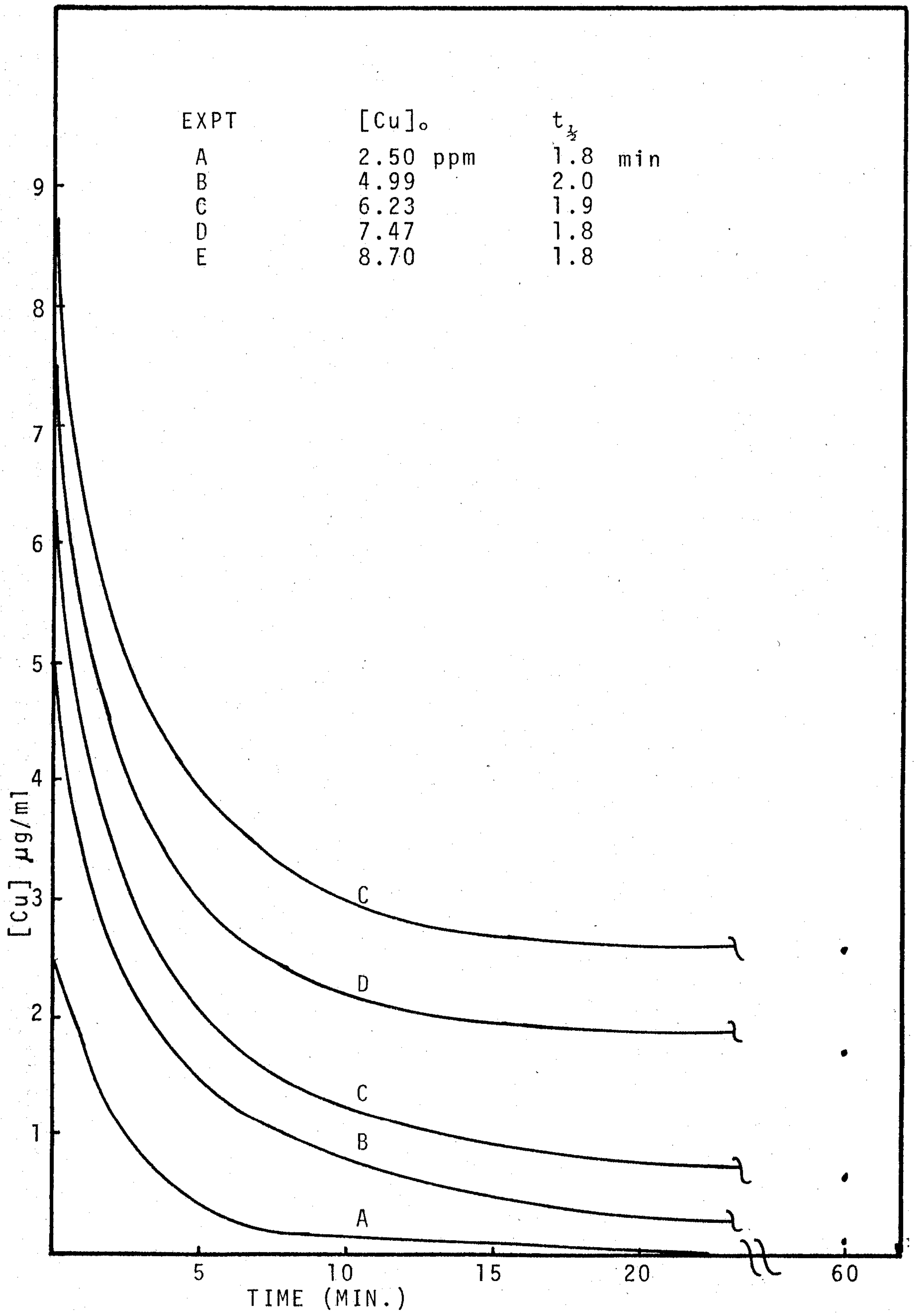

.5
.4
.3
.2
.1
DIFFUSION CURRENT (μamps)
1
2
3
4
5
[Cu] (μg/ml)

Figure 6: Rate f $[Cu]_o$

(see Appendix II)


EXPT
[Cu]o
$t_{1/2}$
A
2.50 ppm
1.8 min
B
4.99
2.0
C
6.23
1.9
D
7.47
1.8
E
8.70
1.8
[Cu] µg/ml
9
8
7
6
5
4
3
2
1
C
D
C
B
A
5
10
15
20
60
TIME (MIN.)

4. Effect of particle size and exchanging cation: The effect of particle size further indicates the absence of a chemically controlled slow step and gives positive indication of a diffusion controlled rate limiting step. The values of the $t_{1/2}$ for 4 particle size ranges are shown in Figure 7 for $[Cu]_o$ = 4.98 mg/ml and in Figure 8 for $[Ni]_o$ = 4.98 mg/ml. Both experiments show a marked dependency on particle size which is characteristic of diffusion controlled processes.

Further, the rates of exchange are the same (within experimental error) for both nickel (II) and copper (II) for equivalent particle sizes. These data indicate that the rate of exchange of both metal ions is limited by diffusion. A noted exception to the equivalency of rates for the two metals is in comparison of the <150 micron particle size. This is explained by the possibility that, when the particle size is <150 microns, the chemical reaction becomes limiting for the exchange of the more stable nickel (II). This seems to be the case when we examine the results of applying the equations of Kressman and Kitchener (1949) to this experiment. By plotting F vs t (eqtn. #2) and -log (1-F) vs t (eqtn. #1), we can determine the type of diffusion controlling the rate of exchange for copper (II) and nickel (II). The nonlinearity observed in Figures 9 and 10 indicates that particle diffusion is not the predominate

Figure 7: Rate f (Particle Size)

Copper (II)

(see Appendix IV)

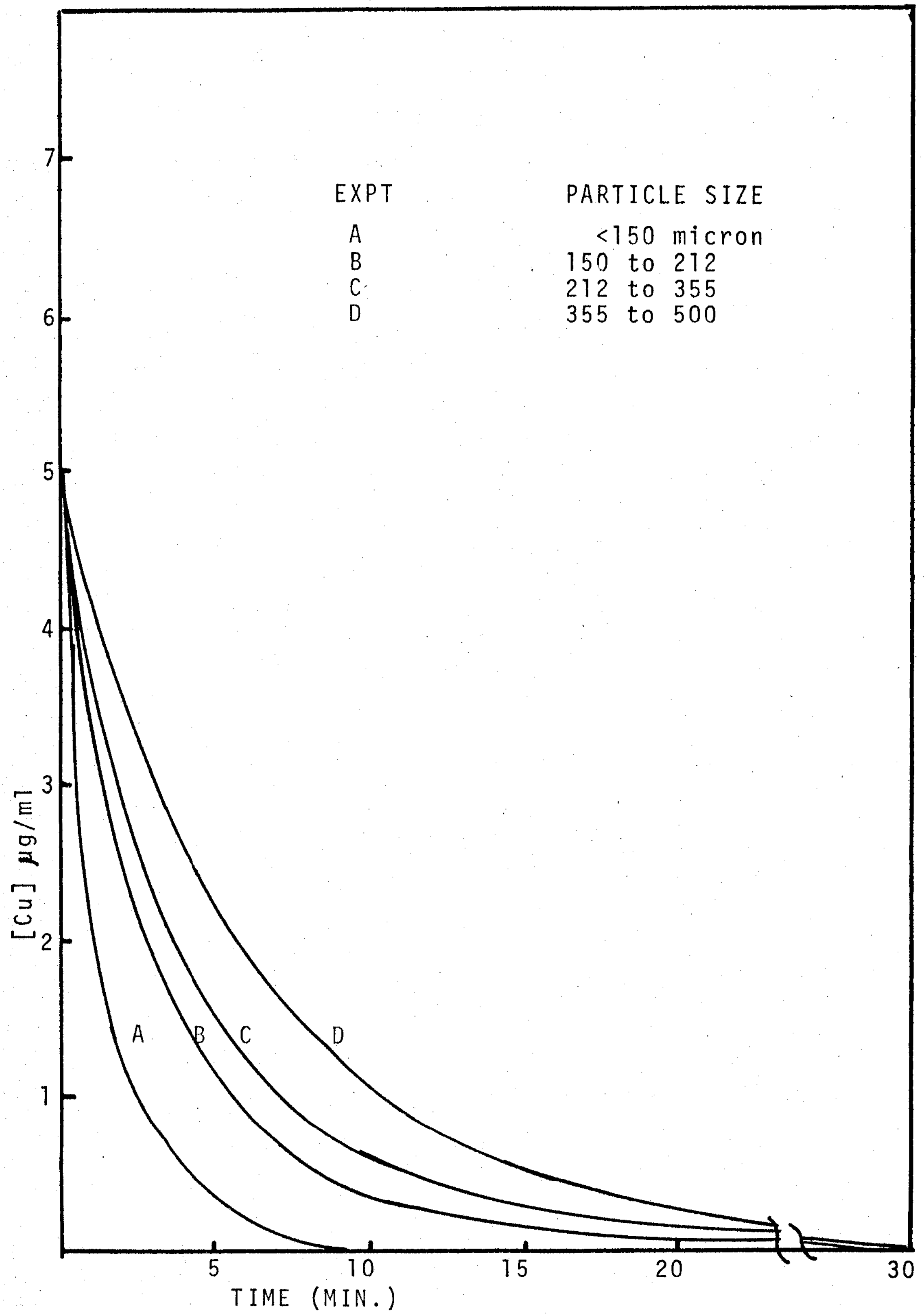

EXPT
PARTICLE SIZE
A
<150 micron
B
150 to 212
C
212 to 355
D
355 to 500
A
B
C
D
[Cu] µg/ml
1
2
3
4
5
6
7
5
10
15
20
30
TIME (MIN.)

Figure 8: Rate f (Particle Size)

Nickel (II)

(see Appendix V)

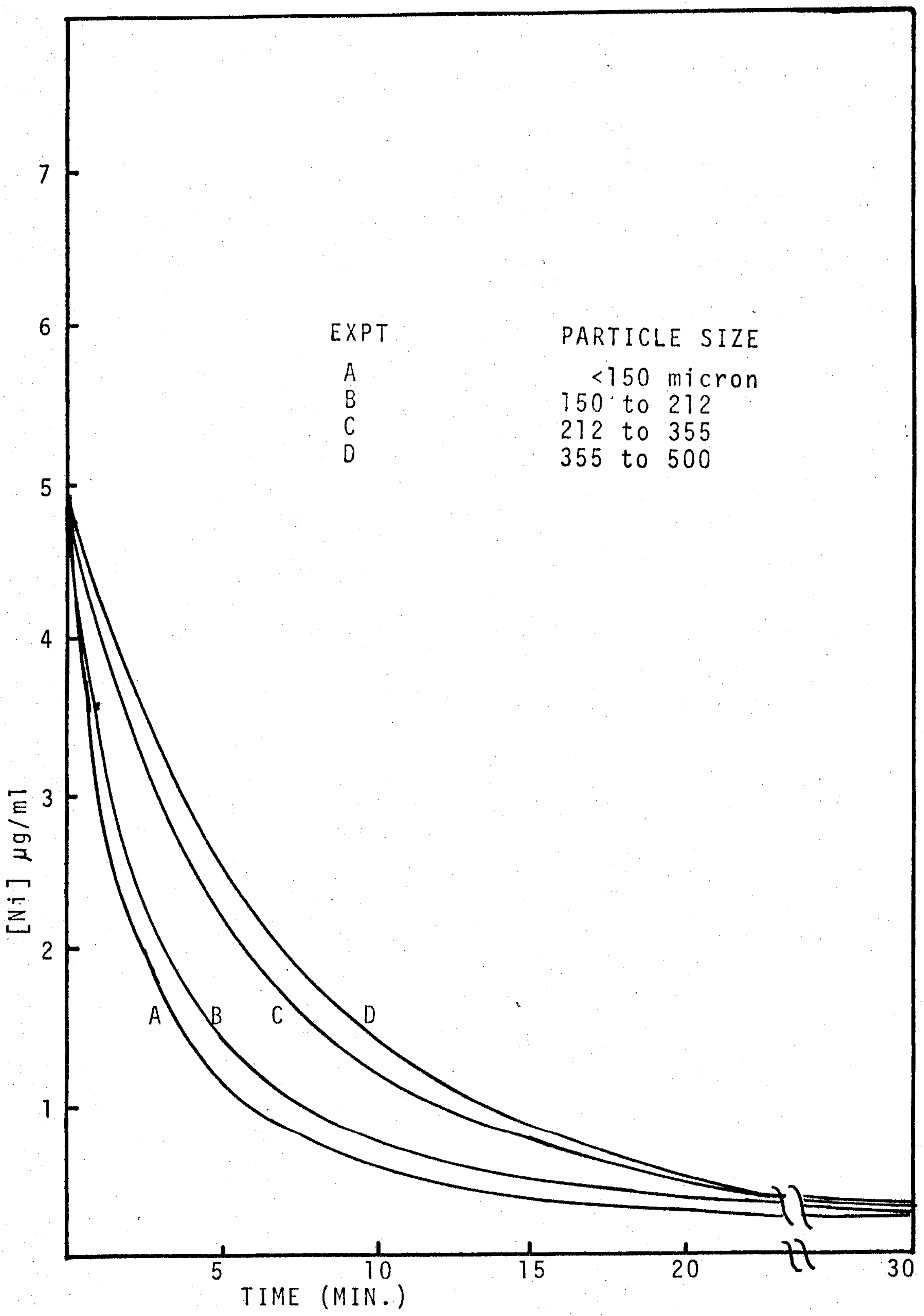

7
6
5
4
3
2
1
[Ni] μg/ml
EXPT
A
B
C
D
PARTICLE SIZE
<150 micron
150 to 212
212 to 355
355 to 500
A
B
C
D
5
10
15
20
30
TIME (MIN.)

Figure 9: F vs. $\sqrt{t}$

Copper (II)

(see Appendix IV)

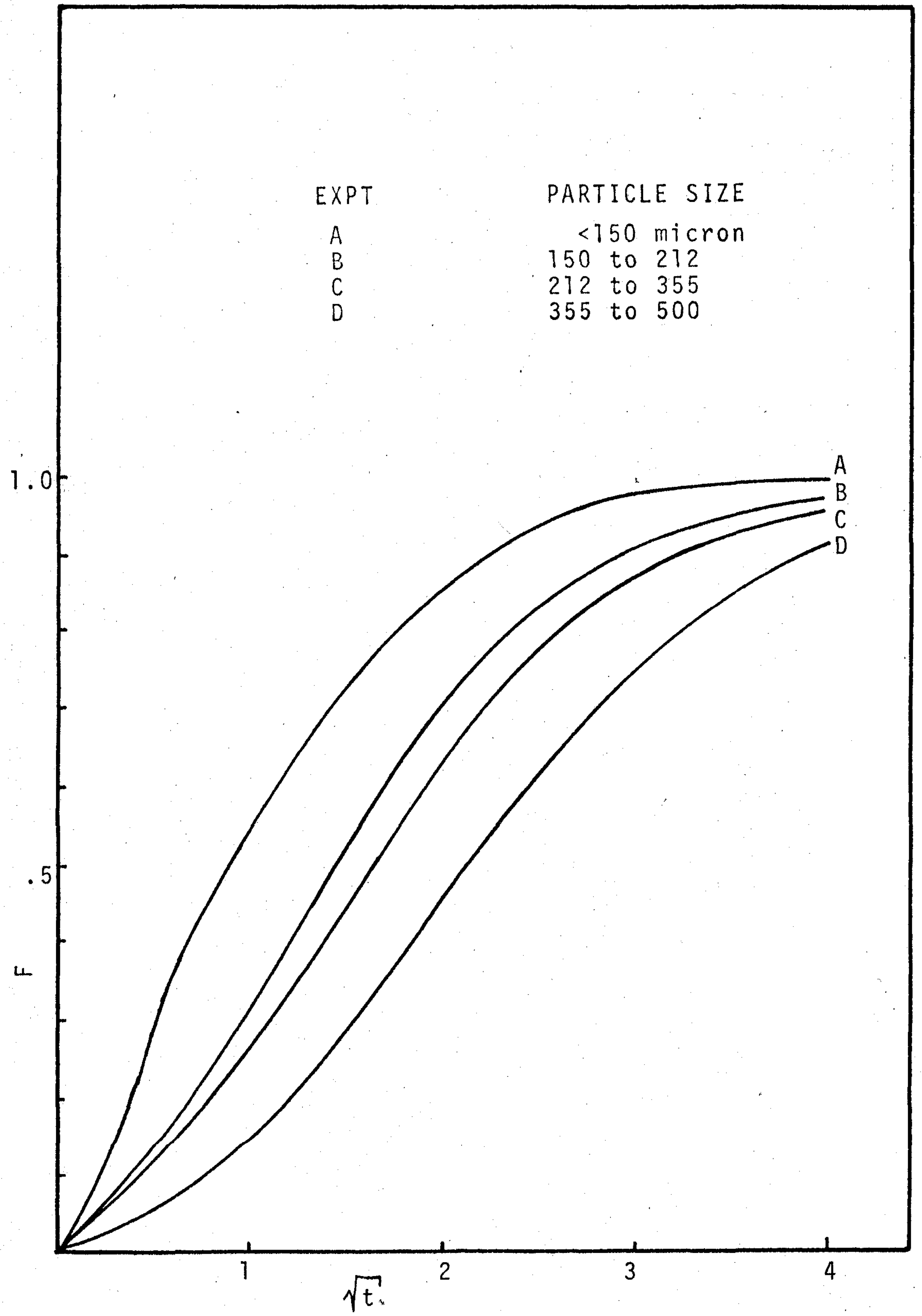

EXPT
PARTICLE SIZE
A
<150 micron
B
150 to 212
C
212 to 355
D
355 to 500
1.0
.5
F
1
2
3
4
√t
A
B
C
D

