TREATMENT OF PLATING PLANT WASH WATERS BY ION EXCHANGE

BY

TREVOR BADEN SYDNEY GIDDEY

The University of Cape Town

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ABSTRACT

The treatment by ion exchange of the wash waters from a mixed electroplating operation has been investigated. The loading characteristics of a strong acid resin has been studied experimentally and by mathematical simulation.

The ability to separate the loaded metals by complexation techniques during elution has been demonstrated. Good agreement between predicted and actual elution conditions for the particular separations have been achieved.

The loading of free and metal-complexed cyanide and chromate on a strong base resin has been shown to be effective under certain resin conditions.

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CHAPTER 1

INTRODUCTION

1.1 NATURE OF THE PROBLEM

The electroplating industry consumes and discharges a considerable volume of water into drains and sewers every year. This effluent discharge contains a high proportion of toxic materials which have a deleterious effect on marine, plant and microbial growth [1]. The toxicity of the discharged effluent is due to the concentration of heavy metals present in the waste waters, the metals all originating in the respective plating operations or cleaning treatments prior to a plating operation.

The standard layout of a plating plant would consist of a series of tanks, each of which contains the solutions necessary for the plating operation. An article to be plated, would first be washed and then immersed in the plating solution. After completion of plating, the article is rinsed in either one or a series of wash water tanks. The latter are either continuously or intermittently discharged, this being the major source of the effluent emanating from the plating works.

The toxicity of the metals and cyanide in the waste has led to Municipalities and Water Authorities imposing restrictions on the quality of the water that may be discharged from plating operations (Table 1.1).

The average effluent quality arising from the rinse operations (Table 1.2) does not comply to the standards imposed for Cape Town municipal sewer discharge, and is considerably higher than drinking water standards, the ultimate aim of any form of pollution treatment.

TABLE 1.1

WATER AUTHORITY STANDARDS

Toxic Material	mg/ℓ[1]	mg/ℓ[2]	mg/ℓ[3]	mg/ℓ[4]
Cu	1,0	1,0	1,0	50
Ni	-	-	2,0	50
Zn	5,0	5,0	5,0	50
Cr	0,5	0,05	1,0	50
Cd	-	0,05	0,01	50
Fe	-	0,3	0,3	-
CN^-	0,5	0,01	0,01	20
pH	5,5-9,5	6,0-9,0	-	5,5-12,0

[1] - S.A. General Standards for discharge to streams

[2] - S.A. Drinking Water Standards

[3] - U.S. Drinking Water Standards

[4] - Cape Town Municipal Effluent Regulations.

TABLE 1.2

PLATING WASH WATER QUALITY

Toxic Material	mg/ℓ[1]	mg/ℓ[2]
Cu	130	52
Ni	80	120
Zn	90	68
Cr	30	322
Fe	-	40
CN^-	180	23
pH	2,3	2,4

(1,2) - Samples obtained from local plating operations.

1.2 PRESENT TREATMENT METHODS

The methods used for the treatment of the wash waters emanating from plating operations are considerable and varied. Where the concentration of the heavy metals is not too low, chemical precipitation followed by filtration has up to now been the standard treatment procedure. The waste in question is generally neutralised with a readily available alkali (generally lime) to a certain pH, at which the insoluble metal hydroxides are precipitated. Kantawala and Tomlinson [2] have demonstrated the effectiveness of this technique in the treatment of a nickel-zinc waste water.

When dilute solutions require treatment, some form of concentrating step is required. The method outlined by Ceresa and Lancy [3] for water contaminated with only a single metal is evaporation. This treatment allows reuse of the condensate and the return of the concentrated solution to the plating tank.

The other techniques utilised for dilute wastes involve firstly a concentrating step and secondly a chemical treatment or recovery step. The concentrating step varies widely and can be distillation [4], ion exchange [5], electrodialysis, or reverse osmosis.

When chromate and cyanide are present in the waste solution, the concentrating step is generally followed by a chemical oxidation. The oxidation of cyanide is achieved by the addition of either chlorine or ozone, with consequent cyanide breakdown. The chromate is reduced by a bisulphite treatment to the trivalent state which precipitates as the hydroxide under high pH conditions.

Treatment methods which are still in the developmental stage as regards plating wash waters are liquid-liquid extraction and freezing [6]. The former aims at selective metal extraction which can then be recovered for reuse.

