

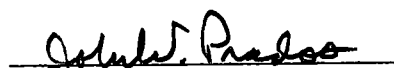
To the Graduate Council

I am submitting herewith a thesis written by Lilla B Cunningham entitled, "Prediction of Breakthrough Curve for Multicomponent Ion Exchange Systems" I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering


J S Watson, Major Professor

We have read this thesis
And recommend its acceptance


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Accepted for the Council


Associate Vice Chancellor and
Dean of The Graduate School

**PREDICITON OF BREAKTHROUGH CURVE FOR MULTICOMPONENT
ION EXCHANGE SYSTEMS**

**A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville**

**Lilla B Cunningham
May 2000**

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ABSTRACT

A simple method/procedure to predict the shape of the breakthrough curve for multi-component ion exchange systems with favorable isotherms was developed. The procedure was based on an earlier procedure developed by Watson for binary ion exchange and adsorption processes. The procedure uses a calculational method to determine the NTU (ratio of the change in concentration to the driving force) from a plot of the equilibrium curve and operating line for a favorable isotherm. The procedure is applicable only to favorable isotherms because it only addresses constant pattern breakthrough fronts. If a constant pattern front does not exist, the calculations will not be valid. The effective equilibrium curve was developed using binary equilibrium data, mass balance equations for the ions in solution and the ions on the resin, and some simplifying assumptions applicable to constant pattern fronts. Development of the equilibrium curve for an n-component system was generalized and the methodology illustrated with 3 and 4 components ion exchange systems. The shape of the breakthrough curve was predicted for both binary and ternary ion exchange systems and compared to experimental data. Systems evaluated experimentally included 1) $\text{Na}^+ - \text{H}^+$, 2) $\text{Cu}^{++} - \text{Na}^+$, 3) $\text{Cu}^{++} - \text{Co}^{++}$, 4) $\text{Ca}^{++} - \text{Co}^{++}$, 5) $\text{Ca}^{++} - \text{H}^+ - \text{Na}^+$, 6) $\text{Ca}^{++} - \text{Co}^{++} - \text{Na}^+$ and 7) $\text{Cu}^{++} - \text{H}^+$ in dilute chloride solutions using a strong cation ion exchange resin (DOWEX). The calculated breakthrough curves agreed favorably to the experimental breakthrough curve. Some deviation at the low concentration range was observed and is probably due to a "constant" pattern front not being developed. A constant pattern front had probably not

developed due to the short length of the column (15.4") or the high flow rates (8.5 and 16.5 ml/min) employed with the systems evaluated. For the ternary systems, the calculated NTUs were a little higher than the experimental NTUs at the high concentration range due to the approximation employed – concentration of the least preferred ion(s) is equal to its feed concentration. In real cases, the concentration of this ion(s) would be higher but approaching the feed concentration. The HTUs, defined as $V_s/k_f a$, were calculated from the experimental data. The effects of flow rate and feed concentration on the NTUs, therefore the length of the front, were also evaluated. The feed concentration had little effect on the NTUs. The HTU increased with flow rate as expected for the Na-H system, however, no noticeable differences were seen in the HTU for the Cu-H-Na system when the flow rate was increased. Molar selectivity was also calculated for Cu-Na and Co-Cu systems and agreed somewhat with the literature values. The resin capacity was determined experimentally from the breakthrough curve.

TABLE OF CONTENTS

	Page
CHAPTER 1: INTRODUCTION	1
CHAPTER 2. LITERATURE REVIEW	7
CHAPTER 3 DEVELOPMENT OF PROCEDURE TO PREDICT BREAKTHROUGH IN MULTICOMPONENT ION EXCHANGE	14
CHAPTER 4: EXPERIMENTAL EVALUATION	26
CHAPTER 5: DISCUSSION OF RESULTS	50
CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS	78
REFERENCES	81
APPENDICES	84
APPENDIX A: Comparison of the front velocity	85
APPENDIX B. Derivation of the equilibrium curve for divalent ion exchanging with an univalent ion on the resin	89
APPENDIX C: Equations for 4 and 5 component Ion Exchange Systems	90
APPENDIX D: Program Listing	92
APPENDIX E: Pump Calibration Data	104
APPENDIX F: DOW Chemical Company – Resin data	105
APPENDIX G: Determination of Cu and Co Concentration using Spectrophometric Analyses.	108
APPENDIX H: Effect of the pH measurement (H Concentration) on the shape of the breakthrough curve	116
APPENDIX I: Experimental Concentration versus Time data	118
APPENDIX J Experimental Molar Selectivity Data	137

APPENDIX K: Determination of Resin Capacity from Experimental	
Data.	. 144
VITA.	. 149

LIST OF SYMBOLS

A	Absorbance
a	Surface area
$\overline{A}, \overline{B}, \overline{C}$, etc.	Concentration of Component or Ion A, B, C etc on the resin, (meq/ml)
A, B, C , etc.	Concentration of component or ion A, B, C, etc in solution, (moles/liter, meq/ml)
A_0, B_0 , etc	Concentration of Component A, B, etc. in the feed (moles/liter, meq/ml)
$\overline{A}_0, \overline{B}_0$, etc.	Concentration of Component A, B, etc. on the resin
$\overline{C}_p$	solid phase concentration (eq/L)
c	Dimensionless concentration
D_s	intraparticle pore diffusivity (cm ² /min)
ξ	Dimensionless particle position
K_{AB}	Molar selectivity for ion A exchanging with ion B
K_A, K_B , etc.	Relative molar selectivity of component A, B, etc
k_f	Liquid film mass transfer coefficient
L	column length (cm)
k_+	adsorption (forward) reaction rate constant
k_-	desorption (reverse) reaction rate constant
N	Ratio of surface diffusion rate to convection rate
n	Ratio of n_1 to n_2
n_1	Charge of component 1

n_2	Charge of component 2
p	particle phase
Q	Total solution concentration, (moles/liter, meq/ml).
$\bar{Q}$	Resin Capacity, (meq/ml)
Q_s	Volumetric flow rate
R	particle radius (cm or micron)
r	particle position (cm)
τ	percolation time (min)
t	time (min)
θ	dimensionless time
u_o	interstitial fluid velocity (cm/min)
V_s	Solution Velocity (cm/min)
V_f	Front Velocity (cm/min)
Y	dimensionless generation term by reaction
z	column position (cm)

LIST OF FIGURES

Figure	Page
1.1 A Favorable Isotherm – Concentration of the solute on the resin ($\bar{Q}$) versus concentration of the solute in solution (C) is concave downward	3
3.1 Typical breakthrough curve for a 3 component system where the selectivity preference is $A > B > C$ and no C is present in the feed	18
3.2 Movement of a constant pattern front down an ion exchange column	23
4.1 Run 1- 0.0472 M Cupric chloride on sodium loaded resin (16.5 ml/min)	32
4.2 Run 2- 0.104 M Cobalt chloride on Copper loaded resin (16.20 ml/min)	33
4.3 Run 3- 0.096 M Calcium chloride on Cobalt loaded resin (16.14 ml/min)	34
4.4 Run 4- 0.046 M Cupric chloride on Sodium loaded resin (15.87 ml/min)	35
4.5 Run 5 – 0.049 M Cobalt chloride on Copper loaded resin (15.97 ml/min)	36
4.6 Run 7 – 0.098 M Cupric chloride on Sodium loaded resin (16.12 ml/min)	37
4.7 Run 8- 0.099 M Cobalt chloride on Copper loaded resin (8.5 ml/min)	38
4.8 Run 10 – 0.023 M Cupric chloride and 0.025 M Cobalt chloride on Sodium loaded resin (16.32 ml/min)	39
4.9 Run 12 – 0.023 M Cupric chloride and 0.0257 M Hydrogen chloride on Sodium loaded resin (15.97 ml/min)	40
4.10 Run 14 – 0.05 M Sodium chloride on Hydrogen loaded resin (16.24 ml/min)	41
4.11 Run 15 – 0.049 M Cupric chloride and 0.0661 M Hydrogen chloride on Sodium loaded resin (8.52 ml/min)	42
4.12 Run 17 – 0.023 M Cupric Chloride and 0.025 M Sodium chloride on Hydrogen loaded resin (16.15 ml/min)	43
4.13 Run 19 – 0.037 M Cupric chloride and 0.01 M Sodium chloride on Hydrogen loaded resin (15.57 ml/min)	44

Figure	Page
4 14 Run 21 – 0.091 M Sodium chloride on Hydrogen loaded resin (16.0 ml/min)	45
4 15 Run 22 – 0.05 M Hydrogen chloride on Sodium loaded resin (15.8 ml/min)	46
4 16 Run 23 – 0.0231 M Cupric chloride and 0.0251 M Hydrogen chloride on Hydrogen loaded resin (16.78 ml/min)	47
4 17 Run 25 – 0.0272 M Sodium chloride on Hydrogen loaded resin (8.47 ml/min)	48
4 18 Run 26 – 0.037 M Cupric chloride and 0.0155 M Hydrogen chloride on Sodium loaded resin (8.47 ml/min)	49
5 1 Breakthrough curve for exchange of 0.0472 M Cupric chloride on sodium loaded resin at 16.5 ml/min (Run 1)	54
5 2 Breakthrough curve for exchange of 0.104 M Cobalt chloride on Copper loaded resin at 16.2 ml/min (Run 2)	55
5 3 Breakthrough curve for exchange of 0.096 M Calcium chloride on cobalt loaded resin at 16.14 ml/min (Run 3)	56
5 4 Breakthrough curve for exchange of 0.046 M Cupric chloride on Sodium loaded resin at 15.87 ml/min (Run 4)	57
5.5 Breakthrough curve for exchange of 0.049 M Cobalt chloride on copper loaded resin at 16.24 ml/min (Run 5)	58
5 6 Breakthrough curve for exchange of 0.098 M Cupric chloride on sodium loaded resin at 16.12 ml/min (Run 7)	59
5 7 Breakthrough curve for exchange of 0.099 M Cobalt chloride on Copper loaded resin at 8.5 ml/min (Run 8)	60
5 8 Breakthrough curve for exchange of 0.023 M Cupric chloride and 0.025 M Cobalt chloride on sodium loaded resin at 16.32 ml/min (Run 10)	61
5 9 Breakthrough curve for exchange of 0.023 M Cupric chloride and 0.0257 M Hydrogen chloride on sodium loaded resin at 15.97 ml/min (Run 12)	62

Figure	Page
5.10 Breakthrough curve for exchange of 0.05 M Sodium chloride on Hydrogen loaded resin at 16.23 ml/min (Run 14)	63
5.11 Breakthrough curve for exchange of 0.049 M Copper chloride and 0.0661 M Hydrogen chloride on sodium loaded resin at 8.52 ml/min (Run 15)	64
5.12 Breakthrough curve for exchange of 0.023 M Cupric chloride and 0.025 M Sodium chloride on hydrogen loaded resin at 16.15 ml/min (Run 17)	65
5.13 Breakthrough curve for exchange of 0.037 M Cupric chloride and 0.01 M Sodium chloride on hydrogen loaded resin at 15.57 ml/min (Run 19)	66
5.14 Breakthrough curve for exchange of 0.091 M Sodium chloride on hydrogen loaded resin at 16 m/min (Run 21)	67
5.15 Breakthrough curve for exchange of 0.05 M Hydrogen chloride on sodium loaded resin at 15.8 ml/min (Run 22)	68
5.16 Breakthrough curve for exchange of 0.0231 M Cupric chloride and 0.0252 M Hydrogen chloride on hydrogen loaded resin at 16.78 ml/min (Run 23)	69
5.17 Breakthrough curve for exchange of 0.072 M Sodium chloride on hydrogen loaded resin at 8.47 ml/min (Run 25)	70
5.18 Breakthrough curve for exchange of 0.037 M Cupric chloride and 0.0155 M Hydrogen chloride on sodium loaded resin at 8.47 ml/min (Run 26)	71
5.19 Equilibrium Curve for 4 and 5 Component Ion Exchange Systems	77
A.1 Hydrogen Concentration as a function of front velocities for Cu and H exchanging with Na	87
G.1 Schematic of the HP8452A Optical system	108
G.2 Absorbance Spectrum of 0.2 M Cupric Chloride solution	111
G.3 Absorbance Spectrum of 0.2 M Cobalt Chloride solution	112

Figure	Page
G 4 Cupric Chloride Calibration Curve	115
G.5 Cobalt Chloride Calibration Curve	115
H 1 Run 12 – 0.023 M Cupric Chloride and 0.0257 M Hydrogen chloride on sodium loaded resin	117
H 2 Run 12 – 0.023 M Cupric Chloride and 0.0257 M Hydrogen chloride on sodium loaded resin – reanalyzed	117
K 1 Na Electrode Calibration Curve	146

LIST OF TABLES

Table	Page
4 1 Experimental Plan	28
4 2 Experimental Run – Summary	29
4 3 Comparison of measured and standard hydrogen concentration of 4 01, 7.00 and 10 01 buffer solutions	31
5.1 Experimental HTU	52
5.2 Parameters used to calculate a general equilibrium curve for 4 and 5 component ion exchange systems	76
A.1 Input Parameters for comparing front velocities	86
E 1 Pump Calibration – Master Flex with 7014 pump head	104
G.1 Cupric Chloride Calibration Data	114
G.2 Cobalt Chloride Calibration Data	114
I 1 Run 1 Experimental and Calculated Breakthrough Data- 0 0472 M Cupric chloride on Sodium loaded resin (16.5 ml/min)	119
I 2 Run 2 Experimental and Calculated Breakthrough Data- 0.104 M Cobalt chloride on Copper loaded resin (16.2 ml/min)	120
I.3 Run 3 Experimental and Calculated Breakthrough Data- 0096 M Calcium chloride on Cobalt loaded resin (16 ml/min)	121
I.4 Run 4 Experimental and Calculated Breakthrough Data - 0 046 M Cupric chloride on Sodium loaded resin (15 87 ml/min)	122
I.5 Run 5 Experimental and Calculated Breakthrough Data – 0 049 M cobalt chloride on Copper loaded resin (15.97 ml/min)	123
I 6 Run 7 Experimental and Calculated Breakthrough Data - 0.098 M Cupric chloride on sodium loaded resin (16.12 ml/min)	124
I 7 Run 8 Experimental and Calculated Breakthrough Data – 0 099 M Cobalt chloride on Copper loaded resin 98 5 ml/min)	125

Table	Page
I 8 Run 10 Experimental and Calculated Breakthrough Data – 0.023 M Cupric chloride and 0.025 M Cobalt chloride on Sodium loaded resin (16.32 ml/min)	126
I 9 Run 12 Experimental and Calculated Breakthrough Data – 0.023 M Cupric chloride and 0.0257 M Hydrogen chloride on Sodium loaded resin (15.97 ml/min)	127
I.10 Run 14 Experimental and Calculated Breakthrough Data – 0.05 M Sodium Chloride on Hydrogen loaded resin (16.24 ml/min)	128
I 11 Run 15 Experimental and Calculated Breakthrough Data – 0.049 M Cupric chloride and 0.0661 M Hydrogen chloride on a Sodium loaded resin (8.52 ml/min)	129
I 12 Run 17 Experimental and Calculated Breakthrough Data – 0.023 M Cupric chloride and 0.025 M Sodium chloride on a Hydrogen loaded resin (16.15 ml/min)	130
I.13 Run 19 Experimental and Calculated Breakthrough Data – 0.037 M Cupric Chloride and 0.01 M Sodium chloride on a Hydrogen loaded resin (15.57 ml/min)	131
I.14 Run 21 Experimental and Calculated Breakthrough Data – 0.091 M Sodium chloride on Hydrogen loaded resin (15.57 ml/min)	132
I 15 Run 22 Experimental and Calculated Breakthrough Data – 0.05 M Hydrogen chloride on sodium loaded resin (15.8 ml/min)	133
I 16 Run 23 Experimental and Calculated Breakthrough Data – 0.0231 M Cupric chloride and 0.0251 M Hydrogen chloride on a Hydrogen loaded resin (16.78 ml/min)	134
I.17 Run 25 Experimental and Calculated Breakthrough Data – 0.072 M Sodium chloride on Hydrogen loaded resin (8.47 ml/min)	135
I.18 Run 26 Experimental and Calculated Breakthrough Data – 0.037 M Cupric chloride and 0.0155 M Hydrogen chloride on a Sodium loaded resin (8.47 ml/min)	136
J.1 Relative Molar Selectivity Coefficients for Univalent and Divalent Cations on DOWEX 50	138

Table	Page
J.2 DOW Ion Exchange Resin	139
J.3 Molar Selectivity - Experimental and Literature Values	141
J.4 Molar Selectivity used to calculate the NTU for comparison to the experimental system	143
K 1 Sodium Concentration of CuCl_2 solution equilibrated with the ion exchange resin	145

CHAPTER 1

INTRODUCTION

Ion exchange is a solid-liquid process in which a reversible exchange occurs between ions in an insoluble solid resin and ions in solution. The ions in solution diffuse into the resin while the ions on the resin diffuse into the solution as equilibrium is approached. The ions in the solution are removed by the ion exchange material that releases an equivalent amount of ions (to the solution) in order to maintain electroneutrality. A counter-ion is defined as the ion being exchanged with the ion exchange resin and the co-ion is the non-exchanging ion and has the same ionic charge as the resin framework. The co-ions are hindered from entering the resin during the ion exchange process due to Donnan exclusion, but this does not hinder the exchange of the counter ions. In ion exchange operations a fluid is passed through a bed of resin, which has a limited capacity for exchange and eventually the resin is saturated. The saturated ion exchange resin can be regenerated by contacting it with a concentrated solution of the original ion on the resin. This reverses the process thus regenerating the resin.

The first ion exchange materials were naturally occurring porous sands called zeolites [1]. Today, the most common ion exchange solids are typically synthetic resins of polymers containing active groups that can exchange ions between the resin and the solution. There are also some commercial inorganic ion exchange materials [2,3]. Ion exchange applications have included water softening, demineralization of water, purification of chemicals, removal of trace toxins or products, recovery of metals like Cu

from leached ores or wastes, separation of ions by chromatography, treatment of radioactive wastes etc [1,4].

The rate of ion exchange depends on:

- 1) mass transfer of ions from the bulk of the liquid to the external surface of the exchanger particle,
- 2) diffusion of the ions through the solid to the exchange site or surface,
- 3) exchange of the ions,
- 4) outward diffusion of the released ions to the surface of the solid, and
- 5) diffusion of the released ions from the surface of the solid to the bulk of solution.

There is usually little resistance from exchange “reactions”; most resistance comes from the diffusion processes, therefore the diffusion of the ions rather than the exchange of the ion is the rate-determining step. Either particle diffusion or film diffusion can be rate controlling. However, in many instances, the mass transfer resistance in the liquid film is the controlling step, especially when very dilute solutions are involved. Most ion exchange operations involve dilute solutions. Other factors that affect the rate of ion exchange (diffusion mechanism) are the amount of cross linkage in the polymer, the particle size of the resin, the degree of agitation, and the concentration of the ionic group. Film resistance control (over solid diffusion resistance) is most likely in systems with ion exchange resin of high concentration of fixed ionic group, low degree of cross linking, and small particle size, with dilute solutions, and with inefficient agitation

Operations of most ion exchange processes are similar in many ways to adsorption operations. They are usually treated together in textbooks because the design methods used for ion exchange and adsorption are similar. Most processes employing ion exchange and adsorption have a favorable isotherm. In a favorable isotherm the equilibrium between the concentration of the solute in solution and the concentration of the solute on the adsorbent (resin) is concave downward as shown in Figure 1.1. Here, the ion in the feed is preferred over the ion initially on the resin. If a favorable isotherm does not exist, ion exchange is less likely to be selected for that particular separation.

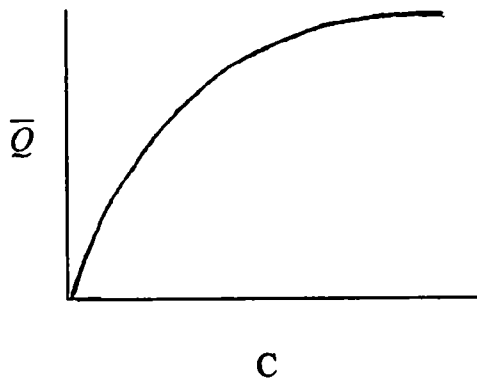


Figure 1.1 A Favorable Isotherm- Concentration of the solute on the resin ($\bar{Q}$) versus concentration of the solute in solution (C) is concave downward

Systems with favorable isotherms develop a constant pattern front (the mass transfer zone is constant as it travels through the column) when long bed lengths are used [5]. This is due to a balance between the dispersion forces that tend to spread the front and the sharpening forces which tend to cause the front to decrease in length or straighten with time. The sharpening force results because the back of the mass transfer zone (high concentration region) wants to move faster than the leading or (forward) edge of the zone (low concentration region). The balance between the dispersion and sharpening forces produces the constant pattern front, "self sharpening", in the column. The stronger the preference for the ion in solution, the sooner the constant pattern is attained and the sharper the boundary. With unfavorable equilibrium the boundary becomes more and more diffuse as it moves down the column thus producing a "non-sharpening" boundary. Constant shape fronts are common in many industrial ion exchange and adsorption operations.

Watson [6,7] developed a procedure to predict the shape of constant pattern adsorption and ion exchange processes in fixed beds for binary systems using ion exchange equilibria. The procedure was based on well-known graphic or numerical procedures used for analyzing countercurrent extraction and absorption operations. The main objective of this work is to extend Watson's procedure to multi-component ion exchange systems. For multi-component systems equilibrium curves based on binary exchanges and mass balances will be developed to use in Watson procedure for calculating breakthrough. This work will allow one to determine more easily the size of the ion

exchange system that is needed for a multi-component system without requiring the use of more complex computer codes or experimental evaluation. A procedure for multi-component ion exchange systems is important because simpler methods are not available for multi-component ion exchange systems and many of the codes calculational schemes for binary and multi-component systems are complicated, difficult to use, or not readily available to all users. The results of this study will be useful to those looking to use or evaluate ion exchange, but are not sufficiently involved in ion exchange to have access to the more complex numerical codes.

In this work, a procedure was developed that can be used relatively easily to predict breakthrough in a multi-component ion exchange system without the use of unusual or extensive computers or software codes. Breakthrough curves for both binary and ternary ion exchange systems were determined experimentally and compared to the calculated data.

This thesis consists of six chapters and ten appendices. Chapter 2 is a literature review which includes a discussion of the method developed by Watson for binary ion exchange and adsorption and other models and calculational codes used to predict breakthrough in binary and multi-component ion exchange systems. The equations and assumptions used to determine the equilibrium curve for a 3 component ion exchange system are presented in Chapter 3. Generalization for cases when more than 3 components are involved in an ion exchange system are also included. The setup of the experimental apparatus, the

experimental procedure and the experimental breakthrough curves for Cu-Na, Cu-Co, Cu-H-Na, H-Na and Cu-Co-Na systems are presented in Chapter 4 Chapter 5 discusses the results of the calculations and its comparison to the experimental data The conclusions of this study with recommendations for further research are given in Chapter 6 Analytical procedures and analyses, the computer programs used to calculate the breakthrough curves, as well as the experimental data and various calculations and experiments are provided in the Appendices

CHAPTER 2

LITERATURE REVIEW

Numerous models have been developed to predict the performance or breakthrough for binary and multi-component ion exchange systems. Some of these models are rather complex and require the use of special computer codes to simultaneously solve a system of non-linear differential equations [8,9,10,11]. Other simpler models are based on drastically simplifying assumptions (no mass transfer resistance, mass transfer resistance are not accounted for separately, etc.) that only give approximate results [3,12]. In general, the various theories to describe column performance are divided into 1) equilibrium theories and 2) rate theories. In the equilibrium theory model, it is assumed that local equilibrium between the liquid and the ion exchange material is attained and all mass transfer resistances are neglected. These assumption results in a vertical breakthrough curve (step function) for systems with favorable isotherms, a result that is unrealistic for most practical single-front ion exchange processes. Although the breakthrough boundary becomes sharper as the performance of the ion exchange resin for the counter ion increases, the front is never completely vertical. These models, although simple to use, do not adequately predict ion exchange systems with significant diffusion resistance. Nevertheless, these simple models can be helpful in explaining the movement of various fronts with very slow flow rates (frontal chromatography) where equilibrium conditions can be approached. Favorable isotherms are the focus of this work so these models will not be addressed further

In the rate theory models, local equilibrium is not assumed and mass transfer resistances are taken into account. The calculations with the rate models are based on continuous flow through the column and finite rates of ion exchange. These models entail complex mathematics; and simple solutions can only be obtained with drastic simplification. The advantage is that they predict column performance from fundamental parameters. Many models have been developed based on the rate theory. In general, the models based on the rate theories require simultaneous solution of 1) the reaction rate equations, 2) ion exchange equilibrium equations, 3) material balances, and 4) Nernst-Planck flux equations for all the ions in the multi-component ion exchange processes. Initial and boundary conditions must also be applied to solve the set of equations. Assumptions are needed to obtain analytical solutions; however, solutions are generally obtained by numerical integration.

Computer simulation models are useful for studying and understanding complex column dynamics in ion exchange processes. One typical computer simulation model that can be used for multi-component ion exchange is VERSE-LC, (VERsatile Reaction and Separation simulator for Liquid Chromatography)[13]. VERSE-LC, a dynamic computer simulation package for adsorption and liquid chromatography systems was developed at Purdue University. VERSE-LC is a detailed rate model that was originally developed to study the complex dynamic behavior of biochemicals in chromatographic separations and to aid in the scale up issues in those types of systems. It is capable of handling multiple components, detailed mass transfer mechanisms, equilibrium and non-equilibrium

adsorption etc. The major assumptions required by the model are: 1) the column is packed with homogenous spherical particles with uniform particle and pore size, 2) the column has uniform packing and pore size, 3) all processes in the column are isothermal, 4) concentration gradients in the radial direction of the column and concentration gradients in the angular direction in the particle are negligible, and 5) mass-transfer coefficients are constant and independent of other components. Implementation of various rate models in VERSE-LC has been made. One recent model incorporated into VERSE-LC was developed by Ernest [14] to predict column performance and behavior in multi-component ion exchange. The model is based on non-equilibrium mass action laws and accounts for surface and pore diffusion. The general rate equations developed by Ernest for surface diffusion for multi-component processes for non-equilibrium systems are illustrated below to show the complexity of a general rate model.

$$\frac{\partial \bar{c}_{p,i}}{\partial \theta} = Y_{1,i} + \bar{Y}_{p,i} + N_{s,i} \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left[\xi^2 \frac{\partial \bar{c}_{p,i}}{\partial \xi} \right] \quad 2.1$$

$$\xi = 0, \quad \frac{\partial \bar{c}_{p,i}}{\partial \xi} = 0 \quad 2.2$$

$$\xi = 1, \quad \frac{\partial \bar{c}_{p,i}}{\partial \xi} = Y_{1,i} + \frac{2D_{s,i}L}{R^2 u_0} \frac{\partial \bar{c}_{p,i}}{\partial \xi} \quad 2.3$$

$$\theta = 0, \quad \bar{c}_{p,i} = \bar{c}_{p,i}(0) \quad 2.4$$

The adsorption isotherm is given by:

$$Y_{1,i} = \frac{\tau}{C_{T,i}} \left[\frac{d\bar{C}_{p,i}}{dt} \right] \quad 2.5$$

Therefore, for components 2 through N_c

$$Y_{l,i}|_{i>1} = \frac{\tau}{C_T} \left[l_{+,i} C_{p,i}^{z_i} \bar{C}_{p,1}^z - l_{-,i} \bar{C}_{p,i}^{z_i} C_{p,1}^z \right] \quad 2.6$$

and for component 1:

$$Y_{l,1} = -\frac{\tau}{C_T} \sum_{i=2}^{N_c} \frac{d\bar{C}_{p,i}}{dt} \quad 2.7$$

These equations were made dimensionless with characteristic values:

$$x = \frac{z}{L}, \quad \xi = \frac{r}{R}, \quad \theta = \frac{t}{\tau}, \quad \tau = \frac{L}{u_0} \quad 2.8$$

The solid phase concentration is made dimensionless using

$$\bar{c}_{p,i} = \frac{\bar{C}_{p,i}}{C_{T,i}} \quad 2.9$$

This set of nonlinear equations (2.1 –2.9) has been added to the VERSE-LC code where they are solved simultaneously. Other rate theory models have been developed to simulate the column behavior of multi-component ion exchange systems. These models are complex and require sophisticated computer codes or numerical calculations such as the orthogonal collocation finite element method. [15] DASSL, A Differential/Algebraic System Solver developed by Lawrence Livermore National Laboratory, Livermore, CA [16] is another software package used to solve a system of equations derived from the various rate model theory for multi-component ion exchange and adsorption systems.

A simple procedure whereas one could predict the shape of the breakthrough curve for binary absorption and ion exchange systems for constant pattern fronts was developed by Watson [5,6,7] The procedure is based on the rate theory and uses graphical and

numerical procedures developed for designing countercurrent extraction and absorption processes. However, no complex computer codes are required and only minimal calculations are needed. The methodology employed by Watson uses essentially the same design equations that are used in the VERSE code but limited the analyses to single front, constant patterns in infinite columns, and film resistances. For mass transfer resistance in the fluid phase, the rate of mass transfer is expressed as

$$V_s \frac{dC}{dZ} = k_f a (C - C^*) \quad 2.10$$

V_s is the flow rate of the fluid down the bed, k_f is the fluid film mass transfer coefficient; a is the area of adsorbent or ion exchange per unit volume of bed, Z is the distance from the mid-point of the breakthrough curve, C is the concentration of solute in solution, and C^* is the concentration of the solute in the fluid that is in equilibrium with solid loading.

Rearranging and solving for Z gives

$$Z = \frac{V_s}{k_f a} \int_{C_1}^{C_2} \frac{dC}{C - C^*} = [HTU][NTU] \quad 2.11$$

The HTU is defined as $\frac{V_s}{k_f a}$ and is called the height of a transfer unit (units are in

distance), NTU, $\int_{C_1}^{C_2} \frac{dC}{C - C^*}$ is the number of transfer units (dimensionless) required

between to concentrations C_1 and C_2 . Equation 2.11 assumes that the velocity and the mass transfer coefficient are constant. This is valid for dilute systems or systems in

which the volume of the fluid does not change greatly with concentration of the solute

Using equation 2.11, the shape of the front for a favorable isotherm can be predicted.

The length of the front required to change the concentration of the solute from one value to another value can then be determined by evaluating the NTU and multiplying by the HTU. The HTU is determined independently for the system of interest. Watson obtained values for the NTU as a function of concentration on the front by integrating for different distances from the midpoint using the following approach

- 1) Obtain values of C^* corresponding to C on the operating line and $\bar{C}$ or (Q) on the equilibrium curve (C^* is determined by looking horizontally to the equilibrium curve from the operating line for a value of C).
- 2) The NTU is obtained by integrating a plot of C as a function of $\frac{1}{C^* - C}$ between 2 concentration values (C and $C_{1/2}$).
- 3) The shape of the front is then obtained from a plot of C as a function of NTU
- 4) The length of the front, Z , for a desired separation is obtained by multiplying the corresponding NTU by the HTU. The HTU can be determined experimentally or calculated from $HTU = \frac{V_s}{k_f a}$, using an empirical correlation for $k_f a$

This procedure/method can be performed graphically or analytically, if an expression for the equilibrium isotherm is obtained. Normalized, breakthrough curves were predicted by Watson for both binary ion exchange and adsorption systems for resistance in the fluid and solid phase as well as in both phases.

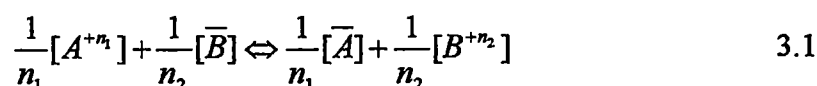
In this work, the methodology developed by Watson will be extended to predict breakthrough in multi-component ion exchange systems for favorable isotherms. The

equilibrium isotherms will be developed based on the last front, where the ion with the highest affinity for the resin is removed from solution. The last front is the one usually of most interest since ion exchange resins are usually selected for their ability to remove a key ion. Because of the high affinity of the resin for this ion, the equilibrium isotherm is very likely to be favorable. If this is not the case, then ion exchange is not likely to be employed or another resin will be selected. The analysis will assume 1) constant pattern front, 2) a favorable (non-linear) isotherm, 3) mass transfer coefficients that do not vary with concentration throughout the front, 4) all mass transfer resistance is in the fluid film, and 5) a linear operating line. This alternate procedure/method to predict the shape of the breakthrough front for multi-component ion exchange systems will aid one in specifying an ion exchange system without building expensive test bed and performing time consuming and costly experiments. Those with large computers and specialized software and codes that have been developed to analyze multi-component ion exchange systems are likely to stay with the available complex codes. The drawbacks of this alternate procedure as opposed to the models solved using the computational codes are 1) mass transfer resistance must be described as a film resistance, 2) only the last front is evaluated, and 3) detailed analyses of a column dynamics (transient conditions) can not be performed.

CHAPTER 3

DEVELOPMENT OF PROCEDURE TO PREDICT BREAKTHROUGH IN MULTICOMPONENT ION EXCHANGE

Many practical applications involve more than two ions. Ion exchange systems with more than two competing ions are a more complex phenomenon than binary ion exchange. However, binary ion exchange equilibrium can be applied along with mass balances and some simplifying assumptions to develop an equilibrium curve that adequately defines the shape of the front of interest, usually the last front, if it is a constant pattern front. The equilibrium curve along with the Watson procedure developed to predict breakthrough for binary ion exchange or adsorption can then be used to calculate the NTU which gives the shape of the breakthrough curve for a constant pattern front. The operating line is easily obtained from a material balance across the column. In general, the mechanism describing the exchange of ions between an ion exchange material containing B and a solution containing A is described by equation 3.1



A and B are the concentration of ions A with an ionic charge n_1 and B with an ionic charge n_2 in the solution, respectively. $\bar{A}$ and $\bar{B}$ are the concentrations of ions A and B on the ion exchange resin, respectively. At equilibrium, the molar selectivity coefficient (K_{AB}) for ion A entering the ion exchange resin and displacing ion B is defined as

$$K_{AB} = \frac{(\bar{A}^* / A)}{(\bar{B}^* / B)^n} \quad 3.2$$

$\bar{A}^*$ and $\bar{B}^*$ are the concentration of ions A and B in the resin (meq/gm) that is in equilibrium with ions A and B in the solution (meq/ml), and n is the ratio of n_1 to n_2 . This definition assumes that the activity coefficients do not change in either the solution or the resin during the exchange, K_{AB} is then constant which is usually valid for dilute solution. If the solution is not dilute, then the solutions activity coefficients must be added to the above expression. An equation for the equilibrium isotherm/curve is then obtained by rearranging equation 2 as follows:

$$\bar{A}^* = K_{AB} A \left(\frac{\bar{B}^*}{B} \right)^n \quad 3.3$$

Equation 3.2 (or 3.3) can be written for $n-1$ components that are in solution exchanging with the resin. The interest lies in ion A and the ion(s) on the resin that is (are) being displaced by A. Only the case where A is the most preferred ion by the resin (or the most preferred ion with significant concentration) will be addressed since ion exchange resins are normally selected for their ability to remove a key ion. This is usually the ion with the highest affinity for the resin. The ion(s) being replaced by the A ion could be the original ion on the resin or an ion in the feed that has exchanged with the initial ion on the resin before the A front.

For a 3 component system (A, B, & C) where component A is the material of interest (the ion most preferred by the resin) and C is the component on the resin, then 2 cases are possible depending on the exchange sequence.

1. B is preferred over C

2. C is preferred over B

In the first case, the loaded resin would be concentrated in A, the preferred ion, but would contain equilibrium concentrations of B and C, if there were any C in the feed solution. The A-front would be preceded by a B-front where B and A displace C from the resin. The distance between the B-front and the A-front could be short for a finite column if the concentration of B is low, but for an infinitely long column there will always be sufficient B to form a front. The concentration of C across the A-front will remain approximately constant and equal to the concentration in the feed. This case could be expanded to include more ions ($A > B > C > D$ etc). The concentration of the least preferred ions (C, D, etc) would remain constant across the A-front depicting binary exchange.

In the 2nd case, for a 3 component system defined as C being preferred over B, B is displacing C as well as A displacing C (and B). Although the A-front is favorable, the B-front is not favorable since the resin has a higher affinity for C than B. Therefore, the B-front will not be a constant pattern, and will be constantly spreading and becoming very broad in an infinite column. Similarly for a system with more than 3 components, for illustration say 4 components with $A > D > B > C$ and D being initially on the resin, both the B and C-fronts will be unfavorable. Their fronts will not be a constant pattern and will be broad in an infinitely long column. The selectivity of the resin and the concentration of the ions in the feed will determine the center of the broad fronts. When the concentration of B and C ions (or B ion for a 3 component system) are sufficiently low that even with low selectivity, the B and C-fronts will progress down the column

slower than the A front. The B and C ions would be trying to displace ion A. However, since the resin prefers ion A to ions B and C, the equilibrium concentration of the B and C components will be low in the resin. That is, the ratio of the concentration of the trace components to the concentration of A will be even lower in the resin than in the feed solution. In this case, for an infinitely long column, the concentrations of B and C can be assumed to be essentially zero throughout the A-front. There will be traces of these materials far upstream within the resin loaded with A. The amount of impurities will be determined by the selectivity of the resin for component A.

When the concentration of B and C are sufficiently high and/or the selectivity of B and C are sufficiently low, the B and C-fronts will pass the A-front. The A-front will displace the next slowest ion front or the front with the next highest preference for the resin. For the 4 component system when the selectivity sequence is $A > D > B > C$, this is defined as component D. In this scenario, the problem can be approximated by assuming the concentrations of B and C are constant over the A front and equal to the concentration in the feed ($B=B_0$ and $C=C_0$). However in reality, the concentrations are usually higher and tend to approach the feed concentration. Comparison of the A and B-front velocities is given in Appendix A.

These concepts can be expanded to cover any n-component system. An n-component system would behave similar to one of the cases discussed above so no new concepts or relationships are needed to define such a system. There will only be $n + 1$ equations to be

solved simultaneously when a constant pattern front has developed for the component of interest, A. The development of the equilibrium curve will now be illustrated for a 3 component system and will then be generalized for similar situations when more than 3 ions are present.

For case 1 (B is preferred over C), there is no C present on the resin or in the solution for an infinitely long column. A schematic of a typical breakthrough curve for a 3 component system when the selectivity is $A > B > C$, and no C is in the solution, is shown in Figure 3.1. The equation for the equilibrium curve is more complex when unequal charge ions are exchanged (n_1 is not equal to n_2) than when the ions carry the same charge. Therefore, to simplify the equations and derivations used for this illustration, the equilibrium curve will be derived here for the case when $n_1 = n_2$.