Figure 10: F vs. $\sqrt{t}$

Nickel (II)

(see Appendix V)

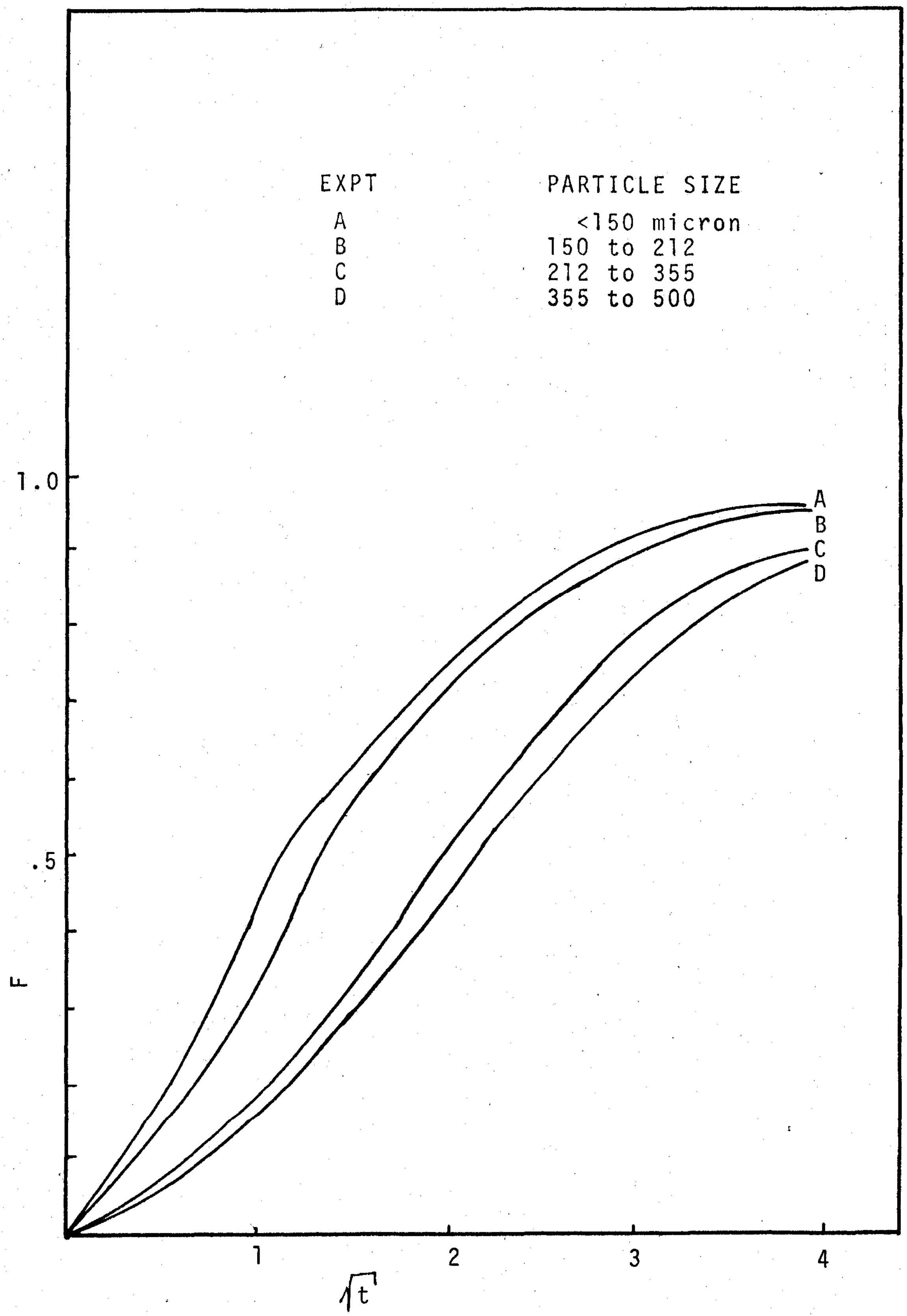

EXPT
PARTICLE SIZE
A
<150 micron
B
150 to 212
C
212 to 355
D
355 to 500
1.0
.5
F
1
2
3
4
√t
A
B
C
D

Figure 11: -log (1-F) vs. t

Copper (II)

(see Appendix IV)

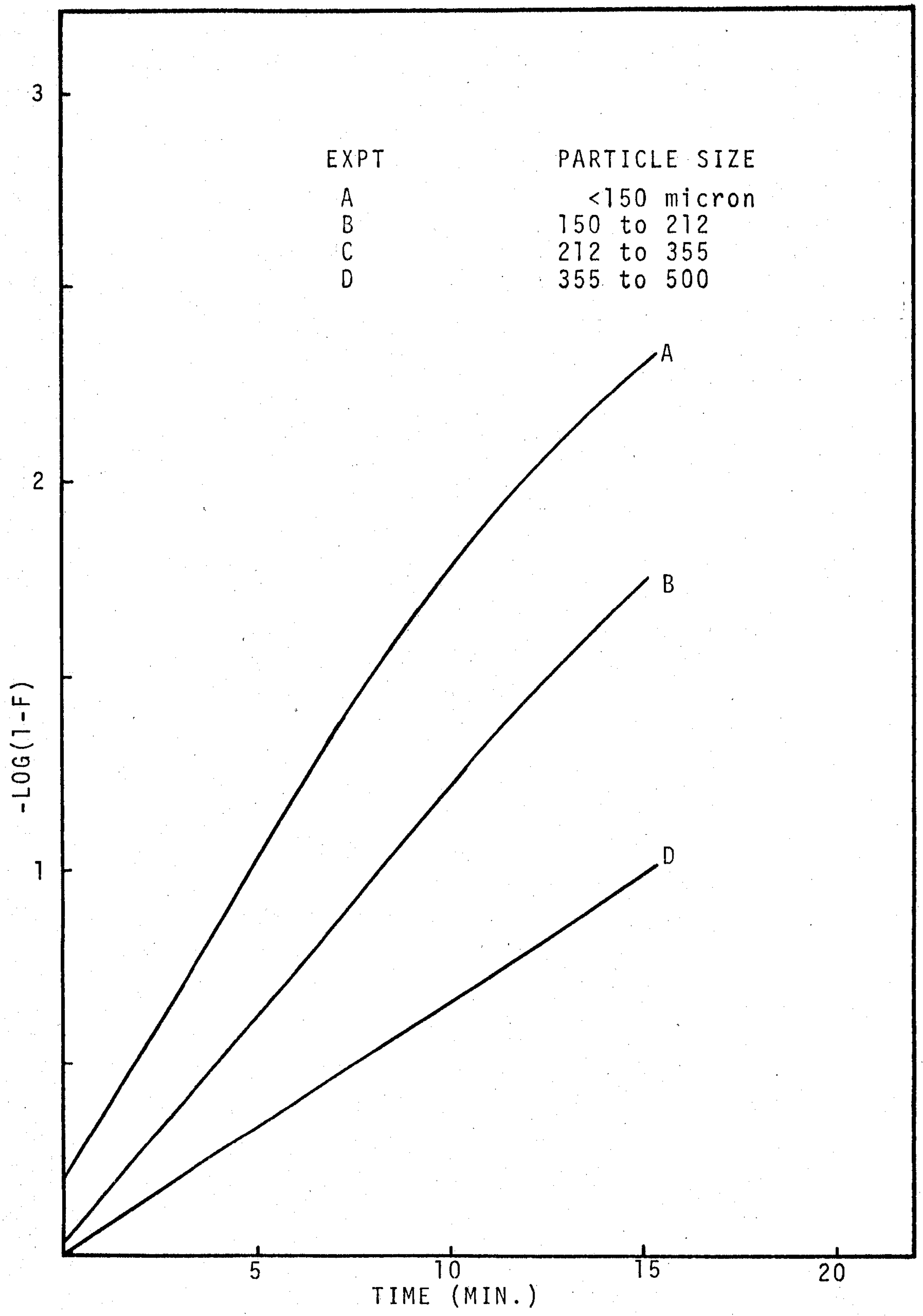

3
2
1
-LOG(1-F)
5
10
15
20
TIME (MIN.)
EXPT
PARTICLE SIZE
A
<150 micron
B
150 to 212
C
212 to 355
D
355 to 500
A
B
D

Figure 12: -log (1-F) vs. t

Nickel (II)

(see Appendix V)

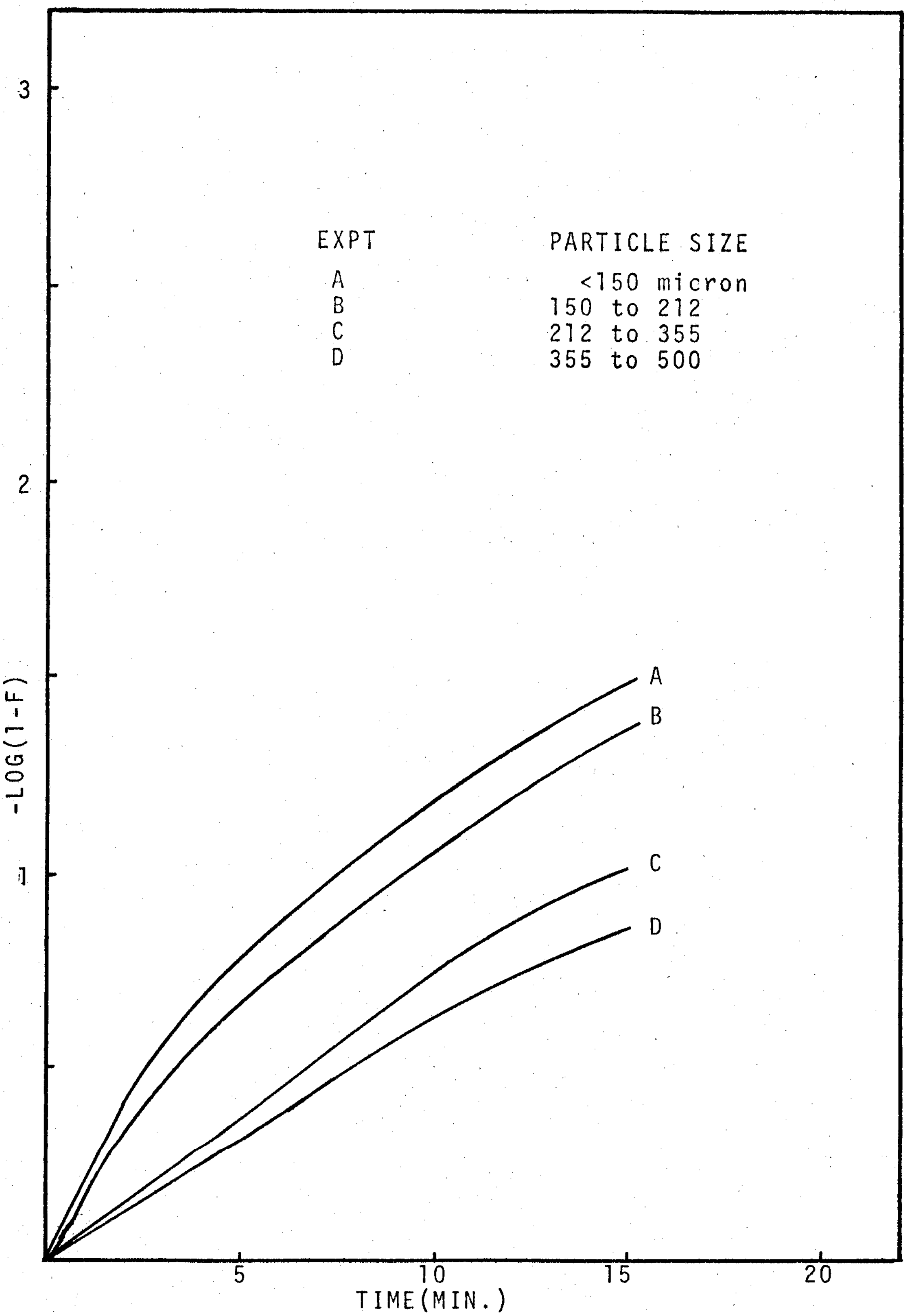
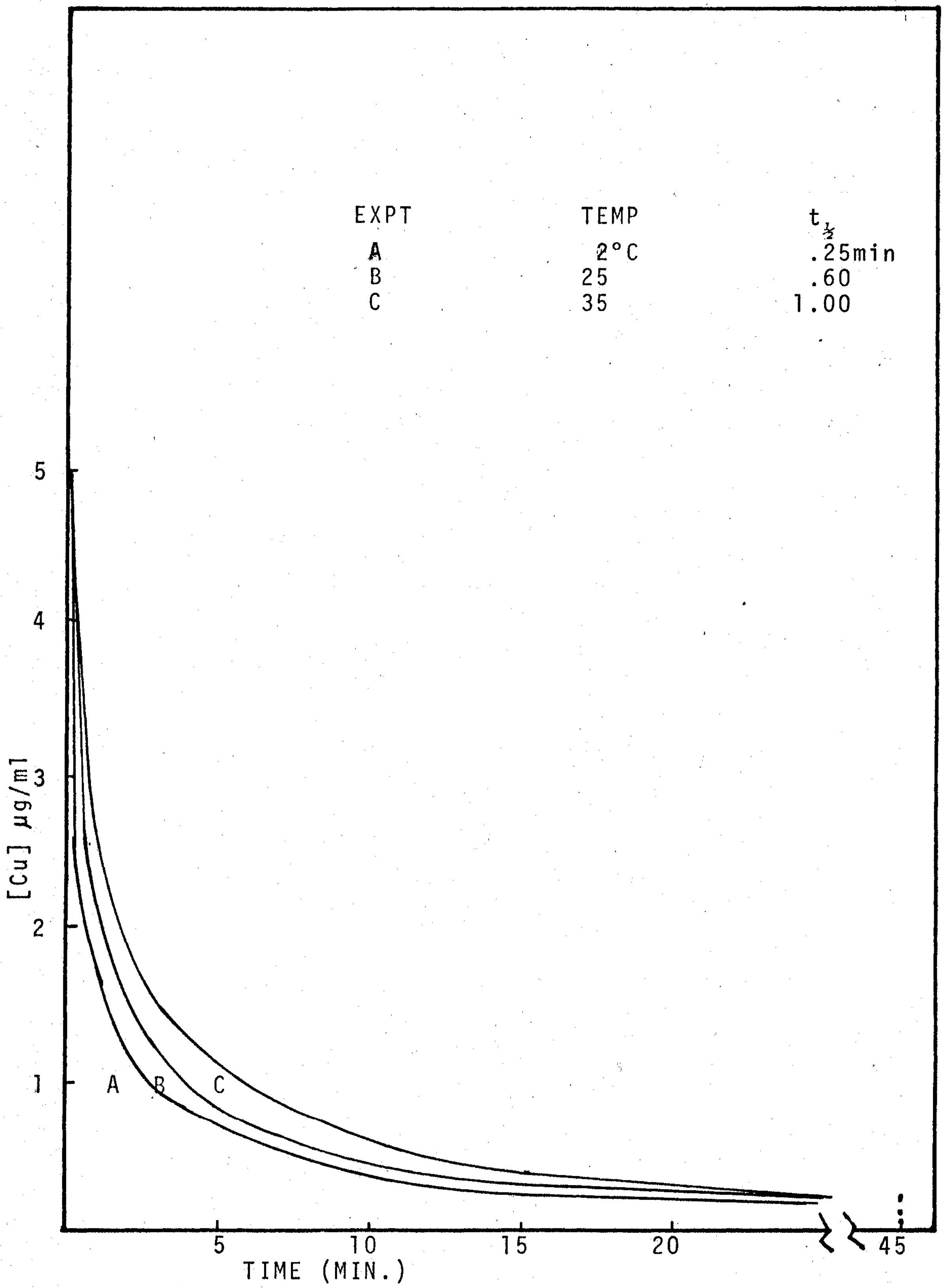

EXPT
PARTICLE SIZE
A <150 micron
B 150 to 212
C 212 to 355
D 355 to 500
3
2
1
-LOG(1-F)
A
B
C
D
5
10
15
20
TIME(MIN.)