1.3 NECESSITY FOR METAL SEPARATION IN WASTE WATER TREATMENT

The reasons for treating a waste water are normally threefold:

(1) A desire to prevent pollution;
(2) Necessity to recover water for reuse;
(3) An attempt to recover metal values.

The first two objectives are easily fulfilled when treating any waste water by ion exchange techniques. The third objective can only be fulfilled with present technology to a certain extent.

In many plating industries, the operating area may involve several different plating baths, the wastes of which cannot conveniently be segregated [7]. In order to recover metal values from such a mixed waste, some form of segregation is necessary.

The recovery of metal values from a plating operation will also determine the economics of the treatment process. A recent survey in Johannesburg revealed that plating firms between them were dumping R270 000 worth of nickel and R40 000 worth of chrome plating solution every year [8].

If either of the above solutions are mixed with each other or with other metals, no usable metal recovery can be achieved without a metal separation step. Without metal recovery, the cost of an ion exchange treatment is estimated by Sawyer [9] to be greater than 40c/1000 gallons.

In order to fulfill the three requirements of waste treatment on a mixed electroplating operation wash water, it was decided to study the treatment process incorporating a metal separation step. The examination of techniques, on a bench-scale in the laboratory, was undertaken in an attempt to evaluate the technical feasibility of the treatment process.

CHAPTER 2

MECHANISM AND THEORY OF ION EXCHANGE

2.1 STRUCTURE OF ION EXCHANGE RESINS

The most important class of ion exchangers are resins produced synthetically from organic materials. These are the only ones considered in this work, as experiments have shown them to be far more stable under extreme conditions of temperature and pH than the naturally occurring exchangers. They also have a higher capacity and higher exchange rates than the inorganic ion-exchanger gels or the naturally occurring zeolites [10,11].

The framework of the organic resins is an irregular hydrophobic macromolecule of hydrocarbon chains, generally a crosslinked styrene - divinylbenzene polymer. Hydrophilic groups are introduced into the resin by incorporation of ionic groups such as $-S\bar{O}_3H^{+}$ for strong acid resins and $=N^{+}$ in strong base resins. The crosslinking of the hydrocarbon chains serves to make the resin insoluble in water and any other solvent which does not destroy the resin.

Since the dissolution of these organic resins requires the rupture of carbon-carbon bonds, they tend to be stable under extremes of conditions except when being used at elevated temperatures (above $\pm 100^{\circ}C$) in the presence of strong oxidising agents.

The degree of crosslinking of the resins affects the resin's ability to swell when immersed in solution as well as its ability to exchange with large counter-ions and the rate at which exchange occurs. The higher the degree of crosslinking of the resin, the higher is its thermal stability and its ability to withstand mechanical attrition.

The ion-exchange behaviour of these polymers is chiefly determined by the fixed ionic groups that have been introduced into the polymeric structure. The number of these groups determines the capacity of the resin whilst the nature of the groups determines the ion exchange equilibrium that will occur. The most important property possessed by the ionic groups is their acid or base strength. The strong acid group $-SO_3^-H^+$ will remain ionised at low pH conditions whilst the strong base group $-N^+(CH_3)_3$ remains ionised at high pH conditions.

The choice of a strong acid resin for this particular study was based on the above considerations, since the waste streams that would have to be treated would generally be at a lower pH than the recommended operating pH of a weak acid resin. The strong base resin was chosen because of its ability to take up free CN^- ions.

2.2 MECHANISM OF ION EXCHANGE

In order to explain the mechanism of ion exchange, it is necessary to consider a spherical ion exchanger bead containing a counter-ion A being placed in a solution of an electrolyte BY, where B is another counter-ion. As equilibrium is approached, ions A diffuse out of the beads into the solution and ions B diffuse from the solution into the beads.

In order to maintain the electroneutrality requirement, any counter-ions which leave the exchanger are replaced by an equivalent amount of other counter-ions. This results in ion exchange being a stoichiometric process, with deviations occurring, however, due to electrolyte sorption by the resin. The co-ions (the functional groups linked to the resin e.g. $-SO_3^-$) do not participate in the exchange and thus have little effect on the rate of the exchange [12].