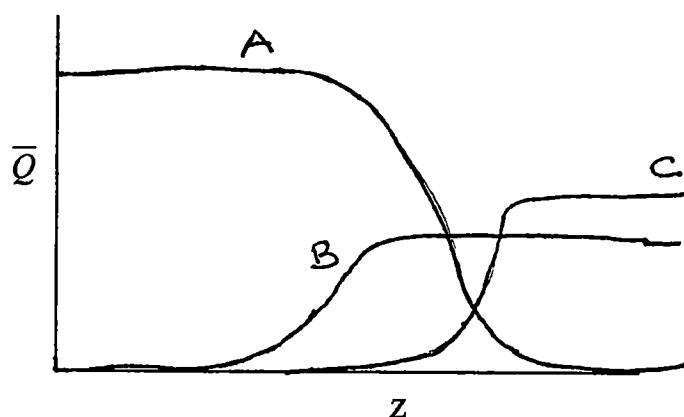


Figure 3.1 – Typical breakthrough curve for a 3 component system where the selectivity preference is $A > B > C$ and no C is present in the feed

For exchange of ions with equal charges ($n_1=n_2$), the equilibrium relation (equation 3)

reduces to

$$\bar{A}^* = K_{AB} A \left(\frac{\bar{B}^*}{B} \right) \quad 3.4$$

Since, the total ionic concentration of the solution leaving the column can be no greater than it was when it entered the column, the following relations are written for the solution and the column:

$$A+B+C=Q \quad 3.5$$

$$\bar{A}^* + \bar{B}^* + \bar{C}^* = \bar{Q}^* = \bar{Q} \quad 3.6$$

where Q - concentration of the solution

$\bar{Q}$ - resin capacity

Near the A-front when B has displaced C, no C is present on the resin or in the solution for an infinitely long column ($\bar{C}^* = 0$ and $C = 0$), therefore, equations 3.5 and 3.6 reduce to

$$A + B = Q \quad 3.7$$

$$\bar{A}^* + \bar{B}^* = \bar{Q}^* = \bar{Q} \quad 3.8$$

Substituting equations 3.7 and 3.8 into equation 3.4 and rearranging gives the following equation for the equilibrium curve:

$$\bar{A}^* = \frac{AK_{AB}\bar{Q}}{Q + (K_{AB} - 1)A} \quad 3.9$$

Equation 3.9 gives the concentration of ion A in the resin as a function of A for the case where $A > B > C$ and $n_1=n_2$. This is the effective equilibrium curve for the A-front K_{AB} ,

Q and $\bar{Q}$ are constant for a particular system. A similar equation can be derived for component B. Note, this is much like the simpler binary exchange cases considered by Watson, but in this case, there is always some B in the A front because there is B in the feed. The principal difference between this case and the simple binary cases studied by Watson is in the operating line, not in the equilibrium curve. Derivation of the equilibrium curve for divalent ion exchanging with a univalent ion on the resin ($n_1=2$ and $n_2=1$) is given in Appendix B for this case

For the case when C is preferred over B (Case 2), the equilibrium curve will depend on whether the B front advances faster or slower than the A- front down the column. When the B front is behind the A- front, then ion A is essentially exchanging with C, and $\bar{B}^*$ and B are approximately zero across the A-front. The equilibrium relationship is then

$$\bar{A}^* = \frac{K_{AC} \bar{A} \bar{C}^*}{C} \quad 3.10$$

(To simplify the derivation, $n_1=n_2$ was assumed.) Equations 3.5 and 3.6 then become

$$A + C = Q \quad 3.11$$

$$\bar{A}^* + \bar{C}^* = \bar{Q} \quad 3.12$$

Substituting equations 3.11 and 3.12 into 3.10 and rearranging gives the following equation for the equilibrium curve

$$\bar{A}^* = \frac{AK_{AC}\bar{Q}}{Q + (K_{AC} - 1)A} \quad 3.15$$

This equation is similar to the equation for the equilibrium curve derived for Case 1 for a 3 component system with the exchange being between ions A and C instead of A and B because C has a higher affinity for the resin than B

Finally, when the B-front is in front of the A-front for a selectivity sequence of $A > C > B$, then the concentration of B would eventually be constant and equal to its feed concentration ($B=B_0$). There are now 2 equilibrium relations that must be used along with equation 3.5 and 3.6:

$$\bar{A}^* = K_{AB}A \left(\frac{\bar{B}^*}{B} \right) \quad 3.14$$

$$\bar{A}^* = K_{AC}A \left(\frac{\bar{C}^*}{C} \right) \quad 3.15$$

The equation for the equilibrium curve is now obtained by rearranging equations 3.5, 3.6, 3.14, and 3.15 and solving for $\bar{A}^*$ as a function of A:

$$\bar{A}^* = \frac{K_{AB}K_{AC}\bar{Q}}{B_0K_{AC} + K_{AC}(AK_{AB} + Q - A - B_0)} \quad 3.16$$

Equation 3.16 gives an explicit expression for $\bar{A}^*$ as a function A when the concentration of component B is approximated as B_0 , feed concentration

Equations 3.5, 3.6, 3.14, and 3.15 could also be solved simultaneously using a solving function such as "fsolve" in MATLAB. For the case where $n_1 \neq n_2$ it would be difficult to obtain an explicit expression for the effective equilibrium and a solving routine would be essential.

Expanding the derivation to more than 3 components does not add any new relations or types of equations. For an n -component system, $2n-1$ equations would be needed to define the equilibrium curve for the component of interest if no assumptions were made. The equilibrium relations, the total ionic concentration in solution, and the total ionic concentration of the resin only provide $n+1$ equations. A list of equations and assumptions for a system with 4 and 5 components are provided in Appendix C. Unlike the simpler case of binary and ternary exchange an explicit expression for the equilibrium curve for component A can not be easily written or derived. An equation solver is needed for larger numbers of components especially when $n_1 \neq n_2$.

A schematic showing the movement of a constant pattern front down a column is shown in Figure 3.2. When the bed and the front are viewed from a moving "imaginary" plane that crosses the bed and moves with the velocity of the front, the bed appears to be at steady state and the front appears to be fixed in the moving space. Therefore, the resin appears to be moving upward with the same velocity by which the front is moving down the bed and the fluid appears to be moving down the bed with a velocity equal to the fluid

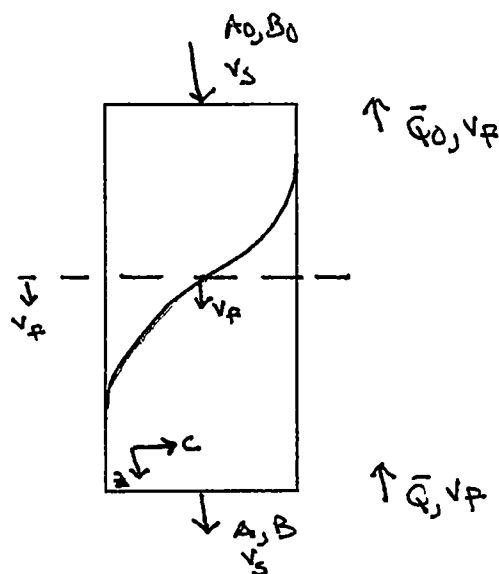


Figure 3.2 Movement of a constant pattern front down an ion exchange column

velocity minus the front velocity, $V_s - V_f$. Viewed from the position of the moving front, material balances for components A and B are written as

$$\bar{A} - \bar{A}_0 = (A - A_0) \frac{(V_s - V_f)}{V_f} \quad 3.17$$

$$\bar{B} - \bar{B}_0 = (B - B_0) \frac{(V_s - V_f)}{V_f} \quad 3.18$$

where V_f = velocity the front moves down the column

V_s = velocity (flow rate) of the fluid down the column

A, B – concentration of components A and B in solution that is in equilibrium with the column far below the front

$\bar{A}, \bar{B}$ - concentration of components A and B in the solid that is in equilibrium with the inlet fluid

Equations 3.17 and 3.18 give the operating line for components A and B in an ion exchange system

From the equilibrium curve and the operating line, the NTU for a multi-component ion exchange system can be easily determined using the approach developed by Watson as described in Chapter 2. For this study, computer programs were written in MATLAB [17] to calculate the NTU for 2, 3, 4 and 5 component ion exchange systems. MATLAB is a computation, data analysis, and visualization software provided by the MathWorks, Inc. The program uses the equilibrium curve derived for the A-front and Watson's procedure assuming liquid film mass transfer. The programs for the binary and ternary ion exchange systems generate a breakthrough curve and tabulates the NTU as a function of concentration of A. Breakthrough curves for 4 and 5 component systems can be calculated in the same way once the effective equilibrium curve is determined. Input values required are concentrations of components in the feed solution, the resin capacity, the molar selectivity (K_{AB} , K_{AC} , etc.), and the ionic charge of components A and B. A copy of the programs is provided in Appendix D. A function in MATLAB called "fsolve" was used to solve the set of equations for the 3 component system when $n_1 \neq n_2$ and the 4 and 5 component systems. "Fsolve" is a built-in function in MATLAB designed to solve a system of nonlinear equations of the form $F(x)=0$ using the nonlinear least squares method. "Fsolve" solves the systems of equations by finding a root or value for the variables that satisfy the equations. However, an initial value must be specified

and only a maximum number of iterations are allowed by the routine. If a solution is not found in the maximum number of iterations or the function does not converge, the search routine exits and gives the message the optimizer is stuck at a minimum that is not a root- try again with a new starting guess. Wrong routes could also be determined if the initial values specified are higher than the actual root. Once the equilibrium curve ($\bar{A}^*$ versus A) is calculated from the set of equations, the NTU can be easily obtained using Watson's procedure

CHAPTER 4

EXPERIMENTAL EVALUATION

Experimental Apparatus and System

Breakthrough curves were determined experimentally by measuring the concentration of the ions in solution leaving an ion exchange column as a function of time. The experimental setup consisted of a XK16 glass column by Pharmacia and a Master Flex peristaltic pump. The XK16 column is 16 mm ID x 60 cm long. It has an end adaptor that allows a range of bed heights to be selected. The Master Flex peristaltic pump used a 7014 pump head that is capable of delivering 0.21 to 21 ml/min of solution at atmospheric pressure. Pump calibration data are given in Appendix E.

The resin used was the DOWEX-HCR-W2 in the sodium form. The DOWEX-HCR-W2 is a high capacity, strong acid cation exchange resin used primarily for mixed bed demineralization and condensate polishing applications. It has a styrene-DVB copolymer matrix (8% cross linkage) with a sulfonic acid functional groups. The Na form has a particle size density of 1.28 g/ml with a minimum exchange capacity of 2 eq/l. The manufacturer product information on the DOWEX-HCR resin is provided in Appendix F. The resin bed length was 15.4 inches.

The H-Na-Cu system was evaluated experimentally. This system was chosen because there were sufficient differences in their selectivity to obtain good separation. Initially, the Cu-Co-Ca system was chosen to study since the Co and Cu could be analyzed easily

using a spectrophotometer. The Ca concentration was to be determined by difference. The system for evaluation was changed to H-Na-Cu because precipitates formed in the solution when CaCl_2 was added to the resin loaded with Co. The precipitates distorted the spectrophotometer analyses. The system was also changed because very little difference was observed in the selectivity of the Cu and Co with the DOW HCR-W2. Based on the manufacturer data, the selectivity sequence for the DOW resin is $\text{Ca} > \text{Co} > \text{Cu} > \text{Na} > \text{H}$. The initial experimental plan was based on these selectivity preferences; however after the first run with cobalt on a copper loaded resin it was obvious that copper and cobalt had essentially the same selectivity for the resin. Chloride solutions were chosen since chloride solutions are not an oxidizer or reducing agent and they are compatible with most ion exchange materials.

The chloride solutions (Cu^{++} , Co^{++} , Ca^{++} , Na^+ , H^+) were prepared by weighing or measuring the amount of material needed and dissolving in deionized water in a volumetric flask. Volumetric flasks were used in preparing the solutions to obtain concentrations as close as possible to the desired concentration. The chloride compounds used to prepare the solutions were $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, CaCl_2 , and NaCl . Both 5 N and 6 N HCl solutions were used as the feedstock for the HCl solutions. HCl solutions with lower concentration were prepared by pipetting the 5 N or 6 N HCl solutions and mixing with deionized water in a volumetric flask.

Experimental Procedure

Chloride solutions containing only 1 or 2 ions were used in the experimental runs. The desired chloride solution was prepared as outlined above, mixed if necessary, and pumped through the ion exchange column at a specified rate until the 80 to 100% breakthrough had occurred. Two flow rates, approximately 16 and 8.5 ml/min, and two concentrations (approximately 0.05 and 0.1 moles/l) were evaluated for both binary and ternary ion exchange systems. An outline of the experimental runs/plan is shown in Table 4.1. A summary of the experimental runs is provided in Table 4.2. Samples of the

Table 4.1 – Experimental Plan

Total solution concentration (M)			0.05		0.1	
Resin	Solution Components		Flow rate (ml/min)		Flow rate (ml/min)	
	A	B	8	16	8	16
C	A	B	8	16	8	16
Na ⁺	H ⁺	---	---	Run 22	---	---
Na ⁺	Cu ⁺⁺	---	---	Run 1 & 4	---	Run 7
H ⁺	Na ⁺	---	---	Run 14	Run 25	Run 21
H ⁺	Cu ⁺⁺	Na ⁺	---	Run 17 and 19	---	---
Na ⁺	Cu ⁺⁺	H ⁺	Run 26	Run 12	Run 15	---
H ⁺	Cu ⁺⁺	H ⁺	---	Run 23	---	---
Na ⁺	Cu ⁺	Co ⁺	---	Run 10	---	---
Cu ⁺⁺	Co ⁺⁺	---	---	Run 5	Run 8	Run 2
Co ⁺⁺	Ca ⁺⁺	---	---	---	---	Run 3

Table 4.2 Experimental Run - Summary

Run No.	Solution	Resin Form	Flow rate (ml/min)	Run Time (min)
1	0.0472 M CuCl_2	Na	16.5	140
2	0.104 M CoCl_2	Cu	16.2	75
3	0.096 M CaCl_2	Co	16.14	120
4	0.046 M CuCl_2	Na	15.87	140
5	0.049 M CoCl_2	Cu	15.97	180
7	0.098 M CuCl_2	Na	16.12	90
8	0.099 M CoCl_2	Cu	8.5	185
10	0.023 M CuCl_2 and 0.025 M CoCl_2	Na	16.32	150
12	0.023 M CuCl_2 and 0.0257 M HCl	Na	15.97	220
14	0.05 M NaCl	H	16.24	240
15	0.049 M CuCl_2 and 0.0661 M HCl	Na	8.52	227
17	0.023 M CuCl_2 and 0.025 M NaCl	H	16.15	270
19	0.037 M CuCl_2 and 0.01 M NaCl	H	15.57	235
21	0.091 M NaCl	H	16.0	124
22	0.05 M HCl	Na	15.8	247
23	0.0231 M CuCl_2 and 0.0251 M HCl	H	16.78	267
25	0.072 M NaCl	H	8.47	235
26	0.037 M CuCl_2 and 0.0155 M HCl	Na	8.47	380

Solution leaving the ion exchange column were taken and analyzed at various time intervals depending on the position of the front of interest in the column. In general, samples were taken more frequently when the front was close to the end of the column (near breakthrough) than when it was at the top of the column. Samples for analyses were taken for 1 min for flow rates around 16 ml/min and 2 minutes for flow rates around 8.5 ml/min. The column was eluted with approximately 1 M NaCl or HCl in order to convert it back to the Na or H form, when necessary. These "runs" were numbered 6, 9, 11, 13, 16, 18, 20 and 24 and are not included in Table 4.1 or 4.2. After eluting with 1 M NaCl or HCl, 0.05 M HCl or NaCl was pumped through the column for at least 3 bed lengths to minimize the effect of the high concentration and resin shrinking and expanding on the shape of the front.

The samples from each run were analyzed, and the concentration was plotted as a function of time. Both Cu and Co concentrations were determined using spectrophotometric analysis technique. The Cu and Co calibration data are provided in Appendix G.

The hydrogen ion concentration was calculated from the pH of the sample ($\text{pH} = -\log_{10} [\text{H}^+]$). One problem encountered with this method was the inconsistency in the pH measurements. Prior to analyzing each set of samples, the pH probe was calibrated with 4.01, 7.0 and 10.01 pH buffer solutions. After calibration, the pH of the buffer solutions was measured for accuracy. Errors ranging from 7.3 to 23% were seen as indicated by

the data shown in Table 4.3. Although there were discrepancies in the pH measurements, therefore the H^+ and Na^+ concentrations, the general shape of the breakthrough curve was unchanged. This is illustrated in Appendix H where breakthrough curves are shown for the same run with 2 different pH measurements.

Table 4.3 Comparison of measured and standard hydrogen concentration of 4.01, 7.00 and 10.01 Buffer Solutions

Buffer	Measured pH	$[H^+]_{\text{measured}}$	$[H^+]_{\text{calculated}}$	% Error
4.01	3.98	1.048×10^{-4}	9.772×10^{-5}	7.3
7.00	7.04	9.120×10^{-8}	1.0×10^{-7}	8.8
10.01	9.92	1.202×10^{-10}	9.772×10^{-11}	23.0

The sodium concentration was determined by difference since no simple or inexpensive analysis for sodium was available. A sodium electrode was purchased but was not used to analyze the samples because a pH range of 6 to 12 is required for accurate sodium measurements. At low pH, the hydrogen ion interferes with the measurements for low levels of sodium ions.

Breakthrough curves for the experimental runs are provided in Figures 4.1 through 4.18.

The experimental data from each run are located in Appendix I.

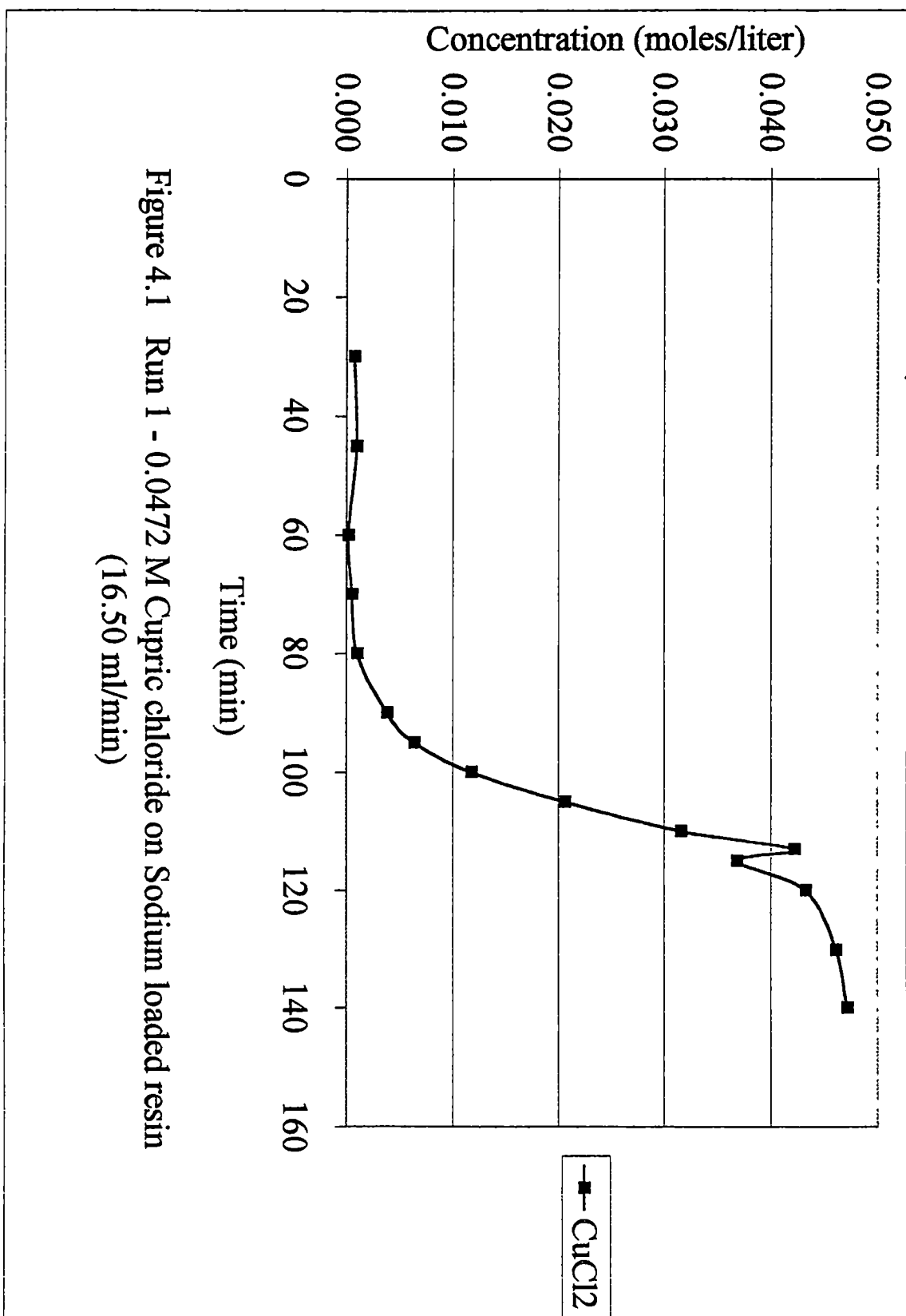


Figure 4.1 Run 1 - 0.0472 M Cupric chloride on Sodium loaded resin
(16.50 ml/min)

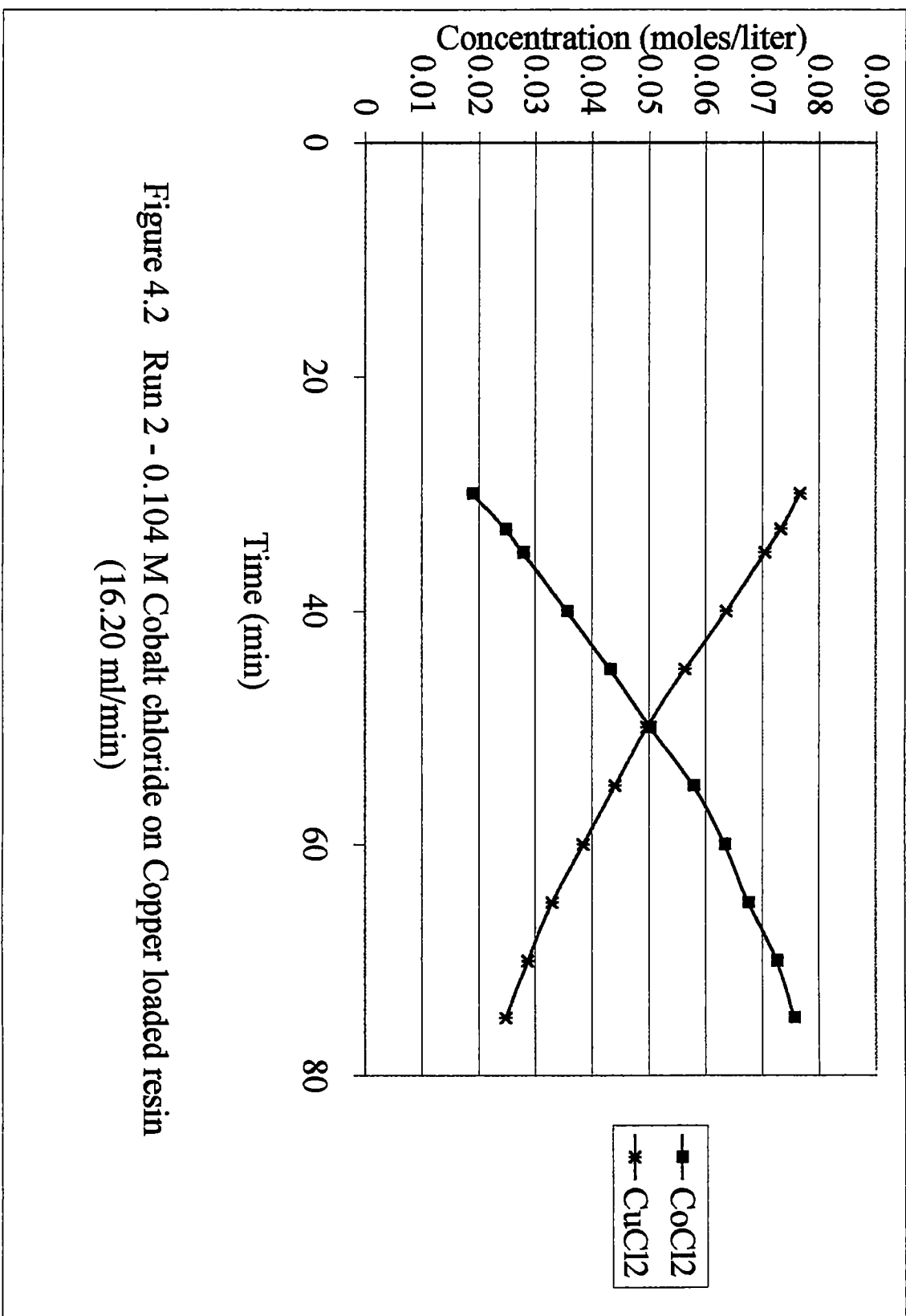


Figure 4.2 Run 2 - 0.104 M Cobalt chloride on Copper loaded resin
(16.20 ml/min)

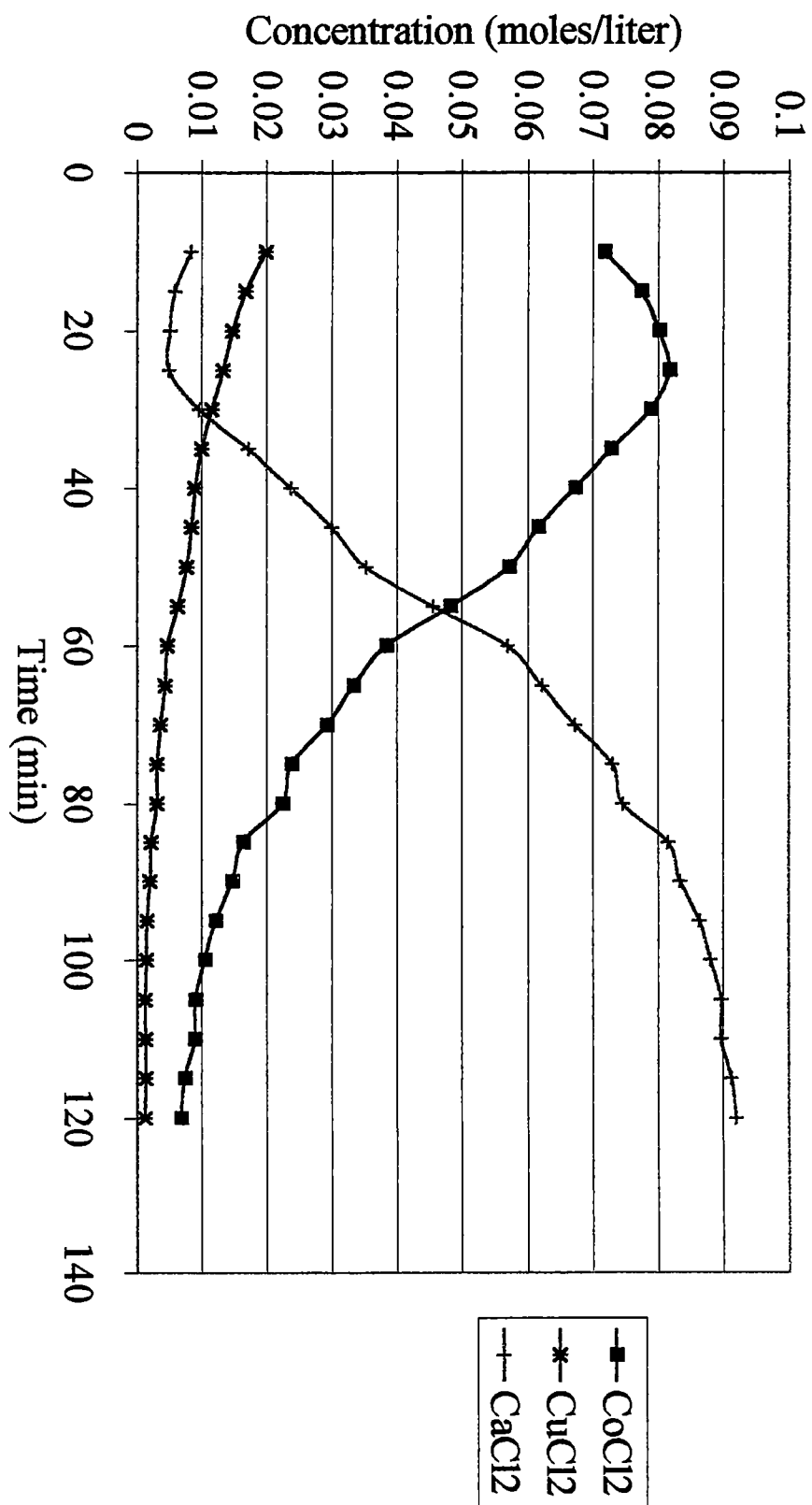


Figure 4.3 Run 3 - 0.096 M Calcium chloride on Cobalt loaded resin
(16.14 ml/min)

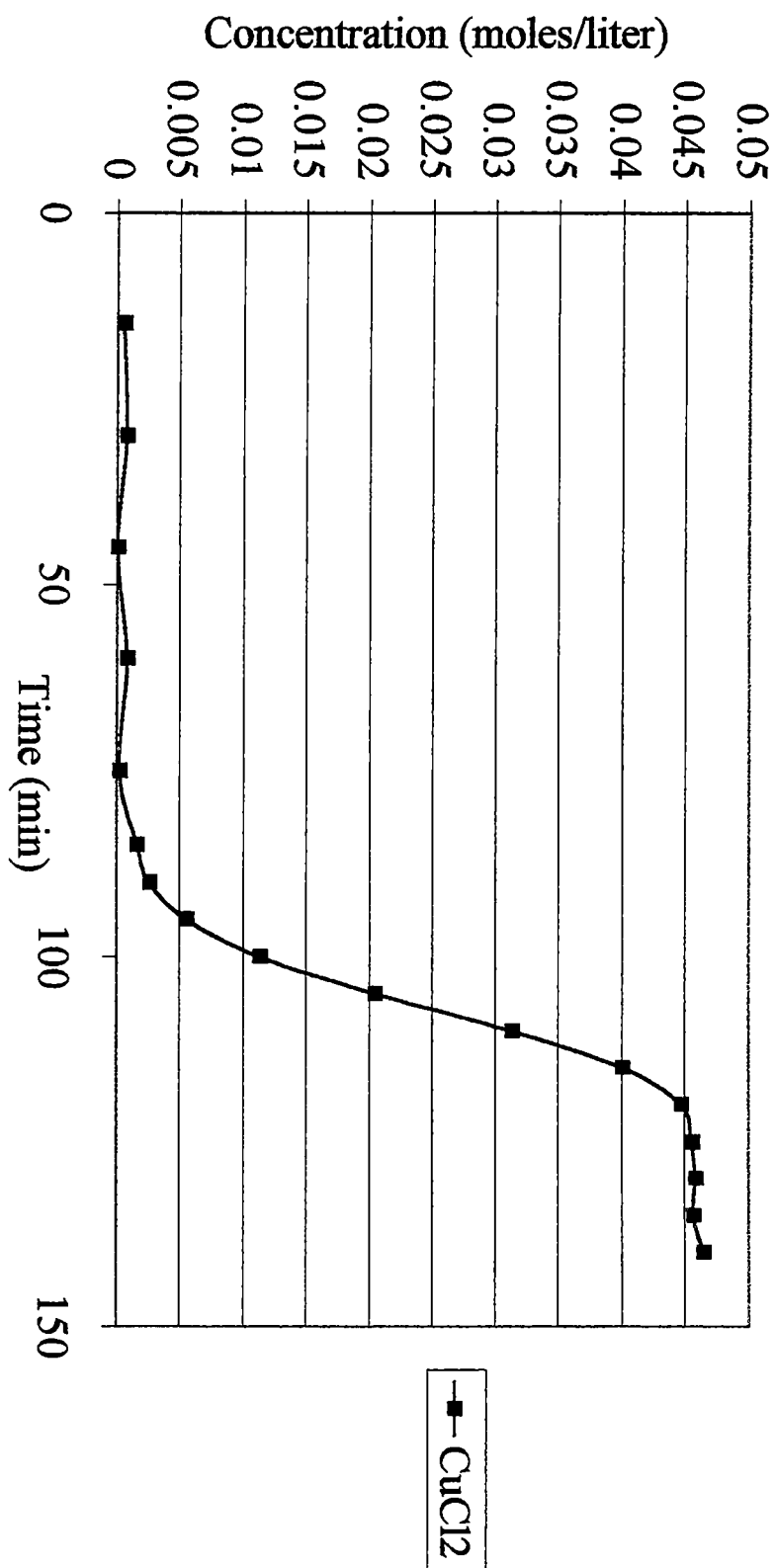


Figure 4.4 Run 4 - 0.046 M Cupric chloride on Sodium loaded resin
(15.87 ml/min)

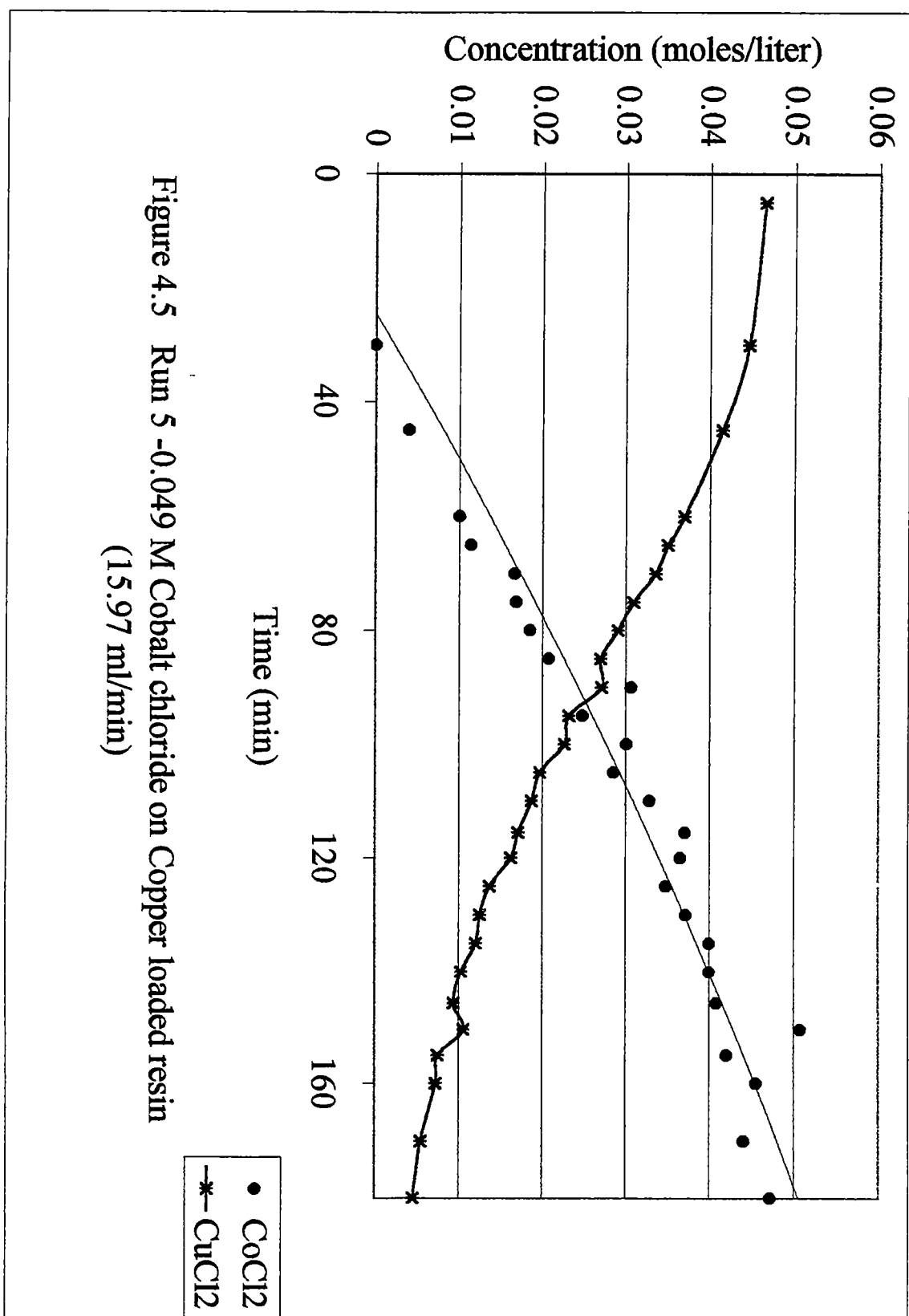


Figure 4.5 Run 5 -0.049 M Cobalt chloride on Copper loaded resin
(15.97 ml/min)

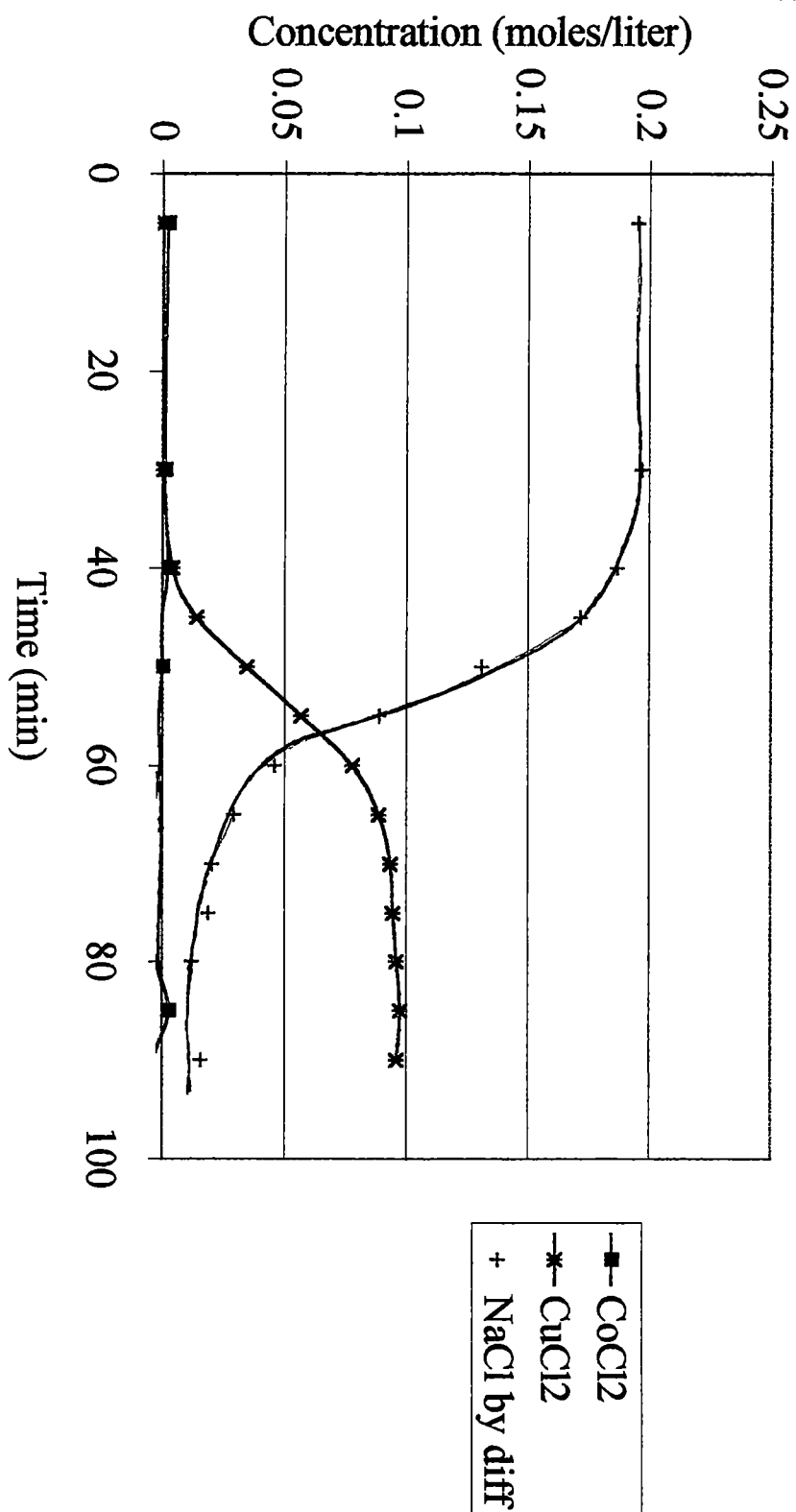


Figure 4.6 Run 7 - 0.098 M Cupric chloride on Sodium loaded resin
(16.12 ml/min)