Figure 13: Rate f (T)

(see Appendix III)


EXPT TEMP t½
A 2°C .25min
B 25 .60
C 35 1.00
[Cu] µg/ml
1
2
3
4
5
A
B
C
5
10
15
20
45
TIME (MIN.)

controlling mechanism. If equation 2 did fit these experimental results, linearity would be expected up to F = 0.6 or 0.8.

Figures 11 and 12 demonstrate that film diffusion controls the rate of exchange for both copper (II) and nickel (II) except at the <150 micron particle size for nickel (II). The slopes of the graphs are proportional to the effective rate constants. Comparing the slopes for each particle size and corresponding metal ion for the 355 to 500 micron particle size, the slopes and therefore, rate constants are the same for the exchange of nickel (II) and copper (II). This is true for each particle size except the very small <150 micron. Here, the initial slope for nickel (II) is the same as that of copper (II) but decreases quickly. This nonlinearity indicates a change in the rate controlling mechanism, to perhaps, a chemically controlled step. Because the initial slopes are the same, but change during the ion exchange, there are probably a mixture or combination of mechanisms occurring in this particular case.

5. Effect of Temperature: Figure 13 illustrates the minimal effect temperature has on the rate of chelation of copper (II) with CPG-8HOQ. The rate actually increases slightly with a decrease in temperature. This effect indicates a non-trivial mechanism where the rate

law possibly includes an equilibrium constant. The effect of temperature is, however, very small.

The data in Figure 13 have been corrected for the effect temperature has on the measurement of current. Changes in temperature affect the diffusion characteristics at the DME. However, a correction of 1.7 per cent per degree C has been used. The raw data and corrections are shown in Appendix II.

6. Equilibrium Capacity Measurements: By allowing the immobilized 8-HOQ to equilibrate with a slight excess of copper (II) and measuring the amount left in solution, the capacity of the CPG-8HOQ can be determined.

$$\text{capacity} = \frac{Cu_0 - Cu_\infty}{\text{gm CPG-8HOQ}}$$

where Cu_0 and Cu_∞ refer to the number of milligrams or milliequivlents initially and at equilibrium. The results are summarized in Table IV for a variety of immobilized chelate samples.

The capacity of the alkylamine glass was determined to evaluate the effect on capacity of unreacted intermediate products from the synthesis which may be present in the CPG-8HOQ. As indicated in Table IV it does have a small capacity, however this information gives no indication regarding the stability of the complex formed.

Neither does it rule out the possibility of adsorption on the glass particles as does the procedure used for XRF analysis because in that case, the sample was rinsed with buffer solution to remove adsorbed, non-complexed metal ion.

The presence of weakly adsorbed copper (II) in the batch polarographic method also would explain the higher capacity for sample 050572 measured by this method compared to that determined by XRF (1.05 mg Cu/gm).

TABLE IV

Equilibrium Capacity Measurements by Polarography

Sample	Capacity
CPG-Alkylamine	0.324 mg Cu gm^{-1}
050572 CPG-8HOQ	1.38
062974 CPG-8HOQ	1.13
Corning CPG-8HOQ	1.45
Corning CPG-8HOQ	1.47
Corning CPG-EDTA	0.93

CHAPTER IV

KINETICS: FLOW SYSTEM

A. Introduction

For *in situ* preconcentration sampling, the immobilized 8-hydroxyquinoline would be used in a column configuration. It is therefore clear that the optimum flow rate and column configuration should be determined. This set of experiments makes use of one of the recently developed ion specific electrodes which have become commercially available. The particular electrode used here was received without supporting documentation about applications, interferences, etc. It was therefore necessary to first examine the electrode response under conditions used in these experiments. Once characterized, the electrode was used to monitor the copper (II) concentration at the column outlet.

B. Experimental

1. *Instrumentation*: The copper ion specific electrode was obtained from Chemtrix (Model CU800, Seattle, Washington) but was manufactured by Luminon (Los Angeles, Calif.). The millivoltmeter used was an Orion (Cambridge, Mass.) Model 801 digital pH meter. The output of the

meter was connected to a Sargent Model TR strip chart recorder through a Heathkit (Benton Harbor, Mich.) summing amplifier and precision voltage source. The latter was needed to compensate for the offset of -50 millivolts so that recorder sensitivites of 1 and 2 millivolts/inch could be used.

2. Column preparation: Two different size columns were prepared. The 36 mm I.D. glass columns were prepared by tapering one end to seat a frit of porous polyethylene. The 1.6 mm I.D. glass columns were prepared by first fusing on a segment of 3.6 mm I.D. glass to one end and inserting the other into a tapered length of polyethylene tubing fitted with a porous polyethylene frit as shown in Figure 14. Both columns were easily attached to the Tygon tubing flow system using Nylon Swagelock fittings and contained 100 mg. of dry CPG-8HOQ.

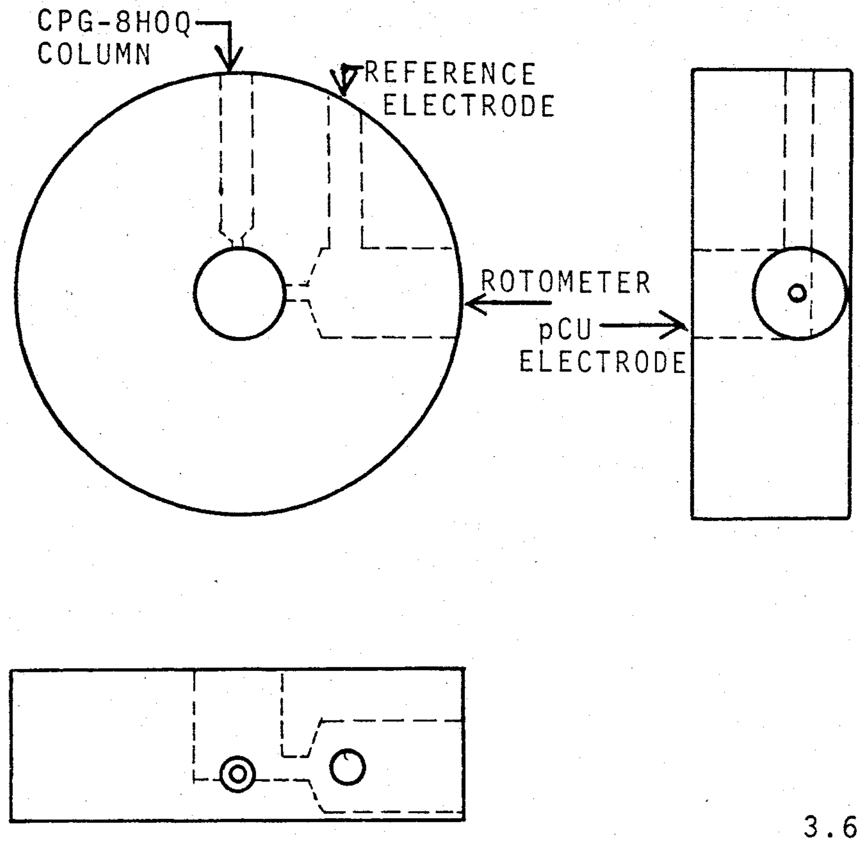
The columns were wet packed by adding 100 mg. of dry CPG-8HOQ to 10 ml of buffer solution. The sample was vacuum degassed as described above to remove air entrapped in the porous glass. An empty disposable polyethylene syringe was attached to the top of the column with a short length of Tygon tubing to act as a funnel. After the CPG-8HOQ had settled, the remaining buffer solution was forced through the column to test for channeling around the porous polyethylene. The column was capped full of buffer to prevent the column from drying or air bubbles forming.

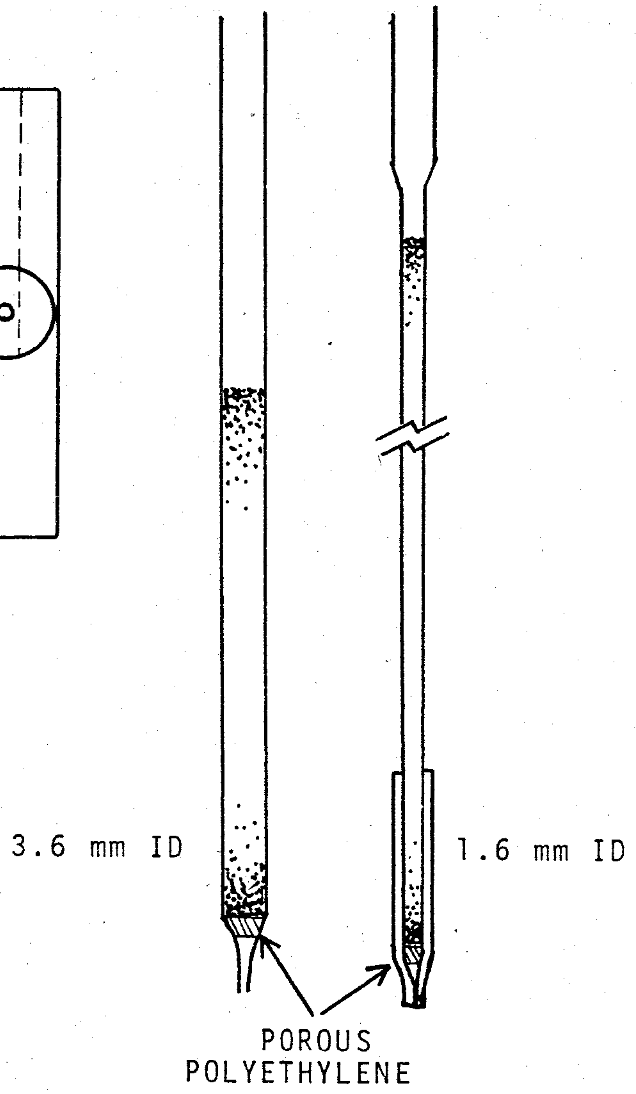
3. Flow cell and electrode holder: The function of the flow cell is to direct the flow from the column over the surface of the ion specific electrode and the reference electrode junction. Several configurations were tried, the major difficulties being reduction of the sample volume at the specific ion electrode while maintaining unrestricted flow, and the prevention of bubble accumulation. Figure 14 shows the flow cell configuration used for the data taken in the subsequent experiments. The volume of the sampling cell is 0.0785 cm^3 when the electrode is 1.0 mm from the back surface. A saturated calomel reference electrode was connected to the cell via a double junction saturated KCl salt bridge.

4. Rate control and Measurement: The flow rate was controlled using a Masterflex variable speed peristaltic pump (Cole Parmer, Chicago, Ill.) and was measured with a rotometer (Ace Glass Co., Vineland, N. J.).

5. Reagents and Solutions: Phosphate buffers were prepared in 25 liter quantities from reagent grade K_2HPO_4 and KH_2PO_4 with a pH = 6.7 and $\mu = 0.1$ M. Copper (II) solutions were prepared by adding a measured volume of the previously described stock solution to a one liter volumetric flask and diluting to volume with buffer solution.

Figure 14: Flow Cell
and Columns


CPG-8HOQ COLUMN
REFERENCE ELECTRODE
ROTOMETER
pCU ELECTRODE


3.6 mm ID
1.6 mm ID
POROUS POLYETHYLENE

Fresh copper (II) solutions were prepared for each experiment.

A solution of Instant Ocean (Aquarium Systems, Eastlake, Ohio) which is synthetic mixture intended to simulate sea water, was prepared according to instructions and substituted for the buffer solution in the indicated experiment.

6. Procedures: While determining the electrode response to various experimental factors, an empty column was used in the flow system diagramed in Figure 15. Buffer solution was pumped through the system until a stable baseline at -50 to -70 millivolts was established. The stopcock was rotated to change over to the copper solution and the electrode response observed. This procedure was repeated during each subsequent experiment prior to the use of a packed column.

The blank column was then exchanged for a packed column and rinsed with buffer solution until a stable baseline was established. The copper (II) solution was then pumped through the system and the electrode response observed.

C. Results

1. Cell Design: The first objective was to obtain a fast electrode response, which necessitated reducing the

cell volume to a minimum. Figure 16 shows a comparison of the electrode response with an earlier cell design with the flow cell used here and which is described in Figure 14. Using the copper ion selective electrode in the horizontal position eliminated the problem of air bubbles accumulating on the electrode surface which would interfere with its response.

2. Electrode Response: The electrode, which is of the solid state epoxy type, required several days to equilibrate in buffer solution after it was first received. Even then, significant variations in response were observed.

Day to day variations in electrode response included changes in both relative and absolute response. Figure 17 shows extremes in the variation in relative electrode response to copper (II) solutions of the same concentration. While small variations of this type could be caused by solutions of different concentrations, variations of the magnitude of 20 to 30% are attributed to changes in the response of the electrode.

Absolute variations were observed where the baseline for the same buffer solution was from -30 to -80 millivolts. No relationship was observed between the relative and absolute variations.

Short term variations in the repeatability of the electrode response using the same solutions were just a

Figure 15: Flow System

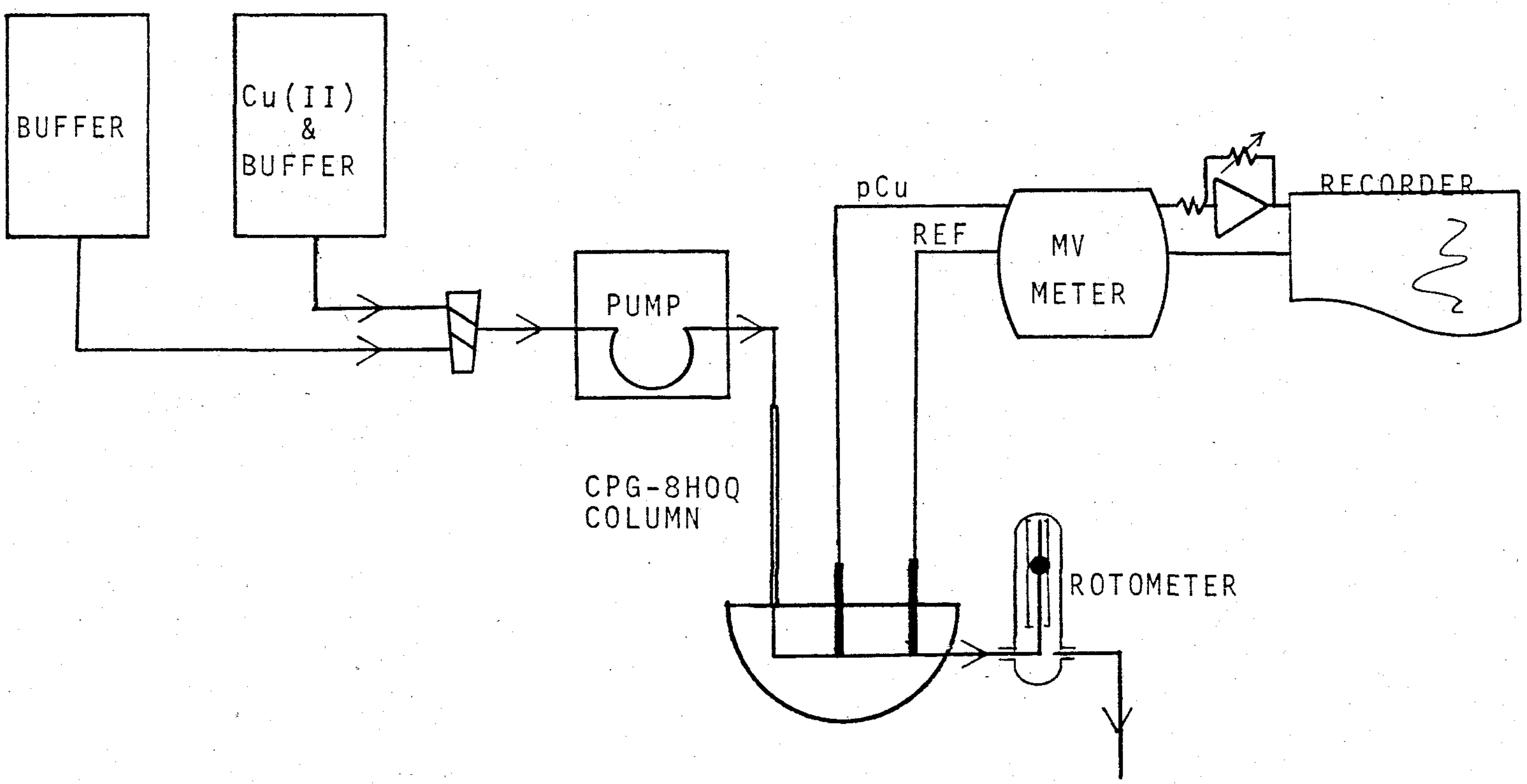

BUFFER
Cu(II) & BUFFER
PUMP
CPG-8HOQ COLUMN
pCu
REF
MV METER
RECORDER
ROTOMETER

Figure 16: Electrode Response

f (cell volume)