The overall rate of transfer between an electrolyte and an ion exchange resin has been shown experimentally to depend on either one of two mechanisms [13]. The steps involved in the exchange of two counter-ions were first proposed by Boyd et al [14]. These steps are

(a) Diffusion of A^+ through the solution to the resin particles;

(b) Diffusion of A^+ through the resin particle;

(c) Chemical exchange between A^+ and BR at the exchanging positions in the interior of the particle;

(d) Diffusion of the displaced B^+ out of the resin particle;

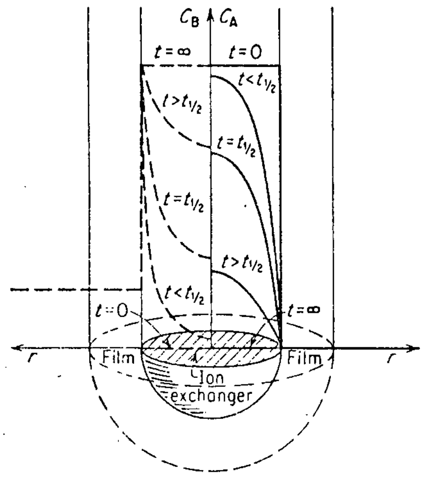
(e) Diffusion of B^+ through the solution away from the resin particle.

The overall rate of exchange is governed by the slowest step of the above sequence, the latter being to a large exgent dependent upon the actual experimental conditions [15]. It is generally agreed, however, that either particle diffusion is controlling, or that liquid film diffusion is controlling. In each case the theory is approached differently and this accounts for the two mechanisms proposed by Eichorn and Bauman [16].

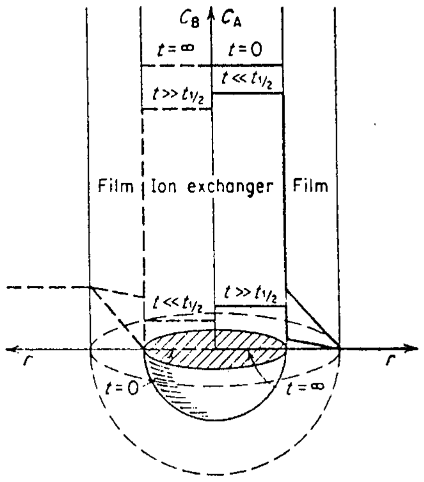
The difference in the two rate determining steps can be represented schematically (Figures 2.1, 2.2) for species A initially in the resin particle and species B initially in the solution.

Film diffusion control prevails in systems where the ion exchangers contain high concentrations of fixed ionic groups, a low degree of crosslinking, and small particle size, with dilute solutions and with inefficient agitation.

The technique employed to determine which of the above mechanisms is rate controlling is the simple interruption test. This requires the termination of solution flow during column operations for a certain length of time. Analysis of the effluent before and after termination determines the rate controlling step. If film diffusion is rate controlling no deviation in the effluent concentration-volume curve should result, whilst for particle diffusion control this is not the case. Here, a step change in concentration is evident [17]. Schematically this is represented by the curve shown in Figure 2.3.