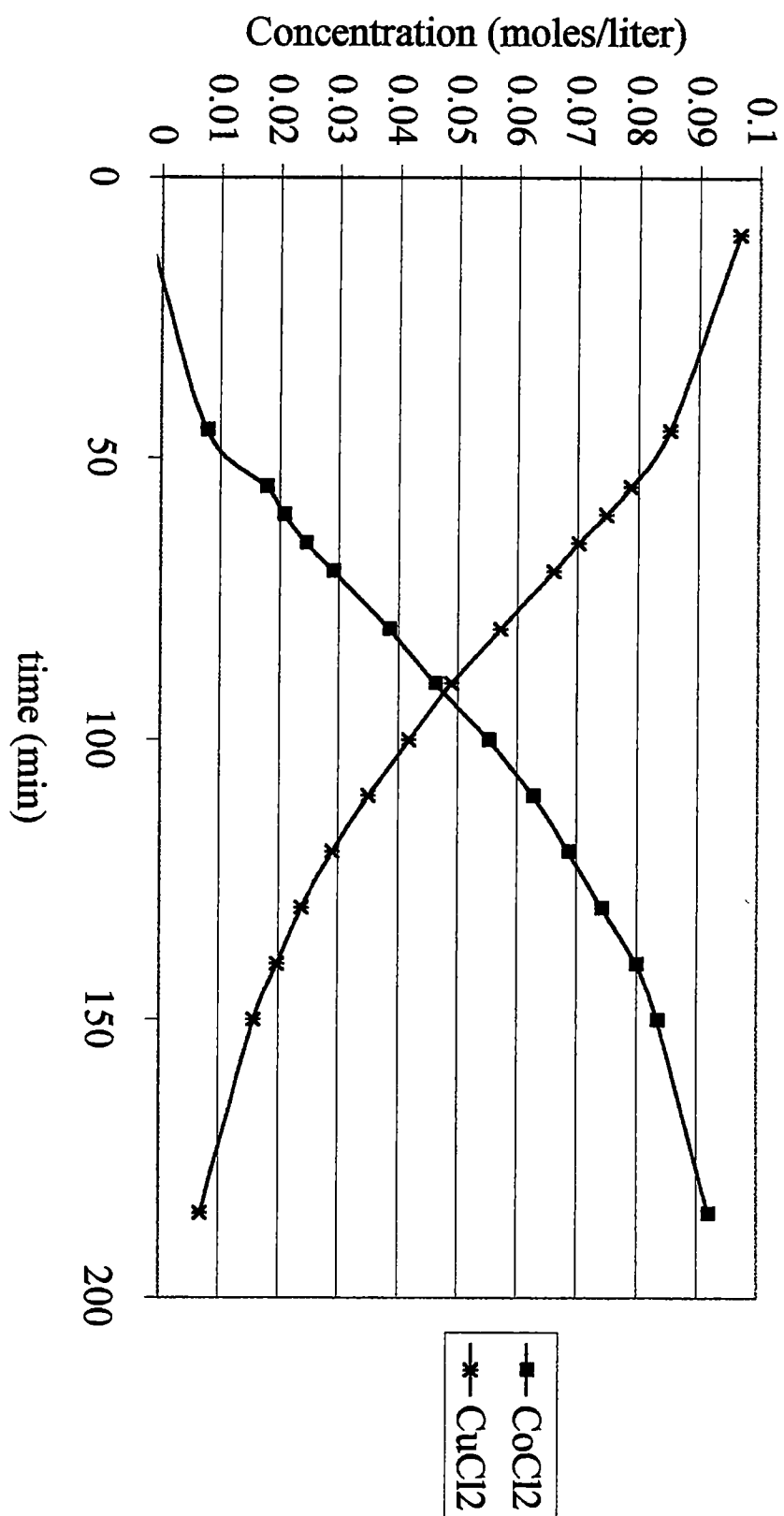


Figure 4.7 Run 8 - 0.099 M Cobalt chloride on Copper loaded resin
(8.5 ml/min)

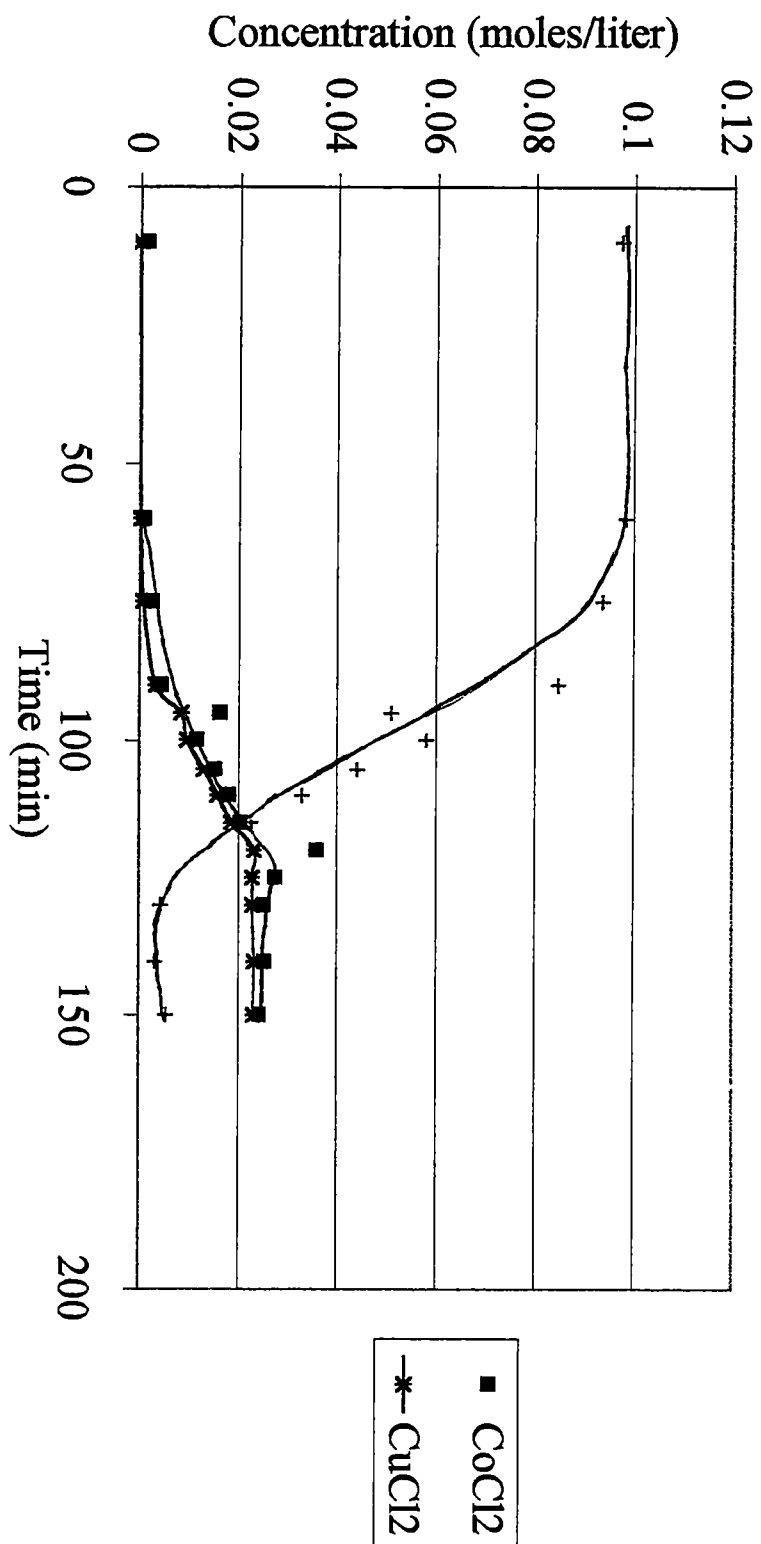


Figure 4.8 Run 10 - 0.023 M Cupric chloride and 0.025 M Cobalt chloride on Sodium loaded resin (16.32 ml/min)

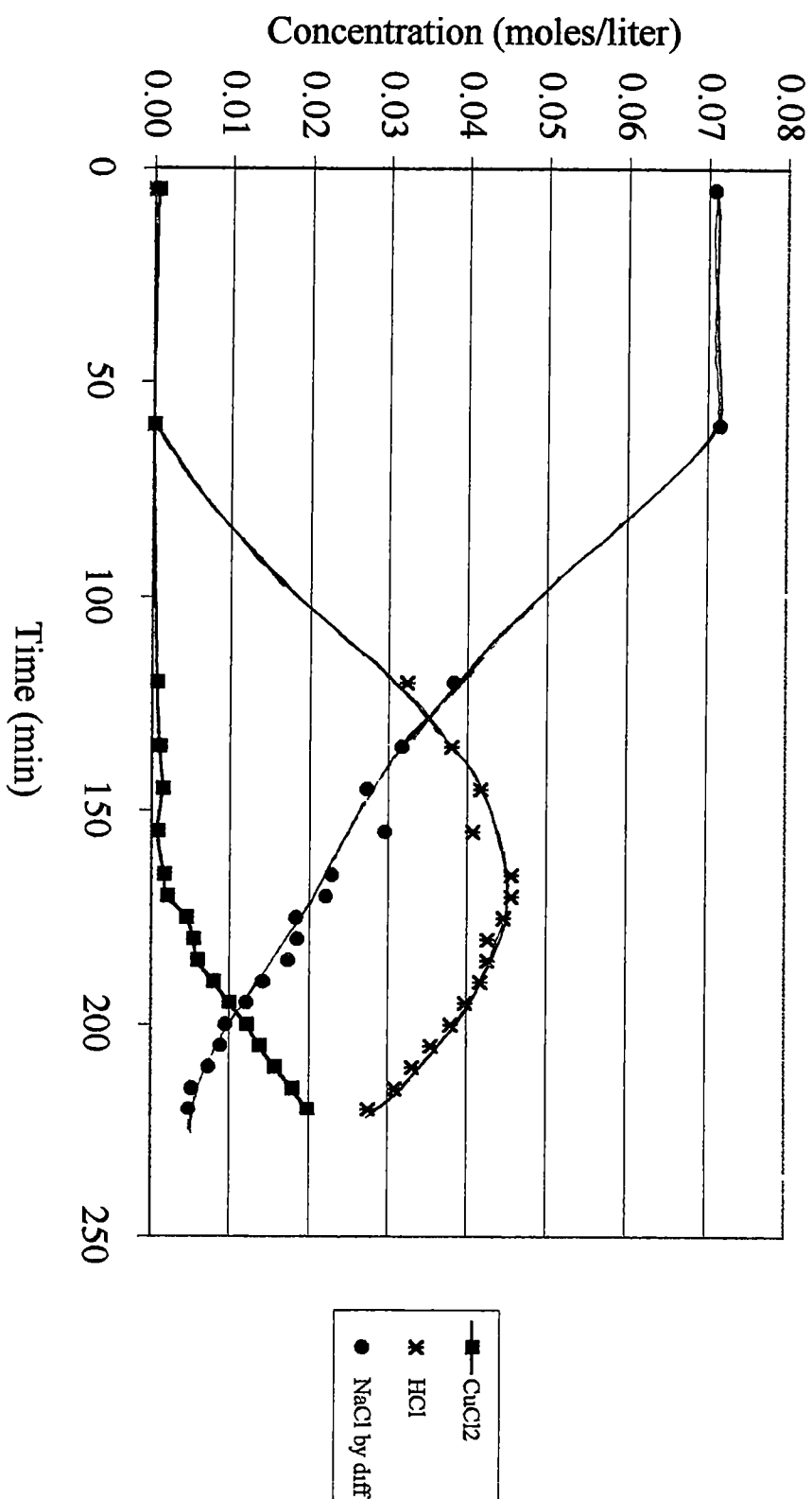


Figure 4.9 Run 12 - 0.023 M Cupric Chloride and 0.0257 M Hydrogen chloride on Sodium loaded resin (15.97 ml/min)

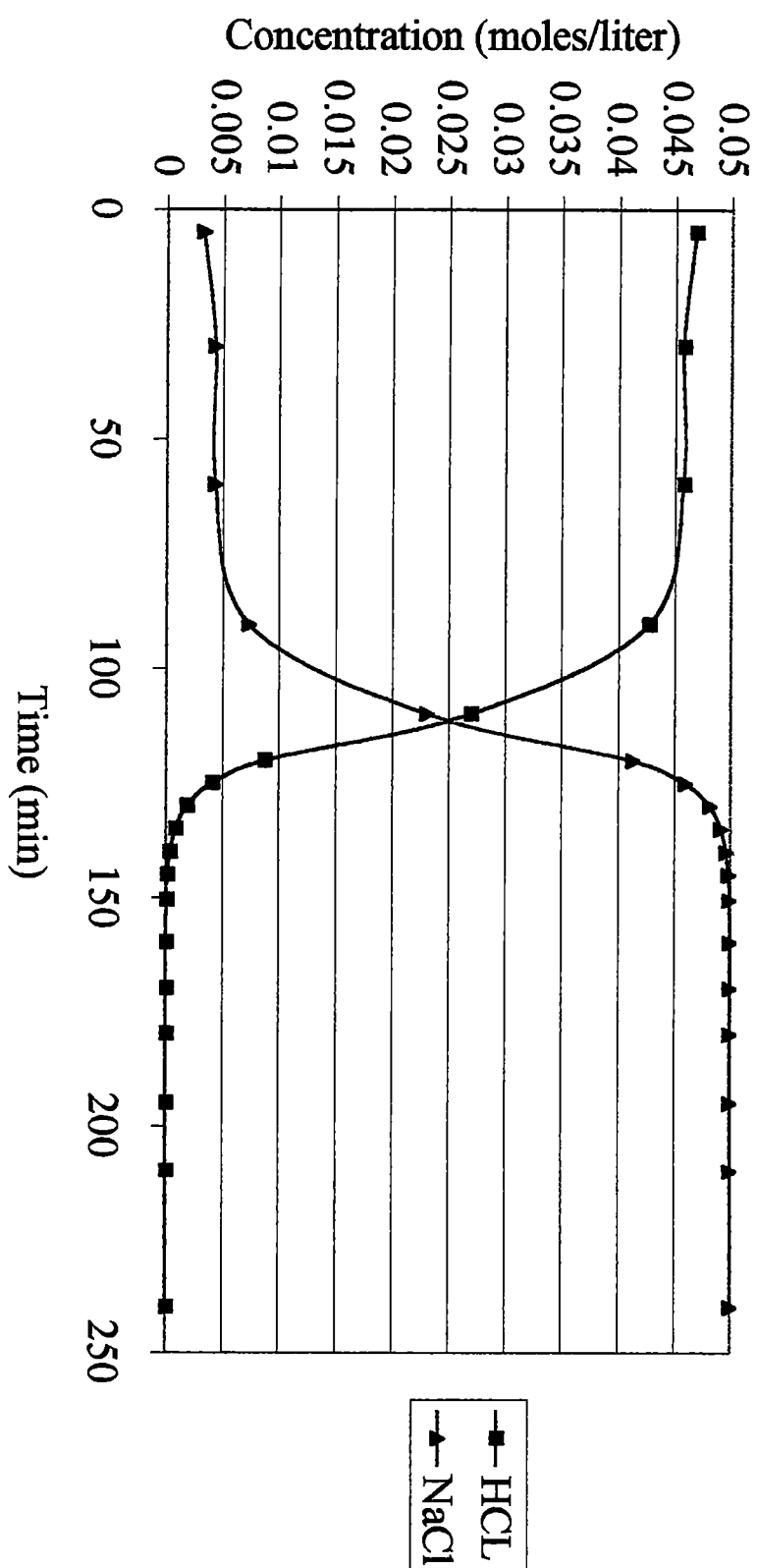


Figure 4.10 Run 14 - 0.05 M Sodium chloride on Hydrogen loaded resin
(16.24 ml/min)

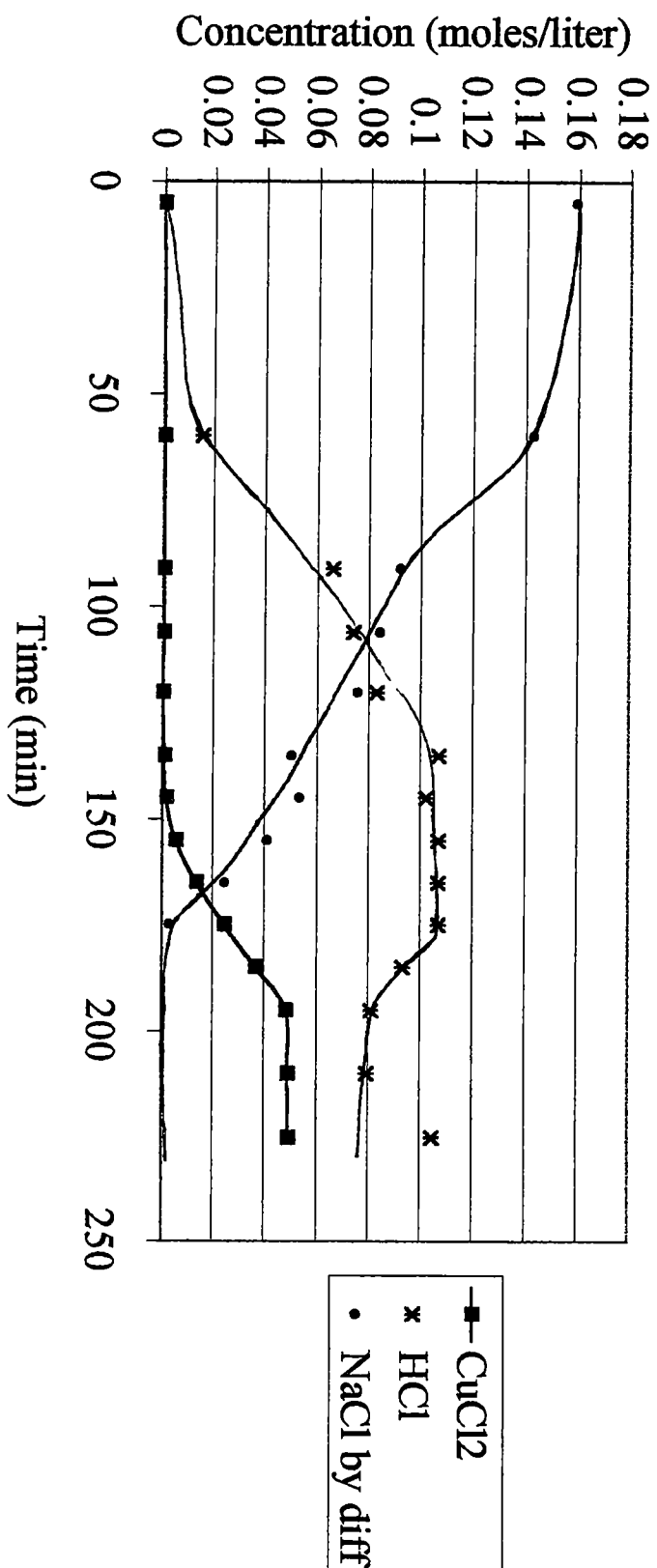


Figure 4.11 Run 15 - 0.049 M Cupric chloride and 0.0661 M Hydrogen chloride on Sodium loaded resin (8.52 ml/min)

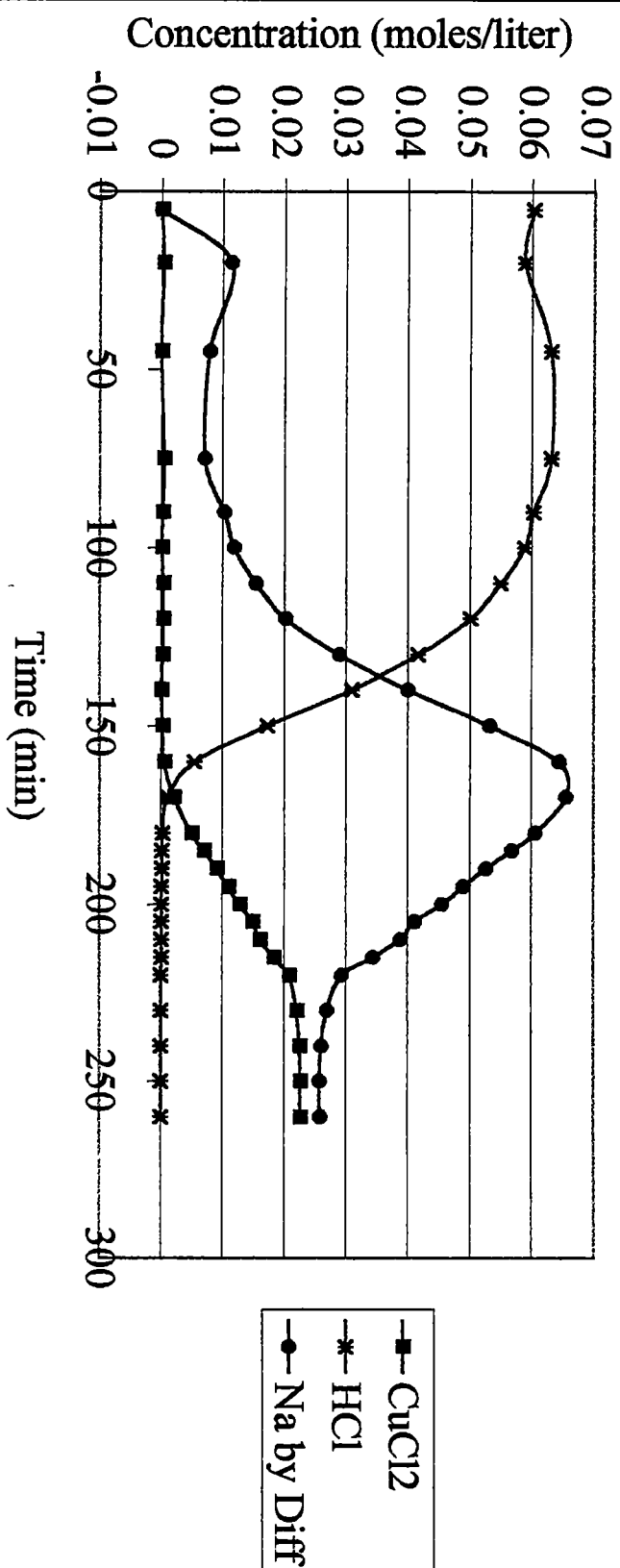


Figure 4.12 Run 17 - 0.023 M Cupric Chloride and 0.025 M Sodium chloride on Hydrogen loaded resin (16.15 ml/min)

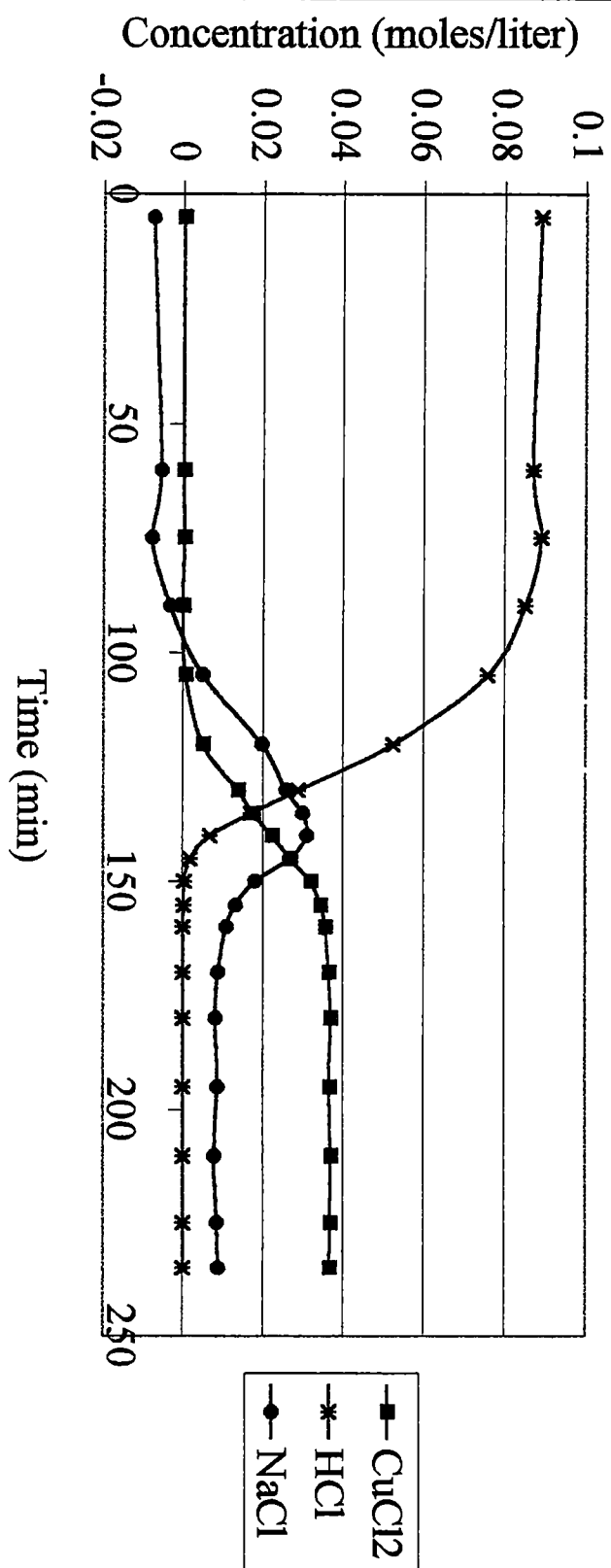


Figure 4.13 Run 19 - 0.037 M Cupric chloride and 0.01 M Sodium chloride on Hydrogen loaded resin (15.57 ml/min)

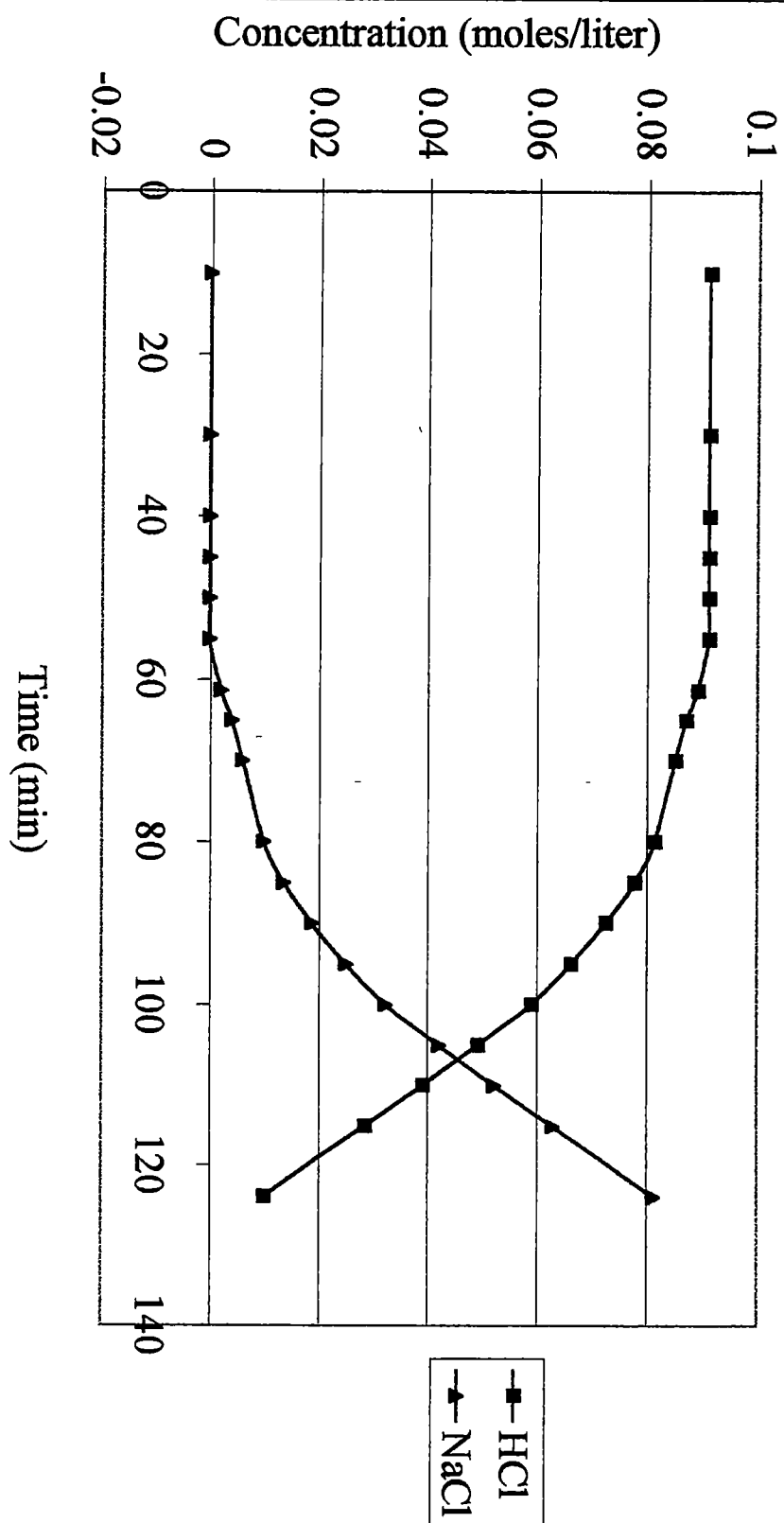


Figure 4.14 Run 21 - 0.091 M Sodium chloride on a Hydrogen loaded resin (16.0 ml/min)

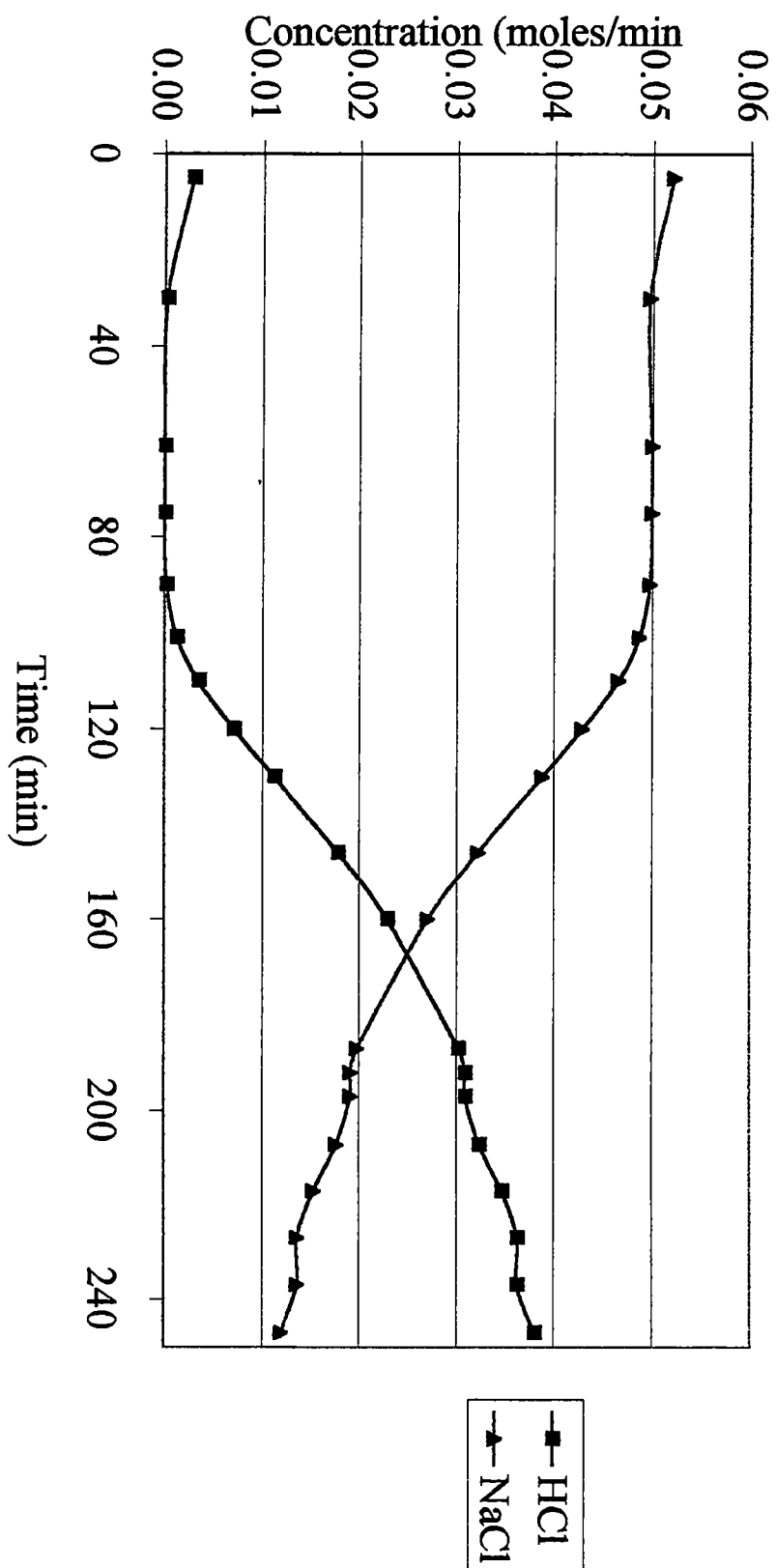


Figure 4.15 Run 22 - 0.05 M Hydrogen chloride on Sodium loaded resin (15.8 ml/min)

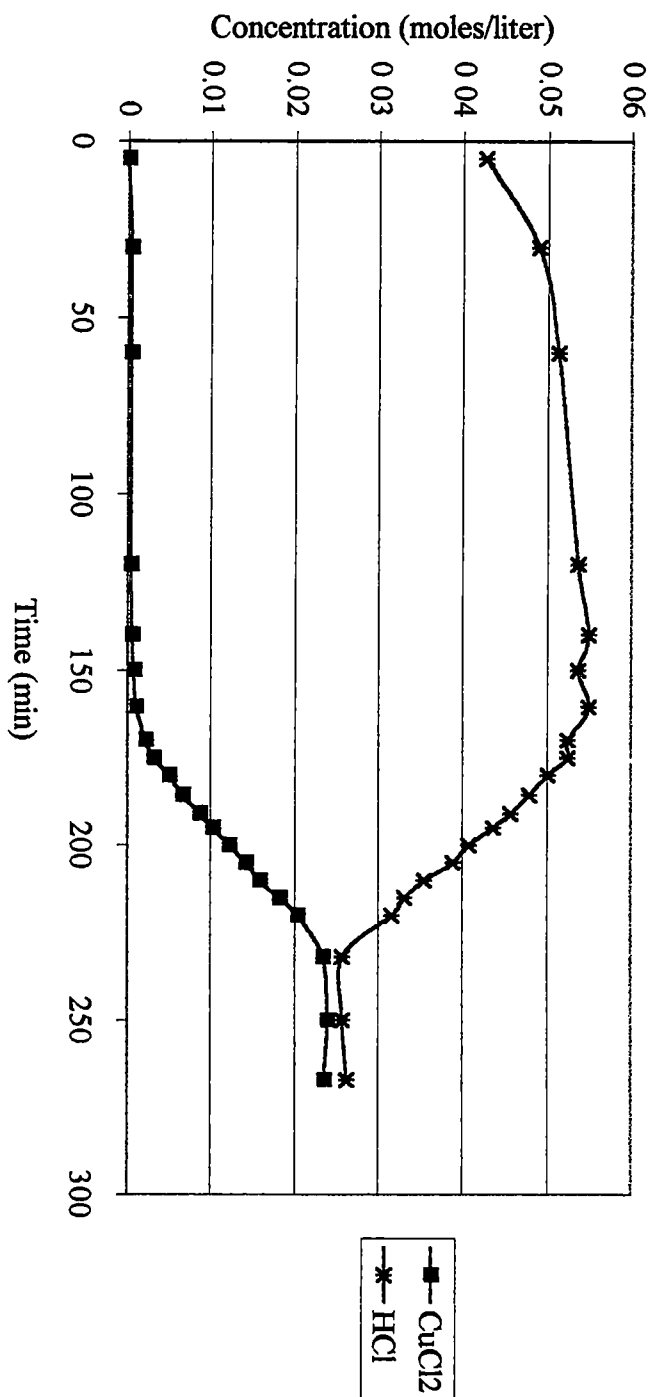


Figure 4 16 Run 23 - 0.0231 M Cupric chloride and 0.0251 M Hydrogen chloride on Hydrogen loaded resin (16.78 ml/min)

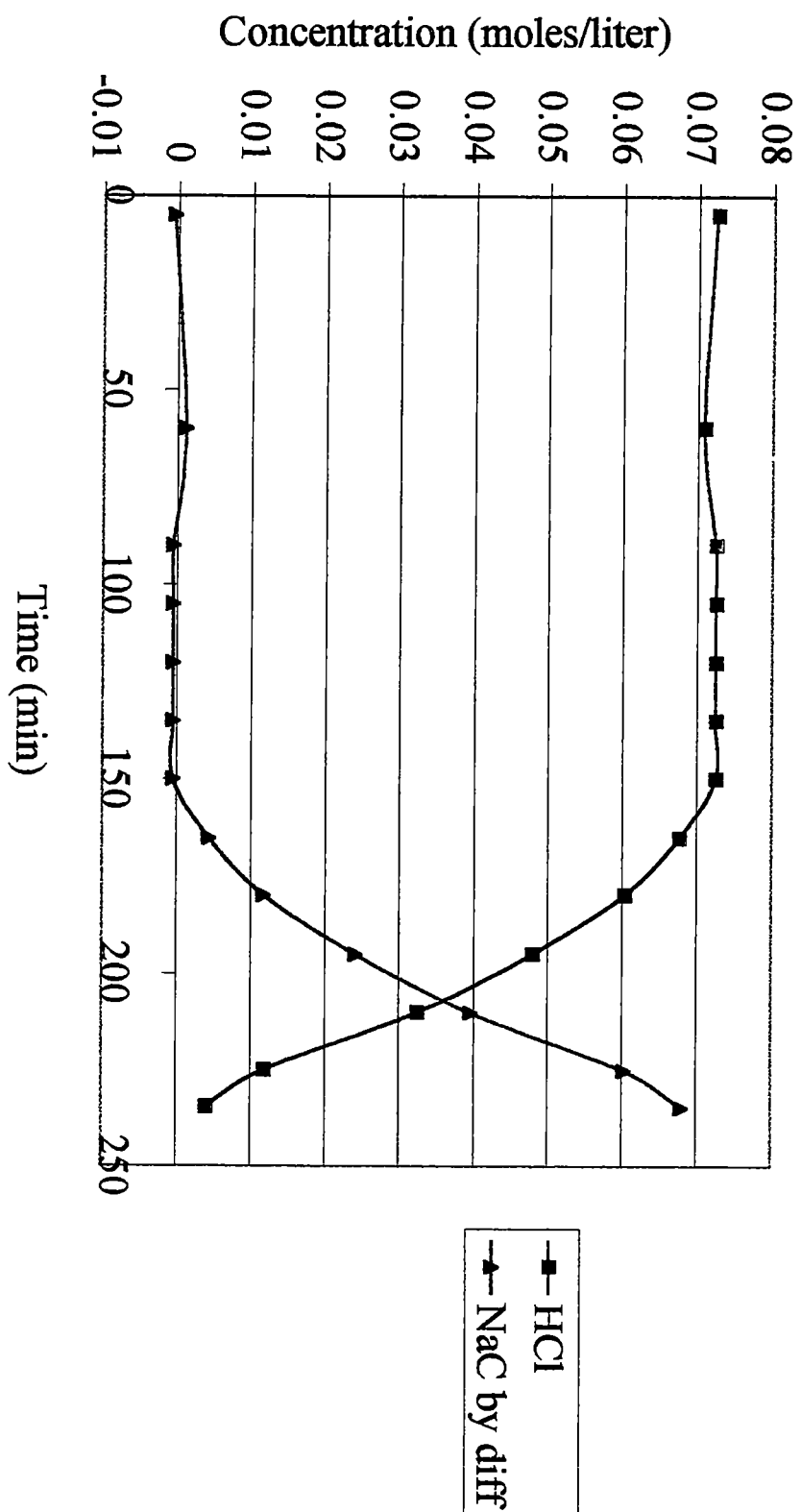


Figure 4.17 Run 25 - 0.072 M Sodium chloride on Hydrogen loaded resin (8.47 ml/min)