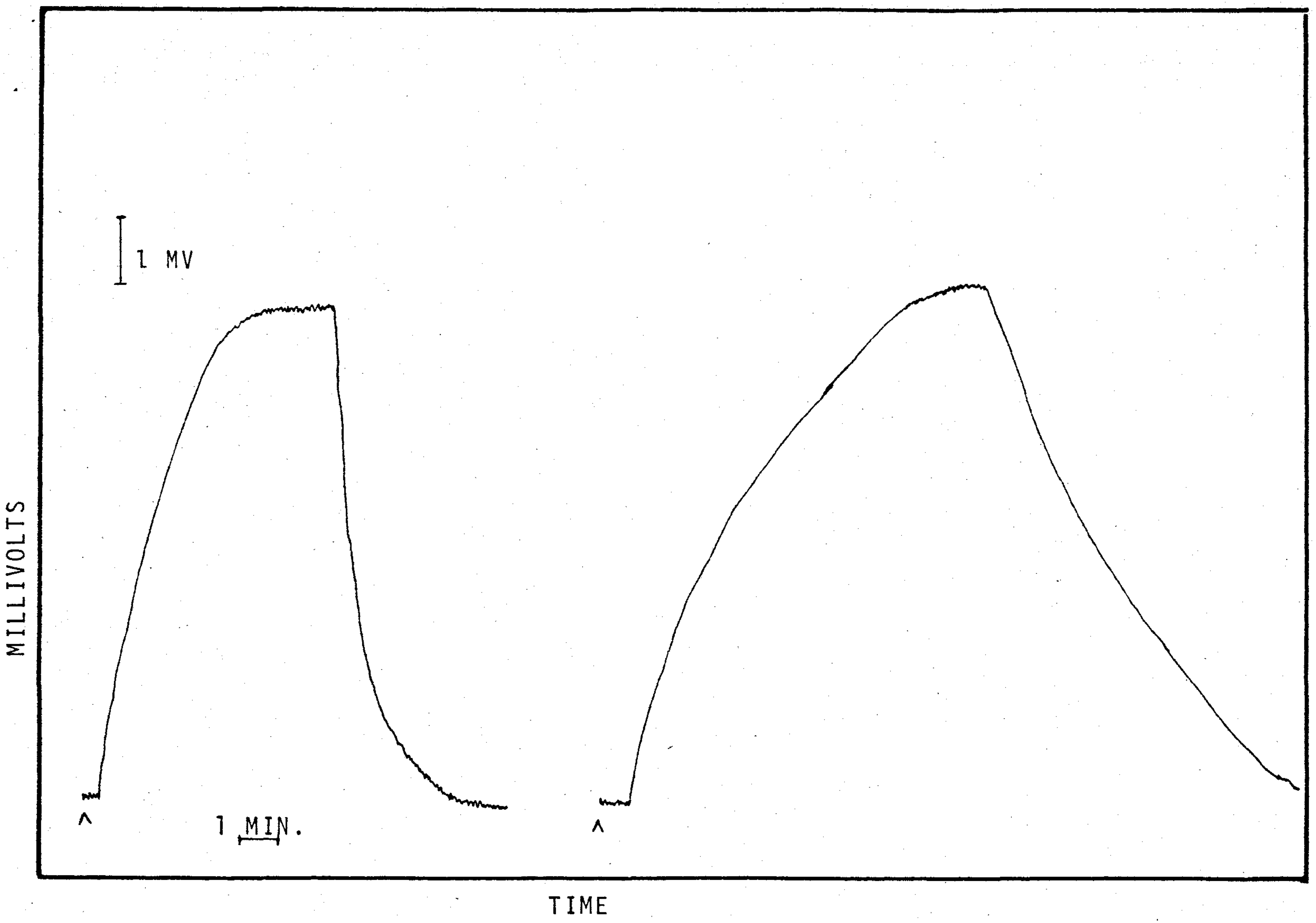

1 MV
1 MIN.
^
^
MILLIVOLTS
TIME

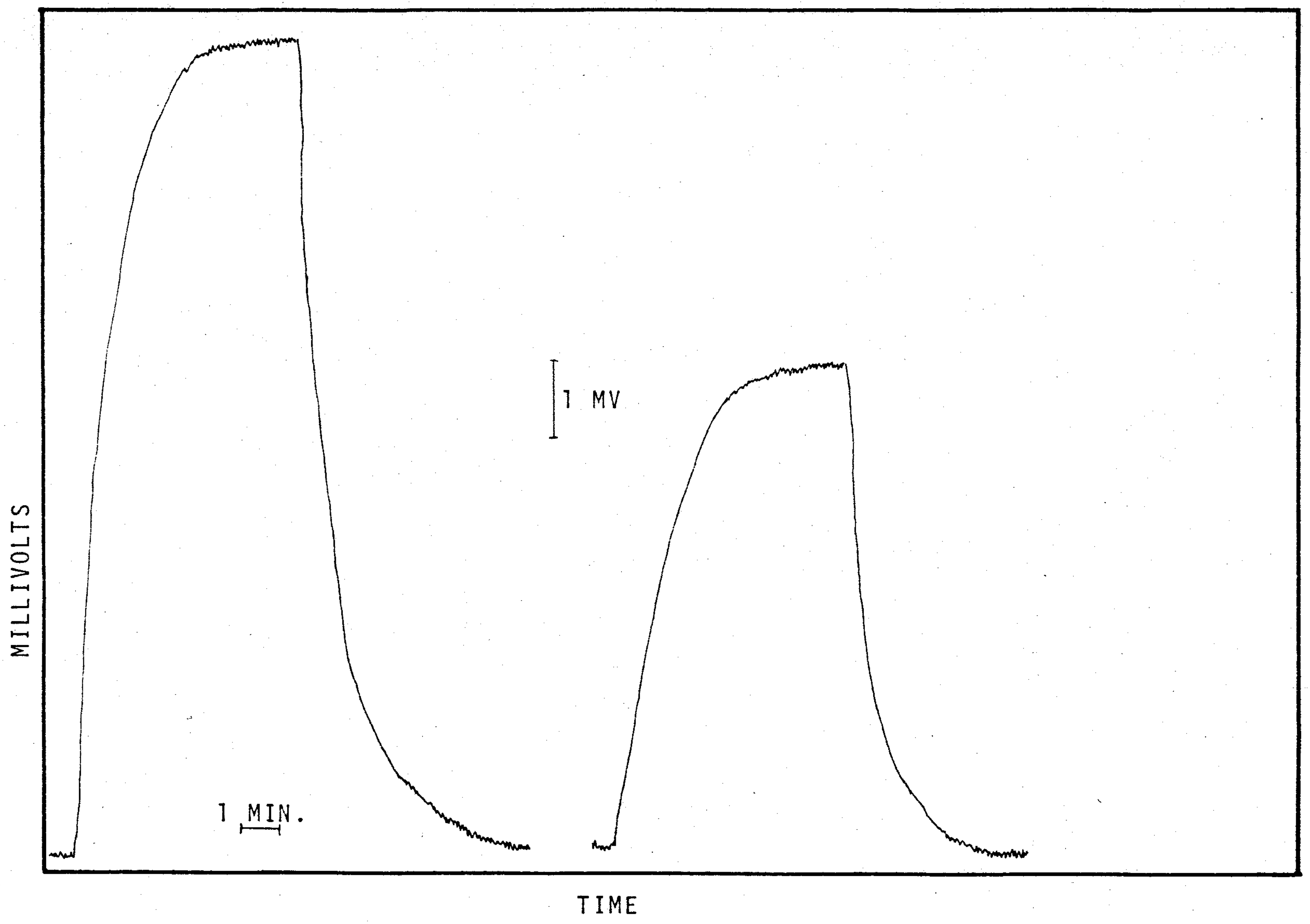
Figure 17: Electrode Response

Relative Variations

[Cu] = 5 ppm

pH = 6.0

μ = 0.1


1 MV
1 MIN.
MILLIVOLTS
TIME

few per cent. This effect is shown in Figure 18 where solutions of copper (II) and buffer were alternately cycled. The electrode response is logrithmic with concentration as shown in Figure 19. A calibration curve provided with the electrode indicated linear log response over three decades of concentration.

Flow rate had two measurable effects. Higher flow rates resulted in more rapid changeover in the solution in the sample cell which had the effect of increasing the rise time of the electrode response without affecting the absolute, or equilibrium response in the same way as cell volume. The other effect of increased flow rate was to reduce the dead time between changeover of solutions. The volume of tubing through the pump between the stopcock and column were kept to a minimum and so dead times were kept below 1.5 minutes.

Information about interfering ions was not provided by the supplier. Epoxy-type electrodes have been found to be susceptable to interference from Ag^+, Cl^-, Br^-, and I^- and give erratic response in solutions of low ionic strength (Olson (1975)). None of these interferences were encountered in experiments using the buffer solutions but in using the synthetic sea water, Cl^- caused considerable interference which made the use of this electrode impractical in this application.

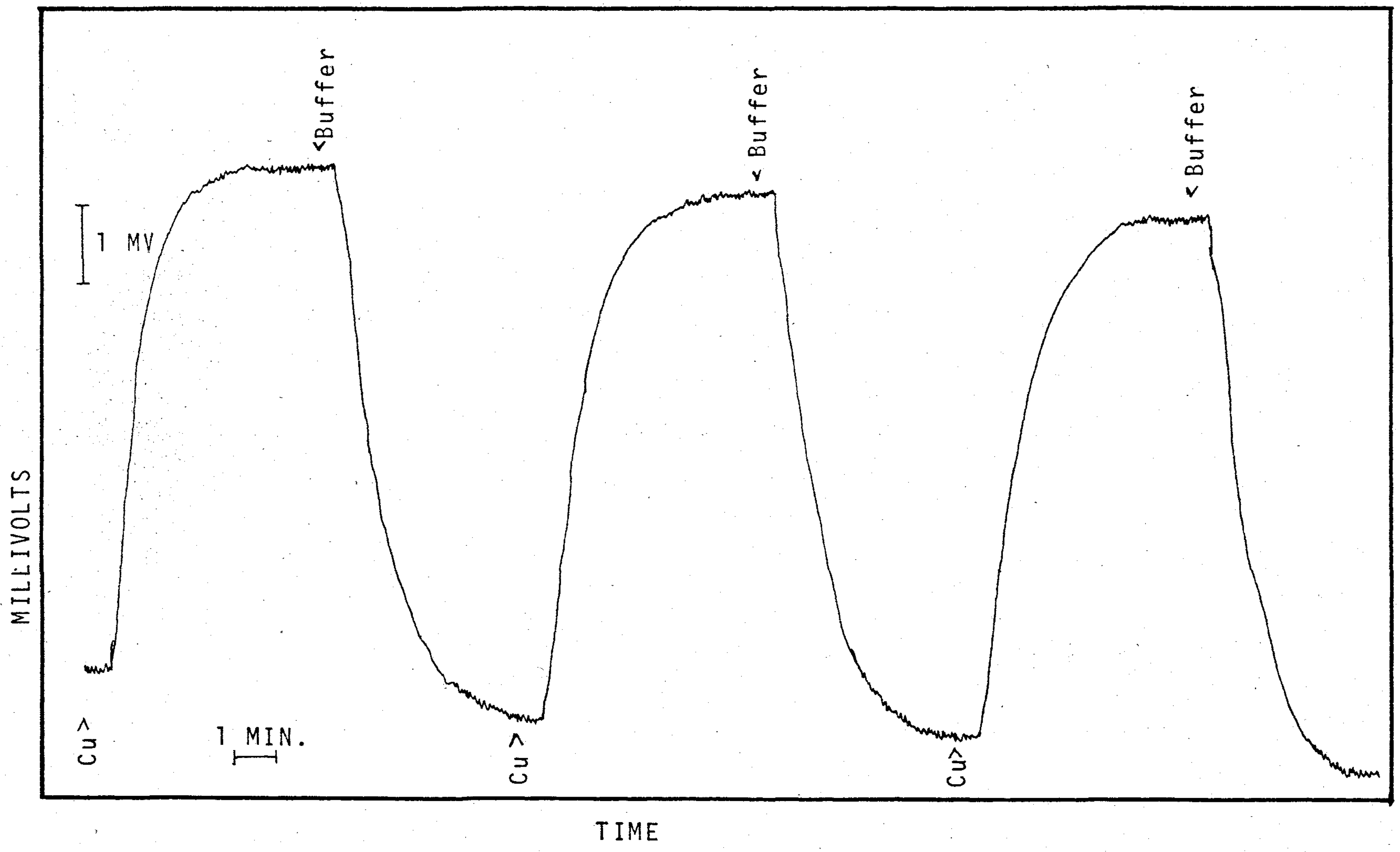
Figure 18: Electrode Response

Repeatability

[Cu] = 1 ppm

pH = 6.7

$\mu = 0.1$



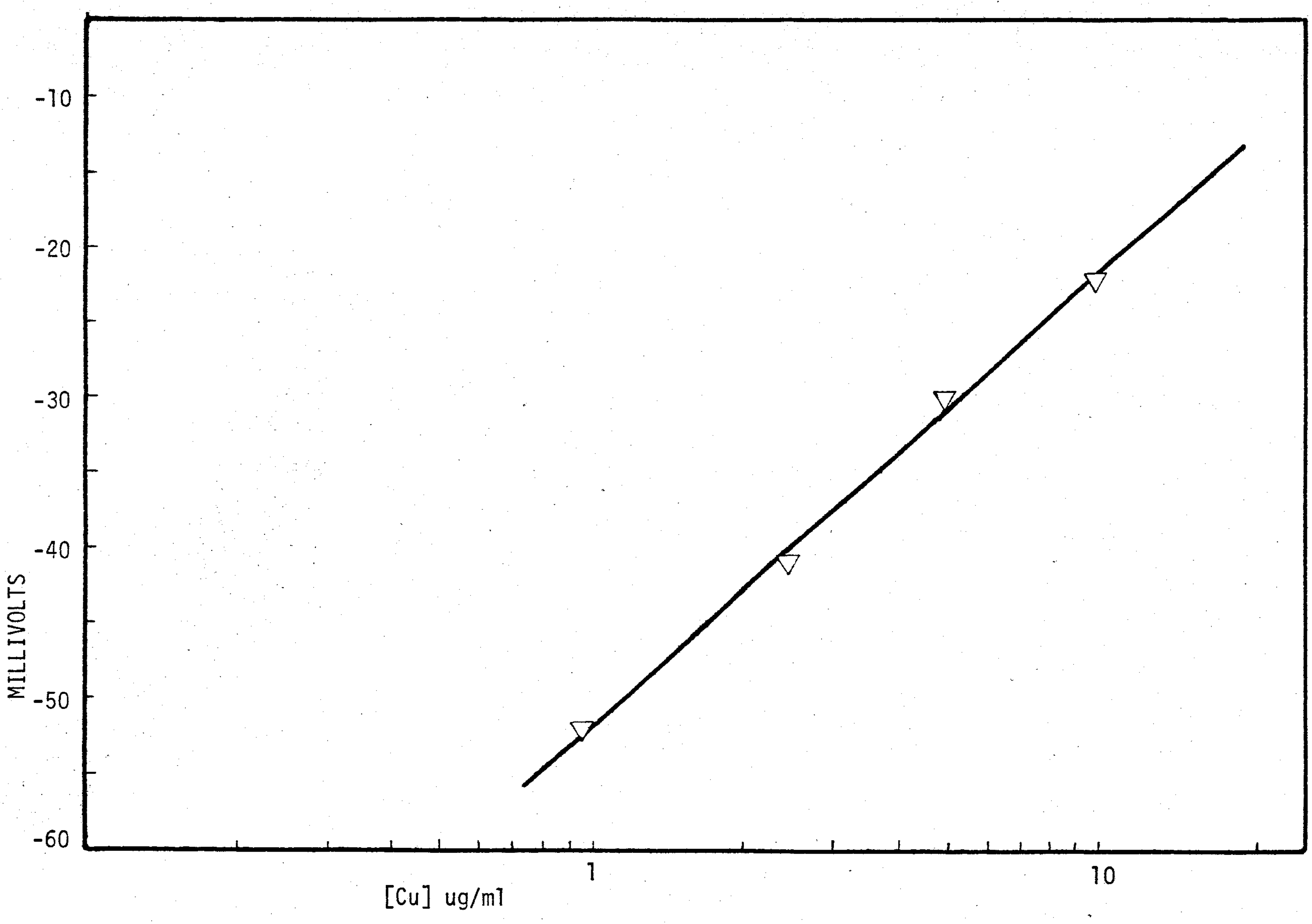
<Buffer
< Buffer
< Buffer
1 MV
MILLIVOLTS
Cu>
1 MIN.
Cu>
Cu>
TIME

Figure 19: Electrode Response

f [m]

pH = 6.0

μ = 0.1


-10
-20
-30
-40
-50
-60
MILLIVOLTS
1
10
[Cu] ug/ml

The continued use of an empty column prior to a packed column in subsequent experiments was necessary for several reasons. First, because of the previously described variations in the electrode response, a calibrated maximum response had to be determined for each experiment. This gave the maximum response expected and could be used as a comparison for determining at what point the CPG-8HOQ was saturated with copper (II). The second reason for calibration with an empty column was to determine the dead time for each experiment. This was then subtracted from the overall time measured for the time response of the electrode when the packed column was used. Figure 20 shows typical tracings of an experiment; the calibration curve with the empty column and the experimental curve using a packed column.