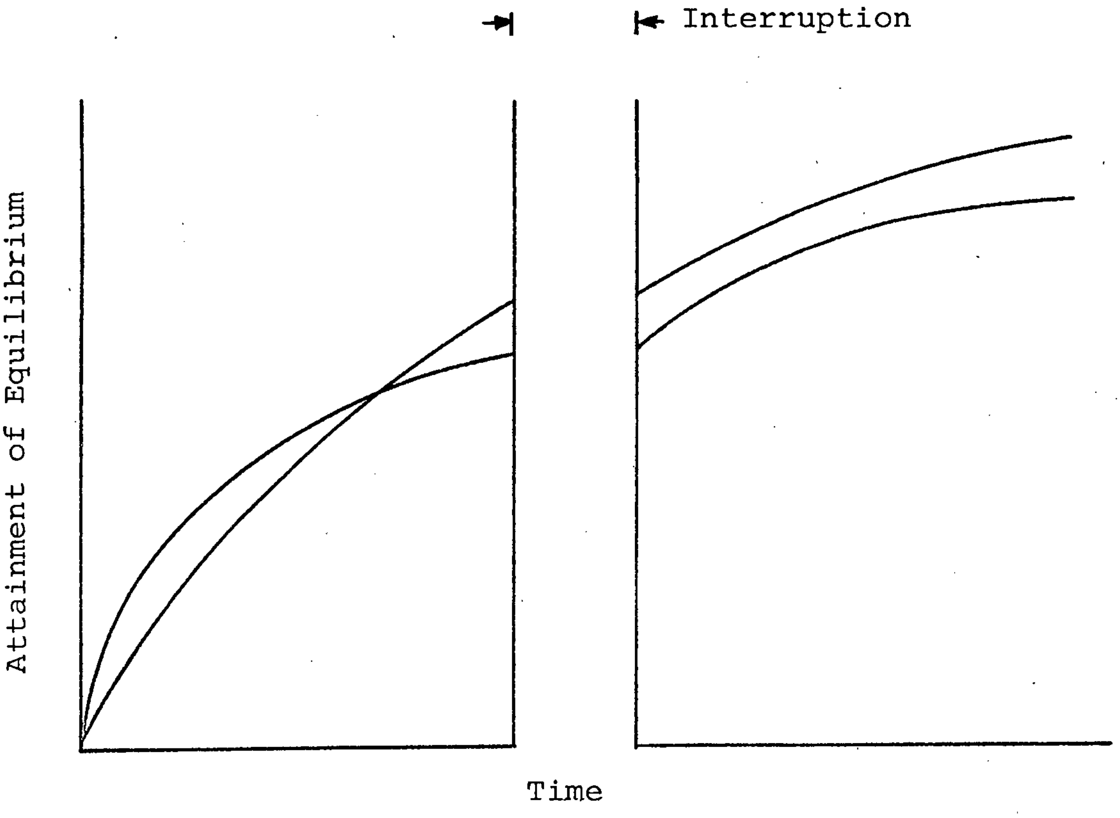
Particle-diffusion control



Film-diffusion control

FIGURE 2.1

FIGURE 2.2



INTERRUPTION TEST

FIGURE 2.3

This has an important bearing on column operations, for if particle diffusion is rate controlling (as it was found to be in this experimental work) the performance of ion exchange columns is independent of column geometry (i.e. L/D ratio typically) if fluid flow rate, column volume, and breakthrough criteria are held constant [18,19].

2.3 EQUILIBRIUM AND SELECTIVITY OF ION EXCHANGE RESINS

Exchange reactions are perfectly reversible (except in certain cases where poisoning of the resin occurs) for synthetic organic exchangers and can be represented by the reaction

$$RA + B^{+}_{(aq)} \rightleftharpoons RB + A^{+}_{(aq)} \qquad (2.1)$$

for the exchange of monovalent counter-ions. The position of equilibrium is quite reproducible and independent of the side from which it is approached, whilst the position of the equilibrium depends on the relative proportions of RA and B^+ present as well as the chemical nature of the counter-ions A^+ and B^+ [20]. The latter determines the selectivity of the resin for one ion as opposed to another.

The practical selectivity of the exchanger is represented by the expression

$$K_A{}^B = \frac{[B^+]_R[A^+]_{aq}}{[A^+]_R[B^+]_{aq}} \qquad (2.2)$$

where $[B^+]_R$ - resin phase
$[A^+]_{aq}$ - aqueous phase

The function $K_A{}^B$ is the selectivity coefficient and generally includes the valence of the counter-ions in the expression.

The valence of the counter-ion is one of the factors which affect the selectivity of the resin for that particular ion. In general, the higher the valence of the counter-ion, the greater the selectivity of the resin for that ion. The preference increases with dilution of the solution. This forms the basis of separation techniques using complexing agents which either decrease or reverse the charge on the counter-ion prior to its participation in the exchange reaction.

The second important factor which affects selectivity is the solvated equivalent volume of the counter-ion. This is a consequence of the elastic properties of the matrix. The smaller the hydrated radius of the counter-ion, the greater the selectivity of the resin for that ion [21,22].

Other factors which affect selectivity, and lead to the following selectivity sequence for strong acid resins

viz. $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < Ag^+$

and $Mg^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} < Cd^{2+} < Ni^{2+}$

are

(a) The ion exchanger prefers the counter-ion with the greater polarizability;
(b) The counter-ion which interacts more strongly with the fixed ionic groups;
(c) The counter-ion which participates least in complex formation with the co-ion [23].

2.4 THEORETICAL PREDICTION OF BREAKTHROUGH IN COLUMN OPERATIONS

Consider the reaction:

$$A^{a+} + B\cdot Resin \rightleftharpoons B^{a+} + A\cdot Resin$$

The rate of ion exchange at the surface for ions of the same valence may be expressed as:

$$\frac{d(A\cdot Resin)}{d\tau} = k[(A^{a+})(B\cdot Resin) - \frac{1}{K}(B^{a+})(A\cdot Resin)] \quad (2.3)$$

where ( ) - concentration

τ - time variable

k - specific rate constant for reaction in forward direction

K - equilibrium constant for reaction.