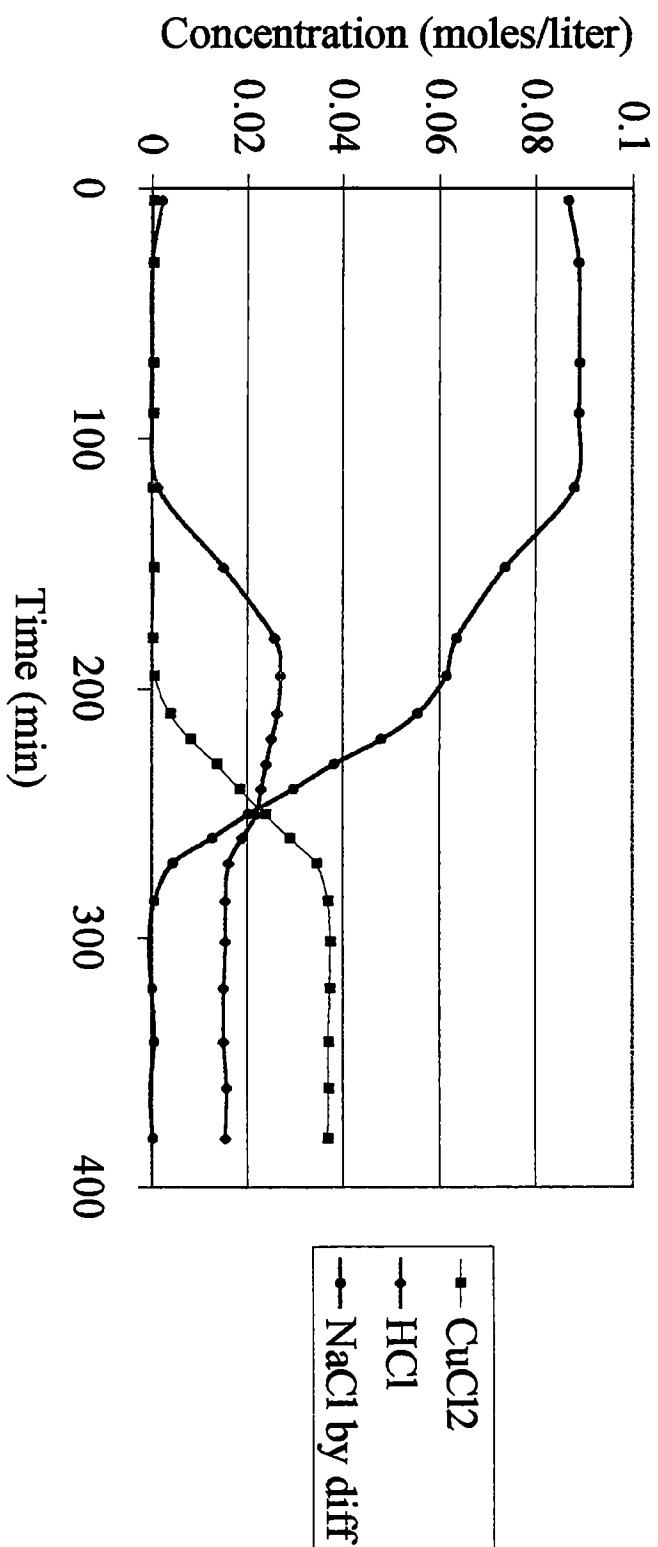


Figure 4.18 Run 26 - 0.037 M Cupric chloride and 0.0155 M Hydrogen chloride on Sodium loaded resin (8.47 ml/min)

CHAPTER 5

DISCUSSION OF RESULTS

This study looked at a relatively simple approach to predicting the breakthrough curve for multi-component ion exchange systems assuming a constant pattern front exist for the component of interest. The dimensionless breakthrough curves (concentration versus NTU) were calculated using the calculational procedure based upon an earlier procedure by Watson. In the Watson procedure, the NTU is determined from a plot of the equilibrium curve and the operating line. The equilibrium curve for the multi-component system was determined using mass action equilibrium and mass balance relationships assuming a constant pattern front as described in Chapter 3. The assumption of a constant pattern front is applicable for dilute solutions with favorable isotherms

Comparison of experimental and calculated breakthrough curve

The calculated breakthrough front (concentration as a function of NTU) was compared to experimental data for the 2 and 3 component ion exchange systems. The experimental breakthrough data were converted to Z, length of the front, using the following equation:

$$Z = (t_{@ 50\% \text{ breakthrough}} - t) V_f \quad 5.1$$

The NTUs were then calculated from the equation $Z = [HT][NTU]$. Alternatively, the calculated breakthrough curves could have been compared to the experimental curves in dimensionless length, Z, but the comparison would be equivalent. The HTU, which is assumed to be constant across the mass transfer zone (MTZ) for the system, was determined by taking the ratio of the Z as determined from the experimental data to the

calculated NTU at the breakthrough point. The HTU could have been calculated using

$HTU = \frac{V_s}{k_f a}$ and an empirical correlation for $K_f a$. Table 5.1 gives the calculated HTU as

a function of percent breakthrough for the 9 systems evaluated. A negative HTU signifies an unfavorable isotherm. For a constant pattern front, the HTU should be constant across the MTZ, however; some variation in the HTU as a function of percent breakthrough was observed. In general, the HTU was approximately constant for points above 50% breakthrough. Two-point linear interpolation was used to estimate the values for Z between the data points to calculate the HTUs. This could have resulted in some spread in the data, also. Below the 50% breakthrough point, the values for the HTUs were generally lower. This is probably due to the fact that a constant pattern front had not fully developed by the time 50% breakthrough had occurred. The front probably did not have time to reach constant pattern due to 1) the length of the column and/or 2) the high flow rate. The low concentration portion of the front should be the last to approach constant pattern. If the front started as a step function, the low concentration data should fall below the predicted value. Increasing the column length or decreasing the flow rate would result in a constant pattern front being approached more closely. The runs that employed the lower flow rates (~8.5 ml/min as opposed to 16 ml/min) seemed to have a little less spread in the HTU values. Because the fronts appeared to be still spreading, especially at the lower concentrations, the HTUs calculated at the 80% breakthrough point were used to convert the length of the front, Z , from the experimental data to NTUs.

Table 5.1 Experimental HTU

System.			Flow rate (ml/min)	HTU at % breakthrough				
Solution	Resin	Run		90	80	60	40	20
CuCl ₂	Na	1	16.5	5.59	5.58	3.62	4.59	3.02
		4	15.9	4.22	3.93	3.16	3.42	2.18
		7	16.1	7.74	6.86	6.65	5.60	4.49
CoCl ₂	Cu	2	16.2	—	-1.82	-1.90	-1.78	-1.48
		5	16.0	-1.42	-1.41	-1.55	-1.29	-1.22
		8	8.5	-1.80	-1.59	-1.43	-1.45	-1.33
CaCl ₂	Co	3	16.1	10.42	10.18	5.95	5.07	6.22
NaCl	H	14	16.2	0.59	0.60	0.79	0.77	0.90
		21	16.0	1.30	1.51	1.67	1.58	1.70
		25	8.5	0.77	0.82	.97	1.02	.98
HCl	Na	22	15.8	—	-4.65	-3.71	-3.27	-2.61
CuCl ₂ and HCl	Na	12	15.9	3.99	5.80	6.46	3.50	2.60
		15	8.52	2.58	3.53	3.78	3.23	1.85
		26	8.47	3.79	5.44	5.48	4.26	2.10
CuCl ₂ and NaCl	H	17	16.1	5.25	5.95	5.13	4.50	3.40
		19	15.57	5.998	5.69	5.43	5.25	3.78
CuCl ₂ and CoCl ₂	Na	10	16.32	3.58	3.94	3.62	3.68	2.11
CuCl ₂ and HCl	H	23	16.78	6.18	6.02	4.49	4.66	3.75

Nine ion exchange systems were evaluated experimentally:

- 1 CuCl_2 on Na loaded resin
2. CuCl_2 on Cu loaded resin
- 3 CaCl_2 on Co loaded resin
4. NaCl on H loaded resin
5. HCl on Na loaded resin
- 6 CuCl_2 and HCl on Na loaded resin
- 7 CuCl_2 and NaCl on H loaded resin
8. CuCl_2 and CoCl_2 on Na loaded resin
- 9 CuCl_2 and HCl on H loaded resin

The experimental data along with the experimental and calculated NTUs as a function of concentration for each run are tabulated in Appendix I Figures 5.1 through 5.18 compare the experimental NTU to the calculated NTU. In general, good agreement is seen between the calculated and experimental curves. The curves fit better at the higher concentration region (above 50% breakthrough) then the lower region as expected because the NTU was determined using the HTU at the 80% breakthrough point due to variations in the HTUs across the MTZ as shown in Table 5 1

The experimental data fell below the calculated data (at the low concentration range) for all the systems except the binary exchange of sodium with hydrogen on the resin. In the Na-H system, the calculated data fell below the experimental data for Run 14, and good agreement was observed with Runs 21 and 25 over the entire concentration range. The

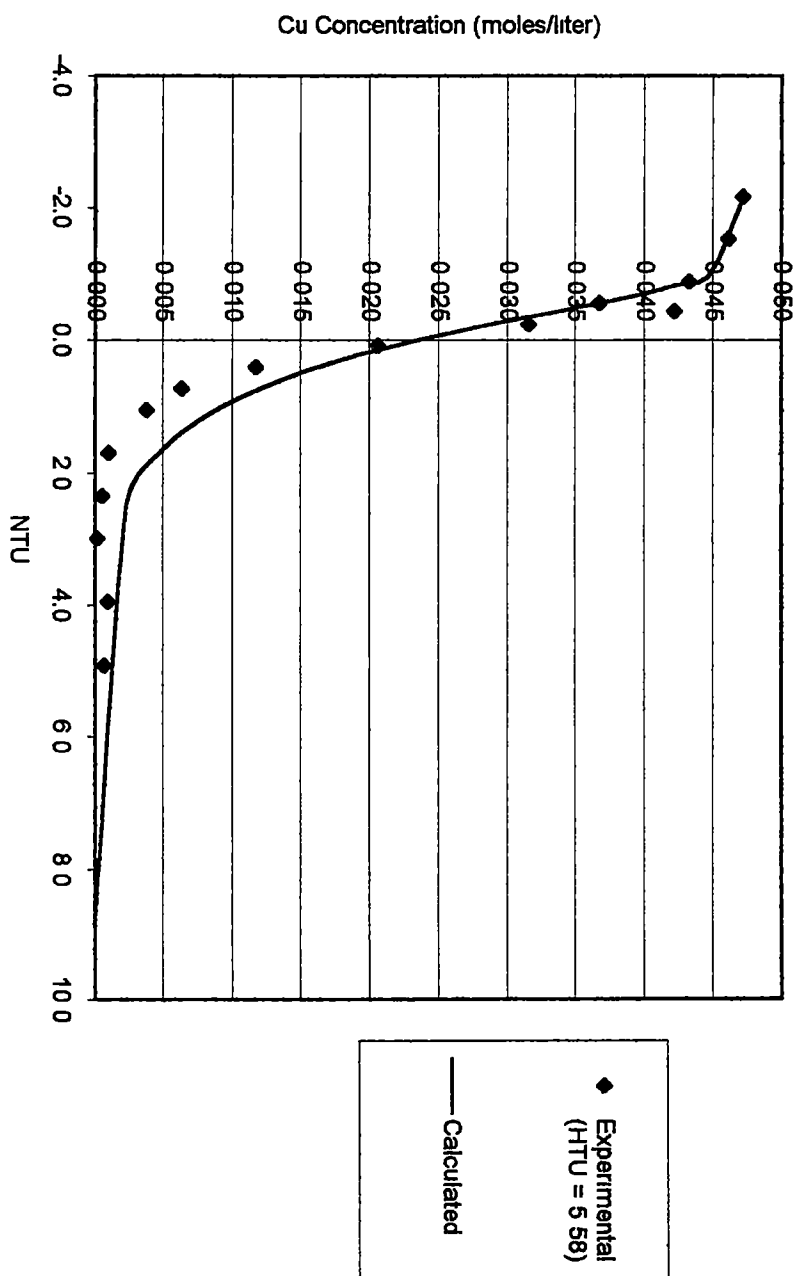


Figure 5 1 Breakthrough curve for exchange of 0.0472 M Cupric chloride on sodium loaded resin at 16.5 ml/min (Run 1)

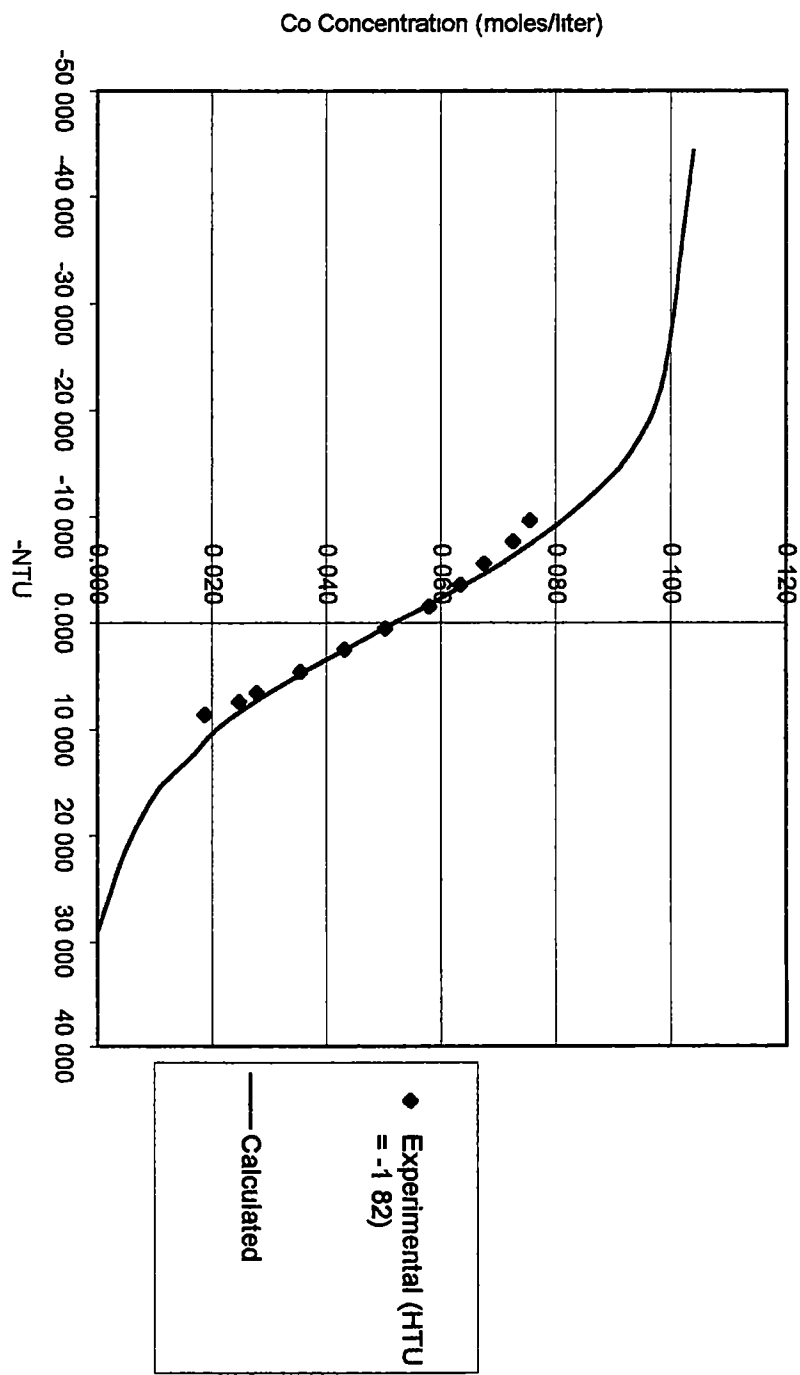


Figure 5.2 Breakthrough curve for exchange of 0.104 M Cobalt Chloride on Copper loaded resin at 16.2 ml/min (Run 2)

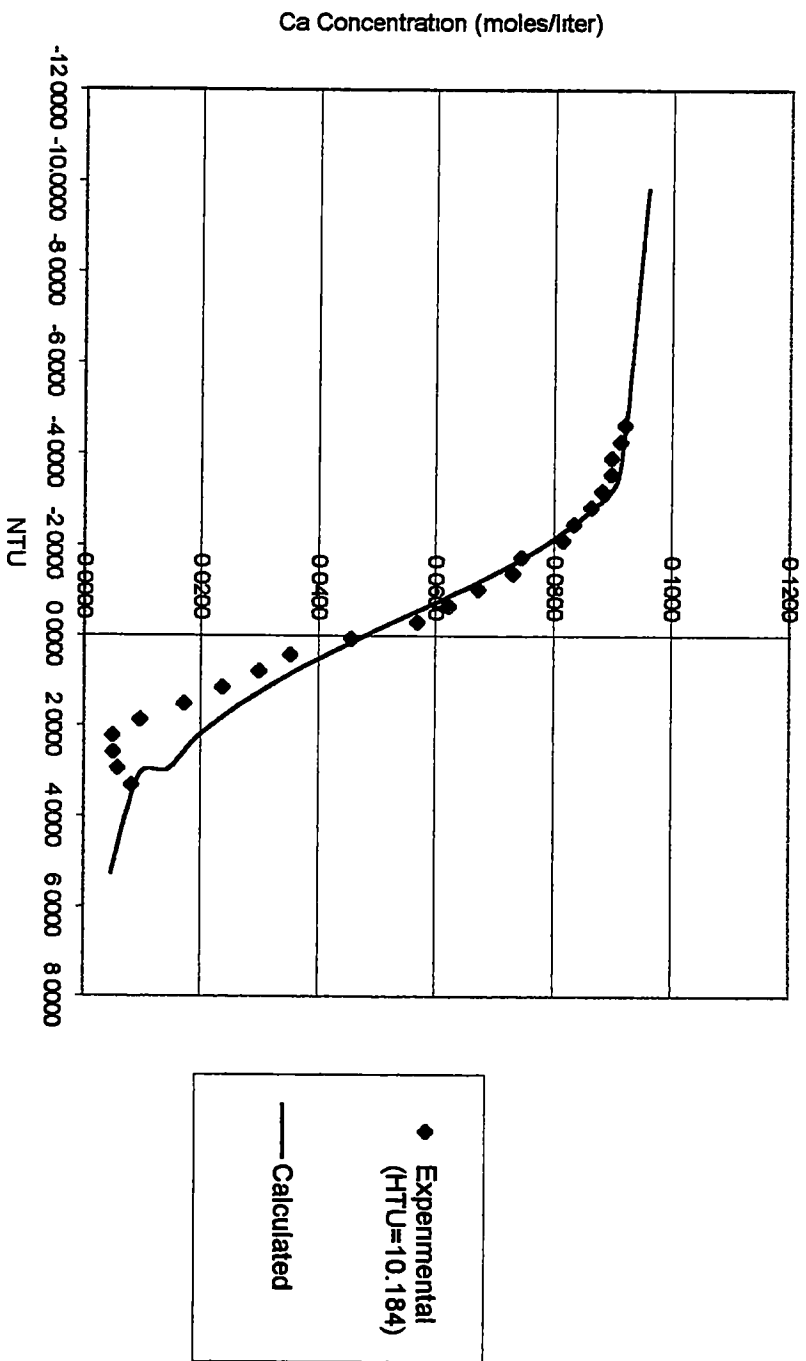


Figure 5.3 Breakthrough curve for exchange of 0.096 M Calcium chloride on cobalt loaded resin at 16.14 ml/min (Run 3)

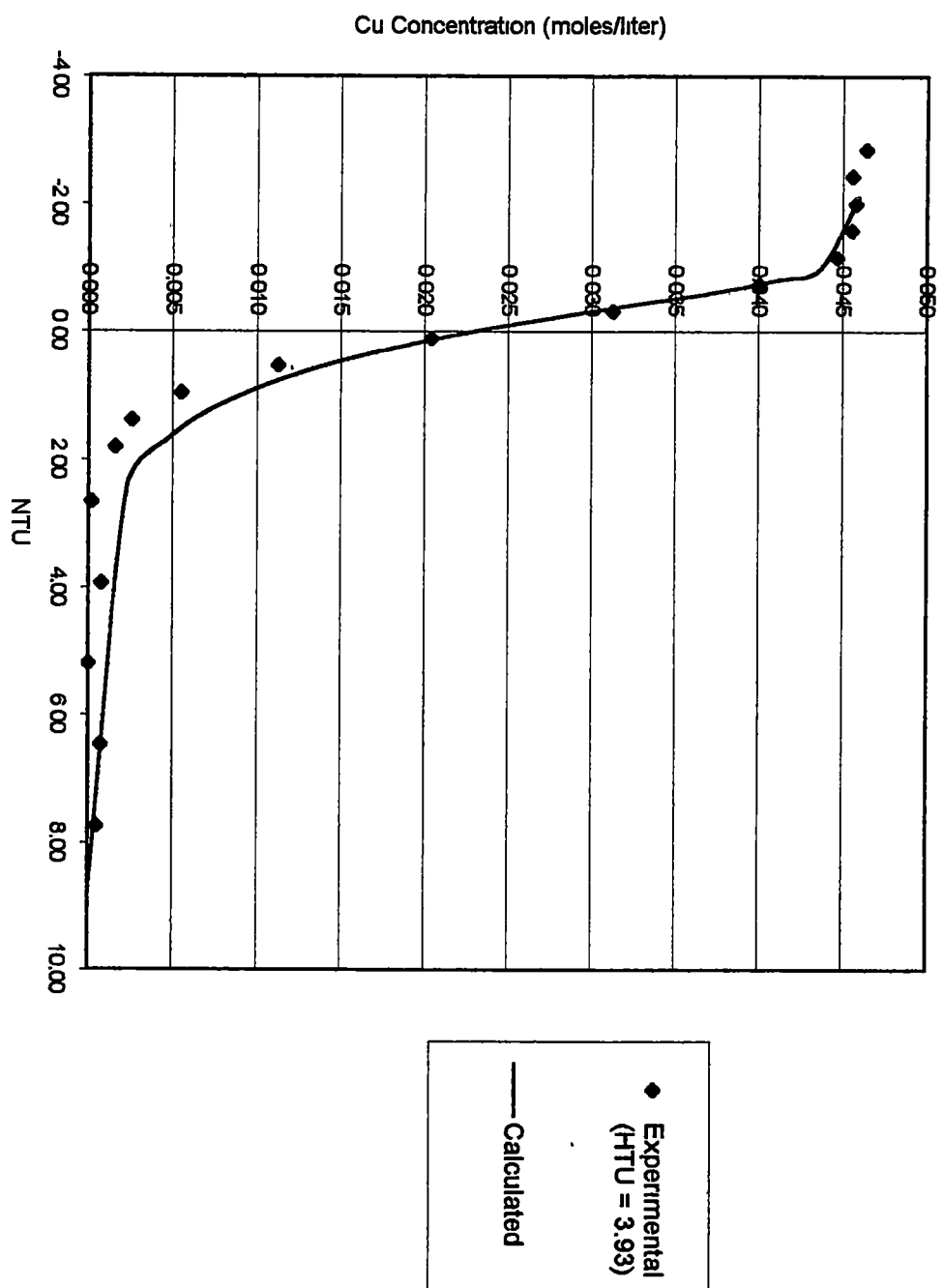


Figure 5.4 Breakthrough curve for exchange of 0.046 M Cupric Chloride on sodium loaded resin at 15.87 ml/min (Run 4)

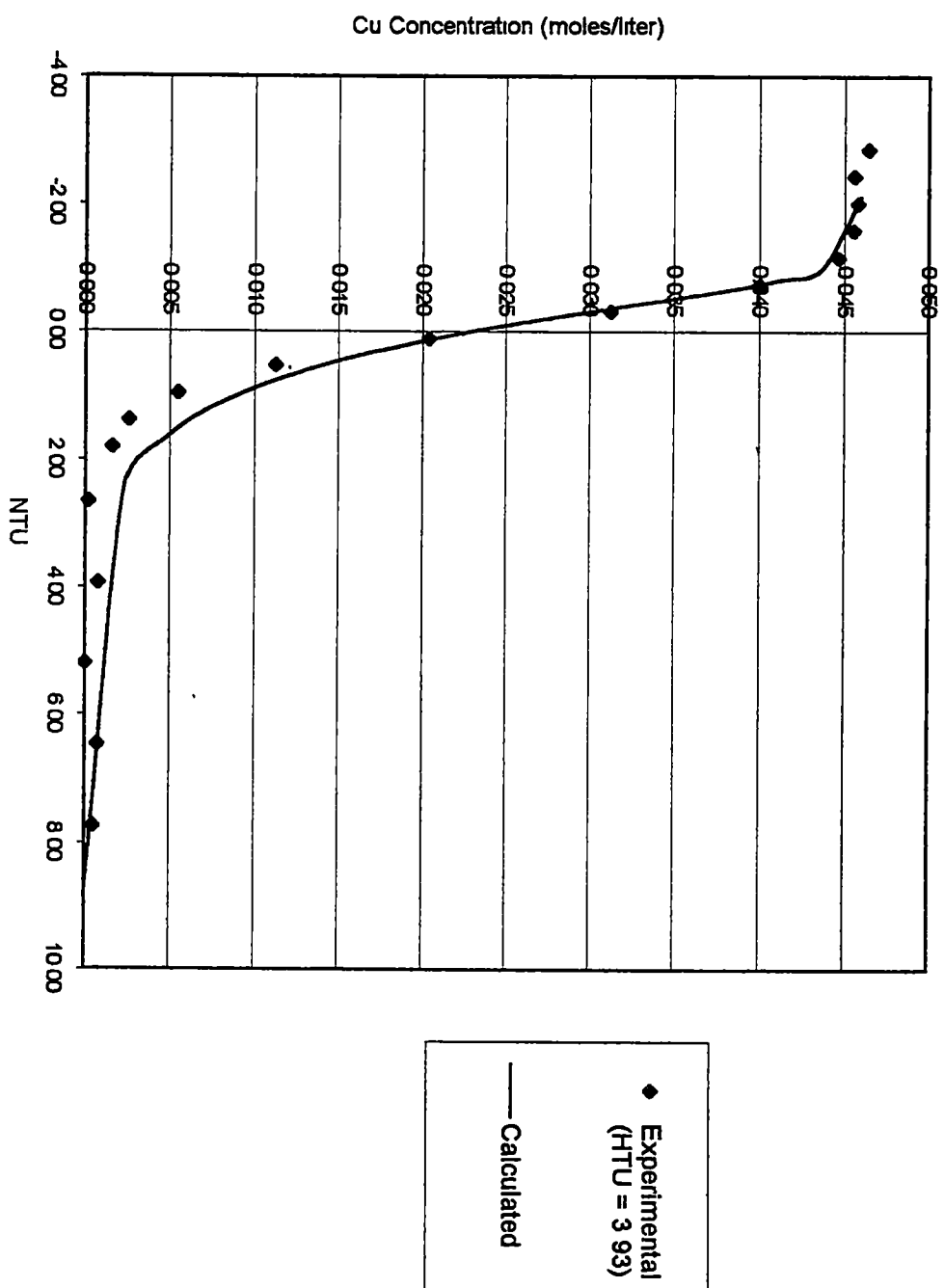


Figure 5.4 Breakthrough curve for exchange of 0.046 M Cupric Chloride on sodium loaded resin at 15.87 ml/min (Run 4)

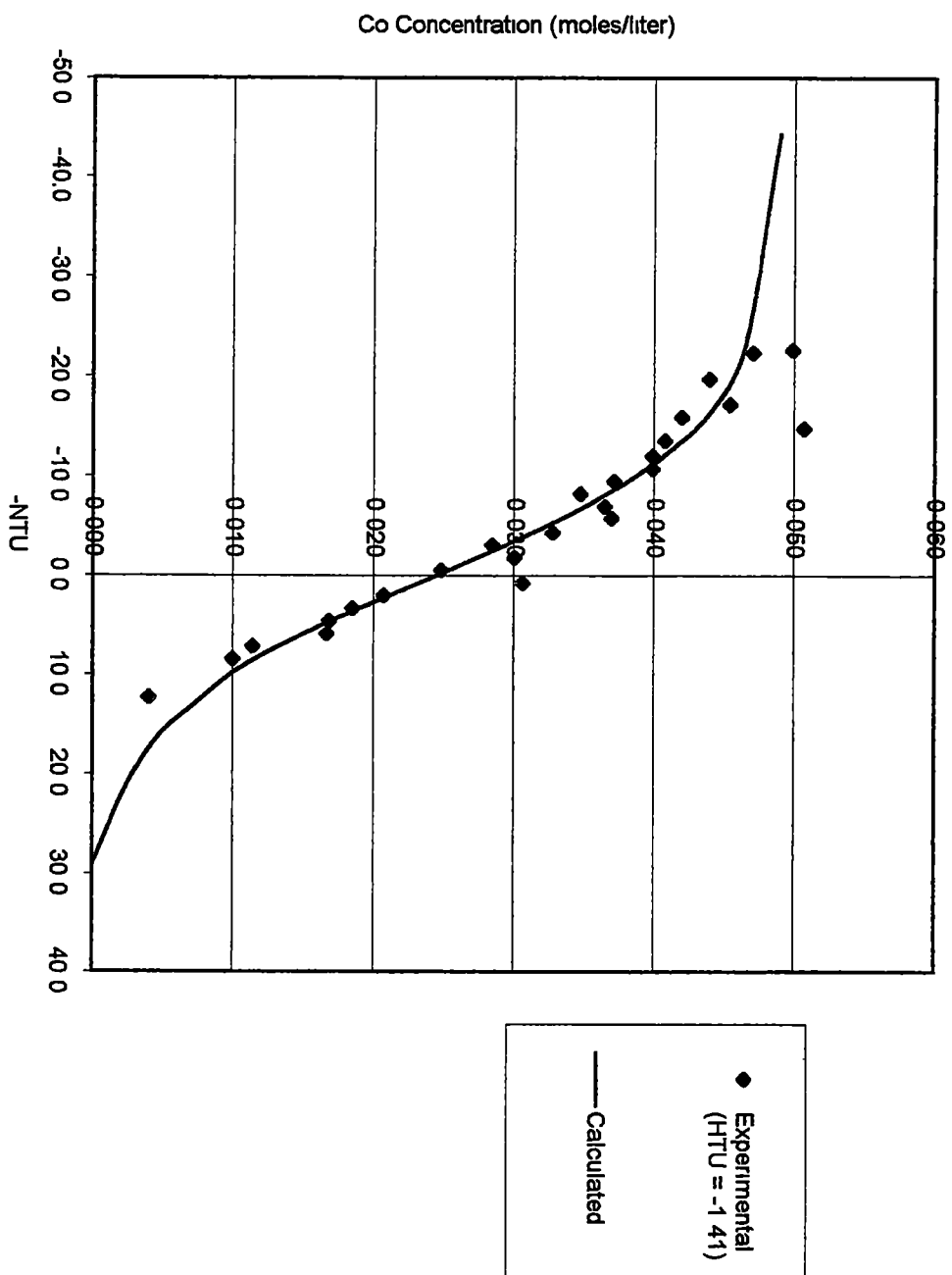


Figure 5.5 Breakthrough curve for exchange of 0.049 M Cobalt chloride on copper loaded resin at 15.97 ml/min (Run 5)

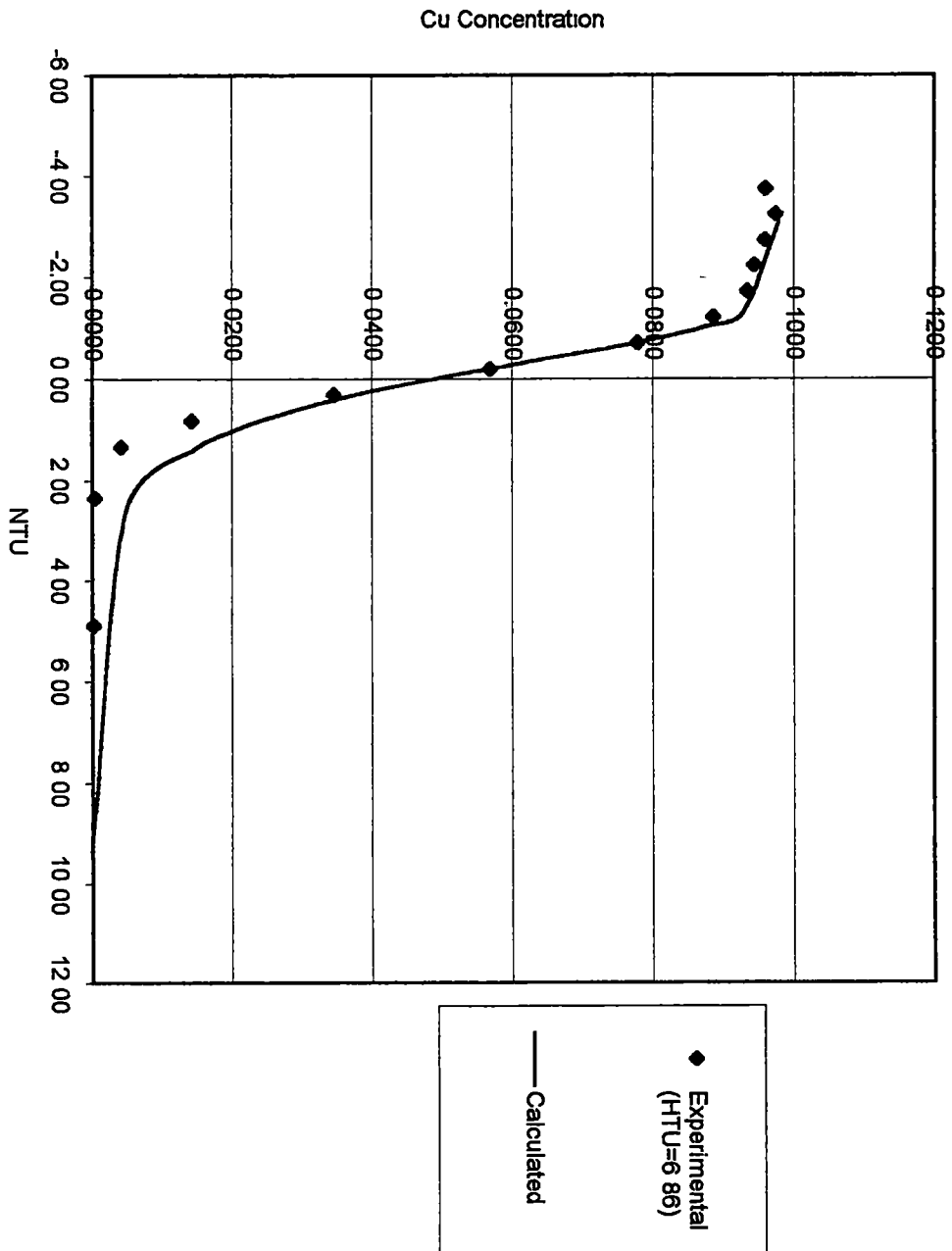


Figure 5.6 Breakthrough curve for exchange of 0.098 M Cupric chloride on sodium loaded resin at 16.12 ml/min (Run 7)

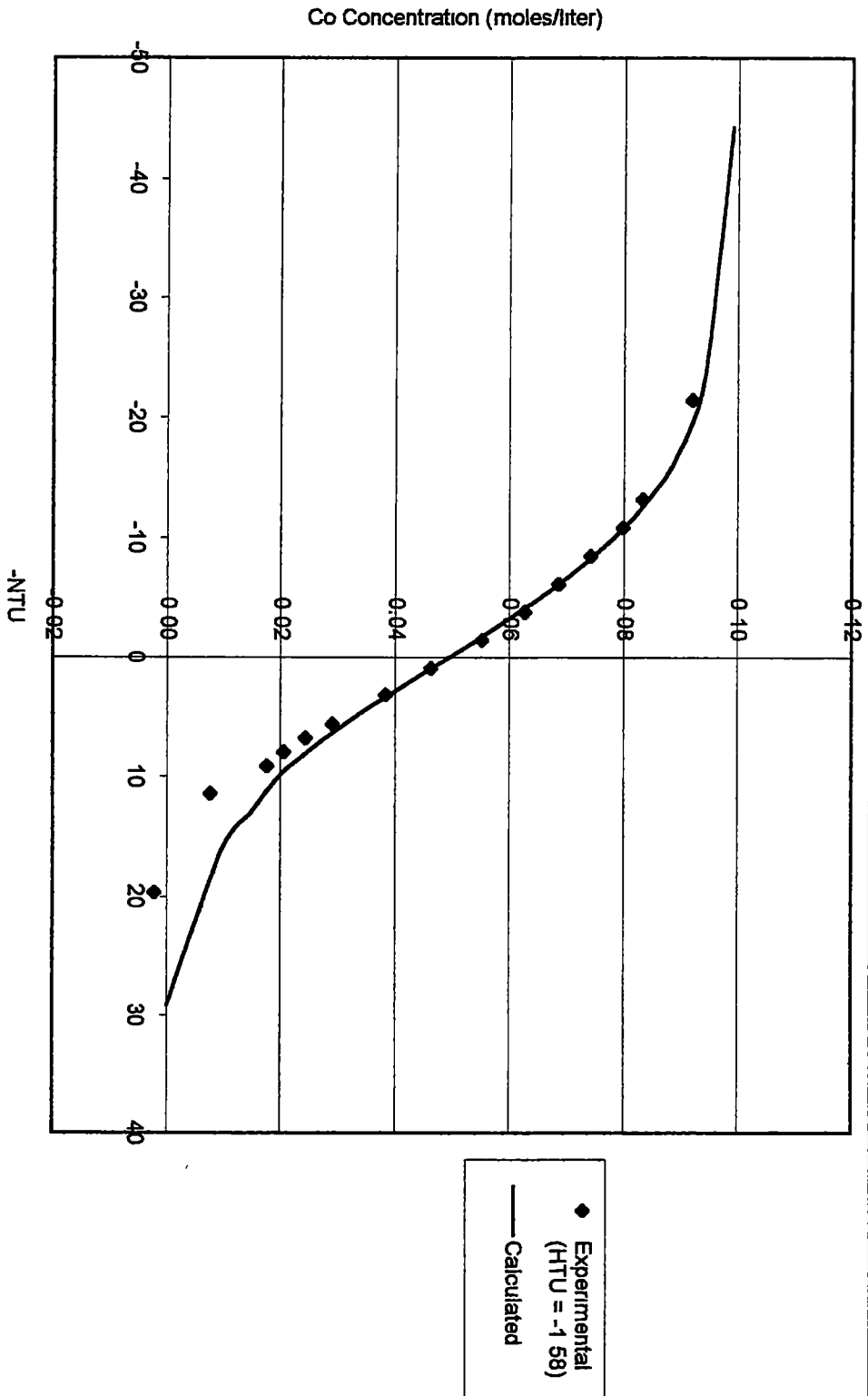


Figure 5.7 Breakthrough curve for exchange of 0.099 M Cobalt chloride on copper loaded resin at 8.5 ml/min (Run 8)