Table V summarizes the results of different column configurations, flow rates and particle sizes which have been corrected for dead time. As would be expected, smaller particle size increases the extraction efficiency for an equal quantity of CPG-8HOQ. The 150 to 212 micron material was therefore used for the remaining experiments where column diameter and flow rates were altered.

Decreasing column diameter had little effect in increasing extraction efficiency and was determined to be a disadvantage. The resulting longer column length resulted

Figure 20: Experiment
No. 03047502

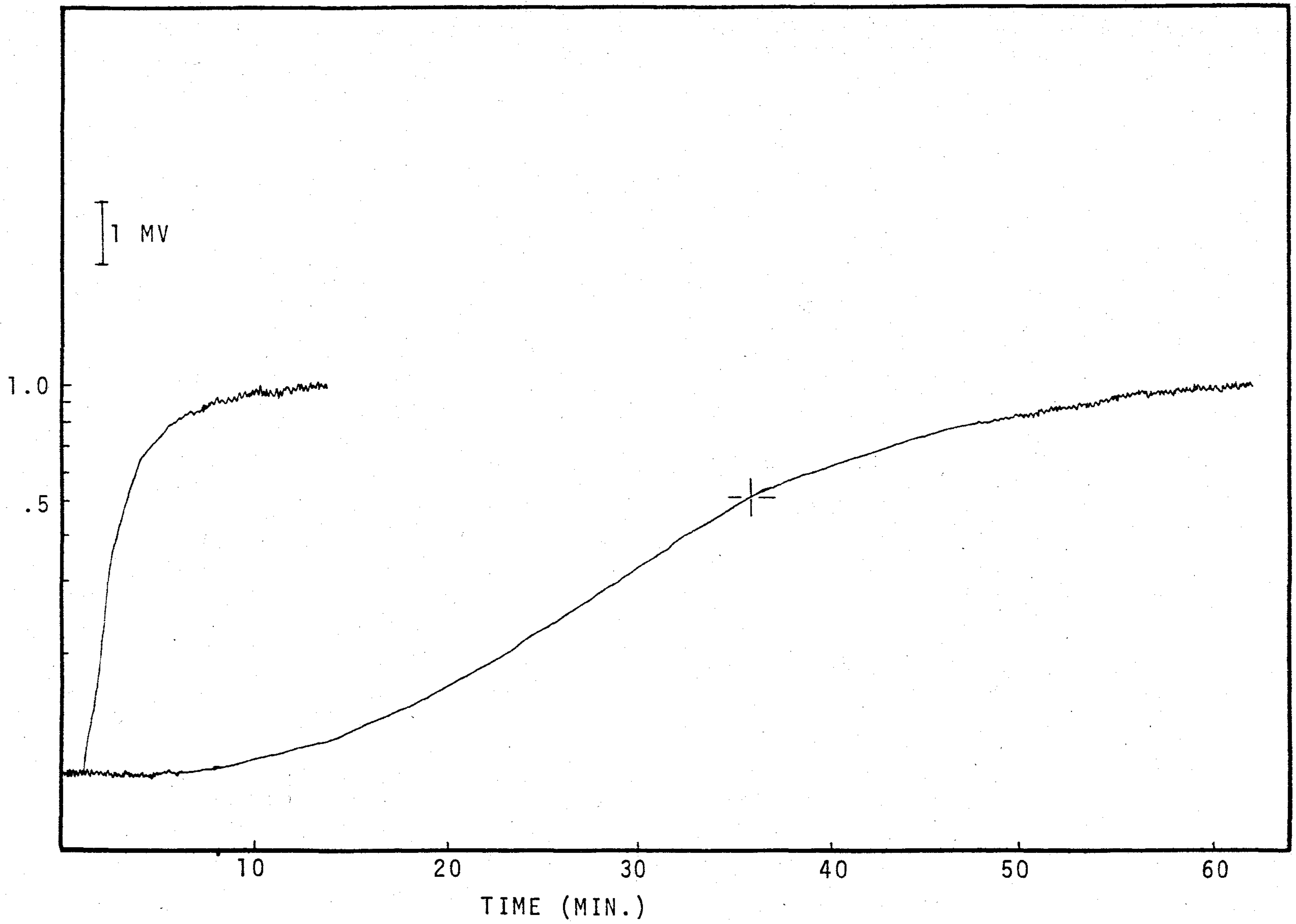

1 MV
1.0
.5
10
20
30
40
50
60
TIME (MIN.)

TABLE V

Column, Particle Size and Flow Conditions

Column	Particle Size	Flow	t_{50}
1.6 mm ID	355 to 500 micron	5.5 ml/min.	3 min.
1.6 mm ID	212 to 355	5.5 ml/min.	11 min.
1.6 mm ID	150 to 212	5.5 ml/min.	33 min.
1.6 mm ID	150 to 212	2.5 ml/min.	42 min.
3.6 mm ID	150 to 212	5.5 ml/min.	9 min.

in higher pressure drop through the column so that flow rates grater than 5.5 ml/min were beyond the capacity of the pump used in these experiments.

CHAPTER V

APPLICATION OF GLASS IMMOBILIZED 8-HYDROXYQUINOLINE TO IN SITU PRECONCENTRATION SAMPLING

Trace metal ions in natural water sources are found in a soup rich in organics where they are highly complexed with both organic and inorganic complexing agents. Much recent work has been directed at determining the speciation of trace metals for purposes of describing the properties of sea water and determining biological availability of those trace metals. Anodic stripping voltammetry has been used to characterize trace metal complexes in aquatic samples (Chau (1973); Chau, and Lum-Shue-Chan (1974); Allen, Matson, and Mancy (1970); Schrimff (1971)). These methods require the addition of reagents which radically alter the character of the metals analyzed. Even for the determination of labile metals, electrolyte must be added and oxygen removed in order to carry out the analysis. This changes the ionic strength, anion concentration and, because CO_2 is displaced along with oxygen by nitrogen, the pH of the solution. A four electrode system has been devised to eliminate deoxygenation and is a partial improvement (Schrimff (1971)) but the other affects are still present. Strongly complexed metals are determined by a variety of preliminary acid digestion methods with subsequent analysis by anodic stripping voltammetry.

The CPG-8HOQ will be useful not only for trace metal analysis, but will also give an indication of speciation when used in conjunction with a total metal analysis. Without adding any additional chemicals or otherwise altering the character of the trace metals prior to sampling, the CPG-8HOQ will complex only with metals from complexes less stable than the CPG-8HOQ/metal complex. Total metal concentration could be determined _in situ_ using a column of CPG-8HOQ followed by a column of activated carbon (Boczkowski (1973)). A column of activated carbon would adsorb the metal complexes too stable to be converted to the CPG-8HOQ complex. Using this as a functional differentiation between labile and stable complexes, the labile metals would be determined on CPG-8HOQ, the stable complexes on activated carbon, and the total would be the sum of these two.

The results of the kinetics experiments has made it possible to identify the best conditions for using the CPG-8HOQ for trace metal preconcentration sampling. Flow will have to be between 2 and 5 ml/min. This represents a compromise between the very high flow rates required to minimize the film diffusion layer thickness, therefore the observed exchange rate, and the necessary time the solution must be in contact with the immobilized chelating agent.

Small particle size is desirable for increasing the extraction efficiency but is limited by the high pressure drop across a column that results with very small particles of CPG-8HOQ. The 150 to 212 micron particle size has good flow characteristics when used in columns under 10 cm. long and with the low pressure pumping system. The 100 mg. of CPG-8HOQ sample provided a high enough preconcentration factor in the single element studies to be easily analyzed by x-ray fluorescence. Larger sampling matrices may be desirable for multi-element preconcentrations.

Two difficulties which were encountered but not identified at the time of the field studies have been eliminated from further work. The columns for the field study were packed dry without pretreatment to remove entrapped air from the porous glass. Failure to do so resulted in the solution not wetting the entire surface and so not preventing its complexation with the metal ions in solution. Conclusions drawn from the work of Turse and Reiman (1961) indicating that the slow step in the exchange kinetics would be the chemical reaction and that that reaction is fast, resulted in the use of optimistically high flow rates (15 to 20 ml/min) in the field studies. On the basis of the kinetic experiments presented here, more realistic flow rates have been suggested.

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APPENDIX I

Data and Calculations for Calibration Curves

```
                CONC(μg/ml)        I (μamps)         W FACTOR        CALC'D CONC
     EXPT:
     01027501
     1          0.0              0.0              1.000000        0.001046
     2          0.499800         0.046000         1.000000        0.039962
     3          0.999900         0.084000         1.000000        0.078901
     4          1.497999         0.120000         1.000000        0.117684
     5          1.995999         0.156000         1.000000        0.156460
     6          2.493999         0.195000         1.000000        0.195235
     7          2.990000         0.212000         1.000000        0.233855
     8          3.488000         0.270000         1.000000        0.272631
     9          3.980000         0.308000         1.000000        0.310939
    10          4.480000         0.354000         1.000000        0.349871
    11          4.974999         0.400000         1.000000        0.388412
 NO. OF POINTS     11

 INTERCEPT      0.1046E-02        STD DEV   0.2937E-02

 SLOPE          0.7786E-01        STD DEV  0.1707E-02

 OVERALL STD DEV              0.8905E-02


     EXPT:
    02037501
    1          0.0              0.0              1.000000        0.063080
    2          0.499800         0.103500         1.000000        0.112556
    3          0.999900         0.150000         1.000000        0.162062
    4          1.497999         0.206000         1.000000        0.211370
    5          1.995999         0.262000         1.000000        0.260668
    6          2.493999         0.316000         1.000000        0.309967
    7          2.990000         0.381000         1.000000        0.359067
    8          3.488000         0.460000         1.000000        0.408365
    9          3.980000         0.488000         1.000000        0.457069
   10          4.480000         0.536000         1.000000        0.506565
   11          4.974999         0.611200         1.000000        0.555566
   12          5.964000         0.632000         1.000000        0.653469
   13          6.457999         0.684000         1.000000        0.702372
   14          6.950000         0.728000         1.000000        0.751076
   15          7.443999         0.784000         1.000000        0.799978
   16          7.936999         0.848000         1.000000        0.848781
   17          8.429999         0.880000         1.000000        0.897584
   18          8.919999         0.936000         1.000000        0.946090
 NO. OF POINTS     18

 INTERCEPT      0.6308E-01        STD DEV   0.8002E-02

 SLOPE          0.9899E-01        STD DEV  0.2540E-02

 OVERALL STD DEV              0.2993E-01
```

```
                 CONC(µg/ml)      I (µamps)        W FACTOR          CALC'D CONC
     EXPT:
      01257501
       1         0.0              0.0              1.000000          0.010829
       2         0.250000         0.035000         1.000000          0.033719
       3         0.499800         0.058000         1.000000          0.056591
       4         0.749400         0.085000         1.000000          0.079444
       5         0.999900         0.109000         1.000000          0.102380
       6         1.247999         0.135000         1.000000          0.125096
       7         1.497999         0.157000         1.000000          0.147986
       8         1.750000         0.196000         1.000000          0.171059
       9         1.995999         0.212000         1.000000          0.193583
      10         2.245000         0.210000         1.000000          0.216381
      11         2.493999         0.228000         1.000000          0.239179
      12         2.493999         0.222000         1.000000          0.239179
      13         2.740000         0.246000         1.000000          0.261703
      14         2.990000         0.270000         1.000000          0.284593
      15         3.240000         0.318000         1.000000          0.307483
      16         3.488000         0.328000         1.000000          0.330190
      17         3.735999         0.362000         1.000000          0.352897
      18         3.980000         0.374000         1.000000          0.375237
      19         4.231999         0.400000         1.000000          0.398311
      20         4.480000         0.424000         1.000000          0.421017
      21         4.730000         0.450000         1.000000          0.443907
      22         4.730000         0.412000         1.000000          0.443907
      23         4.974999         0.448000         1.000000          0.466340
      24         5.230000         0.492000         1.000000          0.489687
      25         5.469999         0.504000         1.000000          0.511662
      26         5.716999         0.536000         1.000000          0.534277
      27         5.964000         0.548000         1.000000          0.556892
      28         6.457999         0.616000         1.000000          0.602123
      29         6.950000         0.640000         1.000000          0.647170
      30         7.443999         0.700000         1.000000          0.692401
      31         7.936999         0.748000         1.000000          0.737540
      32         8.429999         0.788000         1.000000          0.782679
      33         8.919999         0.832000         1.000000          0.827543
  NO. OF POINTS       33

  INTERCEPT        0.1083E-01        STD DEV    0.2328E-02

  SLOPE            0.9156E-01        STD DEV   0.8613E-03

  OVERALL STD DEV              0.1200E-01
```

```
              CONC(µg/ml)       I  (µamps)        W FACTOR         CALC'D CONC
    EXPT:
    02037502
    1         0.0               0.0               1.000000         0.001658
    2         0.999000          0.120000          1.000000         0.103705
    3         1.995999          0.200000          1.000000         0.205546
    4         2.990000          0.290000          1.000000         0.307082
    5         3.980000          0.400000          1.000000         0.408209
    6         4.969999          0.520000          1.000000         0.509336
    7         5.964000          0.624000          1.000000         0.610872
    8         6.950000          0.704000          1.000000         0.711590
NO. OF POINTS        8

INTERCEPT       0.1658E-02        STD DEV    0.5088E-02

SLOPE           0.1021E 00        STD DEV   0.2009E-02

OVERALL STD DEV              0.1292E-01


    EXPT:
    02187501
    1         0.0               0.0               1.000000        -0.002573
    2         0.499800          0.054000          1.000000         0.048971
    3         0.999900          0.111000          1.000000         0.100545
    4         1.497999          0.150000          1.000000         0.151913
    5         1.995999          0.195000          1.000000         0.203271
    6         2.493999          0.238000          1.000000         0.254629
    7         2.990000          0.290000          1.000000         0.305781
    8         3.488000          0.363000          1.000000         0.357139
    9         3.980000          0.426000          1.000000         0.407878
   10         4.480000          0.460000          1.000000         0.459442
NO. OF POINTS       10

INTERCEPT      -0.2573E-02        STD DEV    0.4151E-02

SLOPE           0.1031E 00        STD DEV   0.2597E-02

OVERALL STD DEV              0.1174E-01
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```
               CONC(µg/ml)      I(µamps)         W FACTOR          CALC'D CONC
    EXPT:
     03027501,06
      1          0.0             0.0              1.000000          0.013334
      2          0.499000        0.070000         1.000000          0.062056
      3          1.000000        0.117600         1.000000          0.110973
      4          1.500000        0.165000         1.000000          0.159793
      5          2.000000        0.212000         1.000000          0.208613
      6          2.490000        0.254000         1.000000          0.256456
      7          2.990000        0.302000         1.000000          0.305276
      8          3.490000        0.342000         1.000000          0.354095
      9          3.980000        0.392000         1.000000          0.401939
     10          4.480000        0.450000         1.000000          0.450758
     11          0.0             0.0              1.000000          0.013334
     12          0.499000        0.058000         1.000000          0.062056
     13          1.000000        0.116000         1.000000          0.110973
     14          1.500000        0.164000         1.000000          0.159793
     15          2.000000        0.216000         1.000000          0.208613
     16          2.490000        0.273000         1.000000          0.256456
     17          2.990000        0.305000         1.000000          0.305276
     18          3.490000        0.359000         1.000000          0.354095
     19          3.980000        0.398000         1.000000          0.401939
     20          4.480000        0.453000         1.000000          0.450758
 NO. OF POINTS     20

 INTERCEPT       0.1333E-01        STD DEV    0.2042E-02

 SLOPE           0.9764E-01        STD DEV   0.1275E-02

 OVERALL STD DEV             0.8151E-02


    EXPT:
     03037501
      1          0.0             0.0              1.000000          0.004394
      2          0.499000        0.060000         1.000000          0.056144
      3          1.000000        0.110000         1.000000          0.108102
      4          1.500000        0.173000         1.000000          0.159956
      5          2.000000        0.208000         1.000000          0.211810
      6          2.490000        0.254000         1.000000          0.262626
      7          2.990000        0.298000         1.000000          0.314480
      8          3.490000        0.372000         1.000000          0.366334
      9          3.980000        0.426000         1.000000          0.417151
 NO. OF POINTS      9

 INTERCEPT       0.4394E-02        STD DEV    0.3678E-02

 SLOPE           0.1037E 00        STD DEV   0.2554E-02

 OVERALL STD DEV             0.9848E-02
```

```
            CONC(µg/ml)     I  (µamps)       W FACTOR          CALC'D CONC
   EXPT:
    03037505
    1        0.0            0.0              1.000000          0.012221
    2        0.500000       0.052000         1.000000          0.056157
    3        1.000000       0.099000         1.000000          0.100093
    4        1.500000       0.146000         1.000000          0.144029
    5        2.000000       0.193000         1.000000          0.187965
    6        2.490000       0.250000         1.000000          0.231022
    7        2.990000       0.282000         1.000000          0.274958
    8        3.490000       0.324000         1.000000          0.318893
    9        3.980000       0.359000         1.000000          0.361950
   10        4.480000       0.398000         1.000000          0.405886
   11        4.980000       0.440000         1.000000          0.449822
NO. OF POINTS    11

INTERCEPT      0.1222E-01       STD DEV   0.3157E-02

SLOPE          0.8787E-01       STD DEV  0.1807E-02

OVERALL STD DEV              0.9430E-02

   EXPT:
    03157502
    1        0.0            0.0              1.000000          0.010346
    2        0.500000       0.071000         1.000000          0.063713
    3        1.000000       0.121000         1.000000          0.117080
    4        1.500000       0.170000         1.000000          0.170448
    5        2.000000       0.229000         1.000000          0.223815
    6        2.490000       0.276000         1.000000          0.276115
    7        2.990000       0.326000         1.000000          0.329482
    8        3.490000       0.380000         1.000000          0.382849
    9        3.980000       0.436000         1.000000          0.435149
NO. OF POINTS      9

INTERCEPT      0.1035E-01       STD DEV   0.2123E-02

SLOPE          0.1067E 00       STD DEV  0.1466E-02

OVERALL STD DEV              0.5651E-02
```

```
                 CONC(µg/ml)     I(µamps)        W FACTOR        CALC'D CONC
   EXPT:
04187503
      1          0.0             0.0             1.000000        -0.018723
      2          0.499800        0.030000        1.000000         0.023385
      3          0.999900        0.063000        1.000000         0.065518
      4          1.497999        0.096000        1.000000         0.107483
      5          1.995999        0.138000        1.000000         0.149439
      6          2.493999        0.186000        1.000000         0.191396
      7          2.990000        0.231000        1.000000         0.233184
      8          3.488000        0.274000        1.000000         0.275140
      9          3.980000        0.312000        1.000000         0.316591
     10          4.480000        0.362000        1.000000         0.358716
     11          4.974999        0.418000        1.000000         0.400420
     12          2.493999        0.174000        1.000000         0.191396
     13          2.990000        0.234000        1.000000         0.233184
     14          3.488000        0.285000        1.000000         0.275140
     15          3.980000        0.328000        1.000000         0.316591
     16          4.480000        0.357000        1.000000         0.358716
     17          4.974999        0.390000        1.000000         0.400420
NO. OF POINTS      17

INTERCEPT       -0.1872E-01       STD DEV    0.2931E-02

SLOPE            0.8425E-01       STD DEV   0.1729E-02

OVERALL STD DEV              0.1059E-01
```