For reaction $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$

$$K = \frac{k_1}{k_2}$$

$$\text{and} \quad \frac{dR}{dt} = k_1 C_A C_B - k_2 C_R C_S$$

$$= k_1 C_A C_B - \frac{k_1}{K} C_R C_S$$

$$= k_1 [C_A C_B - \frac{1}{K} C_R C_S]$$

At equilibrium,

$$\frac{k_1}{k_2} = \frac{C_R C_S}{C_A C_B} = K$$

Since k_1, k_2 and K are constants independent of concentration, $\frac{k_1}{k_2} = K$ at any concentration [24].

Substituting into equation (2.3)

$$(A^{a+}) = C_A \qquad (B^{a+}) = C_o - C_A$$

$$(A \cdot \text{Resin}) = q_A \qquad (B \cdot \text{Resin}) = Q - q_A$$

where C_o - total solution concentration

Q - exchanger capacity

q_A - gm-equivalent of A combined with unit weight/vol of exchanger.

Equation (2.3) becomes:

$$\frac{dq_A}{d\tau} = k[C_A (Q - q_A) - \frac{1}{K} q_A (C_o - C_A)] \tag{2.4}$$

In column operation, τ is the time measured from the first entry of fluid into the column. This time must be corrected by subtracting the time required to fill the column,

$$\text{viz.} \quad t = kC_o(\tau - \frac{v\varepsilon}{R}) \qquad (2.5)$$

where v - bulk volume of column
R - volumetric flowrate
ε - void fraction of column
$\frac{v\varepsilon}{R}$ - is the time required to fill the column
and $V = \tau R$
where V - total volume of feed that has entered the column
and $V - v\varepsilon$ is the volume of effluent from the column.

Substituting for τ in equation (2.5) we get the 'solution-capacity parameter' [25],

$$t = kC_o(\frac{V-v\varepsilon}{R}) \qquad (2.6)$$

An analagous 'exchanger-capacity parameter' S, can now be defined such that

$$S = kQ\rho_b(\frac{v}{R})$$

where ρ_b - bulk density of resin.

The relation between t and S then gives rise to a throughput parameter [26],

$$\text{viz.} \quad \frac{t}{S} = T = \frac{C_o(V-v\varepsilon)}{QV\rho_b} \qquad (2.7)$$

which is the ratio of the equivalents of solution to equivalents of exchanger, and 1/T is a dimensionless bed volume [27].

Under equilibrium conditions with uniform presaturation of the bed and constant feed composition, a unique concentration history is obtained if the effluent concentration is plotted against the throughput parameter [26]. A corresponding normalized concentration profile is obtained within a column of finite length by representing the concentrations as functions of 1/T.

Normalized liquid + solid-phase concentrations can then be defined as

$$x_i = \frac{C_i}{C_o} \tag{2.8}$$

and $$y_i = \frac{q_i}{Q_o} \tag{2.9}$$

Since the overall concentration in the system is effectively constant,

$$\sum_{i=1}^{k} x_i = 1 \tag{2.10}$$

and $$\sum_{i=1}^{k} y_i = 1 \tag{2.11}$$

where k - number of species present in the system.

The conservation equation for an infinitesimal thickness of bed at any cross-section perpendicular to the direction of flow is represented by

$$\left(\frac{\partial C_i}{\partial v}\right)_V + \rho_b\left(\frac{\partial q_i}{\partial V}\right)_v + \varepsilon\left(\frac{\partial C_i}{\partial V}\right)_v = 0 \tag{2.12}$$

Substituting equations (2.8) and (2.9) for C_i and q_i leads to

$$\left(\frac{\partial x_i}{\partial v}\right)_V + \frac{Q\rho}{C_o}\left(\frac{\partial y_i}{\partial V}\right)_v + \varepsilon\left(\frac{\partial x_i}{\partial V}\right)_v = 0 \tag{2.13}$$

If the volume of solution that has passed through the infinitesimal bed thickness is considered instead of the feed volume, we can then replace V in equation (2.13) by V-v which leads to

$$\left(\frac{\partial x_i}{\partial v}\right)_{V-v\varepsilon} + \rho_b\left(\frac{\partial y_i}{\partial (V-v\varepsilon)}\right)_v = 0 \qquad (2.14)$$

Substituting S, the exchanger capacity parameter and t, the solution capacity parameter into equation (2.14) gives

$$\left(\frac{\partial x_i}{\partial S}\right)_t + \left(\frac{\partial y_i}{\partial t}\right)_S = 0 \qquad (2.15)$$

which together with equation (2.13), has been transformed by Sillén [28] into the ordinary differential equation

$$\left(\frac{dy_i}{dx_i}\right)_{path} = T \qquad (2.16)$$

for uniform presaturation and constant feed composition.