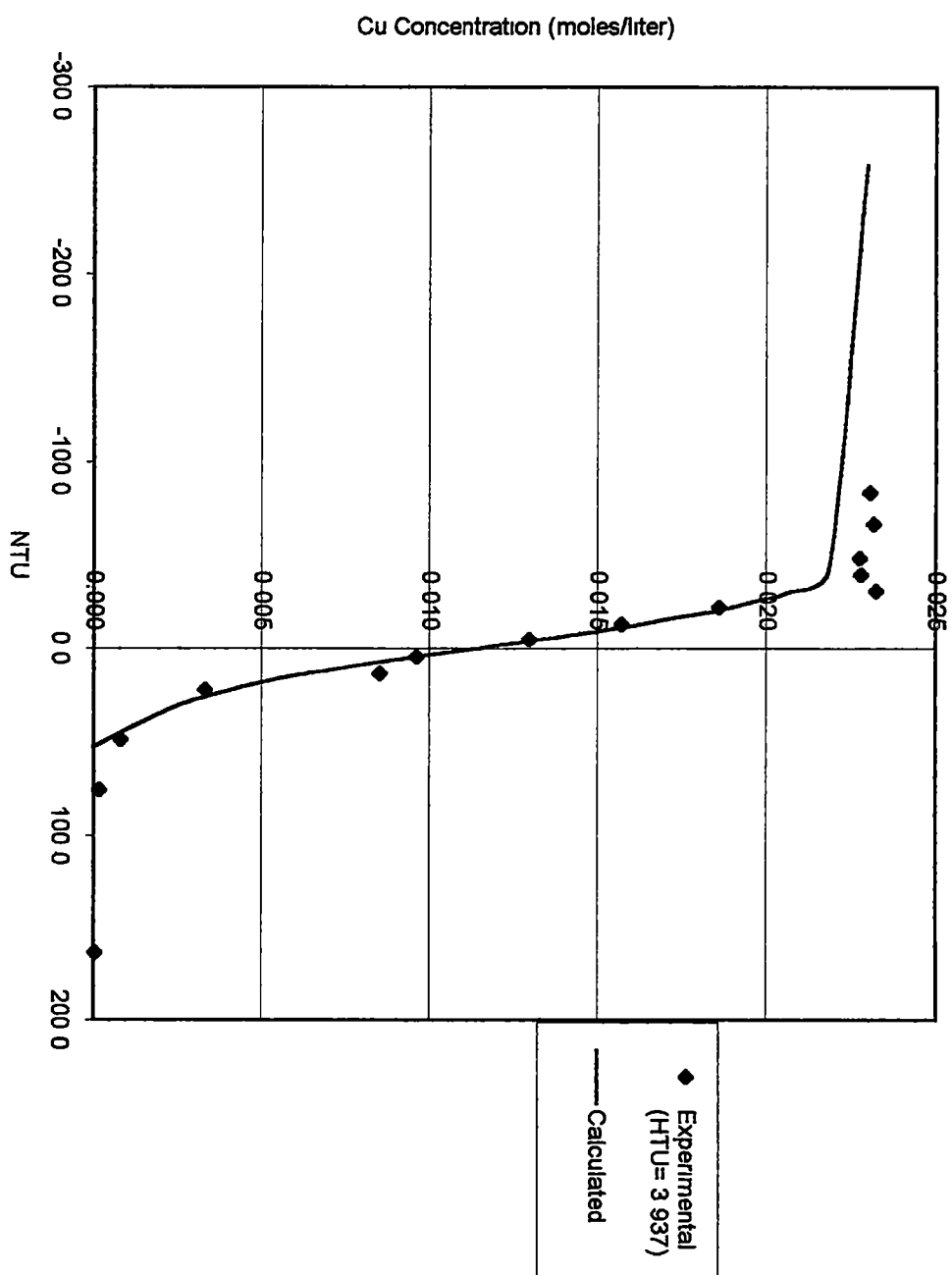


Figure 5.8 Breakthrough curve for exchange of 0.023 M Cupric chloride and 0.025 M Cobalt chloride on sodium loaded resin at 16.32 ml/min (Run 10)

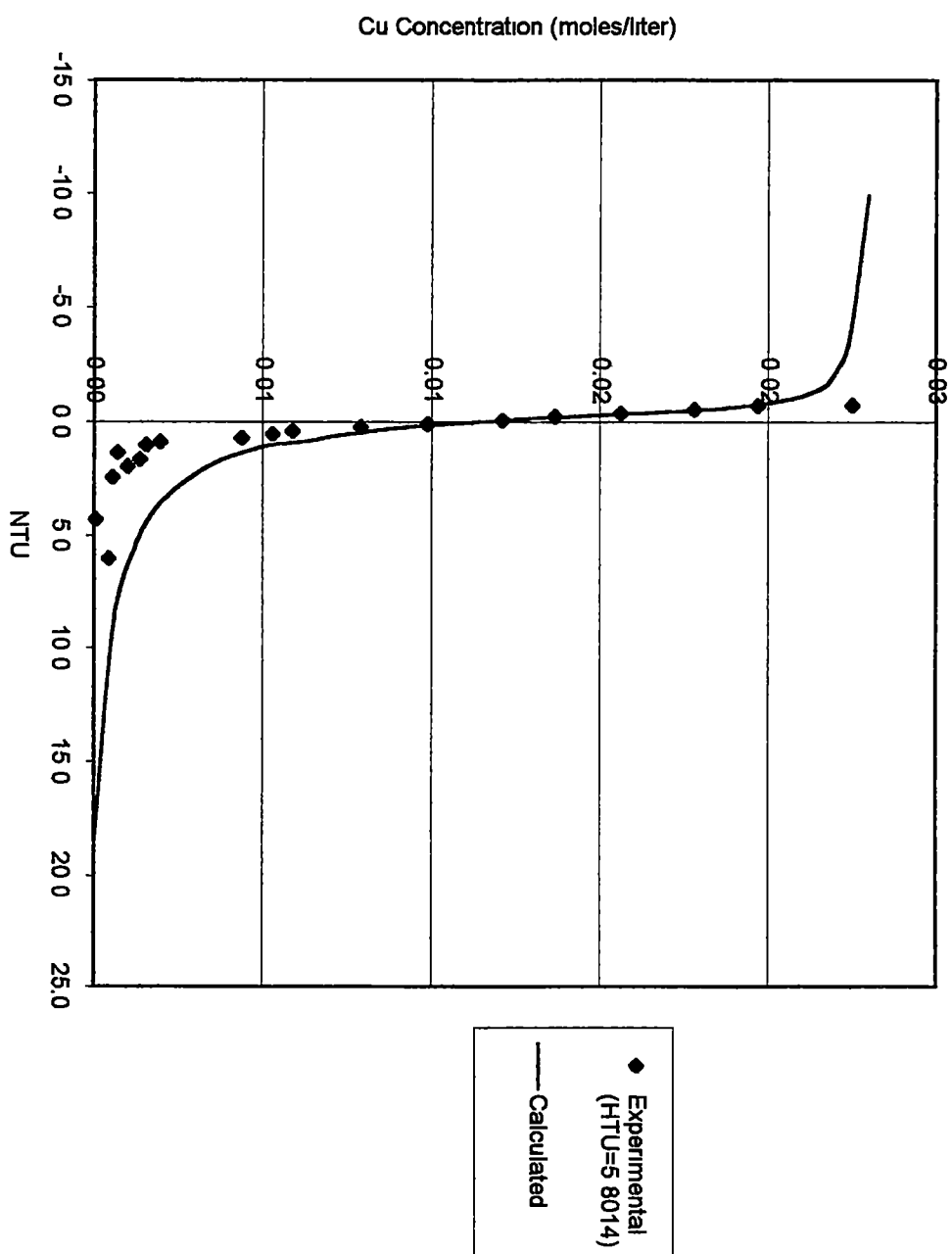


Figure 5.9 Breakthrough curve for exchange of 0.023 M Cupric chloride and 0.0257 M Hydrogen chloride on sodium loaded resin at 15.97 ml/min (Run 12)

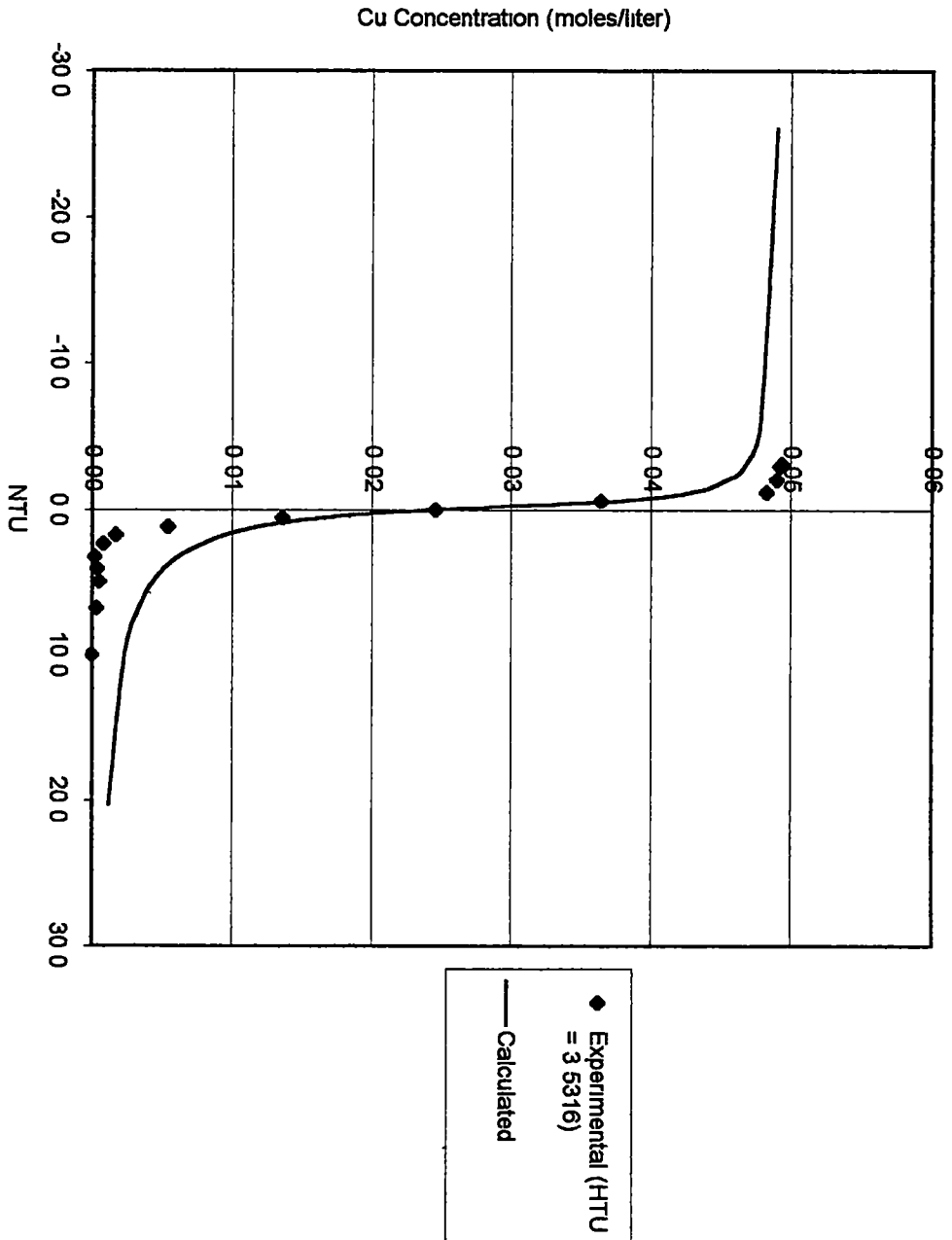


Figure 5.11 Breakthrough curve for exchange of 0.049 M Copper chloride and 0.0661 M Hydrogen chloride on sodium loaded resin at 8.52 ml/min (Run 15)

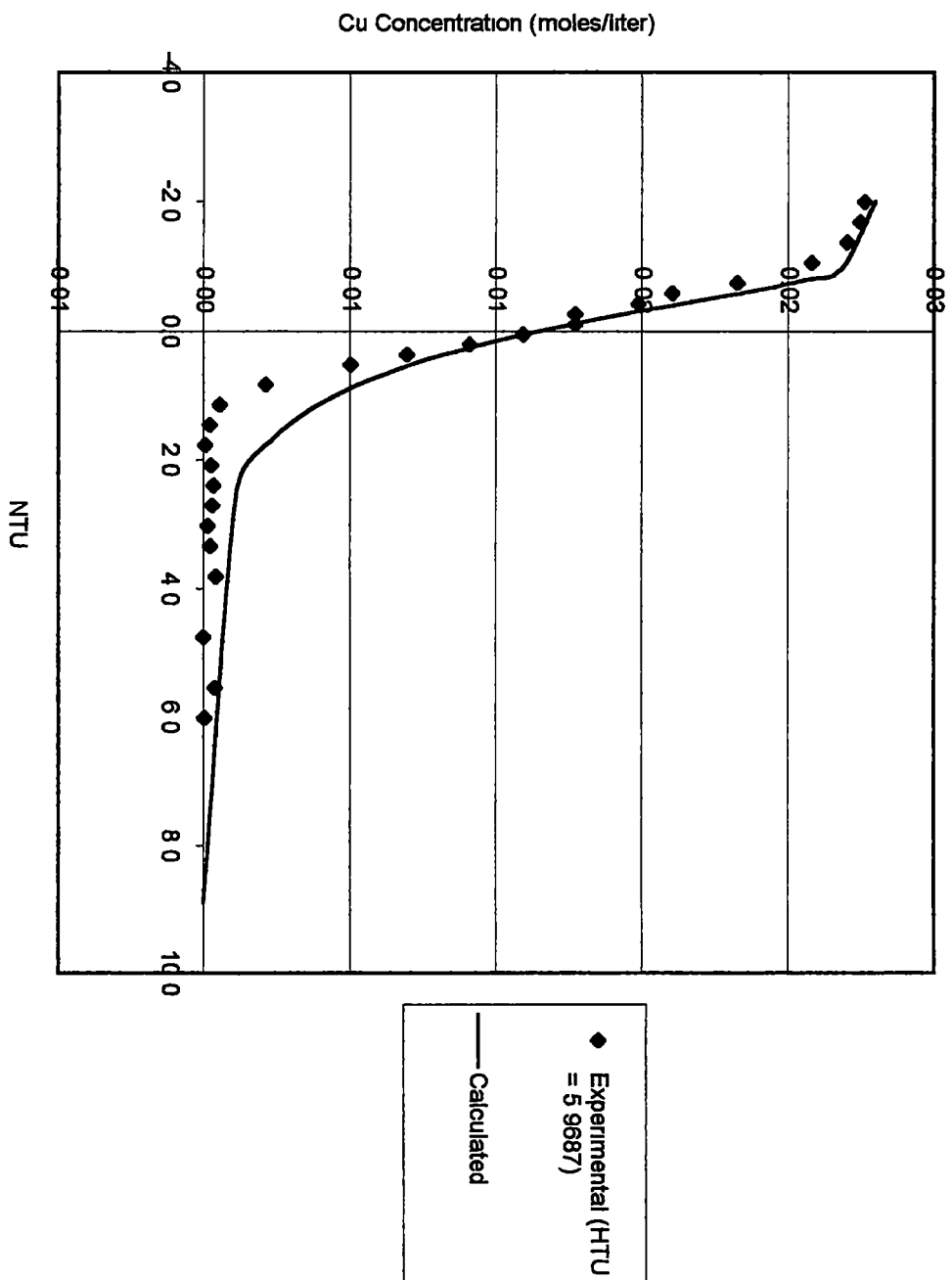


Figure 5.12 Breakthrough curve for exchange of 0.023 M Copper chloride and 0.025 M Sodium chloride on hydrogen loaded resin at 16.15 ml/min (Run 17)

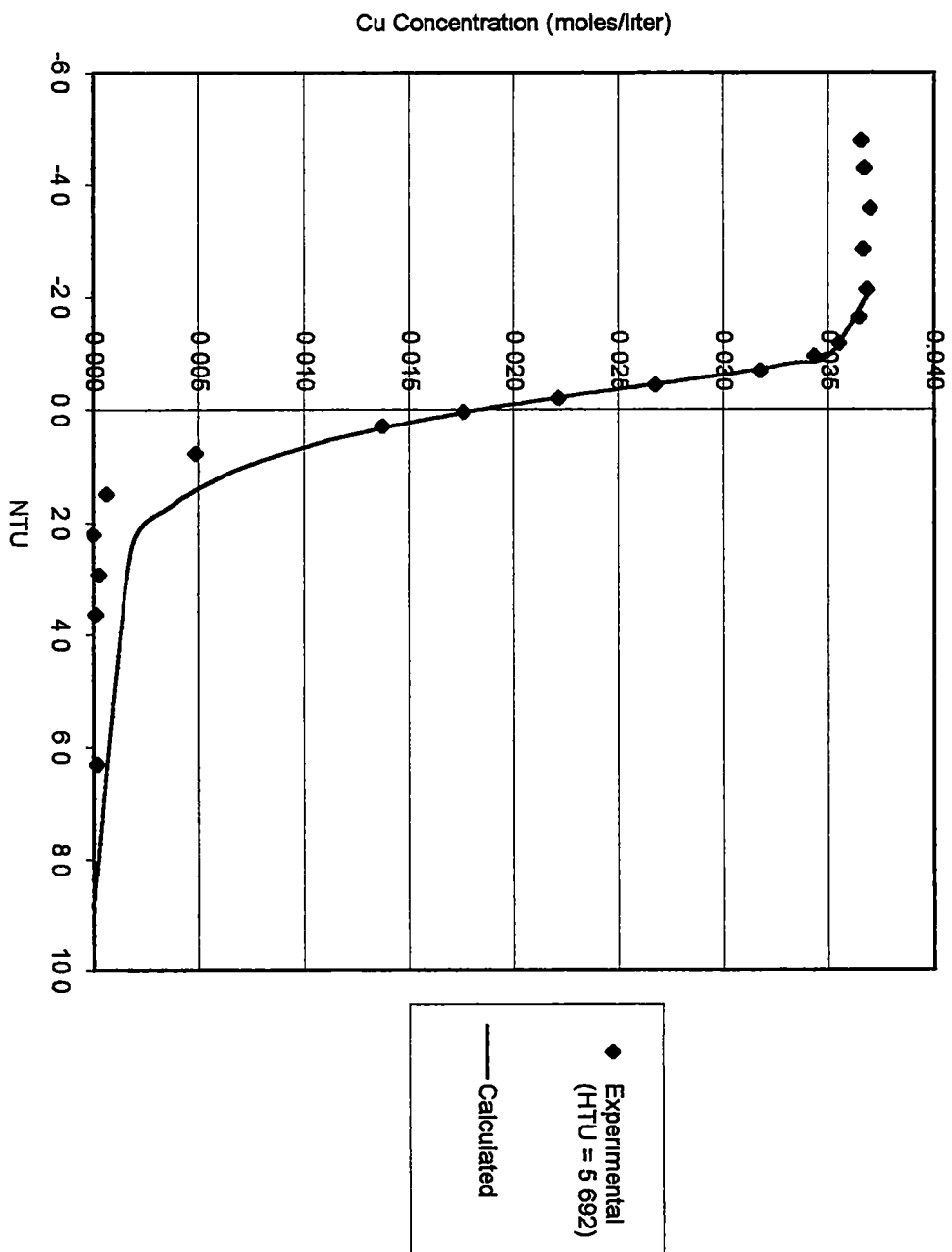


Figure 5 13 Breakthrough curve for exchange of 0.037 M Cupric chloride and 0.01 M Sodium chloride on hydrogen loaded resin at 15.57 ml/min (Run 19)

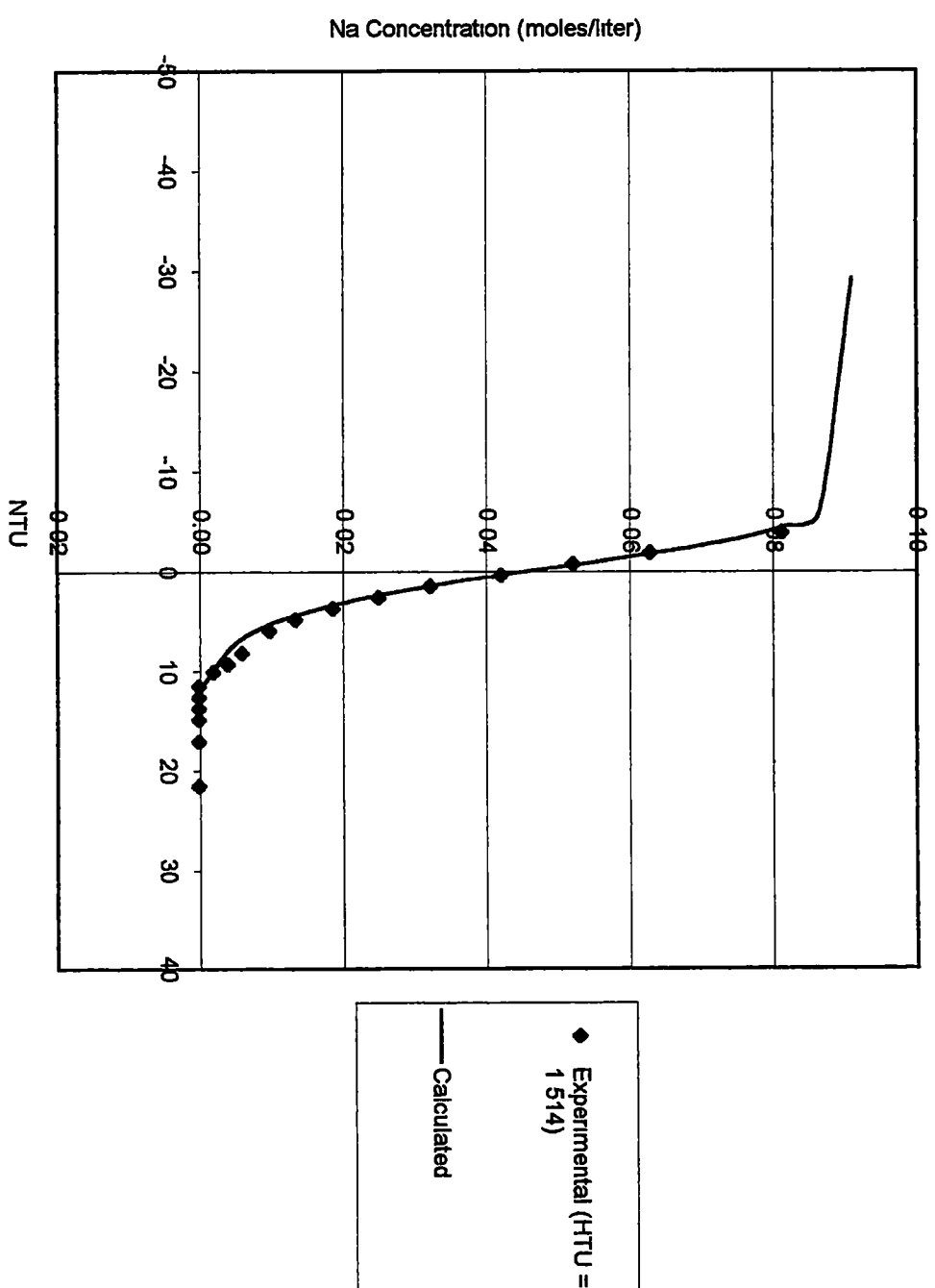


Figure 5 14 Breakthrough curve for exchange of 0.091 M Sodium chloride on hydrogen loaded resin at 16 ml/min (Run 21)

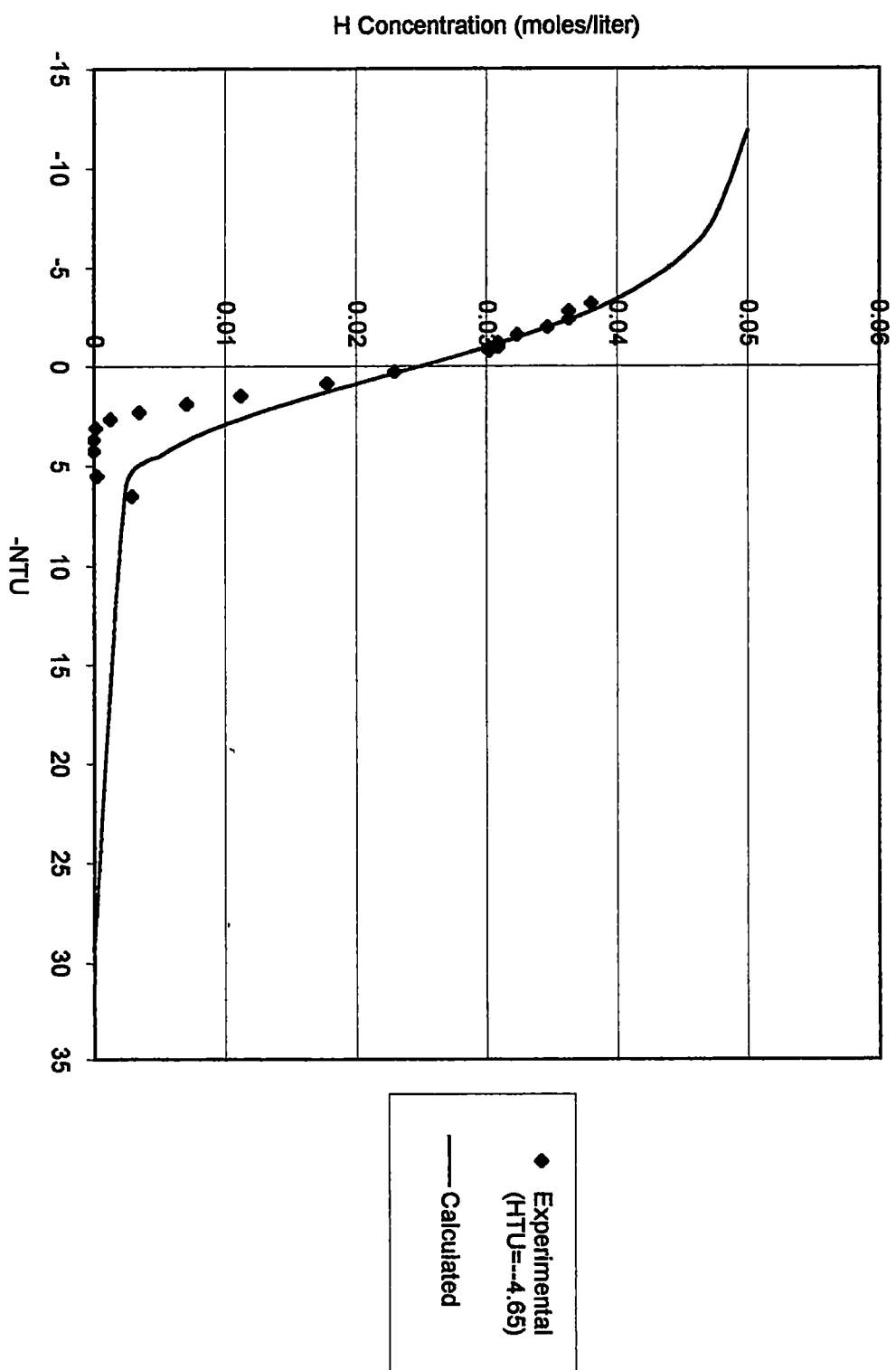


Figure 5.15 Breakthrough curve for exchange of 0.05 M Hydrogen chloride on sodium loaded resin at 15.8 ml/min (Run 22)

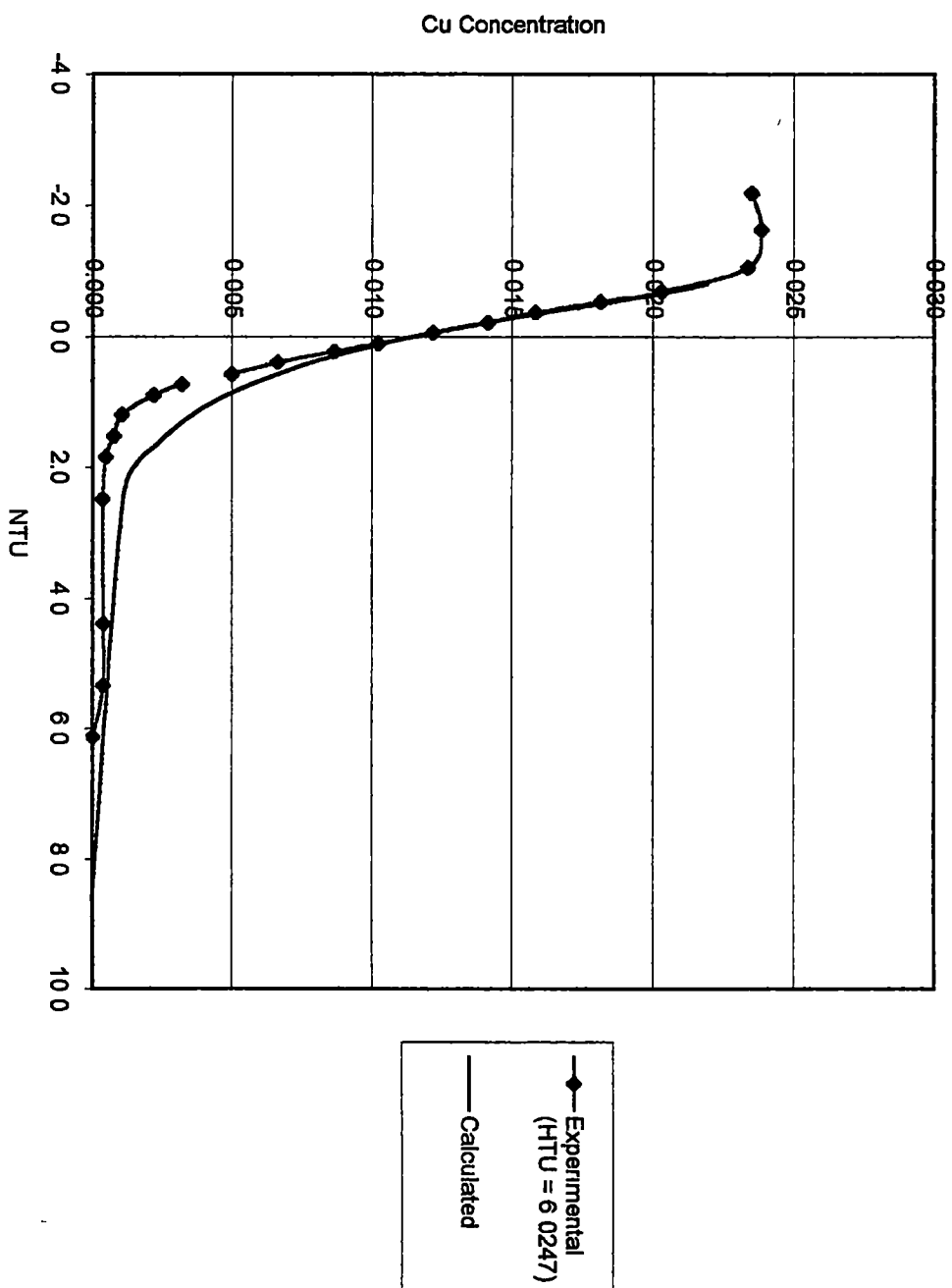


Figure 5.16 Breakthrough curve for exchange of 0.0231 M Cupric chloride and 0.0252 Hydrogen chloride on hydrogen loaded resin at 16.78 ml/min (Run 23)

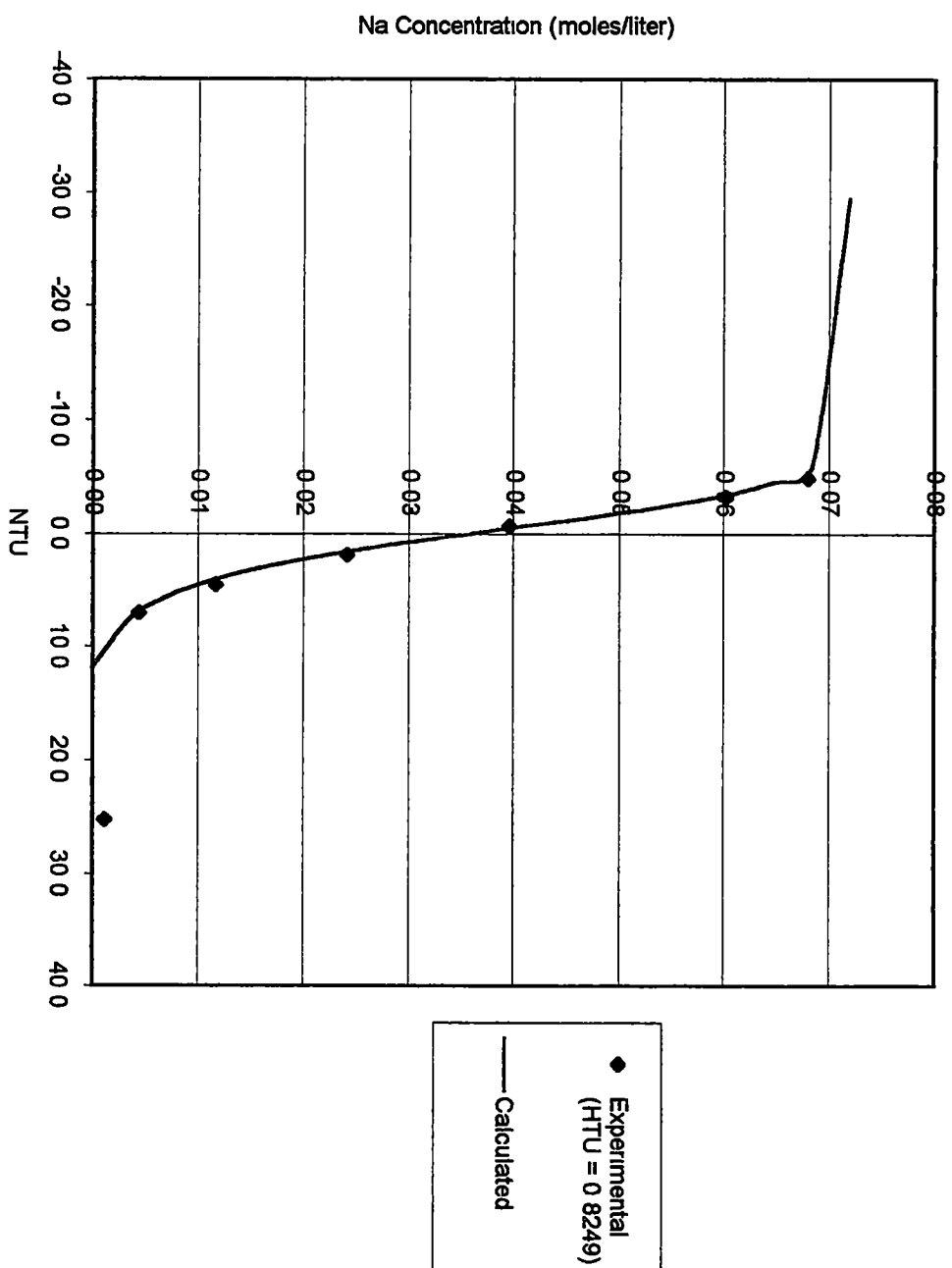


Figure 5.17 Breakthrough curve for exchange of 0.072 M Sodium chloride on hydrogen loaded resin at 8.47 ml/min (Run 25)

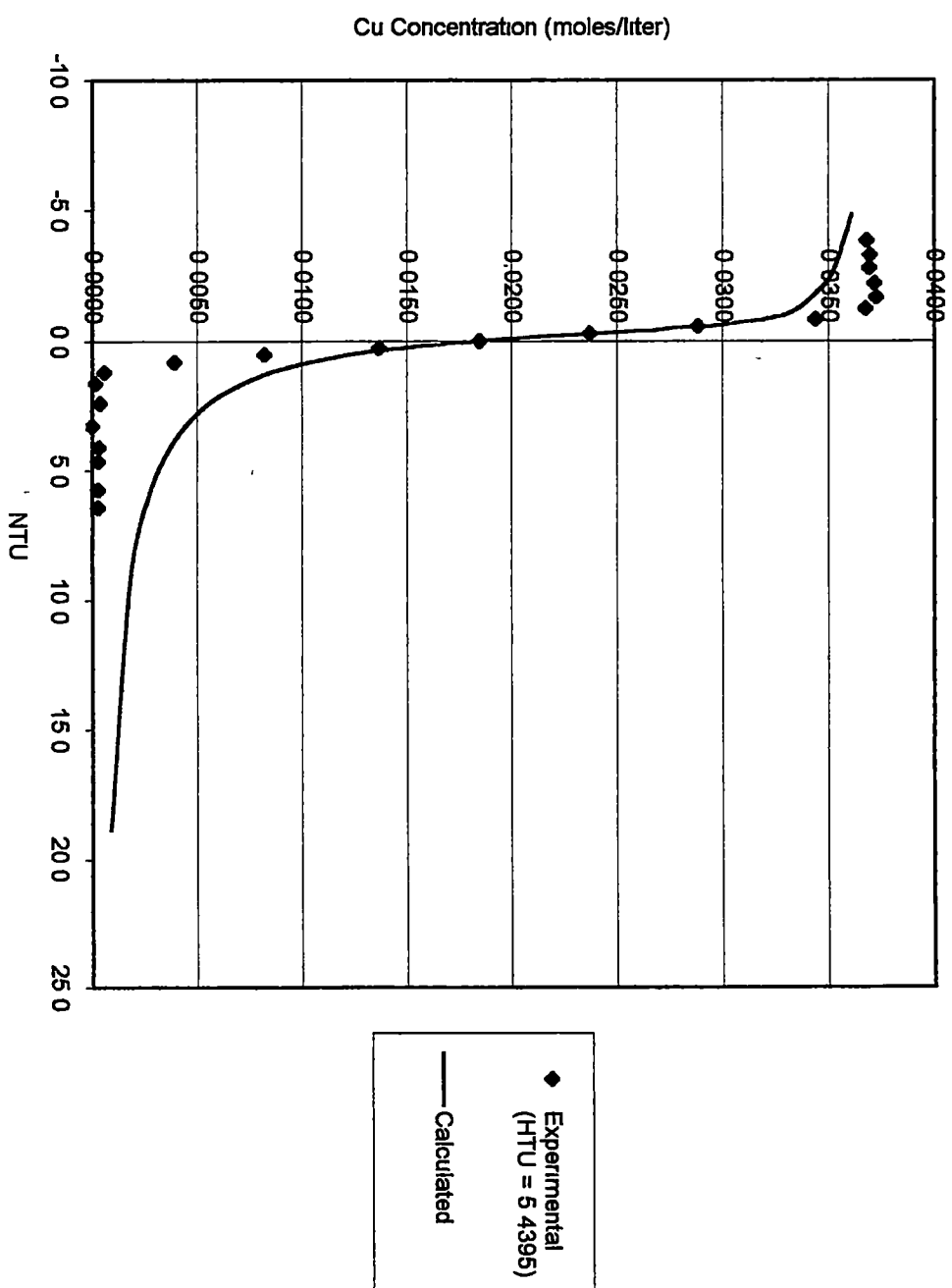


Figure 5 18 Breakthrough curve for exchange of 0.037 M Cupric chloride and 0.0155 M Hydrogen chloride on Na loaded resin at 8.47 ml/min (Run 26)

hydrogen concentration was determined using a pH meter and the sodium concentration was determined by difference. In Run 14, the sodium content was never zero indicating an erroneous measurement on the hydrogen ion concentration. This caused the experimental curve to appear above the calculated curve.