APPENDIX II

Rate f $([Cu]_o)$

$[Cu]_o$ = 2.50 ppm
pH = 6.7
μ = 0.1

```
EXPT      1137502          NO. OF POINTS        8
SLOPE           0.7786E-01   DEV=   0.1707E-02
INTERCEPT     0.1046E-02   DEV=   0.2937E-02
        CURRENT        CONC UG/ML      DEV                UM/ML          TIME(
    1   0.133E 00      0.169E 01     0.267E-01      0.269E-01    1.00
    2   0.585E-01      0.738E 00     0.407E-01      0.117E-01    3.00
    3   0.210E-01      0.255E 00     0.978E-01      0.407E-02    6.00
    4   0.110E-01      0.128E 00     0.183E 00      0.203E-02    9.00
    5   0.600E-02      0.636E-01     0.334E 00      0.101E-02   15.00
    6   0.200E-02      0.123E-01     0.100E 01      0.194E-03   30.00
    7   0.100E-02     -0.591E-03     0.200E 01     -0.938E-05   60.00
    8   0.100E 08     -0.134E-01     0.221E-01     -0.213E-03   90.00


EXPT      1187501          NO. OF POINTS        8
SLOPE           0.7786E-01   DEV=   0.1707E-02
INTERCEPT     0.1046E-02   DEV=   0.2937E-02
        CURRENT        CONC UG/ML      DEV                UM/ML          TIME(
    1   0.150E 00      0.191E 01     0.258E-01      0.304E-01    1.00
    2   0.610E-01      0.770E 00     0.396E-01      0.122E-01    3.00
    3   0.300E-01      0.372E 00     0.702E-01      0.590E-02    5.00
    4   0.140E-01      0.166E 00     0.145E 00      0.264E-02    8.00
    5   0.400E-02      0.379E-01     0.500E 00      0.602E-03   17.00
    6   0.150E-02      0.583E-02     0.133E 01      0.926E-04   30.00
    7   0.100E-02     -0.591E-03     0.200E 01     -0.938E-05   60.00
    8   0.100E 08     -0.134E-01     0.221E-01     -0.213E-03   90.00


EXPT      1187502          NO. OF POINTS        8
SLOPE           0.7786E-01   DEV=   0.1707E-02
INTERCEPT     0.1046E-02   DEV=   0.2937E-02
        CURRENT        CONC UG/ML      DEV                UM/ML          TIME(
    1   0.127E 00      0.162E 01     0.272E-01      0.257E-01    1.00
    2   0.610E-01      0.770E 00     0.396E-01      0.122E-01    3.00
    3   0.325E-01      0.404E 00     0.654E-01      0.641E-02    5.00
    4   0.101E-01      0.116E 00     0.199E 00      0.185E-02   10.00
    5   0.500E-02      0.508E-01     0.401E 00      0.806E-03   20.00
    6   0.300E-02      0.251E-01     0.667E 00      0.398E-03   30.00
    7   0.100E-02     -0.591E-03     0.200E 01     -0.938E-05   60.00
    8   0.500E-03     -0.701E-02     0.400E 01     -0.111E-03   90.00
```

$[Cu]_o$ = 4.90

pH = 6.7

μ = 0.1

```
EXPT      1197501        NO. OF POINTS      10
SLOPE         0.7786E-01  DEV=   0.1707E-02
INTERCEPT     0.1046E-02  DEV=   0.2937E-02
         CURRENT       CONC UG/ML    DEV              UM/ML         TIME(
    1    0.320E 00     0.410E 01     0.230E-01     0.650E-01   1.00
    2    0.180E 00     0.230E 01     0.243E-01     0.365E-01   2.00
    3    0.119E 00     0.151E 01     0.278E-01     0.240E-01   5.00
    4    0.880E-01     0.112E 01     0.317E-01     0.177E-01   7.00
    5    0.590E-01     0.744E 00     0.405E-01     0.118E-01  10.00
    6    0.305E-01     0.378E 00     0.692E-01     0.600E-02  17.00
    7    0.192E-01     0.233E 00     0.106E 00     0.370E-02  25.00
    8    0.800E-02     0.893E-01     0.251E 00     0.142E-02  60.00
    9    0.500E-02     0.508E-01     0.401E 00     0.806E-03  90.00
   10    0.400E-02     0.379E-01     0.500E 00     0.602E-03120.00
```

```
EXPT      1187503        NO. OF POINTS       9
SLOPE         0.7786E-01  DEV=   0.1707E-02
INTERCEPT     0.1046E-02  DEV=   0.2937E-02
         CURRENT       CONC UG/ML    DEV              UM/ML         TIME(
    1    0.252E 00     0.322E 01     0.235E-01     0.512E-01   1.00
    2    0.139E 00     0.241E 01     0.245E-01     0.383E-01   3.00
    3    0.115E 00     0.147E 01     0.281E-01     0.233E-01   5.00
    4    0.575E-01     0.725E 00     0.412E-01     0.115E-01  10.00
    5    0.388E-01     0.485E 00     0.561E-01     0.770E-02  15.00
    6    0.256E-01     0.315E 00     0.812E-01     0.501E-02  30.00
    7    0.110E-01     0.128E 00     0.183E 00     0.203E-02  60.00
    8    0.700E-02     0.765E-01     0.287E 00     0.121E-02  90.00
    9    0.680E-01     0.860E 00     0.368E-01     0.136E-01120.00
```

$[Cu]_o = 6.23$

$pH = 6.7$

$\mu = 0.1$

```
EXPT      1257504        NO. OF POINTS       8
SLOPE          0.9156E-01   DEV=   0.8610E-03
INTERCEPT      0.1083E-01   DEV=   0.2042E-02
         CURRENT        CONC UG/ML    DEV              UM/ML        TIME(
    1    0.416E 00      0.443E 01     0.108E-01      0.702E-01   1.00
    2    0.268E 00      0.281E 01     0.122E-01      0.446E-01   3.00
    3    0.172E 00      0.176E 01     0.151E-01      0.279E-01   6.00
    4    0.124E 00      0.124E 01     0.188E-01      0.196E-01  10.00
    5    0.880E-01      0.843E 00     0.247E-01      0.134E-01  20.00
    6    0.760E-01      0.712E 00     0.280E-01      0.113E-01  30.00
    7    0.730E-01      0.679E 00     0.290E-01      0.108E-01  45.00
    8    0.730E-01      0.679E 00     0.290E-01      0.108E-01  60.00

EXPT      1287503        NO. OF POINTS       8
SLOPE          0.9156E-01   DEV=   0.8610E-03
INTERCEPT      0.1083E-01   DEV=   0.2042E-02
         CURRENT        CONC UG/ML    DEV              UM/ML        TIME(
    1    0.464E 00      0.495E 01     0.105E-01      0.786E-01   1.00
    2    0.294E 00      0.309E 01     0.118E-01      0.491E-01   3.00
    3    0.192E 00      0.198E 01     0.142E-01      0.314E-01   5.00
    4    0.120E 00      0.119E 01     0.192E-01      0.189E-01  10.00
    5    0.880E-01      0.843E 00     0.247E-01      0.134E-01  15.00
    6    0.580E-01      0.515E 00     0.358E-01      0.818E-02  32.00
    7    0.500E-01      0.428E 00     0.411E-01      0.679E-02  45.00
    8    0.480E-01      0.406E 00     0.428E-01      0.644E-02  50.00

EXPT      1287508        NO. OF POINTS      11
SLOPE          0.9156E-01   DEV=   0.8610E-03
INTERCEPT      0.1083E-01   DEV=   0.2042E-02
         CURRENT        CONC UG/ML    DEV              UM/ML        TIME(
    1    0.432E 00      0.460E 01     0.107E-01      0.730E-01   1.00
    2    0.342E 00      0.362E 01     0.113E-01      0.574E-01   2.00
    3    0.284E 00      0.298E 01     0.119E-01      0.474E-01   3.00
    4    0.240E 00      0.250E 01     0.127E-01      0.397E-01   4.00
    5    0.208E 00      0.215E 01     0.136E-01      0.342E-01   5.00
    6    0.148E 00      0.150E 01     0.166E-01      0.238E-01   8.00
    7    0.128E 00      0.128E 01     0.184E-01      0.203E-01  10.00
    8    0.930E-01      0.897E 00     0.236E-01      0.142E-01  17.00
    9    0.850E-01      0.810E 00     0.254E-01      0.129E-01  20.00
   10    0.700E-01      0.646E 00     0.301E-01      0.103E-01  30.00
   11    0.650E-01      0.592E 00     0.322E-01      0.939E-02  60.00
```

$[Cu]_o$ = 7.47
pH = 6.7
μ = 8.1

```
EXPT      1287501          NO. OF POINTS       8
SLOPE          0.9156E-01   DEV=   0.8610E-03
INTERCEPT      0.1083E-01   DEV=   0.2042E-02
        CURRENT        CONC UG/ML    DEV              UM/ML          TIME(
    1   0.348E 00      0.368E 01     0.112E-01        0.585E-01   3.00
    2   0.284E 00      0.298E 01     0.119E-01        0.474E-01   5.00
    3   0.232E 00      0.242E 01     0.129E-01        0.383E-01   8.00
    4   0.214E 00      0.222E 01     0.134E-01        0.352E-01  10.00
    5   0.190E 00      0.196E 01     0.143E-01        0.311E-01  15.00
    6   0.174E 00      0.178E 01     0.150E-01        0.283E-01  23.00
    7   0.171E 00      0.175E 01     0.151E-01        0.278E-01  30.00
    8   0.169E 00      0.173E 01     0.153E-01        0.274E-01  60.00

EXPT      1287507          NO. OF POINTS       8
SLOPE          0.9156E-01   DEV=   0.8610E-03
INTERCEPT      0.1083E-01   DEV=   0.2042E-02
        CURRENT        CONC UG/ML    DEV              UM/ML          TIMEI
    1   0.408E 00      0.434E 01     0.108E-01        0.689E-01   2.00
    2   0.350E 00      0.370E 01     0.112E-01        0.588E-01   3.00
    3   0.308E 00      0.325E 01     0.116E-01        0.515E-01   4.00
    4   0.276E 00      0.290E 01     0.120E-01        0.460E-01   5.00
    5   0.196E 00      0.202E 01     0.140E-01        0.321E-01  10.00
    6   0.165E 00      0.168E 01     0.155E-01        0.267E-01  22.00
    7   0.161E 00      0.164E 01     0.157E-01        0.260E-01  30.00
    8   0.159E 00      0.162E 01     0.158E-01        0.257E-01  45.00


EXPT      1287509          NO. OF POINTS       9
SLOPE          0.9156E-01   DEV=   0.8610E-03
INTERCEPT      0.1083E-01   DEV=   0.2042E-02
        CURRENT        CONC UG/ML    DEV              UM/ML          TIMEI
    1   0.424E 00      0.451E 01     0.107E-01        0.716E-01   2.00
    2   0.308E 00      0.325E 01     0.116E-01        0.515E-01   4.00
    3   0.206E 00      0.213E 01     0.137E-01        0.338E-01   6.00
    4   0.232E 00      0.242E 01     0.129E-01        0.383E-01   8.00
    5   0.210E 00      0.218E 01     0.135E-01        0.345E-01  10.00
    6   0.188E 00      0.194E 01     0.143E-01        0.307E-01  20.00
    7   0.172E 00      0.176E 01     0.151E-01        0.279E-01  30.00
    8   0.156E 00      0.159E 01     0.160E-01        0.252E-01  60.00
    9   0.156E 00      0.159E 01     0.160E-01        0.252E-01  90.00
```

$[Cu]_o$ = 8.70
pH = 6.7
μ = 0.1

```
EXPT      1257503        NO. OF POINTS     7
SLOPE           0.9156E-01   DEV=   0.8610E-03
INTERCEPT       0.1083E-01   DEV=   0.2042E-02
        CURRENT        CONC UG/ML     DEV              UM/ML       TIME(
    1   0.444E 00      0.473E 01     0.106E-01       0.751E-01   3.00
    2   0.364E 00      0.336E 01     0.111E-01       0.612E-01   5.00
    3   0.304E 00      0.320E 01     0.117E-01       0.508E-01   8.00
    4   0.286E 00      0.301E 01     0.119E-01       0.477E-01  10.00
    5   0.258E 00      0.270E 01     0.124E-01       0.428E-01  20.00
    6   0.250E 00      0.261E 01     0.125E-01       0.415E-01  30.00
    7   0.250E 00      0.261E 01     0.125E-01       0.415E-01  60.00

EXPT      1287502        NO. OF POINTS     8
SLOPE           0.9156E-01   DEV=   0.8610E-03
INTERCEPT       0.1083E-01   DEV=   0.2042E-02
        CURRENT        CONC UG/ML     DEV              UM/ML       TIME(
    1   0.624E 00      0.670E 01     0.101E-01       0.106E 00   1.00
    2   0.472E 00      0.504E 01     0.105E-01       0.799E-01   2.00
    3   0.448E 00      0.477E 01     0.106E-01       0.758E-01   3.00
    4   0.372E 00      0.394E 01     0.110E-01       0.626E-01   5.00
    5   0.278E 00      0.292E 01     0.120E-01       0.463E-01  10.00
    6   0.255E 00      0.268E 01     0.124E-01       0.425E-01  15.00
    7   0.244E 00      0.255E 01     0.126E-01       0.404E-01  30.00
    8   0.238E 00      0.248E 01     0.128E-01       0.394E-01  60.00
```