The equilibrium relationships for the reaction of polyvalent ions with an exchanger

$$\text{viz.}\quad bA^{\pm a} + aBR_b \rightleftharpoons aB^{\pm b} + bAR_a$$

are expressed as

$$\bar{K}_B^{\,A} = \left(\frac{q_A}{C_A}\right)^b \left(\frac{C_B}{q_B}\right)^a \qquad (2.17)$$

The 'dimensionless selectivity coefficient' which is then obtained from equation (2.17) by incorporating equations (2.8) and (2.9) is

$$K_B^{\,A} = \left(\frac{y_A}{x_A}\right)^b \left(\frac{x_B}{y_B}\right)^a = \bar{K}_B^{\,A}\left(\frac{Q}{C_o}\right)^{a-b} = \frac{1}{K_A^{\,B}} \qquad (2.18)$$

The selectivity coefficients for a multicomponent system can then all be evaluated from the respective equilibrium values. These values can be related to one another as follows:

$$K_i^{\,j} = \frac{K_k^{\,j}}{K_k^{\,i}} \qquad (2.19)$$

where component k is taken as some reference component.

For any given system, if the x_i's are known a corresponding y_i can be calculated using equations (2.11) and (2.18) which when combined result in a polynomial with only y_i as unknown,

$$y_i + \sum_{j \neq i} x_j (K_i^{\,j})^{\frac{1}{\nu_i}} \left(\frac{y_i}{x_i}\right)^{\frac{\nu_j}{\nu_i}} = 1 \qquad (2.20)$$

where ν_i is the absolute value of the charge of component i.

The other k-2 y's can then be calculated from the equilibrium relationship expressed in equation (2.18)

$$\text{i.e. } y_j = x_j (K_i^{\,j})^{\frac{1}{\nu}} \left(\frac{y_i}{x_i}\right)^{\frac{\nu_i}{\nu_j}} \qquad (2.21)$$

The final y_k value is then calculated using equation (2.11).

If the k y-values are specified, the corresponding k x-values can be calculated, by rearranging equations (2.11) and (2.18), analogously to the calculated y-values.

In order to evaluate the point within the resin bed at which a certain set of y_i values exist, it is necessary to evaluate dy_i/dx_i and consequently 1/T at that point.

Implicit differentiation of the equilibrium equation (2.18) with respect to x_b leads to

$$\frac{dx_i}{dx_k} = \frac{\nu_i}{\nu_b} K_k{}^i \left(\frac{y_k}{x_k}\right)^{\nu_i - 1} \left(\frac{x_i}{y_i}\right)^{\nu_k - 1} \left(\frac{x_i}{x_k}\right)^2 \quad \frac{\frac{dy_k}{dx_k}\ x_k - y_k}{\frac{dy_i}{dx_i}\ x_i - y_i} \tag{2.22}$$

If the $K_k{}^j$ are then replaced by the y_i, x_i values in equation (2.18) and the dy_i/dx_i by the T values from equation (2.16) equation (2.22) yields

$$\frac{dx_i}{dx_k} = \frac{\nu_i}{\nu_k} \; \frac{x_i y_i}{x_k y_k} \; \frac{Tx_k - y_k}{Tx_i - y_i} \tag{2.23}$$

Evaluating dx_i/dx_k from equation (2.10) and substituting into equation (2.23) leads to

$$\sum_{i=1}^{k} \nu_i \frac{x_i y_i}{x_i T - y_i} = 0 \qquad (x_i \neq 0,\ y_i \neq 0) \tag{2.24}$$

which is a polynomial in T containing k-1 positive roots in T for a k component system.

The maximum root corresponds to a value in the first transition zone, the second greatest root to a value in the second transition zone.