At the high concentration range, the calculated data agreed well with the experimental data for the binary exchange systems and for the ternary systems when the selectivity sequence were $A > B > C$, where C is the component on the resin (Case 1) as illustrated by Figures 5.12 and 5.13. For the ternary system, the assumptions that $C = 0$ and $\bar{C} = 0$ at the end of the A-front for an infinitely long column were employed. Based on the 3 component systems this assumption proved valid.

However, for the ternary exchange when the selectivity sequence were $A > C > B$ (Case 2) the calculated data fell slightly below the experimental data at the high concentration range (see Figures 5.9, 5.11, and 5.18). In calculating the equilibrium curve, $B = B_0$ across the A-front was assumed. In reality, the B-front had not progressed far enough in front of the A-front that its concentration has leveled out to its feed concentration. Since B is displacing C on the resin, the concentration of B increases above its feed concentration and then drops until it reaches its feed concentration. When the concentration of B is decreasing, A is exchanging with B as well as C. The exchange of A and B results in a steeper curve, therefore the NTU needed for a specific separation is smaller than the predicted value.

Two of the systems measured experimentally were for unfavorable isotherms – 1) CoCl_2 on Cu loaded resin (Figures 5.2, 5.5, & 5.7) and 2) HCl on Na loaded resin (Figure 5.15). The Co-Cu system was evaluated because the DOW literature had indicated that Co^{++} has a higher selectivity than Cu^{++} on the DOWEX resin. However, that was not the case as evident by the shape of the NTU and the breakthrough curves (Figures 4.2, 4.5 and 4.7). The fronts are dispersed, not approaching a constant pattern shape. The molar selectivity for HCl exchanging with a sodium loaded is also unfavorable ($K_{\text{H-Na}} = 0.64$), as indicated by the literature. Because constant pattern fronts do not develop for unfavorable isotherm, the methodology is not applicable to calculate the NTUs for these 2 systems. The front was measured for the hydrogen exchanging with the sodium because the exchange process was necessary to return the resin to the state needed for the next planned run. The front would have continued to spread if longer columns had been used.

Flow rate effects on NTUs

The effects of the flow rate on the breakthrough curve (NTUs) were examined experimentally by varying the flow rate while maintaining a constant feed concentration. Two flow rates were evaluated – 8.5 and 16 ml/min. All the runs except Runs 8, 15, 25 and 26 were performed at approximately 16 ml/min. Run 8 will not be discussed further since it has an unfavorable isotherm, therefore, does not affect the conditions required for the calculational procedure. Changing the flow rate in an ion exchange system would not

affect the NTU for a constant pattern front. By definition, the NTU is equal to the change

in concentration divided by the driving force, $\int_{c_{1/2}}^c \frac{dC}{C^* - C}$ and therefore, is independent of

the velocity. However, the HTU is proportional to the velocity, $HTU = \frac{V_s}{k_f a}$ and

therefore, should change with a change in velocity. The HTU is not directly proportional to the V_s would since k_f is also a function of velocity. Several empirical correlations for laminar flow in packed beds exist for the k_f . In general, $k_f \propto V_s^{1/3}$ to $V_s^{2/3}$ depending on the correlation. The Onda equation [18], which is based on experimental data for organic liquids and water, gives $k_f \propto V_s^{2/3}$ for Reynolds numbers < 100 . Wilke and Hougen [19] give the following correlation for packed bed operations:

$$k_f a = \frac{10.9V(1-e)}{d_p} \left(\frac{D}{d_p V} \right)^{0.51} \quad 5.2$$

This correlation was developed for laminar flow gas-solid contact. Based on the Wilke-Hougen correlation, $k_f \propto V^{0.49}$. Correlations based on the j-factor [19], show $k_f \propto V^{1/3}$ for Reynolds numbers from 0.0016 to 55 and Schmidt number between 165 and 70600. For the experimental systems used in this study, Reynolds number range from 0.32 to 0.94 and .63 to 1.88 for 8.5 and 16.5 ml/min flow rate, respectively. The particle size range from 0.42 to 1.22 mm. Based on these correlation's, the $HTU \propto V^{1/3}$ to $V^{2/3}$ so increasing the velocity should increase the HTU when liquid mass transfer resistance dominates.

The HTUs should increase from approximately 25 to 56% when the flow rate is increased

from 8.5 to 16.5 ml/min. This would result in a longer front, Z , since $Z=[NTU][HTU]$ and the NTU would remain constant

Based on the experimental data, the HTU increased from 0.82 to 1.51 for the Na-H system when the flow rate was increased from 8.47 to 16 ml/min. However for the Cu-H-Na system, no noticeable difference was seen in the HTU (5.44 and 5.80) for flow rates of 8.5 and 16 ml/min. Any variation in the HTU could have been obscured due to the inaccuracy of the analyses.

Feed Concentration effect on NTUs

Two feed concentrations (0.05 and 0.1 M) were evaluated in the experimental runs to determine the effect of feed concentration on the NTUs. The normalized equilibrium curve for a binary system is

$$\frac{\bar{A}}{\bar{Q}} = \frac{K_{AB} \frac{A}{Q}}{1 + (K_{AB} - 1) \frac{A}{Q}} \quad 5.3$$

A plot of A/Q versus $\frac{\bar{A}}{\bar{Q}}$ would not be affected as the concentration of component A

changes when component B is not present in the feed. Therefore, the NTU is independent of the feed concentration for simple binary exchange. When B is present in the feed, the NTUs depend upon the shape of the equilibrium curve and, thus, the concentration in the feed. For the systems evaluated experimentally, the NTU did not change as the feed concentration increased for the binary exchange systems (Cu-Na and

Na-H) as expected. For the system with copper and hydrogen exchanging with the resin loaded with sodium, the NTU increased for the higher feed concentration. This was expected since the presence of component B spreads out the breakthrough curve for ternary systems

Calculations for Ion Exchange Systems with n-Components

Equilibrium curves for typical 4 and 5 component systems were calculated using the equations and assumptions discussed in Chapter 3. The equilibrium curves are shown in Figure 5.19 and the parameters are listed in Table 5.2. No equipment was available to measure the concentration for more than a 3 component system; therefore, experimental data are not available for comparison. However, based on the 3 component system, good agreement between experimental and calculated data should result. Figure 5.19 is shown only to illustrate how an effective equilibrium curve can be calculated for 4 and 5 component systems.

Table 5.2 Parameters used to calculate a general equilibrium curve for 4 and 5 component ion exchange systems* (Figure 5.19)

Number of Components	4	5
K_{AB}	5	5
K_{AC}	10	10
K_{AD}	--	20
A_0 (moles/l)	0.05	0.05
B_0 (moles/l)	0.05	0.05
C_0 (moles/l)	0.05	0.05
D_0 (moles/l)	--	0.05

*Case $A > B > C > D$

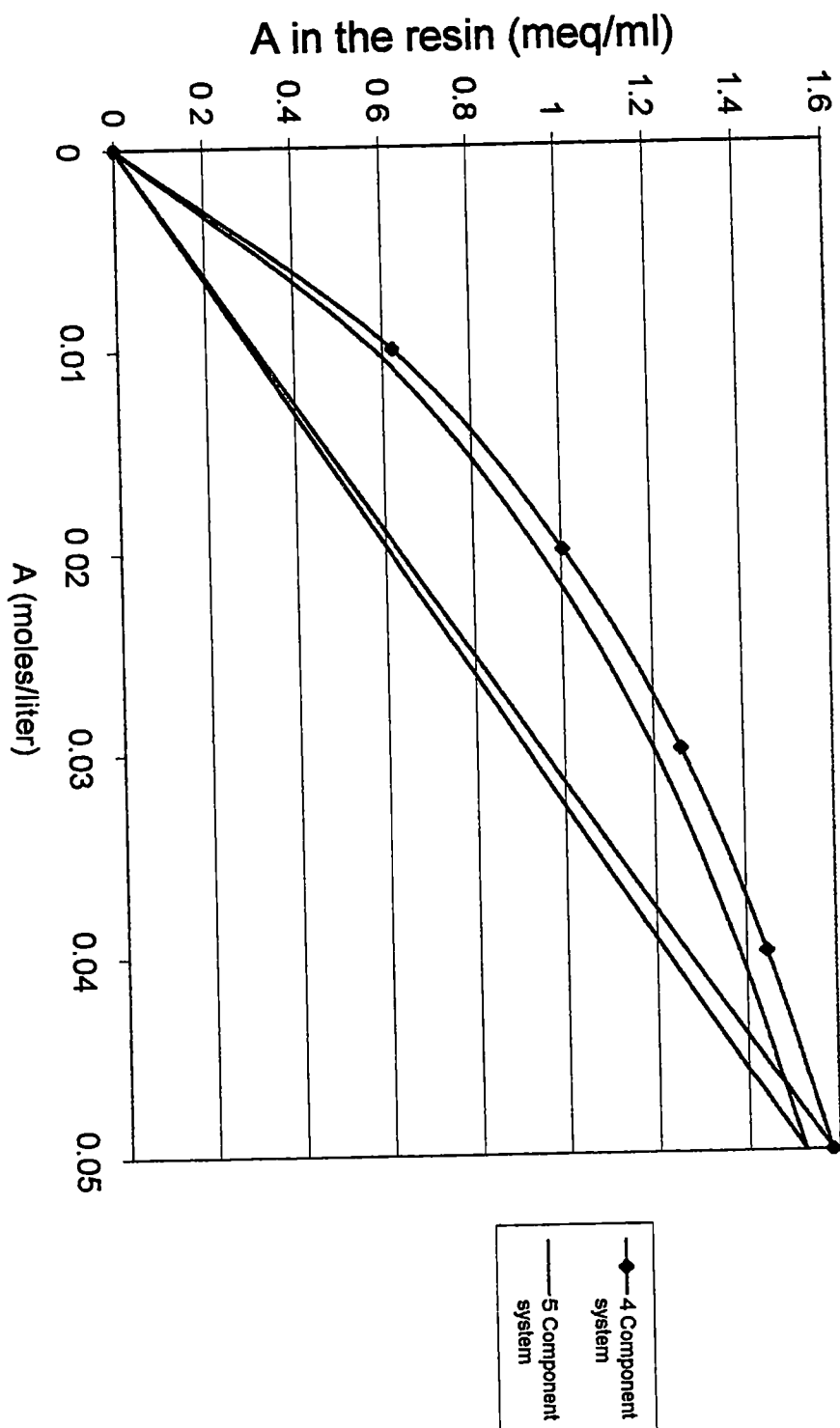


Figure 5.19 Equilibrium Curve for 4 and 5 Component Ion Exchange Systems. Parameters are listed in Table 5.2.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this research was to develop a procedure that would allow one to predict more easily the shape of the breakthrough curve for multi-component ion exchange systems. A simple procedure for predicting breakthrough for multi-component ion exchange systems is a valuable tool because no simple methods are available, and the existing methods are complicated and require the use of sophisticated computer codes and analyses. The results of this study demonstrated that breakthrough curves for binary and ternary ion exchange systems with constant patterns can be predicted approximately using a simple procedure based on rate, mass action equilibrium, and mass balance equations for the system of interest. For systems with 3 or more components, assumptions concerning the concentrations of the ions with the least affinity for the resin must be made in order to predict the equilibrium curve. In general, the concentrations were assumed to be zero or equal to its feed concentration depending on the selectivity sequence of the ions in the system. The assumptions reduce the number of equations needed for an n -component system from $2n-1$ to $n+1$. An explicit expression for the equilibrium curve is also difficult to derive for a system with n -component. The equations must be solved simultaneously in order to obtain a relationship for $\bar{A}$ as a function A (equilibrium curve). The MATLAB function "fsolve" was used to solve the system of non-linear equations for the 3, 4 and 5 component systems.

Breakthrough curves were determined experimentally for binary and ternary ion exchange systems. Only binary and ternary systems were evaluated because limited analytical capabilities were available for measuring the concentration of ions in solution. A total of 18 experimental runs were performed. Good agreement between the calculated and experimental breakthrough curve was seen. The data did show some deviations at the lower concentration range. This is because the concentration in the higher concentration portion of the front was used to calculate the HTU; at the lower concentration range the HTU usually was lower. The HTU was not constant across the MTZ because a constant pattern front had probably not developed by the time breakthrough occurred. The column (15 4" long) was probably not long enough to allow the front to reach a constant pattern at the flow rates employed (8.5 and 16 ml/min). A constant pattern front could be obtained by employing a longer column or decreasing the flow rate. The HTU could also be calculated using $HTU = \frac{V_s}{k_f a}$ with $k_f a$ being determined from empirical correlations.

Overall, the methodology used to predict the shape of the breakthrough curves agreed well with the experimental data for both the binary and ternary ion exchange systems. A longer column is needed or a much slower flow rate to ascertain a constant pattern front has developed fully. Future work might include:

- 1) Using a longer and different length columns and slower flow rate to obtain the HTU to confirm that the variation in the HTU resulted from failure of the front to

reach constant pattern. From the HTU, the k_{fa} could be obtained and compared to the calculated values.

2) Comparing calculated breakthrough curves to experimental data for systems with more than 3 components. This could give further confirmation that the assumption of constant concentration of less selective ions across the A-front is a good approximation for multi-component ion systems. Without these simplifications, additional equations would be needed to predict the equilibrium curve for multi-component ion exchange systems.

3) Using the more accurate (and more complex) computer codes developed by others to evaluate and validate the approximate method for very large number of components, different column lengths, and a wider range of ion selectivities (equilibrium conditions).

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APPENDICES

APPENDIX A

Front Velocity Comparison

The following derivation compares the velocity of the A-front to the B-front as a function of the concentration of B in the feed (B_0) and a fixed concentration of A in the feed (A_0) for the system with CuCl_2 and HCl exchanging with the Na loaded resin

A-front Velocity

Material Balance across the front for component A (operating line)

$$A_0(V - V_{Af}) + \bar{A}V_{Af} = A(V - V_{Af}) + \bar{A}_0V_{Af} \quad \text{A.1}$$

For an infinitely long column, no A will be present very far downstream,

therefore, $A=0$ and $\bar{A} = 0$. Therefore,

$$V_{Af} = \frac{A_0V}{A_0 + \bar{A}_0} \quad \text{A.2}$$

B-front Velocity:

Material Balance across the front for component B (operating line)

$$B_0(V - V_{Bf}) + \bar{B}V_{Bf} = B(V - V_{Bf}) + \bar{B}_0V_{Bf} \quad \text{A.3}$$

For an infinitely long column, no B will be present very far downstream,

therefore, $B=0$ and $\bar{B} = 0$. Also, $B_0 = A_0 + B_0$ because the A-front is behind the

B-front Therefore,

$$V_{Bf} = \frac{(A_0 + B_0)V}{A_0 + B_0 + \bar{B}_0} \quad \text{A.4}$$

Equations A.2 and A.4 give the velocity of the A- and B-fronts, respectively $\bar{A}_0$ and $\bar{B}_0$ are determined from the equilibrium relationship, K_{AB} and mass balance for the resin and the solution. A plot of the A- and B-front velocity as a function of hydrogen concentration is shown in Figure A 1. The parameters used in the calculations are given in Table A.1. The data show that for constant A_0 , no values of B_0 will result in the A-front advancing faster than the B-front when the selectivity of $A > B$. A sensitivity

Table A 1 Input Parameters for comparing the front velocities

Concentration A in feed- A_0 (meq/ml)	0.046
Flow rate (cm/min)	7.96
K_{AB}	3 662
$\bar{Q}$ (meq/ml)	2.06

analysis on the variables K_{AB} and A_0 indicates that only two conditions would result in the A-front advancing faster than the B- front:

- 1) K_{AB} is very small (< 0.06)
- 2) The concentration of A is very large (> 8 meq/ml)

Ion exchange would not be employed for either of these cases. Note: the A-front could lie in the B-front. In this case, the concentration of B in the A-front would not be constant and equal to B_0 . The approximation that the concentration of B across the A-

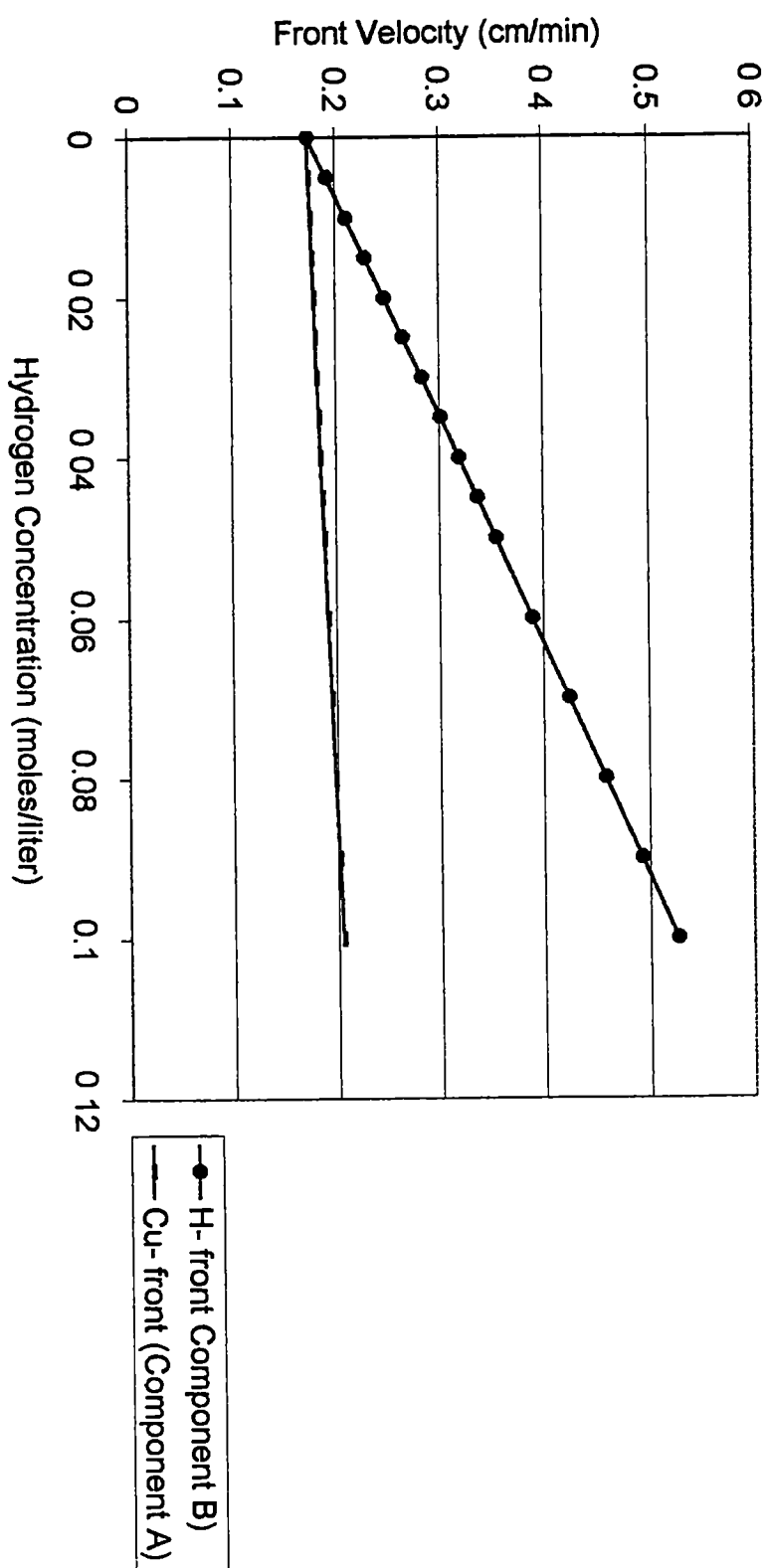


Figure A 1 Hydrogen Concentration as a function of front Velocities for Cu and H exchanging with Na

front is constant for a 3 component system where $A > C > B$ was based upon the estimate that the region is relatively short compared to an infinitely long column and eventually no B would be needed in this region. This would allow the B-front to advance to the next region where no A is present.

Appendix B

Derivation of an Equation for the Equilibrium Curve for a divalent ion exchanging
with an univalent ion on the resin for selectivity sequence of $A > B > C$

$$K_{AB} = \frac{(\bar{A}/A)}{(\bar{B}/B)^n} \quad \text{B 1}$$

For $n = \frac{n_2}{n_1} = 2$, then

$$K_{AB} = \frac{(\bar{A}/A)}{(\bar{B}/B)^2} \quad \text{B.2}$$

Since $C=0$ and $\bar{C} = 0$ for an infinitely long column when $A > B > C$

$$A + B = Q \quad \text{B.3}$$

$$\bar{A} + \bar{B} = \bar{Q} \quad \text{B 4}$$

Combining equations B.2, B.3, and B 4 and solving for $\bar{A}$ gives

$$\bar{A} = - \frac{(2\bar{Q} + \frac{(Q-A)^2}{A+K_{AB}}) \pm \sqrt{\left(2\bar{Q} + \frac{(Q-A)^2}{A+K_{AB}}\right)^2 - 4\bar{Q}}}{2} \quad \text{B 5}$$

The equilibrium curve for component A is given by equation 5. $\bar{A}$ is a function of A, $\bar{Q}$,

Q and K_{AB} only. $\bar{Q}$, Q, and K_{AB} are constant for a given system

APPENDIX C

Equilibrium Curve for 4 and 5 Component Systems

4 Components (Selectivity sequence: $A > D > B > C$)

Equations:

$$K_{AB} = \frac{\bar{A}/A}{(\bar{B}/B)^n}$$

$$K_{AC} = \frac{\bar{A}/A}{(\bar{C}/C)^n}$$

$$K_{AD} = \frac{\bar{A}/A}{(\bar{D}/D)^n}$$

$$A + B + C + D = Q$$

$$\bar{A} + \bar{B} + \bar{C} + \bar{D} = \bar{Q}$$

Unknowns:

$$\bar{A}, \bar{B}, \bar{C}, \bar{D}, A, D$$

Assumptions:

$$B=B_0, C=C_0$$

4 Components (Selectivity sequence: $A > B > C > D$)

Equations:

$$K_{AB} = \frac{\bar{A}/A}{(\bar{B}/B)^n}$$

$$K_{AC} = \frac{\bar{A}/A}{(\bar{C}/C)^n}$$

$$A + B + C + D = Q$$

$$\bar{A} + \bar{B} + \bar{C} + \bar{D} = \bar{Q}$$

Unknowns:

$$\bar{A}, \bar{B}, \bar{C}, A, B$$

Assumptions:

$$\bar{D}=0, D=0, C=C_0$$

5 Components (Selectivity sequence: $A > E > B > C > D$)

Equations:

$$K_{AB} = \frac{\bar{A}/A}{(\bar{B}/B)^n}$$

$$K_{AC} = \frac{\bar{A}/A}{(\bar{C}/C)^n}$$

$$K_{AD} = \frac{\bar{A}/A}{(\bar{D}/D)^n}$$

$$K_{AE} = \frac{\bar{A}/A}{(\bar{E}/E)^n}$$

$$A + B + C + D + E = Q$$

$$\bar{A} + \bar{B} + \bar{C} + \bar{D} + \bar{E} = \bar{Q}$$

Unknowns:

$$\bar{A}, \bar{B}, \bar{C}, \bar{D}, \bar{E}, A, E$$

Assumptions

$$B=B_0, C=C_0, D=D_0$$

5 Components (Selectivity sequence: $A > B > C > D$)

Equations:

$$K_{AB} = \frac{\bar{A}/A}{(\bar{B}/B)^n}$$

$$K_{AC} = \frac{\bar{A}/A}{(\bar{C}/C)^n}$$

$$A + B + C + D + E = Q$$

$$\bar{A} + \bar{B} + \bar{C} + \bar{D} + \bar{E} = \bar{Q}$$

Unknowns:

$$\bar{A}, \bar{B}, \bar{C}, \bar{D}, A, B$$

Assumptions

$$\bar{E}=0, E=0, C=C_0, D=D_0$$

APPENDIX D

Program Listing

Computer programs were written in MATLAB to calculate the NTU required and/or the equilibrium curve for 2, 3, 4, and 5 component systems. The 4 programs were written are as follows:

```

%%%Penny Cunningham          February 18, 2000
%
%
%%% Multi-component Ion Exchange Prediction
%%Thesis2.m
%
%%%This program calculates the NTU required for 3 component ion exchange system when
%%the selectivity of component B > C (component on the resin) and A is the component of
%%interest (Case 1). For an infinitely long column, [Cr]=0, [C]=0, [Q]=Ao+Bo, [Qr]=Aor+Bo
and
%%Kab=[Ar][B]/[Br][A]. An equilibrium curve is generated from these equation and then
Watson's
%%procedure is applied to calculate the NTU for the system.

%%Subprogram associated are DelA.m, and Del.m.

%%Inputs required: [Ao], [Bo], [Co], [Qr], Kab, n1, n2, n3
clear;
global AO AOr Qr Kab Q V;
n1=2;          % n1= charge of component A
n2=2;          % n2= charge of component B
n3=1;          % n3= charge of component C
n=n1/n2
AO=.096*n1;
BO=0*n2;
CO=0*n3;
Qr=2.06;
Kab=2;
Q=Ao+Bo;
Aref=AO/2;
if n==1
    %for n=1
    AOr=AO*Kab*Qr/(BO+AO*Kab);
    V=AOr/AO;
    AI=AO/20;
    Aend=AO-AI;
    Aconc=0:AI:AO;
    [junk num]=size(Aconc);
    for i=1:num
        A=Aconc(i);
        NTU(i)=quad('Del',Aref,A);
        Ar(i)=AOr+(A-AO)*V;
        B(i)=Q-A;
        AEr(i)=A*Kab*Qr/(B(i)+A*Kab);
        Br(i)=Qr-Ar(i);
        AE(i)=Ar(i)*Q/(Br(i)*Kab+Ar(i));
        ZC(i)=1./(A-AE(i));
    end
else
    %for n=2
    a=1;
    b=-(2*Qr+BO^2/(AO*Kab));
    c=Qr^2;
    AOr=(-b-sqrt(b^2-(4*a*c)))/2;

```

```

V=AOx/AO;
AI=AO/20;
Aend=AO-AI;
Aconc=AI:AI:AO-AI;
[junk num]=size(Aconc);
for i=1:num;
    A=Aconc(i);
    NTU(i)=quad('DeIA',Aref,A);
    Ar(i)=AOx+(A-AO)*V;
    Br(i)=Qr-Ar(i);
    B(i)=Q-A;
    b1=(-2*Qr+B(i)^2/(A*Kab));
    AEr(i)=(-b1-sqrt(b1^2-(4*a*c)))/2;
    a=1;
    b2=(-2*Q+(Br(i)^2*Kab/Ar(i)));
    c2=Q^2;
    AE(i)=(-b2-sqrt(b2^2-(4*a*c2)))/2;
    ZC(i)=1./(A-AE(i));
end
end
CA=Aconc(:)/nl;
figure(1);
plot(NTU(:),CA(:),'*-')
ylabel('A Concentration (moles/liter)')
xlabel('NTU')
figure(2);
plot(Aconc(:),ZC(:));
xlabel('A, meq/l')
ylabel('1/(A-A*)')
figure(3);
plot(Aconc(:), Ar(:),Aconc(:),AEr(:))
xlabel('A, meq/l')
ylabel('Aresin')
title('Run 5 - Concentration versus NTU')
fid=fopen('table1.out','w');
frewind(fid);
fprintf(fid,'\n\n\n\nRun 2\n');
fprintf(fid,'A (moles/l)      NTU      AE      1/A-AE\n');
for k=1:num;
    fprintf(fid,'%9.5f      %6.4f      %9.4f      %9.4f\n',CA(k), NTU(k), AE(k), ZC(k))
end
%polyfit(Aconc(:),ZC(:),2)
fclose(fid)
clear;

```

```
function [Z]=Del(A)
global AO AOr Qr Kab Q V;
%Z=1./ (A- (AOr+(A-AO)*V)*Q/ ((Qr- (AOr+(A-AO)*V))*Kab+ (AOr+(A-AO)*V))
Ar=AOr+(A-AO)*V;
Br=Qr-Ar;
AE=Ar*Q/ (Br*Kab+Ar);
Z=1./ (AE-A);
```

```

function [Z]=DelA(A)
global AO AOr Qr Kab Q V;
%Z=1./ (A- (AOr+ (A-AO) *V) *Q/ ( (Qr- (AOr+ (A-AO) *V) ) *Kab+ (AOr+ (A-AO) *V) ) )
Ar=AOr+ (A-AO) *V;
Br=Qr-Ar;
a=1;
b2=- (2*Q+ (Br.^2*Kab/Ar) );
c2=Q^2;
AE=(-b2-sqrt (b2^2- (4*a*c2) ) ) /2;
Z=1./ (AE-A);

```

```

%Equation3new
%General solution for a 3 component system where C, component
%on the resin, is preferred over B.
global xi a aconc ae be ce c ao aor ar bo bor kab kac q qr v z
ao=0.046;          %meq/ml
bo=.0257;          %meq/ml
co=0;
q=ao+bo+co;
qr=2.06;
kab=3.662;
kac=1.5;
bl=-(2*qr+bo^2/(ao*kab));
cl=qr^2;
aor=(-bl-sqrt(bl^2-(4*c1)))/2;
bor=qr-aor;
v=aor/ao;
ai=ao/40;
aconc=0:ai:ao
[junk num]=size(aconc);
for i=1:num;
    a=aconc(i);
    Ar(i)=aor+(a-ao)*v;
    ar=Ar(i);
    ci=q-bo-a;
    bri=(qr-ar)*.2;
    cri=(qr-ar)*.8;
    if i>1
        xi=[ae(i-1);be(i-1);ce(i-1);c(i-1)];
    else
        xi=[0.001;bri;cri;.0460];
    end
    [x,fval]=fsolve('fun3',xi);
    ae(i)=x(1);
    be(i)=x(2);
    ce(i)=x(3);
    c(i)=x(4);
    aref=ao/2;;
    NTU(i)=quad8('Arecanew',aref,a)
    Z1(i)=1/(aconc(i)-ae(i));
    end
    ca=aconc(:)/2;
    plot(aconc(:),Ar(:),ae(:),Ar(:),'*')
    ylabel('A resin')
    xlabel('A solution')
    fid=fopen('table.out','w')
    for k=1:num
        fprintf(fid,'%6.4f %6.4f %6.4f %6.4f %6.4f %6.4f %6.4f\n',ca(k),aconc(k),Ar(k),ae(k),be(k),ce(k),c(k),NTU(k))
    end
    fclose(fid)
    fid=fopen('table2.out','w')
    for k=1:num
        fprintf(fid,'%6.4f %6.4f %5.4f %9.4f\n',aconc(k),ae(k),Z1(k),NTU(k))
    end
    fclose(fid)
    clear all;

```

```

%%m-file for for 3 component ion exchange system
%%with b=bo to be used with equation3

```

```

function F=fun3(x)
global xi a aconc ae be ce c ao aor ar bo bor kab kac q qr v Z
F=[x(2)-sqrt((ar*bo^2)/(x(1)*kab));
  x(1)*x(3)^2*kac-ar*x(4)^2;
  x(1)+bo+x(4)-q;
  ar+x(2)+x(3)-qr]

```

```

function [Z]=Areanew(A)
global xi a aconc ae be ce c ao aor ar bo bor kab kac q qr v Z
A=a
ar=aor+(A-ao)*v;
ci=q-bo-a;
bri=(qr-ar)*.2
cri=(qr-ar)*.8
xi=[0.001;bri;cri;.0460]
[x,fval]=fsolve('fun3',xi)
areq=x(1)
breq=x(2)
creq=x(3)
ceq=x(4)
Z=1./(areq-A);

```

```

%Equation4all
%General solution for a 4 component system where D, component
%on the resin, is preferred over B & C.
global a ao aor ar bo bor co cor do dor kab kac kad q qr
ao=0.05;      %meq/nl
bo=0.05;      %meq/ml
co=0.05;
do=0
q=ao+bo+co
qr=2.06;
kab=3;
kac=4;
kad=2;
bor=qr/(1+kab+kab/kac+kab/kad*do)
aor=kab*bor;
cor=aor/kac;
dor=aor/kad;
v=aor/ao;
ai=ao/20
aend=ao-ai
aconc=0:ai:ao
%aconc=.04:.001:.049
[junk num]=size(aconc);
for i=1:num;
    a=aconc(i);
    Ar(i)=aor+(a-ao)*v;
    ar=Ar(i);
    ai=a*.8;
    bri=(qr-ar)*.5;
    cri=(qr-ar)*.3;
    dri=(qr-ar)*.1;
    boi=bo*.99;
    coi=co*.99;
    doi=ao*.2;
    if i>1
        yi=[aey(i-1);brey(i-1);crey(i-1);drey(i-1);dey(i-1)]
    else
        yi=[ai;bri;cri;dri;doi];
    end
    [y,fval]=fsolve('fun4exp',yi)
    aey(i)=y(1);
    brey(i)=y(2);
    crey(i)=y(3);
    drey(i)=y(4);
    dey(i)=y(5);
end
ARR=ar
plot(aconc(:),Ar(:),aey(:),Ar(:),'*')
ylabel('A resin')
xlabel('A solution')
fid=fopen('table.out','w')
for k=1:num
    fprintf(fid,'%6.5f    %6.4f    %6.4f    %6.4f    %6.4f    %6.4f\n',aconc(k),Ar(k),aey(k),brey(k),crey(k),drey(k),dey(k))
end
fclose(fid)

```

```

%%m-file for for 4 component ion exchange system
%%with assumption b=bo and c=co to be used with equation4all

```

```

function F=fun4exp(y)
global ao aor ar bo bor co cor do dor kab kac kad q qr
F=[ar*bo-y(1)*y(2)*kab;
   ar*co-y(1)*y(3)*kac;
   ar*y(5)-y(1)*y(4)*kad;
   y(1)+bo+co+y(5)-q;
   ar+y(2)+y(3)+y(4)-qr];

```

```
%Main program to calculate ar, br, and b from a simplified set of equations
%Calls fundec - non linear equations
%4 components where A>B>C>D
```

```
global ao bo co q a qr kab kac kbc aor bor cor dor;
ao=0.05;
bo=0.05;
co=0.05;
q=ao+bo+co;
aor=1.584;
bor=0.317;
cor=0.1584;
qr=2.06;
kab=5;
kac=10;
kbc=2;
kad=20;
a=0.01
xo=[1.2;.3;.025];
[x,fval]=fsolve('fundec',xo)
clear all;
```

%Calculates ar, br and b from a simplified set of equations

%Using equatdec to call this m file - fundec

```
function F=fundec(x)
global ao bo co do q a qr kab kac kbc kad aor bor cor dor
F=[x(1)*x(3)-a*kab*x(2);
   x(2)*(a*kab+(q-a)/kbc +x(3)-x(3)/kbc)-2.06*x(3);
   x(2)-bor-(x(1)-aor)*(x(3)-bo)/(a-ao)]
```

APPENDIX E

PUMP CALIBRATION

A Master Flex peristaltic pump with a 7014 head was used to pump the solution to the ion exchange column. The 7014 head is rated to deliver 0.21 to 21 ml/min at atmospheric pressure. The flow rate as a function of set point was determined by pumping water through the ion exchange column for a specified time and measuring the volume of the solution pumped. Calibration data for set points at 4, 5, 7 and 9 are given in Table E.1.

Table E.1 Pump Calibration – Master Flex with 7014 pump head

Set Point	Time (min)	Volume pumped (ml)	Flow rate (ml/min)
4	10	87	8.7
	20	177	8.9
	30	260	8.7
	35	300	8.6
5	4	43	11.0
	10	110	11.0
	25	287	11.5
7	10	160	16.0
	10	161	16.1
	10	162.5	16.3
9	5	110	22.0
	10	215	21.5
	16	338	21.1

Based on this data, set points of 4 (approx. 8.5 ml/min) and 7 (approx. 16 ml/min) were chosen for the experimental study.

APPENDIX F

DOW Chemical Company – DOWEX HCR-W2 product data

PRODUCT INFORMATION



DOWEX HCR-W2

A High Capacity Strong Acid Cation Exchange Resin for Mixed Bed Demineralization and Condensate Polishing Applications

Product	Type	Matrix	Functional group
DOWEX® HCR-W2	Strong acid cation	Styrene-DVB, gel	Sulfonic acid

Guaranteed Sales Specifications		Na ⁺ form	H ⁺ form			
Total exchange capacity, min.	eq/l	2.0	1.8			
	kg/ft ³ as CaCO ₃	43.7	39.3			
Water content	%	45 - 49	48 - 54			
Bead size distribution [†]						
>1.2 mm, max. (16 mesh)	%	2	2			
<0.42 mm, max. (40 mesh)	%	1	1			
Whole uncracked beads, min.	%	95	95			
Crush strength						
Average, min.	g/bead	350	350			
>200 g/bead, min.	%	95	95			
Trace metals, ppm dry resin, max. (H ⁺ form)						
Na	Fe	Cu	Al	Mg	Ca	Heavy Metals (as Pb)
50	50	10	50	50	50	10

Typical Physical and Chemical Properties			Na ⁺ form	H ⁺ form
Total swelling (Na ⁺ → H ⁺)		%	8	8
Particle density		g/ml	1.28	1.22
Shipping weight		g/l lbs/ft ³	820 51	800 50

Recommended Operating Conditions		
Maximum operating temperature		120°C (250 °F)
pH range		0-14
Bed depth, min.		450 mm (1.5 ft)
Flow rates		
Service/fast rinse		5-50 m/h (2-20 gpm/ft ²)
Service/condensate polishing		40-150 m/h (15-60 gpm/ft ²)
Backwash		See figure 1
Regeneration/displacement rinse		1-10 m/h (0.4-4 gpm/ft ²)
Total rinse requirement		3-6 Bed volumes
Regenerant		1-10% H ₂ SO ₄ or 4-8% HCl

[†]For additional particle size information, please refer to the Particle Size Distribution Cross Reference Chart (Form No. 177-01775/CH 171-475-E)

Trademark of The Dow Chemical Company

DOWEX Ion Exchange Resins

DOWEX Ion Exchange Resins

For more information about DOWEX resins,
call Dow Liquid Separations business:

North America 1-800-447-4369
Latin America (+55) 11-5165-9345
Europe (+31) 20-691-6266
Japan (+81) 3-5480-2100
Australia (+61) 2-9776-3266
<http://www.dow.com/liquidspe>

Typical properties and applications:

DOWEX® HCR-W2 strong acid cation exchange resin is a premium grade resin with high exchange capacity, excellent resistance to attrition, and good resistance to thermal and oxidative degradation.