APPENDIX III

Rate f (Temp)

```
      DIMENSION Y(100),T(100),XCALC(100),XCALCP(100)
C INPUT DATA/ NO. DATA SETS
      READ(5,19) NN
C INPUT DATA/ EXPERIMENT NUMBER AND NO. OF POINTS
      DO 10 K=1,NN
      READ(5,19) NLB,N
C IN UT DATA/ SLOPE, STD DEV, INTERCEPT, STD DEV
      READ(5,29) A1,S1,AZ,SZ
      WRITE(6,39) NLB,N,A1,S1,AZ,SZ
      WRITE(6,49)
C INPUT DATA/ CURRENT, TIME(SEC)
      READ (5,59) (Y(I),T(I),I=1,N)
      DO 10 I=1,N
C CORRECT FOR TEMP EFFECT AR 1.7 PER CENT PER DEG C
      TFACT=(50.-25.)*0.017*Y(I)
      Y(I)=Y(I)+TFACT
C CALC CONCN
       XCALC(I)=(Y(I)-AZ)/A1
       MW=63.54
      IF(XCALC(I))5,5,5
    1 XCALC(I)=0
  5   XCALCP(I)=XCALC(I)/MW
C CALC DEV
C ASSUME ERROR IN CURRENT .002 MICRO AMP
      SB=0.002
      IF(Y(I))8,8,9
8     Y(I)=9999999.
    9 SY=((S1/A1)**2+(SB/Y(I))**2)+SZ**2
      DEV=SQRT(SY)
      WRITE(6,69) I,Y(I),XCALC(I),DEV,XCALCP(I),T(I)
10    CONTINUE
19    FORMAT(2I8)
29    FORMAT(4F10.6)
39    FORMAT(//,' EXPT ',2X,I8,5X,' NO. OF POINTS ',I5/,' SLOPE ',
     14X,E12.4,'  DEV=',E12.4,/,' INTERCEPT ',E12.4,'  DEV=',E12.4)
49    FORMAT(7X,' CURRENT ',3X,' CONC UG/ML ',',  DEV  ',5X,
     1'  UM/ML ',5X,' TIME(MIN)')
59    FORMAT(8F10.4)
69    FORMAT(I5,4E12.3,F6.2)
      STOP
      END
```

[Cu] = 4.9 ppm
pH = 6.7
μ = 0.1
T = 2°C

```
EXPT      2187502        NO. OF POINTS      11
SLOPE          0.1031E 00   DEV=    0.2597E-02
INTERCEPT   -0.2573E-02   DEV=    0.4151E-02
        CURRENT        CONC UG/ML     DEV             UM/ML        TIME(
    1   0.154E 00     0.152E 01     0.286E-01      0.241E-01   1.00
    2   0.118E 00     0.117E 01     0.306E-01      0.186E-01   2.00
    3   0.956E-01     0.952E 00     0.330E-01      0.151E-01   3.00
    4   0.798E-01     0.799E 00     0.358E-01      0.127E-01   4.00
    5   0.664E-01     0.669E 00     0.395E-01      0.106E-01   5.00
    6   0.499E-01     0.509E 00     0.475E-01      0.808E-02   7.00
    7   0.329E-01     0.344E 00     0.650E-01      0.546E-02  10.00
    8   0.213E-01     0.232E 00     0.972E-01      0.368E-02  15.00
    9   0.158E-01     0.179E 00     0.129E 00      0.283E-02  22.00
   10   0.122E-01     0.143E 00     0.166E 00      0.227E-02  30.00
   11   0.974E-02     0.119E 00     0.207E 00      0.190E-02  45.00

EXPT      2187504        NO. OF POINTS      11
SLOPE          0.1031E 00   DEV=    0.2597E-02
INTERCEPT   -0.2573E-02   DEV=    0.4151E-02
        CURRENT        CONC UG/ML     DEV             UM/ML        TIME(
    1   0.185E 00     0.181E 01     0.277E-01      0.288E-01   1.00
    2   0.141E 00     0.140E 01     0.292E-01      0.221E-01   2.00
    3   0.116E 00     0.115E 01     0.308E-01      0.182E-01   3.00
    4   0.974E-01     0.970E 00     0.328E-01      0.154E-01   4.00
    5   0.828E-01     0.828E 00     0.351E-01      0.131E-01   5.00
    6   0.621E-01     0.627E 00     0.411E-01      0.996E-02   7.00
    7   0.426E-01     0.438E 00     0.534E-01      0.696E-02  10.00
    8   0.262E-01     0.279E 00     0.805E-01      0.443E-02  15.00
    9   0.177E-01     0.196E 00     0.116E 00      0.312E-02  20.00
   10   0.974E-02     0.119E 00     0.207E 00      0.190E-02  30.00
   11   0.609E-02     0.840E-01     0.329E 00      0.133E-02  50.00
```

[Cu] = 4.9 ppm
cH = 6.7
μ = 0.1
T = 25°C

```
EXPT       2047501         NO. OF POINTS      11
SLOPE            0.1021E 00    DEV=   0.2009E-02
INTERCEPT        0.1658E-02    DEV=   0.5088E-02
          CURRENT        CONC UG/ML     DEV              UM/ML         TIME(
    1     0.218E 00      0.212E 01      0.223E-01        0.336E-01   2.00
    2     0.184E 00      0.179E 01      0.230E-01        0.283E-01   3.00
    3     0.150E 00      0.145E 01      0.243E-01        0.231E-01   4.00
    4     0.122E 00      0.118E 01      0.261E-01        0.187E-01   5.00
    5     0.720E-01      0.689E 00      0.344E-01        0.109E-01   8.00
    6     0.572E-01      0.544E 00      0.404E-01        0.863E-02  10.00
    7     0.340E-01      0.317E 00      0.622E-01        0.503E-02  15.00
    8     0.240E-01      0.219E 00      0.858E-01        0.347E-02  20.00
    9     0.170E-01      0.150E 00      0.119E 00        0.239E-02  30.00
   10     0.100E-01      0.817E-01      0.201E 00        0.130E-02  60.00
   11     0.800E-02      0.621E-01      0.251E 00        0.986E-03  90.00

EXPT       2047502         NO. OF POINTS      11
SLOPE            0.1021E 00    DEV=   0.2009E-02
INTERCEPT        0.1658E-02    DEV=   0.5088E-02
          CURRENT        CONC UG/ML     DEV              UM/ML         TIME(
    1     0.276E 00      0.269E 01      0.216E-01        0.427E-01   1.00
    2     0.180E 00      0.175E 01      0.232E-01        0.277E-01   2.00
    3     0.127E 00      0.123E 01      0.257E-01        0.195E-01   4.00
    4     0.108E 00      0.105E 01      0.274E-01        0.166E-01   5.00
    5     0.784E-01      0.752E 00      0.326E-01        0.119E-01   7.00
    6     0.590E-01      0.562E 00      0.395E-01        0.891E-02  10.00
    7     0.360E-01      0.336E 00      0.592E-01        0.534E-02  15.00
    8     0.270E-01      0.248E 00      0.768E-01        0.394E-02  20.00
    9     0.160E-01      0.140E 00      0.127E 00        0.223E-02  30.00
   10     0.120E-01      0.101E 00      0.158E 00        0.161E-02  45.00
   11     0.110E-01      0.915E-01      0.183E 00        0.145E-02  60.00
```

[Cu] = 4.9 ppm
pH = 6.7
μ = 0.10
T = 35°C

```
EXPT     2237504        NO. OF POINTS      8
SLOPE          0.1031E 00   DEV=   0.2597E-02
INTERCEPT   -0.2573E-02   DEV=   0.4151E-02
          CURRENT       CONC UG/ML    DEV               JM/ML         TIME(
    1    0.218E 00     0.214E 01     0.271E-01       0.339E-01   1.00
    2    0.153E 00     0.151E 01     0.287E-01       0.240E-01   2.00
    3    0.889E-01     0.887E 00     0.340E-01       0.141E-01   4.00
    4    0.655E-01     0.660E 00     0.398E-01       0.105E-01   6.00
    5    0.409E-01     0.422E 00     0.551E-01       0.670E-02  10.00
    6    0.211E-01     0.229E 00     0.983E-01       0.364E-02  20.00
    7    0.164E-01     0.184E 00     0.125E 00       0.292E-02  30.00
    8    0.164E-01     0.184E 00     0.125E 00       0.292E-02  60.00

EXPT     2237505        NO. OF POINTS      8
SLOPE          0.1031E 00   DEV=   0.2597E-02
INTERCEPT   -0.2573E-02   DEV=   0.4151E-02
          CURRENT       CONC UG/ML    DEV               JM/ML         TIME(
    1    0.139E 00     0.138E 01     0.293E-01       0.218E-01   2.00
    2    0.913E-01     0.910E 00     0.336E-01       0.144E-01   4.00
    3    0.655E-01     0.660E 00     0.398E-01       0.105E-01   6.00
    4    0.456E-01     0.468E 00     0.507E-01       0.742E-02   8.00
    5    0.351E-01     0.365E 00     0.624E-01       0.580E-02  10.00
    6    0.187E-01     0.207E 00     0.110E 00       0.328E-02  20.00
    7    0.129E-01     0.150E 00     0.157E 00       0.238E-02  30.00
    8    0.936E-02     0.116E 00     0.215E 00       0.184E-02  60.00
```

```
EX
SL
IN
```

APPENDIX IV

Rate f (particle size)
for Copper (II)

[Cu] = 4.98 pH = 6.7 μ = 0.1
Experiment D particles: 355 to 500 microns

```
EXPT      3027502         NO. OF POINTS      8
SLOPE           0.9764E-01  DEV=   0.1275E-02
INTERCEPT       0.1333E-01  DEV=   0.2042E-02
          CURRENT        CONC UG/ML      DEV             UM/ML         TIME
    1     0.411E 00      0.407E 01      0.141E-01      0.646E-01       1.00
    2     0.352E 00      0.347E 01      0.144E-01      0.551E-01       2.00
    3     0.293E 00      0.286E 01      0.149E-01      0.455E-01       3.00
    4     0.232E 00      0.224E 01      0.158E-01      0.355E-01       5.00
    5     0.170E 00      0.160E 01      0.177E-01      0.255E-01       7.00
    6     0.105E 00      0.939E 00      0.232E-01      0.149E-01      10.00
    7     0.380E-01      0.253E 00      0.543E-01      0.401E-02      15.00
    8     0.700E-02     -0.648E-01      0.286E 00     -0.103E-02      30.00

              F            T          SQRT(T)  LOG(1-F)
     1      0.1782       1.00         1.00     -0.0852
     2      0.2982       2.00         1.00     -0.1538
     3      0.4182       3.00         1.00     -0.2352
     4      0.5423       5.00         1.00     -0.3394
     5      0.6684       7.00         1.00     -0.4794
     6      0.8007      10.00         1.00     -0.7004
     7      0.9369      15.00         1.00     -1.2002

EXPT      3027503         NO. OF POINTS      8
SLOPE           0.9764E-01  DEV=   0.1275E-02
INTERCEPT       0.1333E-01  DEV=   0.2042E-02
          CURRENT        CONC UG/ML      DEV             UM/ML         TIME
    1     0.436E 00      0.433E 01      0.140E-01      0.687E-01       1.00
    2     0.382E 00      0.378E 01      0.142E-01      0.599E-01       2.00
    3     0.332E 00      0.326E 01      0.145E-01      0.518E-01       3.00
    4     0.260E 00      0.253E 01      0.153E-01      0.401E-01       5.00
    5     0.187E 00      0.178E 01      0.170E-01      0.282E-01       7.00
    6     0.125E 00      0.114E 01      0.208E-01      0.182E-01      10.00
    7     0.660E-01      0.539E 00      0.331E-01      0.856E-02      15.00
    8     0.130E-01     -0.338E-02      0.154E 00     -0.536E-04      30.00

              F            T          SQRT(T)  LOG(1-F)
     1      0.1289       1.00         1.00     -0.0599
     2      0.2401       2.00         1.00     -0.1193
     3      0.3431       3.00         1.00     -0.1825
     4      0.4914       5.00         1.00     -0.2936
     5      0.6417       7.00         1.00     -0.4457
     6      0.7694      10.00         1.00     -0.6371
     7      0.8909      15.00         1.00     -0.9620
```

[Cu] = 4.98   pH = 6.7   μ = 0.1
Experiment C   particles: 212 to 355 microns

```
EXPT      3027507         NO. OF POINTS      8
SLOPE           0.9764E-01   DEV=   0.1275E-02
INTERCEPT       0.1333E-01   DEV=   0.2042E-02
          CURRENT       CONC UG/ML      DEV              UM/ML          TIME
      1   0.357E 00     0.352E 01     0.144E-01      0.559E-01        1.00
      2   0.278E 00     0.271E 01     0.150E-01      0.430E-01        2.00
      3   0.221E 00     0.213E 01     0.160E-01      0.338E-01        3.00
      4   0.146E 00     0.136E 01     0.190E-01      0.216E-01        5.00
      5   0.880E-01     0.765E 00     0.263E-01      0.121E-01        7.00
      6   0.460E-01     0.335E 00     0.454E-01      0.531E-02       10.00
      7   0.160E-01     0.273E-01     0.126E 00      0.434E-03       15.00
      8   0.500E-02    -0.853E-01     0.400E 00     -0.135E-02       30.00

               F          T          SQRT(T)   LOG(1-F)
        1    0.2869      1.00        1.00     -0.1468
        2    0.4469      2.00        1.00     -0.2572
        3    0.5624      3.00        1.00     -0.3589
        4    0.7143      5.00        1.00     -0.5442
        5    0.8318      7.00        1.00     -0.7743
        6    0.9169     10.00        1.00     -1.0806
        7    0.9777     15.00        1.00     -1.6520
```

```
EXPT      3035500         NO. OF POINTS      8
SLOPE           0.1037E 00   DEV=   0.2554E-02
INTERCEPT       0.4394E-02   DEV=   0.3678E-02
          CURRENT       CONC UG/ML      DEV              UM/ML          TIME
      1   0.388E 00     0.370E 01     0.254E-01      0.587E-01        1.00
      2   0.300E 00     0.285E 01     0.258E-01      0.452E-01        2.00
      3   0.260E 00     0.246E 01     0.261E-01      0.391E-01        3.00
      4   0.178E 00     0.167E 01     0.273E-01      0.266E-01        5.00
      5   0.118E 00     0.110E 01     0.301E-01      0.174E-01        7.00
      6   0.780E-01     0.710E 00     0.357E-01      0.113E-01       10.00
      7   0.420E-01     0.363E 00     0.537E-01      0.576E-02       15.00
      8   0.300E-02    -0.134E-01     0.667E 00     -0.213E-03       30.00

               F          T          SQRT(T)   LOG(1-F)
        1    0.2550      1.00        1.00     -0.1278
        2    0.4253      2.00        1.00     -0.2406
        3    0.5027      3.00        1.00     -0.3034
        4    0.6614      5.00        1.00     -0.4703
        5    0.7775      7.00        1.00     -0.6526
        6    0.8549     10.00        1.00     -0.8382
        7    0.9245     15.00        1.00     -1.1222
```

[Cu] = 4.98 pH = 6.7 μ = 0.1
Experiment B particles: 150 to 212 microns

```
EXPT      3157501        NO. OF POINTS      8
SLOPE          0.1067E 00   DEV=   0.1466E-02
INTERCEPT      0.1035E-01   DEV=   0.2123E-02
        CURRENT       CONC UG/ML      DEV            UM/ML          TIME
    1   0.370E 00     0.337E 01     0.149E-01      0.535E-01       1.00
    2   0.252E 00     0.226E 01     0.160E-01      0.359E-01       2.00
    3   0.215E 00     0.192E 01     0.167E-01      0.304E-01       3.00
    4   0.128E 00     0.110E 01     0.209E-01      0.175E-01       5.00
    5   0.800E-01     0.653E 00     0.286E-01      0.104E-01       7.00
    6   0.400E-01     0.278E 00     0.519E-01      0.441E-02      10.00
    7   0.240E-01     0.128E 00     0.845E-01      0.203E-02      15.00
    8   0.100E 08    -0.970E-01     0.139E-01     -0.154E-02      30.00


            F          T         SQRT(T)   LOG(1-F)
     1    0.3156      1.00       1.00     -0.1647
     2    0.5339      2.00       1.00     -0.3315
     3    0.6023      3.00       1.00     -0.4005
     4    0.7632      5.00       1.00     -0.6257
     5    0.8520      7.00       1.00     -0.8298
     6    0.9260     10.00       1.00     -1.1309
     7    0.9556     15.00       1.00     -1.3527


EXPT      3157503        NO. OF POINTS      8
SLOPE          0.1067E 00   DEV=   0.1466E-02
INTERCEPT      0.1035E-01   DEV=   0.2123E-02
        CURRENT       CONC UG/ML      DEV            UM/ML          TIME
    1   0.372E 00     0.339E 01     0.149E-01      0.538E-01       1.00
    2   0.290E 00     0.262E 01     0.155E-01      0.416E-01       2.00
    3   0.212E 00     0.189E 01     0.168E-01      0.300E-01       3.00
    4   0.134E 00     0.116E 01     0.204E-01      0.184E-01       5.00
    5   0.800E-01     0.653E 00     0.286E-01      0.104E-01       7.00
    6   0.590E-01     0.456E 00     0.366E-01      0.724E-02      10.00
    7   0.120E-01     0.155E-01     0.167E 00      0.245E-03      15.00
    8   0.200E-02    -0.783E-01     0.100E 01     -0.124E-02      30.00


            F          T         SQRT(T)   LOG(1-F)
     1    0.3131      1.00       1.00     -0.1631
     2    0.4653      2.00       1.00     -0.2719
     3    0.6101      3.00       1.00     -0.4091
     4    0.7549      5.00       1.00     -0.6107
     5    0.8552      7.00       1.00     -0.8392
     6    0.8942     10.00       1.00     -0.9754
     7    0.9314     15.00       1.00     -1.7313
```

```
EXPT      3037503         NO. OF POINTS      8
SLOPE          0.8787E-01  DEV=   0.1807E-02
INTERCEPT   0.1222E-01  DEV=   0.3157E-02
          CURRENT        CONC UG/ML     DEV            UM/ML         TIME
    1     0.298E 00     0.325E 01     0.219E-01     0.516E-01      1.00
    2     0.223E 00     0.240E 01     0.227E-01     0.381E-01      2.00
    3     0.176E 00     0.186E 01     0.237E-01     0.296E-01      3.00
    4     0.104E 00     0.104E 01     0.283E-01     0.166E-01      5.00
    5     0.590E-01     0.532E 00     0.398E-01     0.845E-02      7.00
    6     0.310E-01     0.214E 00     0.678E-01     0.339E-02     10.00
    7     0.100E-01    -0.253E-01     0.201E 00    -0.401E-03     15.00
    8     0.200E-02    -0.116E 00     0.100E 01    -0.185E-02     30.00


                 F          T          SQRT(T)  LOG(1-F)
       1      0.3377      1.00       1.00     -0.1790
       2      0.5055      2.00       1.00     -0.3059
       3      0.6107      3.00       1.00     -0.4097
       4      0.7718      5.00       1.00     -0.6416
       5      0.8725      7.00       1.00     -0.8944
       6      0.9351     10.00       1.00     -1.1878
       7      0.9821     15.00       1.00     -1.7471
```

[Cu] = 4.98   pH = 6.7   μ = 0.1
Experiment A   particles: <150 microns

```
EXPT      3027504         NO. OF POINTS       8
SLOPE            0.9764E-01   DEV=   0.1275E-02
INTERCEPT        0.1333E-01   DEV=   0.2042E-02
         CURRENT       CONC UG/ML     DEV            UM/ML        TIME
    1    0.203E 00     0.194E 01    0.165E-01     0.308E-01      1.00
    2    0.140E 00     0.130E 01    0.195E-01     0.206E-01      2.00
    3    0.100E 00     0.888E 00    0.240E-01     0.141E-01      3.00
    4    0.450E-01     0.324E 00    0.464E-01     0.515E-02      5.00
    5    0.210E-01     0.786E-01    0.962E-01     0.125E-02      7.00
    6    0.800E-02    -0.546E-01    0.250E 00    -0.866E-03     10.00
    7    0.200E-02    -0.116E 00    0.100E 01    -0.184E-02     15.00
    8    0.100E 08    -0.137E 00    0.132E-01    -0.217E-02     30.00

             F            T         SQRT(T)  LOG(1-F)
     1     0.5929       1.00       1.00    -0.3903
     2     0.7192       2.00       1.00    -0.5516
     3     0.7994       3.00       1.00    -0.6978
     4     0.9097       5.00       1.00    -1.0445
     5     0.9579       7.00       1.00    -1.3755
     6     0.9840      10.00       1.00    -1.7947
     7     0.9960      15.00       1.00    -2.3967
```

```
EXPT      3027506         NO. OF POINTS       8
SLOPE            0.9764E-01   DEV=   0.1275E-02
INTERCEPT        0.1333E-01   DEV=   0.2042E-02
         CURRENT       CONC UG/ML     DEV            UM/ML        TIME
    1    0.234E 00     0.226E 01    0.157E-01     0.359E-01      1.00
    2    0.162E 00     0.152E 01    0.181E-01     0.242E-01      2.00
    3    0.108E 00     0.970E 00    0.228E-01     0.154E-01      3.00
    4    0.500E-01     0.376E 00    0.421E-01     0.596E-02      5.00
    5    0.180E-01     0.478E-01    0.112E 00     0.759E-03      7.00
    6    0.120E-01    -0.136E-01    0.167E 00    -0.216E-03     10.00
    7    0.300E-02    -0.106E 00    0.667E 00    -0.168E-02     15.00
    8    0.100E 08    -0.137E 00    0.132E-01    -0.217E-02     30.00

             F            T         SQRT(T)  LOG(1-F)
     1     0.5307       1.00       1.00    -0.3285
     2     0.6751       2.00       1.00    -0.4882
     3     0.7834       3.00       1.00    -0.6643
     4     0.8997       5.00       1.00    -0.9988
     5     0.9639       7.00       1.00    -1.4425
     6     0.9759      10.00       1.00    -1.6186
     7     0.9940      15.00       1.00    -2.2206
```

APPENDIX V

Rate f (particle size)
for Nickel (II)

[Ni] = 4.98   pH = 6.70 μ = 0.1
Experiment A   particles: <150 microns

```
EXPT      4187504         NO. OF POINTS      7
SLOPE          0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT       CONC UG/ML      DEV            UM/ML         TIME
    1     0.293E 00     0.370E 01     0.218E-01     0.638E-01      1.00
    2     0.168E 00     0.222E 01     0.239E-01     0.382E-01      2.00
    3     0.130E 00     0.177E 01     0.258E-01     0.304E-01      3.00
    4     0.760E-01     0.112E 01     0.335E-01     0.194E-01      5.00
    5     0.160E-01     0.412E 00     0.127E 00     0.711E-02     15.00
    6     0.600E-02     0.293E 00     0.334E 00     0.506E-02     25.00
    7     0.200E-02     0.246E 00     0.100E 01     0.424E-02     30.00

            F          T         SQRT(T)  LOG(1-F)
     1    0.2688      1.00      1.00    -0.1360
     2    0.5829      2.00      1.00    -0.3798
     3    0.6784      3.00      1.00    -0.4927
     4    0.8141      5.00      1.00    -0.7307
     5    0.9648     15.00      1.00    -1.4538
     6    0.9899     25.00      1.00    -1.9978

EXPT      4187505         NO. OF POINTS      7
SLOPE          0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT       CONC UG/ML      DEV            UM/ML         TIME
    1     0.228E 00     0.293E 01     0.225E-01     0.505E-01      1.00
    2     0.166E 00     0.219E 01     0.240E-01     0.378E-01      2.00
    3     0.128E 00     0.174E 01     0.260E-01     0.300E-01      3.00
    4     0.700E-01     0.105E 01     0.353E-01     0.182E-01      5.00
    5     0.280E-01     0.555E 00     0.744E-01     0.956E-02     10.00
    6     0.160E-01     0.412E 00     0.127E 00     0.711E-02     15.00
    7     0.200E-02     0.246E 00     0.100E 01     0.424E-02     30.00

            F          T         SQRT(T)  LOG(1-F)
     1    0.4322      1.00      1.00    -0.2458
     2    0.5879      2.00      1.00    -0.3850
     3    0.6834      3.00      1.00    -0.4995
     4    0.8291      5.00      1.00    -0.7674
     5    0.9347     10.00      1.00    -1.1849
     6    0.9648     15.00      1.00    -1.4538
```

[Ni] = 4.98 pH = 6.70 μ = 0.1
Experiment B particles: 150 to 212 microns

```
EXPT      4187506         NO. OF POINTS      8
SLOPE          0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT       CONC UG/ML     DEV           UM/ML          TIME
    1     0.190E 00     0.248E 01     0.232E-01     0.427E-01      2.00
    2     0.147E 00     0.197E 01     0.248E-01     0.339E-01      3.00
    3     0.980E-01     0.139E 01     0.291E-01     0.239E-01      5.00
    4     0.680E-01     0.103E 01     0.360E-01     0.177E-01      7.00
    5     0.420E-01     0.721E 00     0.519E-01     0.124E-01     10.00
    6     0.210E-01     0.471E 00     0.975E-01     0.813E-02     15.00
    7     0.800E-02     0.317E 00     0.251E 00     0.547E-02     30.00
    8     0.400E-02     0.270E 00     0.500E 00     0.465E-02     60.00

              F          T         SQRT(T)  LOG(1-F)
     1     0.5303      2.00      1.41    -0.3282
     2     0.6389      3.00      1.41    -0.4424
     3     0.7626      5.00      1.41    -0.6246
     4     0.8384      7.00      1.41    -0.7915
     5     0.9040     10.00      1.41    -1.0179
     6     0.9571     15.00      1.41    -1.3672
     7     0.9899     30.00      1.41    -1.9956

EXPT      4187507         NO. OF POINTS      7
SLOPE          0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT       CONC UG/ML     DEV           UM/ML          TIME
    1     0.270E 00     0.343E 01     0.220E-01     0.591E-01      1.00
    2     0.138E 00     0.186E 01     0.253E-01     0.321E-01      3.00
    3     0.940E-01     0.134E 01     0.297E-01     0.231E-01      5.00
    4     0.670E-01     0.102E 01     0.363E-01     0.175E-01      7.00
    5     0.420E-01     0.721E 00     0.519E-01     0.124E-01     10.00
    6     0.210E-01     0.471E 00     0.975E-01     0.813E-02     15.00
    7     0.100E-01     0.341E 00     0.201E 00     0.588E-02     30.00

              F          T         SQRT(T)  LOG(1-F)
     1     0.3333      1.00      1.00    -0.1761
     2     0.6718      3.00      1.00    -0.4839
     3     0.7846      5.00      1.00    -0.6668
     4     0.8538      7.00      1.00    -0.8352
     5     0.9179     10.00      1.00    -1.0859
     6     0.9718     15.00      1.00    -1.5497
```

[Ni] = 4.98　pH = 6.70　μ = 0.1
Experiment C　particles:　212 to 355 microns

```
EXPT     4187501        NO. OF POINTS      9
SLOPE         0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT       CONC UG/ML     DEV            UM/ML        TIME
    1     0.342E 00     0.428E 01     0.215E-01     0.738E-01      1.00
    2     0.290E 00     0.366E 01     0.218E-01     0.632E-01      2.00
    3     0.244E 00     0.312E 01     0.223E-01     0.538E-01      3.00
    4     0.214E 00     0.276E 01     0.227E-01     0.476E-01      3.00
    5     0.192E 00     0.250E 01     0.232E-01     0.431E-01      5.00
    6     0.800E-01     0.117E 01     0.325E-01     0.202E-01     10.00
    7     0.450E-01     0.756E 00     0.490E-01     0.130E-01     15.00
    8     0.120E-01     0.365E 00     0.168E 00     0.629E-02     30.00
    9     0.400E-02     0.270E 00     0.500E 00     0.465E-02     45.00

             F          T         SQRT(T)  LOG(1-F)
     1     0.1465      1.00       1.00     -0.0688
     2     0.2778      2.00       1.00     -0.1413
     3     0.3939      3.00       1.00     -0.2175
     4     0.4697      3.00       1.00     -0.2755
     5     0.5253      5.00       1.00     -0.3235
     6     0.8081     10.00       1.00     -0.7169
     7     0.8965     15.00       1.00     -0.9849
     8     0.9798     30.00       1.00     -1.6946

EXPT     4187502        NO. OF POINTS      8
SLOPE         0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT       CONC UG/ML     DEV            UM/ML        TIME
    1     0.322E 00     0.404E 01     0.216E-01     0.697E-01      1.00
    2     0.270E 00     0.343E 01     0.220E-01     0.591E-01      2.00
    3     0.184E 00     0.241E 01     0.234E-01     0.415E-01      4.00
    4     0.161E 00     0.213E 01     0.242E-01     0.368E-01      5.00
    5     0.120E 00     0.165E 01     0.266E-01     0.284E-01      7.00
    6     0.800E-01     0.117E 01     0.325E-01     0.202E-01     10.00
    7     0.460E-01     0.768E 00     0.482E-01     0.132E-01     15.00
    8     0.900E-02     0.329E 00     0.223E 00     0.567E-02     30.00

             F          T         SQRT(T)  LOG(1-F)
     1     0.1995      1.00       1.00     -0.0966
     2     0.3325      2.00       1.00     -0.1755
     3     0.5524      4.00       1.00     -0.3491
     4     0.6113      5.00       1.00     -0.4103
     5     0.7161      7.00       1.00     -0.5469
     6     0.8184     10.00       1.00     -0.7409
     7     0.9054     15.00       1.00     -1.0240
```

[Ni] = 4.98   pH = 6.70   μ = 0.1
Experiment D   particles: 355 to 500 microns

```
EXPT      4197502        NO. OF POINTS      9
SLOPE          0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT        CONC UG/ML     DEV              UM/ML           TIME
   1     0.338E 00      0.423E 01      0.216E-01       0.730E-01        1.00
   2     0.290E 00      0.366E 01      0.218E-01       0.632F-01        2.00
   3     0.258E 00      0.328E 01      0.221E-01       0.566E-01        3.00
   4     0.190E 00      0.248E 01      0.232E-01       0.427E-01        5.00
   5     0.680E-01      0.103E 01      0.360E-01       0.177E-01       10.00
   6     0.400E-01      0.697E 00      0.541E-01       0.120E-01       15.00
   7     0.210E-01      0.471E 00      0.975E-01       0.813E-02       20.00
   8     0.800E-02      0.317E 00      0.251E 00       0.547E-02       30.00
   9     0.600E-02      0.293E 00      0.334E 00       0.506E-02       30.00

             F            T          SQRT(T)   LOG(1-F)
    1     0.1574       1.00        1.00      -0.0744
    2     0.2792       2.00        1.00      -0.1422
    3     0.3604       3.00        1.00      -0.1941
    4     0.5330       5.00        1.00      -0.3307
    5     0.8426      10.00        1.00      -0.8031
    6     0.9137      15.00        1.00      -1.0640
    7     0.9619      20.00        1.00      -1.4194
    8     0.9949      30.00        1.00      -2.2945

EXPT      4197503        NO. OF POINTS      8
SLOPE          0.8425E-01   DEV=   0.1729E-02
INTERCEPT   -0.1872E-01   DEV=   0.2931E-02
          CURRENT        CONC UG/ML     DEV              UM/ML           TIME
   1     0.286E 00      0.362E 01      0.219E-01       0.624E-01        2.00
   2     0.256E 00      0.326E 01      0.222E-01       0.562E-01        3.00
   3     0.196E 00      0.255E 01      0.231E-01       0.439E-01        5.00
   4     0.154E 00      0.205E 01      0.245E-01       0.353E-01        7.00
   5     0.110E 00      0.153E 01      0.276E-01       0.263E-01       10.00
   6     0.630E-01      0.970E 00      0.379E-01       0.167E-01       15.00
   7     0.220E-01      0.483E 00      0.932E-01       0.833E-02       20.00
   8     0.900E-02      0.329E 00      0.223E 00       0.567E-02       30.00

             F            T          SQRT(T)   LOG(1-F)
    1     0.2916       2.00        1.41      -0.1497
    2     0.3683       3.00        1.41      -0.1995
    3     0.5217       5.00        1.41      -0.3203
    4     0.6292       7.00        1.41      -0.4308
    5     0.7417      10.00        1.41      -0.5879
    6     0.8619      15.00        1.41      -0.8598
    7     0.9668      20.00        1.41      -1.4782
```