The resin is specially sized for use in working or polishing mixed beds.

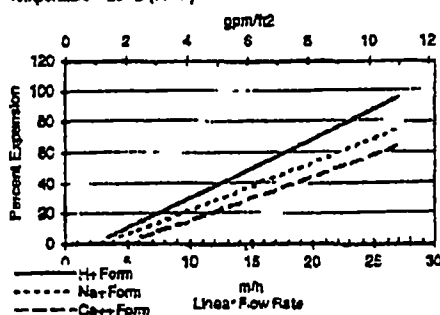
DOWEX HCR-W2 resin is recommended for use alone as a single bed cation or with DOWEX SBR-C (OH) or DOWEX SBR-P C (OH) anion exchange resins in mixed beds for deep-bed condensate polishing.

Packaging

25 liter bags or 5 cubic feet
fiber drums

Figure 1. Backwash Expansion Data

Temperature = 25° C (77° F)



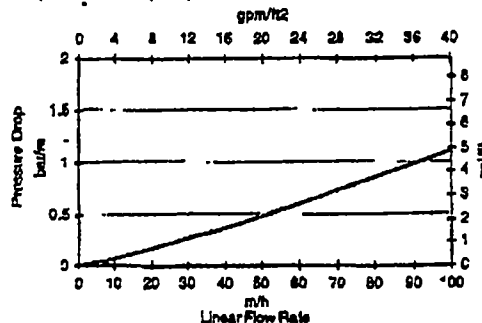
For other temperatures use:

$$F_T = F_{77°F} [1 + 0.008 (T_F - 77)], \text{ where } F = \text{gpm/ft}^2$$

$$F_T = F_{25°C} [1 + 0.008 (T_C - 25)], \text{ where } F = \text{m/h}$$

Figure 2. Pressure Drop Data

Temperature = 20° C (68° F)



For other temperatures use:

$$P_T = P_{20°C} / (0.026 T_C + 0.48), \text{ where } P = \text{bar/m}$$

$$P_T = P_{68°F} / (0.014 T_F + 0.05), \text{ where } P = \text{psi/ft}$$

Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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CH 171-123-E-980A

APPENDIX G

Determination of Cu and Co Concentration using Spectrophotometric Analyses

Solutions of cupric chloride and cobalt chloride were selected for use in the experimental study since they could be analyzed using spectrophotometer analyses. A HP8452 A Spectrophotometer was available to perform the analyses. The HP 8452A spectrophotometer is a single beam microprocessor controlled, UV/VIS spectrophotometer with collimating optics. It uses diode array technology that the manufacturer says makes it much faster than conventional instruments with more precision, sensitivity, and reproducible results. The unit is capable of operating in a wavelength range of 190 to 820 nm. The diode array is a series of 328 individual photodiodes and control circuits etched onto a semiconductor chip 2 mm x 18 mm in size. Each photodiode is assigned a wavelength. A schematic of the HP 8452 A optical system is shown in Figure G.1. Sample cells are available in quartz, glass and plastic. Quartz

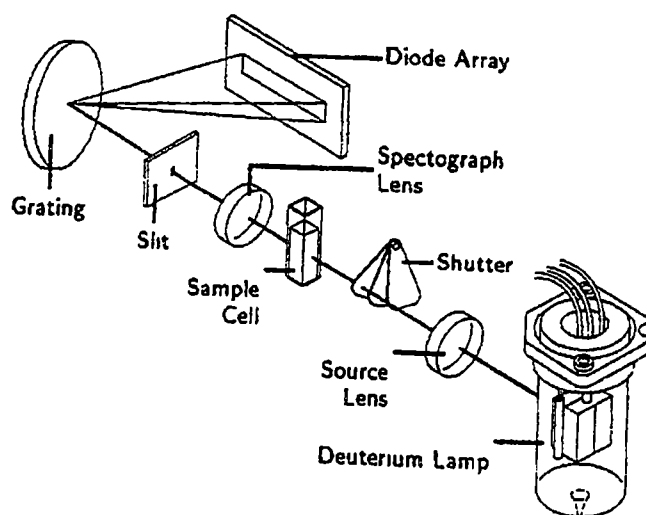


Figure G 1 HP 8452A Optical System

sample cells are required if the full 190 to 820 nm wavelength range is used. For the visible range, good quality glass is adequate. The quality of the disposable plastic cells varies, therefore, plastic cuvettes are generally not recommended

A spectrum was run on a 0.2-M solution of CuCl_2 and CoCl_2 to determine the wavelengths at which they absorb. The wavelength at which a compound absorbs is determined by selecting the wavelength that gives the highest measured value for that component. Solutions of CuCl_2 and CoCl_2 were found to absorb at 800 and 510 nm, respectively. Absorbance spectrums of the 0.2 M CuCl_2 and CoCl_2 solutions are given in Figures G.2 and G.3, respectively. The absorbance (A) of a solution is defined by Beer's Law, $A=abc$, where a is the absorptivity, c is the concentration of the absorbing species in moles/liter, and b is the length of the light path through the absorbing solution in centimeters. The absorptivity, a , is a function of the wavelength that is characteristic of the component. The length of the light path is a function of the spectrophotometer and is usually 1 cm. For a mixture, the absorbance at any selected wavelength is the sum of the contributions of each constituent. Therefore in a mixture, the concentration of each constituent is determined by solving a set of simultaneous equations for each absorbance at the specified wavelength. For a binary mixture of CuCl_2 and CoCl_2 ,

$$A_{@ 510 \text{ nm}} = a_1[\text{Cu}] + a_2[\text{Co}] \quad \text{G.1}$$

$$A_{@ 800 \text{ nm}} = a_3[\text{Cu}] + a_4[\text{Co}] \quad \text{G.2}$$

where a_1 and a_3 are the absorptivity of copper at 510 and 800 nm, respectively, a_2 and a_4 are the absorptivity of cobalt at 510 and 800 nm, respectively, and $[\text{Cu}]$ and $[\text{Co}]$ are the

concentration of copper and cobalt, respectively in moles/liter. These equations are then solved simultaneously for $[\text{Cu}]$ and $[\text{Co}]$.

---> WAVELENGTH SCAN REPORT <---

Date 01-27-1980
Time 13:05:52
Operator Not Entered

Sample Name : CuCl₂
Solvent Name : CuCl₂
Concentration 0.2000
Units M (moles/liter,

Function : Absorbance
Wavelength Range 190 to 820 nanometers
Integration Time 1 seconds
Std Deviation OFF

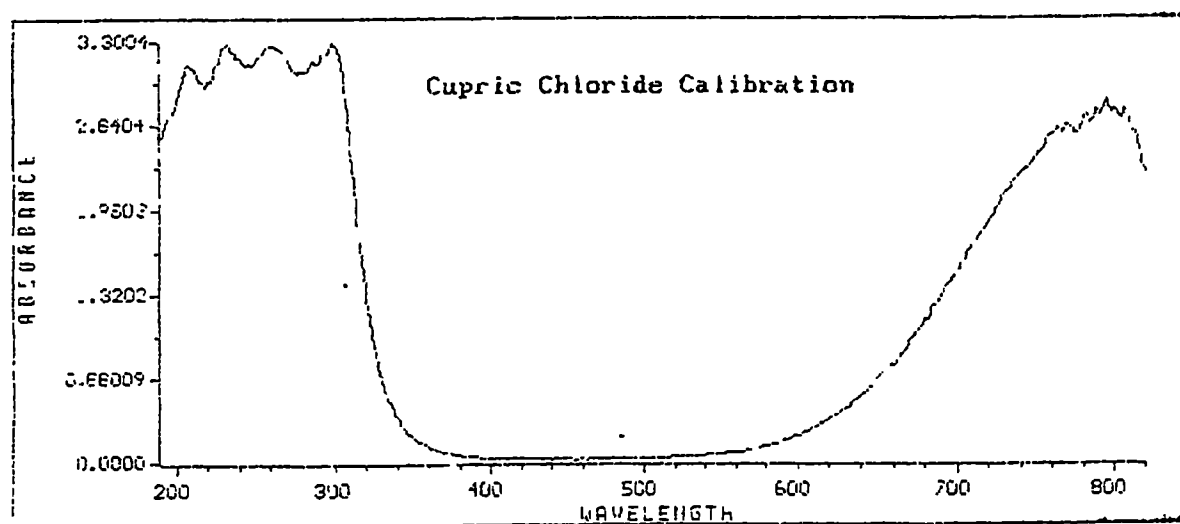


Figure G 2 Absorbance Spectrum of 0.2 M Cupric Chloride Solution

---> WAVELENGTH SCAN REPORT <---

Date : 01-27-1980
Time : 14:34.58
Operator : Not Entered

Sample Name	: Calibration	Function	: Absorbance
Solvent Name	: CoCl_2	Wavelength Range	: 190 to 820 nanometers
Concentration	: 0.2000	Integration Time	: 2 seconds
Units	: M (moles/liter)	Std Deviation	: OFF

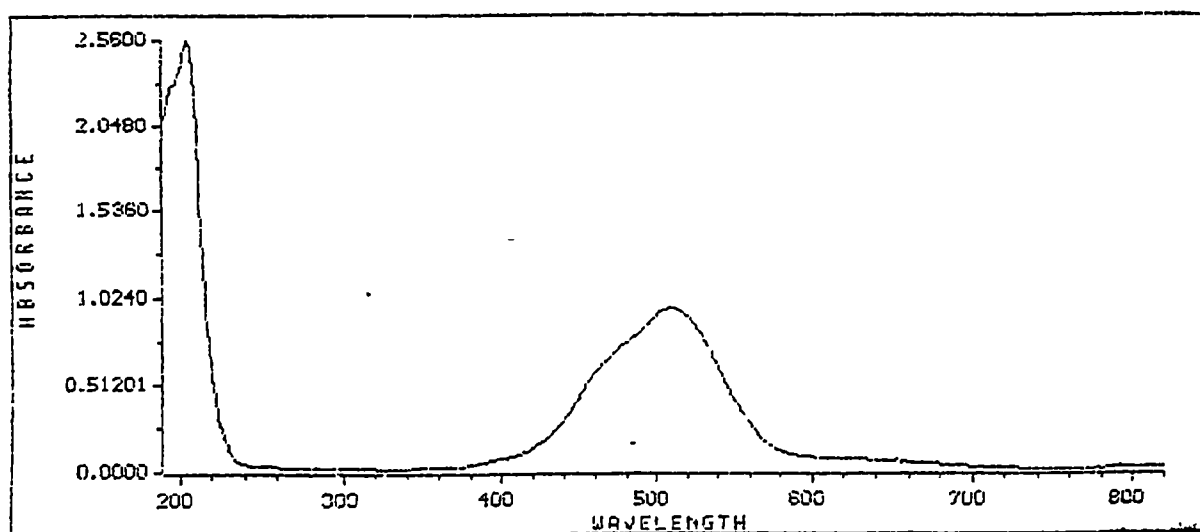


Figure G.3 Absorbance Spectrum of 0.2 M Cobalt Chloride Solution

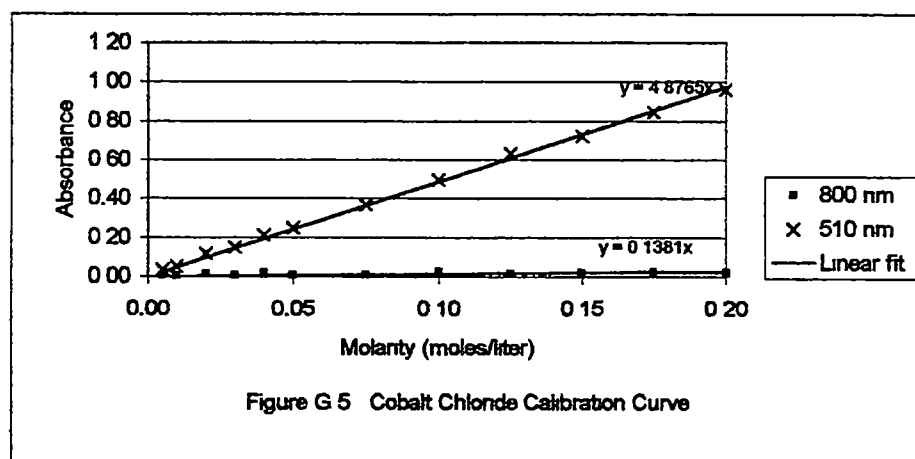
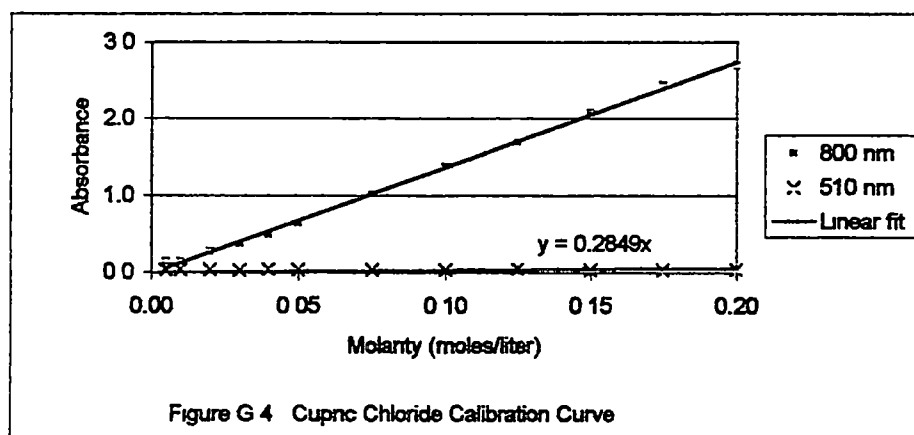
Calibration curves were generated for CuCl_2 and CoCl_2 by measuring the absorbance as a function of solution concentration. The standards were prepared by diluting a 0.2 M solution of CuCl_2 and CoCl_2 . The 0.2 M solutions were prepared by dissolving 3.4 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 4.8 g of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in a 100-ml volumetric flask with deionized water for a total solution volume of 100 ml. The absorbance at 510 and 800 nm wavelengths as a function of the CuCl_2 and CoCl_2 concentrations were measured and are tabulated in Tables G 1 and G.2, respectively. The data was fitted to a linear equation to obtain the relationship between the absorbance and the concentration of the copper and cobalt chloride solutions. Plots of the data for the CuCl_2 and CoCl_2 solutions with a linear fit are shown in Figures G 4 and G.5, respectively. As indicated by the figures, a good fit exists between the data and the linear equation especially at the high concentration range. Based on the data, the absorptivity of Cu at 800 and 510 nm were determined to be 13.69 and 0.2849, respectively, and the absorptivity of Co at 800 and 510 nm are 0.1381 and 4 8765, respectively. The concentrations of copper and cobalt in an unknown solution are determined by measuring the absorbance of the solution at 510 and 800 nm and simultaneously solving the two equations.

Table G.1. Cupric Chloride Calibration Data

M <u>moles/liter</u>	<u>Wavelength</u>	
	<u>800</u>	<u>510</u>
0.005	0.1444	0.0296
0.010	0.1402	0.0308
0.020	0.2708	0.0345
0.030	0.3788	0.0285
0.040	0.4752	0.0423
0.050	0.6437	0.0335
0.075	0.9963	0.0311
0.100	1.3840	0.0315
0.125	1.7049	0.0462
0.150	2.0852	0.0377
0.175	2.4524	0.0349
0.200	2.7006	0.0432

Table G.2. Cobalt Chloride Calibration Data

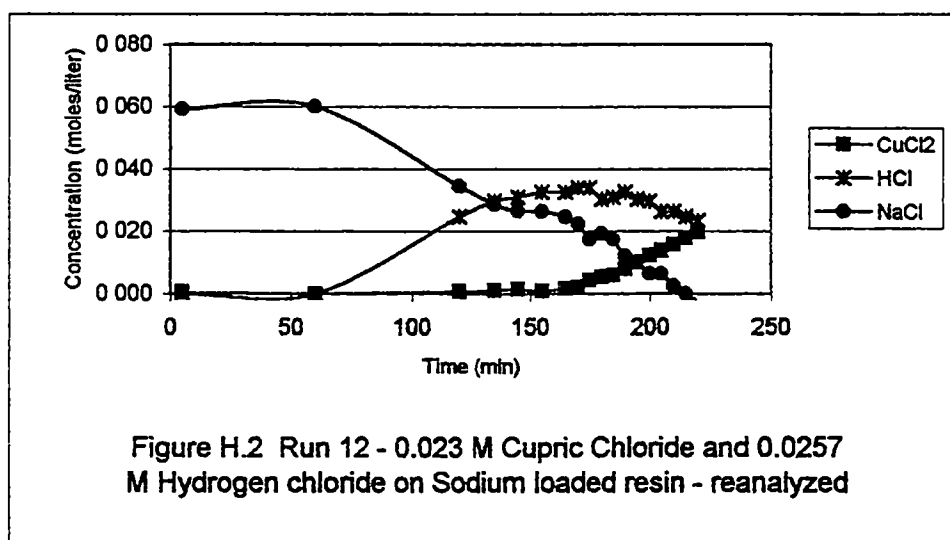
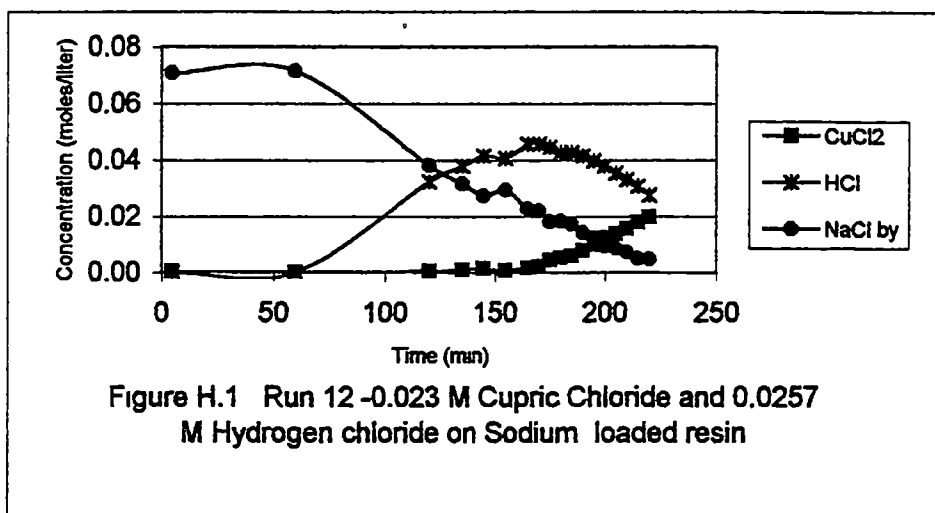
M <u>moles/liter</u>	<u>Wavelength</u>	
	<u>800</u>	<u>510</u>
0.005	0.0051	0.0322
0.010	0.0024	0.0499
0.020	0.0147	0.1163
0.030	0.0062	0.1486
0.040	0.0201	0.2108
0.050	0.0077	0.2498
0.075	0.0111	0.3678
0.100	0.0231	0.4966
0.125	0.0171	0.6335
0.150	0.0193	0.7219
0.175	0.0237	0.8462
0.200	0.0195	0.9614



APPENDIX H

Effect of pH on the Shape of the Breakthrough Curve

Problems with reproducibility with the pH measurements were encountered while analyzing the concentration of the samples that contain HCl. However, although the analyses differed, the shape of the breakthrough curve was not changes. This is shown by Figure H.1 and H.2, same run with 2 different pH measurements. The sodium concentration was determined by difference. The general shape of the breakthrough curve remained the same even though the pH measurement, therefore the sodium concentration did not agree. Analyzing the hydrogen concentration using a pH meter is not recommended unless reproducibility and precision can be obtained.



APPENDIX I**Experimental and Calculated Breakthrough Data**

Table I.1 Run 1 Experimental and Calculated Breakthrough data -
0.0472 M Cupric chloride on Sodium loaded resin (16.5 ml/min)

HTU = 5.58

Sample	time (min)	Absorbance (800 nm)	Concentration (moles/liter)	Z cm	NTU data	Calculated Data NTU	C (moles/l)
1	30	0.00981	0.0007	0.0472	27.5	8.8502	0
2	45	0.01315	0.0010	0.0472	22.1	2.4260	0.00236
3	60	0.00255	0.0002	0.0472	16.7	1.7062	0.00472
4	70	0.00745	0.0005	0.0472	13.1	1.2840	0.00708
5	80	0.01396	0.0010	0.0472	9.5	0.9829	0.00944
6	90	0.05214	0.0038	0.0472	5.9	0.7481	0.01180
7	95	0.08698	0.0064	0.0472	4.1	0.5549	0.01416
8	100	0.16077	0.0117	0.0472	2.3	0.3902	0.01652
9	105	0.28214	0.0206	0.0472	0.5	0.2460	0.01888
10	110	0.43242	0.0316	0.0472	-1.3	0.1171	0.02124
11	113	0.57829	0.0422	0.0472	-2.4	0.0000	0.02360
12	115	0.50377	0.0368	0.0472	-3.1	-0.1082	0.02596
13	120	0.59283	0.0433	0.0472	-4.9	-0.2097	0.02832
14	130	0.63181	0.0462	0.0472	-8.5	-0.3065	0.03068
15	140	0.64639	0.0472	0.0472	-12.1	-0.4006	0.03304
Qresin							
AO	2.06					-0.4945	0.03540
BO	0.0944 meq/ml					-0.5913	0.03776
Kab	0					-0.6968	0.04012
Vs	1.5					-0.8225	0.04248
	8.21 cm/min		(16.5 ml/min)			-1.0047	0.04484
						-2.1365	0.04720
Aoresin							
VI	2.06 meq/ml						
VI	0.360 cm/min						

HTU. -182

Sample	Time (min)	Absorbance 510 nm	CoCl ₂ (moles/liter)	Absorbance 800 nm	CuCl ₂ (moles/liter)	Z (cm)	NTU	----Calculated Data ----	
								NTU	C (moles/l)
1	30	0.11342	0.019	1.06235	0.077	15.71	-8.6306	-29.1389	0.000
2	33	0.14174	0.025	1.00692	0.073	13.49	-7.4122	-21.0219	0.0052
3	35	0.15569	0.028	0.9698	0.070	12.01	-6.5999	-15.843	0.010
4	40	0.19156	0.036	0.87711	0.064	8.32	-4.5692	-12.963	0.016
5	45	0.22639	0.043	0.77872	0.056	4.62	-2.5384	-9.9982	0.021
6	50	0.25914	0.050	0.68718	0.050	0.92	-0.5077	-7.9424	0.026
7	55	0.29488	0.058	0.61044	0.044	-2.77	1.5231	-6.184	0.031
8	60	0.32008	0.063	0.53634	0.038	-6.47	3.5638	-4.5173	0.036
9	65	0.33846	0.067	0.46007	0.033	-10.16	5.5845	-2.9787	0.042
10	70	0.36206	0.073	0.40346	0.029	-13.86	7.6153	-1.4793	0.047
11	75	0.37576	0.076	0.35048	0.025	-17.56	9.6460	0	0.052
12 feed		0.50739	0.104	0.02388	0.001			1.4894	0.057
Qreslin								3.0198	0.062
								4.6137	0.068
								6.3616	0.073
AO	2.06 meq/ml							8.2752	0.078
BO	0.208 meq/ml							10.4571	0.083
Kab	0.8733							13.0932	0.088
Vs	8.06 cm/min	(16.2 ml/min)						16.492	0.094
								23.0272	0.099
Acreslin	2.06 meq/ml							44.28986	0.104
VI	0.7392 cm/min								

[illegible]

1	10	0.35582	0.072	0.28229	0.020	0.0083	33.80247619	3.3192	5.2691	0.0048
2	15	0.38213	0.077	0.23882	0.017	0.0059	30.12028924	2.9576	3.097	0.0096
3	20	0.39484	0.080	0.2132	0.015	0.0051	26.43810229	2.5980	2.9832	0.0144
4	25	0.40225	0.082	0.19333	0.013	0.0050	22.75591534	2.2345	2.2963	0.0192
5	30	0.38773	0.079	0.16843	0.012	0.0097	19.0737284	1.8729	1.7935	0.024
6	35	0.35759	0.073	0.1474	0.010	0.0172	15.39154145	1.5113	1.3586	0.0288
7	40	0.33067	0.067	0.132	0.009	0.0238	11.7093545	1.1498	0.9759	0.0364
8	45	0.30275	0.062	0.12445	0.008	0.0289	8.027167549	0.7882	0.6286	0.0384
9	50	0.28055	0.057	0.11288	0.008	0.0352	4.3449806	0.4266	0.306	0.0432
10	55	0.23647	0.048	0.09331	0.006	0.0455	0.662793651	0.0651	0	0.048
11	60	0.18822	0.038	0.07089	0.005	0.0569	-3.0193933	-0.2965	-0.296	0.0528
12	65	0.16371	0.033	0.0652	0.004	0.0623	-6.70159025	-0.6580	-0.5878	0.0576
13	70	0.14304	0.029	0.05396	0.004	0.0672	-10.3837672	-1.0196	-0.8815	0.0624
14	75	0.11682	0.024	0.04657	0.003	0.0731	-14.0656541	-1.3812	-1.184	0.0672
15	80	0.10976	0.022	0.04549	0.003	0.0746	-17.7481411	-1.7427	-1.5047	0.072
16	85	0.08006	0.016	0.03239	0.002	0.0815	-21.430328	-2.1043	-1.858	0.0768
17	90	0.07188	0.015	0.03006	0.002	0.0833	-25.112515	-2.4659	-2.2879	0.0816
18	95	0.05948	0.012	0.02363	0.002	0.0863	-28.7947019	-2.8274	-2.7821	0.0864
19	100	0.05144	0.010	0.02147	0.001	0.0881	-32.4769889	-3.1890	-3.5858	0.0912
20	105	0.04402	0.009	0.01906	0.001	0.0897	-36.1590758	-3.5506	-9.8255	0.096
21	110	0.04361	0.009	0.02023	0.001	0.0897	-39.8412628	-3.9121		
22	115	0.0361	0.007	0.01978	0.001	0.0913	-43.5234497	-4.2737		
23	120	0.03922	0.007	0.01788	0.001	0.0920	-47.2056367	-4.6353		
24 feed		0.01758	0.004	0.01141	0.001	0.0956				

Variable	Value
Qresin	2.06 meq/ml
AO	0.208 meq/ml
BO	0 meq/ml
Kab	1.5
Vs	8.03 cm/min
Aoresin	2.06 meq/ml
Vf	0.7364 cm/min

VI 0 7364 cm/min

Table I.4 Run 4 Experimental and Calculated Breakthrough Data -
0.046 M Cupric chloride on Sodium loaded resin (15.87 ml/min)

		HTU		3.93			
Sample time (min)	Absorbance (800 nm)	Cu Conc. (moles/liter)	Z (cm)	NTU	-----Calculated Data----- NTU	C (moles/l)	
1	0	0.6328	0.046				
2	15	0.00722	0.001	7.74	8.8389	0	0
3	30	0.01047	0.001	6.47	2.4228	0.0023	0.0023
4	45	0.00063	0.000	5.20	1.7037	0.0046	0.0046
5	60	0.01088	0.001	3.93	1.2819	0.0069	0.0069
6	75	0.00301	0.000	2.66	0.9812	0.0092	0.0092
7	85	0.02211	0.002	1.81	0.7467	0.0115	0.0115
8	90	0.03671	0.003	1.39	0.5538	0.0138	0.0138
9	95	0.07555	0.006	0.96	0.3893	0.0161	0.0161
10	100	0.15463	0.011	0.54	0.2454	0.0184	0.0184
11	105	0.27943	0.020	0.12	0.1168	0.0207	0.0207
12	110	0.42834	0.031	-0.31	0.0000	0.023	0.023
13	115	0.5479	0.040	-0.73	-0.1079	0.0253	0.0253
14	120	0.61139	0.045	-1.16	-0.2090	0.0276	0.0276
15	125	0.62338	0.046	-1.58	-0.3054	0.0299	0.0299
16	130	0.62685	0.046	-2.00	-0.3990	0.0322	0.0322
17	135	0.6243	0.046	-2.43	-0.4823	0.0345	0.0345
18	140	0.63579	0.046	-2.85	-0.5684	0.0368	0.0368
Qresin		2.06 meq/ml			-0.6929	0.0391	0.0391
AO		0.092 meq/ml			-0.8173	0.0414	0.0414
BO		0 meq/ml			-0.9972	0.0437	0.0437
Kab		1.5			-2.1120	0.046	0.046
Vs		7.787 cm/min	(15.87 ml/min)				
Aoresin		2.06 meq/ml					
Vf		0.3329 cm/min					

Table 1.5 Run 5 Experimental and Calculated Breakthrough Data -
0.049 M Cobalt chloride on Copper loaded resin (15.97 ml/min)

Sample	Time (min)	Absorbance 510 nm	CoCl ₂ (moles/liter)	Absorbance 800 nm	CuCl ₂ (moles/liter)	Z (cm)	NTU	-----Calculated Data-----	
								NTU	C (moles/l)
1	0	0.24129	0.049	0.00591	0.000	31.8428703	-22.5836	-29.1389	0.0000
2	5	0.00706	-0.001	0.63531	0.046	22.8094319	-16.1769	-21.0219	0.0025
3	30	0.01256	0.000	0.60889	0.045	17.3893689	-12.3329	-15.8430	0.0049
4	45	0.03131	0.004	0.56827	0.041	11.9693058	-8.4887	-12.9630	0.0074
5	60	0.05927	0.010	0.50697	0.037	10.1626182	-7.20753	-9.9982	0.0088
6	65	0.06563	0.011	0.48041	0.035	8.35593049	-5.92619	-7.9424	0.0123
7	70	0.09093	0.017	0.46097	0.034	6.54924282	-4.64485	-6.1840	0.0147
8	75	0.09102	0.017	0.4249	0.031	4.74255514	-3.36351	-4.5173	0.0172
9	80	0.09857	0.019	0.40062	0.029	2.93586747	-2.08218	-2.9787	0.0196
10	85	0.10876	0.021	0.37241	0.027	1.1291798	-0.80084	-1.4793	0.0221
11	90	0.15695	0.031	0.37491	0.027	-0.6775079	0.4805	0.0000	0.0245
12	95	0.12752	0.025	0.32091	0.023	-2.4841956	1.76184	1.4894	0.0270
13	100	0.15297	0.030	0.31438	0.023	-4.2908832	3.04318	3.0198	0.0294
14	105	0.14452	0.028	0.27417	0.020	-6.0975709	4.32452	4.6137	0.0319
15	110	0.16507	0.033	0.26108	0.019	-8.0849273	5.73399	6.3616	0.0343
16	115.5	0.18523	0.037	0.23965	0.017	-9.7109462	6.8872	8.2752	0.0368
17	120	0.1824	0.036	0.22786	0.016	-11.517634	8.16853	10.4571	0.0392
18	125	0.1732	0.035	0.193	0.014	-13.324322	9.44987	13.0932	0.0417
19	130	0.18465	0.037	0.17719	0.013	-15.131009	10.7312	16.4920	0.0441
20	135	0.19809	0.040	0.17073	0.012	-16.937697	12.0126	23.0272	0.0466
21	140	0.19759	0.040	0.14706	0.010	-19.015388	13.4861	44.2888	0.0490
22	145.75	0.20157	0.041	0.13434	0.009	-20.720901	14.6957		
23	150.47	0.25024	0.051	0.15228	0.011	-22.36776	15.8566		
24	155	0.207024	0.042	0.1086	0.008	-24.164448	17.1379		
25	160	0.22371	0.045	0.10588	0.007	-27.777823	19.7006		
26	170	0.21609	0.044	0.08157	0.006	-31.391198	22.2633		
27	180	0.23103	0.047	0.06903	0.005	-31.752536	22.5195		
28	181	0.24347	0.050	0.00574	0.000				

HTU -1.41

Creslin

2.06 meq/ml
0.098 meq/ml

Kab

0.8733
7.96 cm/min (15.97 ml/min)

Aoreslin

2.06 meq/ml
0.3613 cm/min

Table I.6 Run 7 Experimental and Calculated Data -
0.098 M Cupric chloride on Sodium loaded resin (16.12 ml/min)

HTU: 6.86

Sample time (min)	Absorbance 510 nm	CuCl ₂ (moles/liter)	Absorbance 800 nm	CuCl ₂ (moles/liter)	Na by Diff (moles/liter)	Z (cm)	NTU	-----Calculated Data ----- NTU C (moles/l)
1	0	0.0074	0.00604	0.000	0.196			
2	0	0.02475	1.34135	0.008	0.005		4.894	9.355
3	5	0.01019	0.0042	0.000	0.195	33.575	2.355	2.606
4	30	0.00522	0.00674	0.000	0.197	16.153	1.339	1.816
5	40	0.01256	0.05824	0.004	0.187	9.185	0.831	1.375
6	45	0.0031	0.19576	0.014	0.172	5.700	0.323	1.058
7	50	0.00935	0.47397	0.005	0.131	2.216	-0.165	0.810
8	55	0.00951	0.77798	0.057	0.089	-1.268	-0.693	0.604
9	60	0.01822	1.06615	0.078	0.046	-4.753	-1.201	0.428
10	65	0.00851	1.214	0.089	0.029	-8.237	-1.709	0.271
11	70	0.00844	1.27924	0.093	0.020	-11.721	-2.217	0.130
12	75	0.00731	1.29306	0.094	0.019	-15.205	-2.724	0.044
13	80	0.01643	1.31442	0.096	0.012	-18.690	-3.232	0.054
14	85	0.04095	1.33535	0.098	-0.001	-22.174	-3.740	0.059
15	90	0.00723	1.31488	0.096	0.016	-25.658		0.0637
Qresln	2.06 meq/ml							-0.4674
A0	0.196 meq/ml							-0.7109
B0	0 meq/ml							-0.8538
Kab	1.5							-1.0321
Vs	8.021 cm/min	(16.12 ml/min)						-1.3032
Aoresln	2.06 meq/ml							-3.0863
VI	0.6989 cm/min							0.098

Table I.7 Run 8 Experimental and Calculated Data -
0.099 M Cobalt chloride on Copper loaded resin (8.5 ml/min)

HTU: -1.58

Sample time (min)	Absorbance 510 nm	CoCl ₂ (moles/liter)	Absorbance 800 nm	CuCl ₂ (moles/liter)	Na by Diff (moles/liter)	Z (cm)	NTU	Calculated Data NTU C (moles/l)
1 feed	0.48447	0.099	0.01088	0.000	0.002			
2 10	0.01729	-0.002	1.32445	0.097	0.011	31.114	-19.883	-28.1389 0.000
3 45	0.06187	0.008	1.16782	0.085	0.014	18.133	-11.477	-21.0219 0.005
4 55	0.10863	0.018	1.08194	0.079	0.007	14.424	-9.129	-15.8430 0.010
5 60	0.12151	0.021	1.02594	0.075	0.009	12.570	-7.855	-12.9530 0.015
6 65	0.13881	0.024	0.96359	0.070	0.011	10.715	-6.782	-9.9982 0.020
7 70	0.1604	0.029	0.90858	0.066	0.010	8.861	-5.608	-7.9424 0.025
8 80.333	0.20372	0.038	0.78772	0.057	0.009	5.028	-3.182	-6.1840 0.030
9 90	0.23943	0.046	0.6779	0.049	0.009	1.443	-0.913	-4.5173 0.035
10 100	0.28119	0.055	0.57988	0.042	0.006	-2.266	1.484	-2.9787 0.040
11 110	0.3158	0.063	0.48978	0.035	0.004	-5.975	3.782	-1.4793 0.045
12 120	0.3427	0.069	0.40808	0.029	0.005	-9.684	6.129	0.0000 0.050
13 130	0.36859	0.074	0.33676	0.024	0.004	-13.393	8.477	1.4894 0.054
14 140	0.39552	0.080	0.28107	0.020	0.001	-17.102	10.824	3.0198 0.059
15 150	0.41119	0.083	0.2289	0.016	0.001	-20.811	13.171	4.6137 0.064
16 185	0.45096	0.092	0.10902	0.007	0.001	-33.792	21.387	6.3616 0.069
Qresln	2.06 meq/ml							8.2752 0.07425
AO	0.198 meq/ml							13.0932 0.08415
BO	0 meq/ml							16.4920 0.0891
Kab	0.8733							23.0272 0.09405
Vs	4.2297 cm/min	(8.5 ml/min)						44.2888 0.099
Aoresln	2.06 meq/ml							
VI	0.3709 cm/min							

Table I.8 Run 10 Experimental and Calculated Breakthrough Data -
0.023 M Cupric chloride and 0.025 M Cobalt Chloride on Sodium loaded resin (16.32 ml/min)

Sample time (min)	Absorbance 510 nm	CoCl ₂ (moles/liter)	Absorbance 800 nm	CuCl ₂ (moles/liter)	Na by Diff (moles/liter)	Z (cm)	NTU	---Calculated Data---	
								NTU	C (moles/l)
1 feed	0.12621	0.025	0.32219	0.023	0.004				
2 10	0.00615	0.001	0.00092	0.000	0.097	16.436	4.175	8.657	0.000
3 60	0.00333	0.001	0.00275	0.000	0.098	7.569	1.922	2.371	0.001
4 75	0.01155	0.002	0.01158	0.001	0.094	4.908	1.247	1.663	0.002
5 90	0.02177	0.004	0.04604	0.003	0.085	2.247	0.571	1.248	0.003
6 95	0.08049	0.016	0.11903	0.009	0.051	1.361	0.346	0.953	0.005
7 100	0.05804	0.011	0.13333	0.010	0.058	0.474	0.120	0.724	0.006
8 105.33	0.07655	0.015	0.17989	0.013	0.044	-0.472	-0.120	0.535	0.007
9 110	0.09122	0.018	0.21767	0.0157	0.033	-1.300	-0.330	0.375	0.008
10 115	0.10336	0.020	0.25752	0.0186	0.023	-2.187	-0.556	0.236	0.009
11 120	0.18086	0.036	0.3233	0.023	-0.018	-3.074	-0.781	0.112	0.010
12 125	0.13989	0.027	0.31601	0.023	0.000	-3.961	-1.006	0.000	0.012
13 130	0.12859	0.025	0.31529	0.023	0.004	-4.848	-1.231	-0.103	0.013
14 140.33	0.12809	0.025	0.32072	0.023	0.003	-6.680	-1.697	-0.198	0.014
15 150	0.1243	0.024	0.31915	0.023	0.006	-8.365	-2.132	-0.287	0.015
								-0.373	0.016
								-0.4562	0.01725
								-0.5339	0.0184
								-0.6279	0.01955
								-0.7285	0.0207
								-0.8674	0.02185
								-1.6785	0.023
Qresin	2.06 meq/ml								
AO	0.046 meq/ml								
BO	0 meq/ml								
Kab	1.31								
Vs	8.121 cm/min								
		(16.32 ml/min)							
Aoresin	2.06 meq/ml								
VF	0.1774 cm/min								

HTU: 3.937

Sample time (min)	Absorbance (800 nm)	Cu Conc (moles/liter)	pH	HCl Conc (moles/l)	Na Conc (moles/l)	Z (cm)	NITU
							--Calculated Data-- NTU C (moles/l)

[illegible]

[illegible]

Table I.11 Run 15 Experimental and Calculated Breakthrough Data -
0.049 M Cupric chloride and 0.0661 M Hydrogen chloride on a Sodium loaded resin (8.52 ml/min)

HTU= 3.5316

Sample	Time (min)	Absorbance (800 nm)	Cu Conc (moles/liter)	pH	HCl Conc (moles/l)	Na Conc (moles/l)	Z (cm)	NTU	-Calculated Data- NTU C (moles/l)
1	0	0.00657	0.000	1.01	0.0977	0			20.2763 0.0012
2	0	0.67239	0.049	1.18	0.0661	0			9.6347 0.0024
3	5	0.0013	0.000	4.59	0.0000	0.159	35.22	9.97	6.0868 0.0037
4	60	0.0049	0.000	1.81	0.0155	0.143	23.83	6.75	4.3121 0.0049
5	91.2	0.00722	0.001	1.18	0.0661	0.092	17.36	4.92	3.2467 0.0061
6	106	0.00629	0.000	1.13	0.0741	0.084	14.30	4.05	2.6368 0.0074
7	120	0.00288	0.000	1.08	0.0832	0.075	11.39	3.23	1.6455 0.0098
8	135	0.01169	0.001	0.97	0.1072	0.050	8.29	2.35	1.3479 0.0110
9	145	0.02339	0.002	0.99	0.1023	0.063	6.22	1.76	1.1092 0.0122
10	155	0.07484	0.005	0.97	0.1072	0.041	4.14	1.17	0.9132 0.0135
11	165	0.18668	0.014	0.97	0.1072	0.025	2.07	0.59	0.7492 0.0147
12	175	0.33617	0.025	0.97	0.1072	0.003	0.00	0.00	0.4892 0.0159
13	185	0.489188	0.036	1.03	0.0933	-0.007	-2.07	-0.59	0.6096 0.0172
14	195	0.66113	0.048	1.09	0.0813	-0.019	-4.14	-1.17	0.2808 0.0196
15	210	0.67085	0.049	1.1	0.0794	-0.018	-7.25	-2.05	0.2075 0.0208
16	225.1	0.67358	0.049	0.98	0.1047	-0.044	-10.38	-2.94	0.1322 0.0220
17	227.1	0.67555	0.049	1.03	0.0933	-0.033	-10.79	-3.06	0.0635 0.0233
									0.0000 0.0245
									0.0593 0.0257
									-0.1152 0.027
									-0.1698 0.0282
									-0.2209 0.0294
									-0.2722 0.0306
									-0.3238 0.0319
									-0.4320 0.0343
									-0.4916 0.0355
									-0.5574 0.0368
									-0.6328 0.038
									-0.7212 0.0392
									-0.9700 0.0416
									-1.1615 0.0429
									-1.4437 0.0441
									-1.989 0.0453
									-2.8235 0.0466
									-5.5983 0.0478
									-26.037 0.049
Creslin	2.06 meq/ml								
AO	0.066 meq/ml								
BO	0.0661 meq/ml								
Kab	3.662								
Vs	4.24 cm/min								
			(16 ml/min)						
Aoresin	1.9076 meq/ml								
VI	0.2072 cm/min								

Table I 12 Run 17 Experimental and Calculated Breakthrough Data -
0.023 M Cupric chloride and 0.025 M Sodium chloride on a Hydrogen loaded resin (16.15 ml/min)

HTU = 5.9687

Sample time (min)	Absorbance (800 nm)	Cu Conc (moles/liter)	pH	HCl Conc (moles/l)	Na Conc (moles/l)	Z (cm)	Cu Conc (moles/liter)	NTU	---Calculated Data--- NTU C (moles/l)
1 feed	0.3091	0.023	4.7	0.0000	0.025	35.9	0.000	6.0	8.9
2 5	0.00058	0.000	1.22	0.0603	0	35.9	0.000	6.0	0.0000
3 20	0.00513	0.000	1.23	0.0589	0.011	33.1	0.000	5.5	2.4
4 45	0.00002	0.000	1.2	0.0631	0.008	28.4	0.000	4.8	1.7
5 75	0.0058	0.000	1.2	0.0631	0.007	22.8	0.000	3.8	1.3
6 90	0.00317	0.000	1.22	0.0603	0.010	20.0	0.000	3.3	1.0
7 100	0.00192	0.000	1.23	0.0589	0.012	18.1	0.000	3.0	0.7
8 110	0.00404	0.000	1.26	0.0550	0.015	16.2	0.000	2.7	0.6
9 120	0.00468	0.000	1.3	0.0501	0.020	14.3	0.000	2.4	0.4
10 130	0.00336	0.000	1.36	0.0417	0.029	12.5	0.000	2.1	0.2
11 140	0.00078	0.000	1.51	0.0309	0.040	10.6	0.000	1.8	0.1
12 150	0.00272	0.000	1.76	0.0174	0.053	8.7	0.000	1.5	0.0
13 160	0.00751	0.001	2.26	0.0055	0.064	6.8	0.001	1.1	-0.1
14 170	0.02834	0.002	2.93	0.0012	0.066	5.0	0.002	0.8	-0.2
15 180	0.06892	0.005	3.42	0.0004	0.061	3.1	0.005	0.5	-0.3
16 185	0.09528	0.007	3.56	0.0003	0.057	2.2	0.007	0.4	-0.4
17 190	0.12456	0.009	3.64	0.0002	0.053	1.2	0.009	0.2	-0.5
18 195	0.14883	0.01094	3.78	0.0002	0.049	0.3	0.011	0.0	-0.6
19 200	0.17407	0.01272	3.86	0.0001	0.045	-0.6	0.013	-0.1	-0.7
20 205	0.20369	0.015	3.78	0.0002	0.041	-1.6	0.015	-0.3	-0.8
21 210	0.21986	0.016	3.88	0.0001	0.039	-2.5154	0.0161	-0.4	-1.0
22 215	0.25052	0.01830	3.99	0.0001	0.034	-3.4519	0.01830	-0.6	-2.0
23 220	0.28505	0.02082	4.1	0.0001	0.029	-4.3884	0.02082	-0.7	
24 230	0.30183	0.022	4.1	0.0001	0.027	-6.2614	0.0220	-1.0	
25 240	0.30794	0.022	4.19	0.0001	0.026	-8.1	0.022	-1.4	
26 250	0.31001	0.023	4.16	0.0001	0.026	-10.0	0.023	-1.7	
27 260	0.30885	0.023	4.24	0.0001	0.026	-11.9	0.023	-2.0	
28 270	0.30904	0.023	4.26	0.0001	0.026	-13.8	0.023	-2.3	
Qresln AO BO	2.06 meq/ml 0.046 meq/ml 0.025 meq/ml	Kab Vs	1.5 8.037 cm/min (16.15 ml/min)	Aoresln Vf	1.928 meq/ml 0.187 cm/min				

[illegible][illegible]

Table I. 14 Run 21 Experimental and Calculated Breakthrough Data -
0.091 M Sodium chloride on Hydrogen loaded resin (15.57ml/min)

HTU= 1.51

Sample time (min)	H Concentration pH	Moles/liter	Na by Diff	Z (cm)	NTU	-Calculated Data- NTU C (moles/l)		
1	10	1.04	0.091	-0.0002	32.5642	21.57	11.87	0
2	30	1.04	0.091	-0.0002	25.8291	17.11	7.49	0.00455
3	40	1.04	0.091	-0.0002	22.4616	14.88	5.51	0.0091
4	45	1.04	0.091	-0.0002	20.7778	13.76	4.31	0.01365
5	50	1.04	0.091	-0.0002	19.094	12.65	3.38	0.0182
6	55	1.04	0.091	-0.0002	17.4102	11.53	2.64	0.02275
7	61.33	1.05	0.089	0.0019	15.2786	10.12	2.03	0.0273
8	65	1.06	0.087	0.0039	14.0427	9.30	1.46	0.03185
9	70	1.07	0.085	0.0059	12.3589	8.18	0.94	0.0364
10	80	1.09	0.081	0.0097	8.99136	5.95	0.46	0.04095
11	85	1.11	0.078	0.0134	7.30758	4.84	0.00	0.0455
12	90	1.14	0.072	0.0186	5.62381	3.72	-0.45	0.05005
13	95	1.18	0.066	0.0249	3.94003	2.61	-0.90	0.0546
14	100	1.23	0.059	0.0321	2.25626	1.49	-1.36	0.05915
15	105	1.31	0.049	0.0420	0.57248	0.38	-1.84	0.0637
16	110	1.41	0.039	0.0521	-1.11129	-0.74	-2.35	0.06825
17	115	1.55	0.028	0.0628	-2.79507	-1.85	-2.93	0.0728
18	124	2.01	0.010	0.0812	-5.82586	-3.86	-3.62	0.07735
19 feed		6.04	0.000	0.0910			-4.51	0.0819
							-5.86	0.08645
							-29.28	0.091
Qresin	2.06 meq/ml		Aoresin	2.06 meq/ml				
AO	0.091 meq/ml							
BO	0 meq/ml		VF	0.337 cm/min				
Kab	1.563							
Vs	7.96 cm/min	(15.57 ml/min)						
Aoresin	2.06 meq/ml							
VF	0.3368 cm/min							

Table I.15 Run 22 Experimental and Calculated Breakthrough Data -
0.05 M Hydrogen chloride on Sodium loaded resin (15.8 ml/min)

Sample	time (min)	H Concentration pH	Moles/liter	Na by Diff	Z (cm)	H Conc (moles/liter)	HTU =		-Calculated Data- NTU	C (moles/l)
							NTU	-4.65		
1	0	1.23	0.059	-0.004						
2	0	1.25	0.058	-0.001			-6.51695459		-29.4235	0
3	5	2.54	0.003	0.052	30.30	0.0029	-5.51557866		-5.8638	0.0025
4	30	3.59	0.000	0.050	25.65	0.0003	-4.2738725		-4.5131	0.005
5	61	6.34	0.000	0.050	19.87	0.0000	-3.71310197		-3.6178	0.0075
6	75	6.72	0.000	0.050	17.27	0.0000	-3.11227641		-2.9347	0.01
7	90	3.71	0.000	0.050	14.47	0.0002	-2.671671		-2.3558	0.0125
8	101	2.89	0.001	0.049	12.42	0.0013	-2.31117566		-1.8454	0.015
9	110	2.46	0.003	0.047	10.75	0.0035	-1.91062529		-1.3634	0.0175
10	120	2.15	0.007	0.043	8.89	0.0071	-1.51007491		-0.8033	0.02
11	130	1.95	0.011	0.039	7.02	0.0112	-0.86919431		-0.4521	0.0225
12	146	1.75	0.018	0.032	4.04	0.0178	-0.30842379		0	0.025
13	160	1.64	0.023	0.027	1.43	0.0229	0.773062223		0.4621	0.0275
14	187	1.52	0.030	0.020	-3.59	0.0302	0.97333741		0.9441	0.03
15	192	1.51	0.031	0.019	-4.53	0.0309	1.173612597		1.4579	0.0325
16	197	1.51	0.031	0.019	-5.46	0.0309	1.574162972		2.0298	0.035
17	207	1.49	0.032	0.018	-7.32	0.0324	1.974713947		2.6456	0.0375
18	217	1.46	0.035	0.015	-9.18	0.0347	2.375263721		3.3836	0.04
19	227	1.44	0.036	0.014	-11.04	0.0363	2.775814096		4.3127	0.0425
20	237	1.44	0.036	0.014	-12.91	0.0363	3.17636447		5.5115	0.045
21	247	1.42	0.038	0.012	-14.77	0.0380			7.4996	0.0475
22 feed		1.3	0.050	0.000					11.8942	0.05
Qiresln										
AO			2.06 meq/ml							
BO			0.05 meq/ml							
Kab			0 meq/ml							
Vs			0.64							
Aoresln										
			7.86 cm/min							
			2.06 meq/ml							
VF										
			0.18626 cm/min							

(15.8 ml/min)

Sample	time (min)	Absorbance (600 nm)	Cu Conc (moles/liter)	pH	HCl Conc (moles/l)	Z (cm)	NTU	C (moles/l)	-Calculated Data-- NTU	C (moles/l)
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Qresln	2.06 meq/ml	Acresln	1.974257631 meq/ml
AO	0.0462 meq/ml		
BO	0.0251 meq/ml	Vf	0.190831992 cm/mln
Kab	3.662		
	8.35 cm/mln		
	/s		(16.78 ml/mln)

Table I 17 Run 25 Experimental and Calculated Breakthrough Data -
0.072 M Sodium Chloride on Hydrogen loaded resin (8.47 ml/min)

HTU= 0.825

Sample	time (min)	H Concentration pH	Moles/liter	Na by Diff	Z (cm)	NTU	--Calculated Data-- NTU	C (moles/l)
1	0	5.27	0.000	0.072			11.894	0.000
2	5	1.14	0.072	0.000	28.661	34.744	7.500	0.004
3	60	1.15	0.071	0.001	20.828	25.249	5.512	0.007
4	80	1.14	0.072	0.000	16.555	20.070	4.313	0.011
5	105	1.14	0.072	0.000	14.419	17.480	3.384	0.014
6	120	1.14	0.072	0.000	12.283	14.890	2.646	0.018
7	135	1.14	0.072	0.000	10.147	12.301	2.090	0.022
8	150	1.14	0.072	0.000	8.011	9.711	1.458	0.025
9	165	1.17	0.068	0.004	5.827	7.064	0.944	0.029
10	180	1.22	0.060	0.012	3.736	4.532	0.462	0.032
11	195	1.32	0.046	0.024	1.602	1.942	0.000	0.036
12	210	1.49	0.032	0.040	-0.534	-0.647	-0.452	0.040
13	225	1.93	0.012	0.060	-2.670	-3.237	-0.903	0.043
14	234.5	2.4	0.004	0.068	-4.023	-4.877	-1.363	0.047
Qresin	2.06 meq/ml							
AO	0.072 meq/ml						-1.845	0.050
BO	0 meq/ml						-2.356	0.054
Kab	1.5625						-3.618	0.061
Vs	4.217 cm/min	(8.47 ml/min)					-4.5131	0.0648
							-5.8638	0.0684
Acresin	2.06 meq/ml						-29.4235	0.072
VI	0.14241 cm/min							

Table I.18 Run 26 Experimental and Calculated Breakthrough Data -
0.03 / M Cupric chloride and 0.0155 M Hydrogen chloride on a Sodium loaded resin (8.4 / ml/min)

HTU= 5.4395											
Sample	time (min)	Absorbance (800 nm)	Cu Conc (moles/liter)	pH	HCl Conc (moles/l)	Na Conc (moles/l)	Z (cm)	NTU	-Calculated Data- NTU	C (moles/l)	
1	0	0.50502	0.037	1.78	0.0166	0			18.898	0.0009	
2	0	0.50525	0.037	1.81	0.0155	0			8.985	0.0019	
3	5	0.00412	0.000	2.64	0.0023	0.087	35.058	6.445	5.872	0.0028	
4	30	0.00427	0.000	3.82	0.0002	0.089	31.331	5.760	4.153	0.0037	
5	70	0.00391	0.000	5.12	0.0000	0.089	25.368	4.664	3.121	0.0046	
6	90	0.00443	0.000	5.21	0.0000	0.089	22.386	4.115	2.433	0.0056	
7	120	0.00014	0.000	2.82	0.0015	0.088	17.914	3.293	1.941	0.0065	
8	152	0.00545	0.000	1.82	0.0151	0.074	13.143	2.416	1.572	0.0074	
9	180	0.00233	0.000	1.59	0.0267	0.063	8.989	1.649	1.285	0.0083	
10	195	0.00815	0.001	1.57	0.0269	0.061	6.733	1.238	1.065	0.0093	
11	210	0.05365	0.004	1.58	0.0263	0.055	4.486	0.827	0.708	0.0111	
12	220	0.11217	0.008	1.6	0.0251	0.048	3.005	0.553	0.574	0.0120	
13	230 16	0.18713	0.014	1.62	0.0240	0.038	1.481	0.274	0.459	0.0130	
14	240 16	0.25299	0.018	1.64	0.0229	0.030	0.000	0.000	0.359	0.0139	
15	250 25	0.32484	0.024	1.66	0.0219	0.020	-1.504	-0.277	0.271	0.0148	
16	260	0.39478	0.029	1.72	0.0191	0.013	-2.958	-0.544	0.122	0.0167	
17	270	0.47101	0.034	1.79	0.0162	0.004	-4.449	-0.818	0.068	0.0176	
18	285 25	0.50325	0.037	1.81	0.0155	0.000	-6.722	-1.236	0.000	0.0185	
19	301 5	0.50999	0.037	1.81	0.0155	0.000	-9.145	-1.681	-0.054	0.0194	
20	320 25	0.50873	0.037	1.82	0.0151	0.000	-11.940	-2.195	-0.1039	0.0204	
21	341.75	0.50577	0.037	1.82	0.0151	0.000	-15.145	-2.784	-0.1511	0.0213	
22	360	0.50623	0.037	1.8	0.0158	0.000	-17.866	-3.284	-0.1962	0.0222	
23	380	0.50392	0.037	1.81	0.0155	0.000	-20.848	-3.833	-0.2397	0.0231	
Qresin	2.06 meq/ml								-0.2824	0.0241	
AO	0.074 meq/ml								-0.3253	0.0250	
BO	0.0155 meq/ml								-0.3691	0.0259	
Kalb	3.662								-0.4151	0.0268	
Ve	4.214 cm/min								-0.4949	0.0278	
									-0.5851	0.0296	
Aoresin	2.01771 meq/ml								-0.6636	0.0305	
Vf	0.14908 cm/min								-0.7638	0.0315	
									-0.9007	0.0324	
									-1.6512	0.0342	
									-2.6466	0.0352	
									-4.8478	0.0361	

APPENDIX J

Experimental Molar Selectivity

The molar selectivity for Cu, Co, and H exchanging with Na on the DOWEX HCR-2 resin (Na form) was determined experimentally and compared with the manufacturer and literature value. The experimental molar selectivity was determined by equilibrating a known volume of solution with a known amount of resin. Once the resin and solution was in equilibrium, the concentration of the ions in solution was measured and the concentration of the ions on the resin were calculated using the following equations:

$$\bar{A} = \frac{(A_0 - A_f)V_s \rho_{resm}}{M_{resm}} \quad J.1$$

$$\bar{B} = \bar{Q} - \bar{A} \quad J.2$$

V_s and M_{resm} are volume of the solution and mass of resin, respectively. The resin density of 0.838 gm/ml as determined from the volume of 65 g of resin used in the ion exchange column and a resin capacity of 2.06 meq/ml (See Appendix K) were used. In equation J.1 and J.2, $\bar{A}$ is the concentration of the ion that is exchanging with the ion on the resin, $\bar{B}$, A_0 is the initial concentration of ion A, and A_f is the concentration of ion A in equilibrium with the resin. The molar selectivity, K_{AB} , is then calculated using

$$K_{AB} = \frac{\bar{A}/A}{(\bar{B}/B)^n} \quad J.3$$

n is the ratio of the valence of ion A divided by the valence of ion B.

The literature values were determined from the relative molar selectivity of the individual ion as proposed by Anderson [2]

$$K_{AB} = K_A/K_B \quad \text{J.4}$$

K_A and K_B are the relative molar selectivity of ions A and B, respectively. Relative molar selectivity for several divalent and univalent cations for a DOWEX50 ion exchange resin with 4, 8 and 16% cross linkage was determined experimentally by Bonner [20,21].

Values for several divalent and univalent cations are provided in Table J.1. Selectivity coefficients for various anions and cations on DOW [22] anion and cation exchange resin of different cross linkage are provided in Table J 2. The method of Anderson (Equation J.4) was also used to determine the binary molar selectivity from the DOW data

Table J.1. Relative Molar Selectivity Coefficients for Univalent and Divalent Cations on DOWEX 50

	4% DVB	8% DVB	16% DVB
Univalent Ions			
Li	1.0	1.0	1.0
H	1.32	1.27	1.47
Na	1.58	1.98	2.37
NH ₄	1.90	2.55	3.34
Ag	4.73	8.51	22.9
Divalent Ions			
UO ₂	2.36	2.45	3.34
Mg	2.95	3.29	3.51
Co	3.23	3.74	3.81
Cu	3.29	3.85	4.46
Ca	4.15	5.16	7.27
Ba	7.47	11.5	20.8

The calculated molar selectivity coefficients along with the manufacturer and literature values are given in Table J.3. Two measurements were performed at two different

Table J 2 DOW Ion Exchange Resin



DOWEX Ion Exchange Resins

Using Ion Exchange Resin Selectivity Coefficients

Ion exchange resins, when placed in a solution, reach an equilibrium state between ions in solution and ions on the resin. From this equilibrium state, selectivity coefficients (equilibrium constants) can be derived based on the ratio of ions in solution vs. ions on the resin.

Effectively, these selectivity coefficients are a measurement of a resin's preference for an ion. The greater the selectivity coefficient, the greater the preference for the ion. For example, a strong acid cation resin with 8% crosslink has a selectivity coefficient for sodium vs. hydrogen of 1.58, while the selectivity coefficient for calcium vs. hydrogen is 2.28. As a result, calcium is selectively removed by the ion exchange over the sodium.

In column operation, undesirable ions can be selectively removed by regenerating the resin with any ion of lower selectivity. For example, calcium can be removed from solution by a strong acid cation resin when the resin is regenerated by salt (Na-cycle operation) or by acid (H-cycle operation).

Selectivity coefficients can also be used to determine the order of elution in column operation. In a demineralizer (H-cycle operation), sodium with a selectivity coefficient of 1.58 will elute before ammonium with a selectivity of 2.51, which is followed by potassium with a selectivity of 2.28.

Ionic leakage from demineralizers can also be predicted by the use of selectivity coefficients. With a knowledge of the degree of regeneration, solution pH, and the selectivity coefficient, an estimate of leakage can be calculated.

For a complete treatment of the subject, numerous textbooks can be consulted. One excellent reference is *Ion Exchange*, by Friedrich Helfferich, currently published by Dover Press under ISBN #61-15453.

Selectivity Coefficients of Various Anions (Compared with the Hydroxyl Ion) on Functionalized Styrene-Divinylbenzene Anion Exchange Resins of Different Base Strength

Anion	Selectivity Coefficient	Selectivity Coefficient
OH ⁻	1.0	1.0
Benzene sulfonate	600	76
Bicarbonate	460	86
Citrate	220	22
I ⁻	175	17
Phenolate	110	27
HSO ₄ ⁻	65	15
CO ₃ ²⁻	74	12
NO ₃ ⁻	65	6
Br ⁻	60	6
CN ⁻	26	3
HSO ₃ ⁻	27	3
BrO ₃ ⁻	27	3
NO ₂ ⁻	24	3
Cl ⁻	22	2.3
HCO ₃ ⁻	8.0	1.2
IO ₃ ⁻	5.5	0.5
Formate	4.6	0.6
Acetate	3.2	0.6
Propionate	2.6	0.3
F ⁻	1.6	0.3
HSiO ₃ ⁻	<1.0	<1.0

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DOWEX Ion Exchange Resins

For more information about DOWEX resins,

call Dow Liquid Separations Business:

North America 1-800-447-4369

Latin America (+55) 11-5189-9345

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Japan (+81) 3-5480-2100

Australia (+61) 2-9776-3225

<http://www.dow.com/liquiseps>

Selectivity Coefficients of Various Cations (Compared with the Hydrogen Ion) on
Sulfonated Polystyrene Cation Exchange Resins of Different Crosslinkage

Cation	Degree of Crosslinkage			
	1% DVB	5% DVB	10% DVB	16% DVB
Li^+	0.76	0.79	0.77	0.68
H^+	1.00	1.00	1.00	1.00
Na^+	1.20	1.56	1.61	1.62
NH_4^+	1.44	2.01	2.15	2.27
K^+	1.72	2.28	2.54	3.06
Rb^+	1.86	2.49	2.69	3.14
Cs^+	2.02	2.56	2.77	3.17
Ag^+	3.58	6.70	8.15	15.6
Th^+	5.03	9.76	12.8	19.4
UO_2^{2+}	1.79	1.93	2.00	2.27
Mg^{2+}	2.23	2.59	2.62	2.39
Zn^{2+}	2.37	2.73	2.77	2.57
Co^{2+}	2.45	2.84	2.92	2.59
Cu^{2+}	2.49	2.03	3.15	3.03
Cd^{2+}	2.55	3.06	3.23	3.37
Ni^{2+}	2.81	3.09	3.08	2.76
Ca^{2+}	3.14	4.06	4.42	4.95
Sr^{2+}	3.56	5.13	5.85	6.87
Pb^{2+}	4.97	7.80	8.92	12.2
Ba^{2+}	5.66	9.86	9.42	14.2

Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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DOW

Table J 3 Molar Selectivity - Experimental and Literature Values

Sample	Comp	Mass (gms)	Valence Component	(moles/liter)	Solution (A) Volume(ml)	Valence Absorbance (moles/liter)	Conc A (moles/liter)	Conc B (moles/liter)	A (meq/ml)	B (meq/ml)	A resin (meq/ml)	B resin (meq/ml)	Kab calculated	Kab by DOW	Kab by Bonner
Run 1 - Jan 13															
1	Na	10	1	CaCl ₂	0.1	100	2	0.27655	0.020	0.159	0.041	0.159	1.335	0.725	1.58
2	Na	10	1	CaCl ₂	0.2	50	2	0.72630	0.053	0.284	0.106	0.284	1.231	0.828	1.46
3	Na	10	1	CaCl ₂	0.1	100	2	0.08940	0.020	0.159	0.041	0.159	1.334	0.726	1.58
4	Na	10	1	CaCl ₂	0.2	50	2	0.28326	0.054	0.282	0.106	0.282	1.224	0.839	1.36
Run 2 - Feb 25															
(resample on Feb 17)															
1	Na	10	1	CaCl ₂	0.1	100	2	0.27380	0.020	0.160	0.040	0.160	1.341	0.719	1.66
2	Na	10	1	CaCl ₂	0.2	50	2	0.75461	0.055	0.280	0.110	0.280	1.214	0.846	1.28
3	Na	10	1	CaCl ₂	0.1	100	2	0.11385	0.023	0.153	0.047	0.153	1.285	0.775	1.08
4	Na	10	1	CaCl ₂	0.2	50	2	0.27505	0.056	0.287	0.113	0.287	1.203	0.857	1.20
Run 2 - Feb 25															
1	Na	10	1	CaCl ₂	0.05	300	2	0.20287	0.015	0.070	0.030	0.070	1.769	0.291	3.49
2	Na	10	1	CaCl ₂	0.1	300	2	0.65789	0.063	0.075	0.125	0.075	1.877	0.183	2.50
3	Na	10	1	HCl	0.05	300	1	---	0.01688	0.033	0.017	0.033	0.830	1.230	1.31
4	Na	10	1	HCl	0.1	300	1	---	0.04570	0.054	0.046	0.054	1.395	0.695	2.33
(resample on Feb 29)															
1	Na	10	1	CaCl ₂	0.05	300	2	0.19403	0.014	0.072	0.028	0.072	1.801	0.259	4.88
2	Na	10	1	CaCl ₂	0.1	300	2	0.84872	0.062	0.076	0.124	0.076	1.811	0.149	4.00
3	Na	10	1	HCl	0.05	300	1	---	0.01620	0.032	0.016	0.032	0.800	1.280	1.11
4	Na	10	1	HCl	0.1	300	1	---	0.03546	0.065	0.035	0.065	1.622	0.438	6.73
Resin Capacity Q -															
Resin Density -															
2.06 meq/ml															
0.836 g/ml															

Experimental Data

Literature

solution concentrations for copper exchanging with a sodium loaded resin, and only 1 measurement for cobalt and hydrogen exchanging with a sodium loaded resin. However, for all 3 systems, the solutions were analyzed twice to ascertain the solution and resin had equilibrated. The concentrations of copper and cobalt were determined by spectrophotometer analyses. The hydrogen concentration was calculated from the pH of the solution and the sodium concentration was determined by difference. For hydrogen exchanging with sodium, the calculated molar selectivity ranged from 1.11 to 6.73. However, sodium has a higher selectivity than hydrogen therefore the molar selectivity as reported should be less than 1. This is also confirmed by the sharp front observed when sodium replaced hydrogen and the dispersed front when hydrogen displaced sodium. Indications are that the hydrogen analyses are inaccurate; therefore the literature value of 0.64 was used for the molar selectivity of H exchanging with Na. The molar selectivity determined for Cu exchanging with Na and Co exchanging with Na ranged from 1.29 to 4.88 and 1.08 to 2.33, respectively. As indicated by the data from Run 2, Cu exchanging with Na, a small change in Cu concentration (0.001 moles/liter) results in approximately 40% difference in molar selectivity. As a result of the sensitivity of the molar selectivity to the concentration, it was decided not to use the data from Run 2 for Cu-Na. Based on Run 1 only, the molar selectivity between Cu-Na and Co-Na, averaged 1.50 and 1.31, respectively. These values are somewhat lower than the data reported by Bonner and higher for the Cu^{++} and lower for the Co^{++} in comparison to the data reported by DOW. The measured values along with Bonner indicate that Cu^{++} has a higher selectivity than Co^{++} . According to the DOW literature, Co^{++} selectivity is greater than Cu^{++} . The

experimental runs also confirm that Cu^{++} has a higher selectivity than Co^{++} as given by Bonner . Both DOW and Bonner give similar molar selectivity for H exchanging with Na The molar selectivity used in the calculations for the Cu-Na, Co-Na, H-Na, Co-Cu and Cu-H systems are summarized in Table J.4

Table J.4. Molar Selectivity used to calculate the NTU
For comparison to the experimental system

A-B - Component A exchanging with B on the resin	K_{AB}
Cu-Na	1.5
Co-Na	1.31
H-Na	.64

The K_{AB} for Cu^{++} exchanging with H^+ and Co^{++} exchanging with Cu^{++} were calculated from the other data $K_{\text{Cu}^{++}-\text{H}^+}$ and $K_{\text{Co}^{++}-\text{Cu}^{++}}$ are 3.662 and 0.8733, respectively.

APPENDIX K

Determination of Resin Capacity from Experimental Data

Efforts to determine the resin capacity ($\bar{Q}$) by measuring directly from the resin were unsuccessful. Direct measurements were performed by equilibrating a known volume and concentration of CuCl_2 with a known weight of resin. Once the resin and solution equilibrated, the resin was eluted with concentrated NaCl and the solution loaded with the Cu analyzed for copper. Two separate measurements were performed and are outlined below.

1. Resin Capacity determination - Measurement 1. A weight of 5.21 g of DDOWEX HCR-W2 (Na form) resin was placed in a 500-ml volumetric flask
2. To the flask, 300 ml of 0.05 M CuCl_2 was added to the flask, the flask was then sealed, and shaken for 1 hour using a shaker. The CuCl_2 solution was then decanted. This was repeated for a total of 4 times with the exception that the 3rd batch was shaken overnight instead of 1 hour. This was done to make sure that the resin and the 0.05 M CuCl_2 had reached equilibrium.
3. The residual CuCl_2 solution was then removed by washing the resin with 3-100 ml batches of deionized water once the last batch of CuCl_2 was decanted
4. Finally, 300 ml of 2 M NaCl was added to the resin, the resin and solution were shaken for 1 hr and then the solution analyzed for Cu concentration using spectrophotometer analyses

Resin Capacity Determination – Measurement 2:

1. The above procedure was repeated except that 5.08 g of resin and 300 ml of 0.1 M CuCl_2 was used
2. The sodium content of each batch of CuCl_2 solution that had equilibrated with the resin was also determined using a Na specific ion electrode in an effort to verify the resin capacity. A Ross sodium electrode by ORION (Model 86-11) was used to measure the sodium content of the solutions along with a mV output meter. Calibration data for the Na electrode is shown in Figure K.1. The mV reading of each batch of CuCl_2 that had equilibrated with the resin along with the calculated Na concentration (based on the calibration data from Figure K.1) is presented Table K.1

Table K.1. Sodium Concentration of CuCl_2 solution equilibrated with the ion exchange resin

Batch	MV	Sodium Concentration (moles/liter)
1	-4.9	0.0570
2	-54.6	0.0093
3	-105.9	0.0014
4	-149.4	0.0013

The resin capacity was calculated from the following

$$\bar{Q} = \frac{Cu(eq/l) * NaCl(l) * \rho_{resin}(g/ml)}{M_{resin}(grams)}$$

K.1

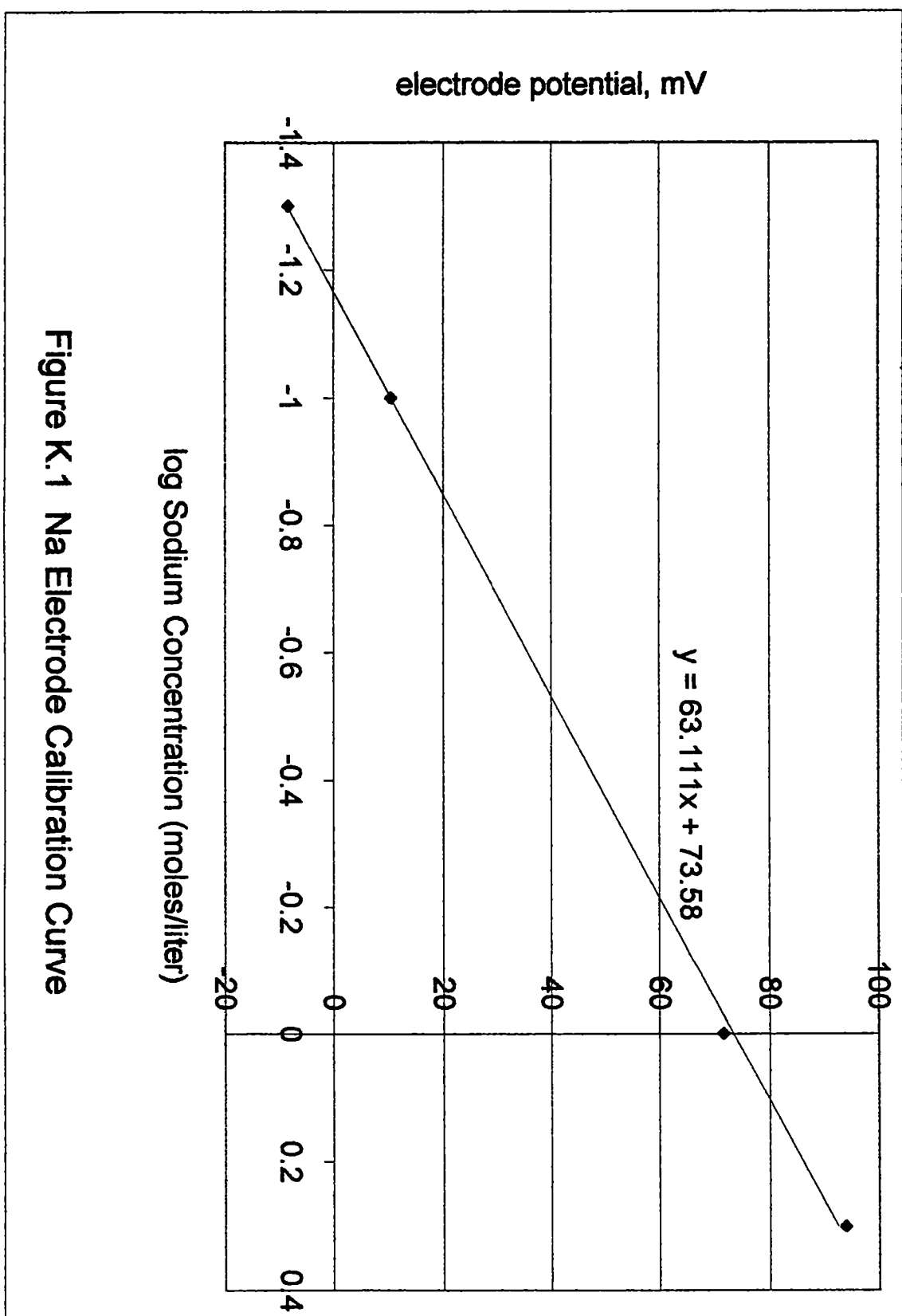


Figure K.1 Na Electrode Calibration Curve

The Cu content of the NaCl solutions in Runs 1 and 2 were determined to be 0.0415 and 0.0413 moles/liter, respectively (as analyzed by spectrophotometer). This corresponds to a resin capacity of 3.8 and 3.9 meq/ml as determined from equation 1. The density of the resin used in the calculation was determined from measuring the volume of a known weight of resin in water using a graduated cylinder. The volume of 4- grams of resin (as received) was 5-ml corresponding to a density of 0.8 g/ml. Based on the sodium concentration of measurement 2, the resin capacity should be approximately 3.26 meq/ml. These measured capacities are high in comparison to the manufacturer value of 2 meq/ml (min) and other resin capacity data observed in the literature. No obvious explanation can be given for why the resin capacity calculated by the above method is high in comparison to the manufacturer data.

The resin capacity was also calculated from the experimental data using the 50% breakthrough point. The approach assumes that the front is symmetrical. The resin capacity is then based on the time it takes the outlet solution concentration to reach 50% of the initial solution concentration (50% of breakthrough). The volume of the resin loaded in the column was 77.5 cm³. The resin capacity calculated from the experimental data for binary ion exchange only is given in Table K.2. Based on the experimental data, the capacity of the DOW HCR-W2 resin averages 2.06 meq/ml. This value corresponds to the 2 meq/ml (min) as reported by DOW. Therefore, the 2.06 meq/ml was used in the calculations of the NTU for both the experimental study and the predictions based on a

constant pattern front. Run 14 had a very low value for the resin capacity in comparison to the other runs; therefore, it was not used in average the value.

Table K.2 Resin Capacity ($\bar{Q}$) based on 50% Breakthrough from the Experimental Runs

Run	Solution	Concentration (moles/liter)	Resin Form	Flow rate (ml/min)	Time to reach 50% breakthrough (min)	Resin Capacity ^a (meq/ml)
1	CuCl ₂	0.048	Na	16.5	106.5	2.12
2	CoCl ₂	0.050	Cu	16.2	50.0	2.09
3	CaCl ₂	0.092 0.095	Co	16.2	51.0 55.0	1.95 2.15
4	CuCl ₂	0.046 0.050	Na	15.9	106.3 107.3	2.01 2.19
5	CuCl ₂	0.050	Cu	16.0	95.0	1.95
7	CuCl ₂	0.098	Na	16.1	53.2	2.16
8	CoCl ₂	0.099 0.098	Cu	8.5	94.4	2.05 1.92
14	NaCl	0.047 0.088	H	16.2	111.9	1.09 1.40
21	NaCl	0.091	H	16.0	106.8	2.01
22	HCl	0.058	Na	15.8	182.2	2.15
25	NaCl	0.091	H	8.5	197.3	1.97
Average Resin Capacity						2.06 ^a

^a Average of all runs except Run 14

VITA

Lilla Cunningham (Penny) was born in Englewood, New Jersey on March 29, 1960. She attended schools in the public system of Englewood, NJ where she graduated from Dwight Morrow High School in June 1977. She attended Stevens Institute of Technology in Hoboken, NJ from September 1977 to May 1981 where she received a Bachelor of Engineering in Chemical Engineering. In June 1981, she was employed by the DOE under subcontract by Union Carbide at the Oak Ridge National Laboratory. She transferred to the Development Division, Y-12 Plant (currently operated by Lockheed Martin Energy Systems) in March 1982 where she is still employed. In August of 1998, she received a technical fellowship award from Lockheed Martin Energy Systems. The award gave her the opportunity to attend the University of Tennessee, Knoxville full time to pursue a Master of Science in Chemical Engineering while maintaining her employment status and benefits. Upon completion of her degree, she will return to Lockheed Martin Energy Systems, Y-12 Plant, Development Division.