2.41 Qualitative Rules for Evaluation of Profiles

(a) Slope rule

The components in the system are represented as A, B, C etc. in alphabetical order, with the separation factors of the components being such that

$$A > B > C > D > E \ldots\ldots \text{ etc.}$$

The slope rule states that in the first upstream transition zone, the profile of A if it exists is positive, whilst all others are negative; in the second zone A and B are positive, in the third zone A, B and C are positive. This applies to both gradual and abrupt transitions; in the latter the profile is termed positive if the concentration of the component is higher in the upstream plateau zone than it is in the downstream zone.

These relations are summarized in Figure 2.4 below.

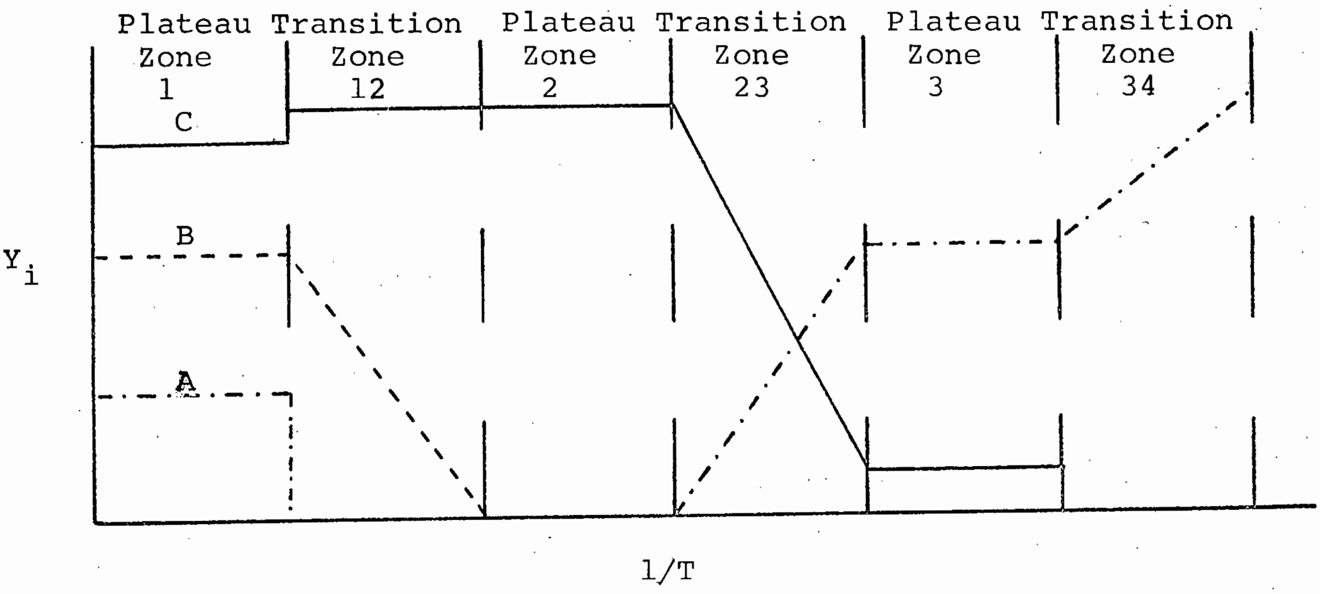


Figure 2.4

SIGN OF TRANSITION - PROFILE SLOPE

Component	Zone 12	Zone 23	Zone 34	Zone 45
A	+	+	+	+
B	–	+	+	+
C	–	–	+	+
D	–	–	–	+

(b) Alphabet Rule

The alphabet rule states that the mathematical profile curves which rise from zero or go to zero, do so at distinct column levels. These levels are arranged in alphabetical order when the components are labelled alphabetically in order of their respective selectivities. Specifically, if the successive zone bounds are designated by (12)', (12)", (23)', (23)" etc., the various components can vanish as indicated below:

Zone bound	(12)'	(12)"	(23)'	(23)"	(34)'	(34)"	(45)'	....
Zero of Component	A	B	B	C	C	D	D	....

2.42 Application of Slope and Alphabet Rules

The profile of each component in the transition zone is evaluated using the mathematical relationships outlined. If, during the evaluation, the slope of the evaluated profile is opposite in sign to that allowable, this indicates a fictitious profile and consequently an abrupt transition. The concentration of the component is then assumed to increase or decrease at a point $(\overline{12})$ the mean of (12)' and (12)" (Figure 2.5).

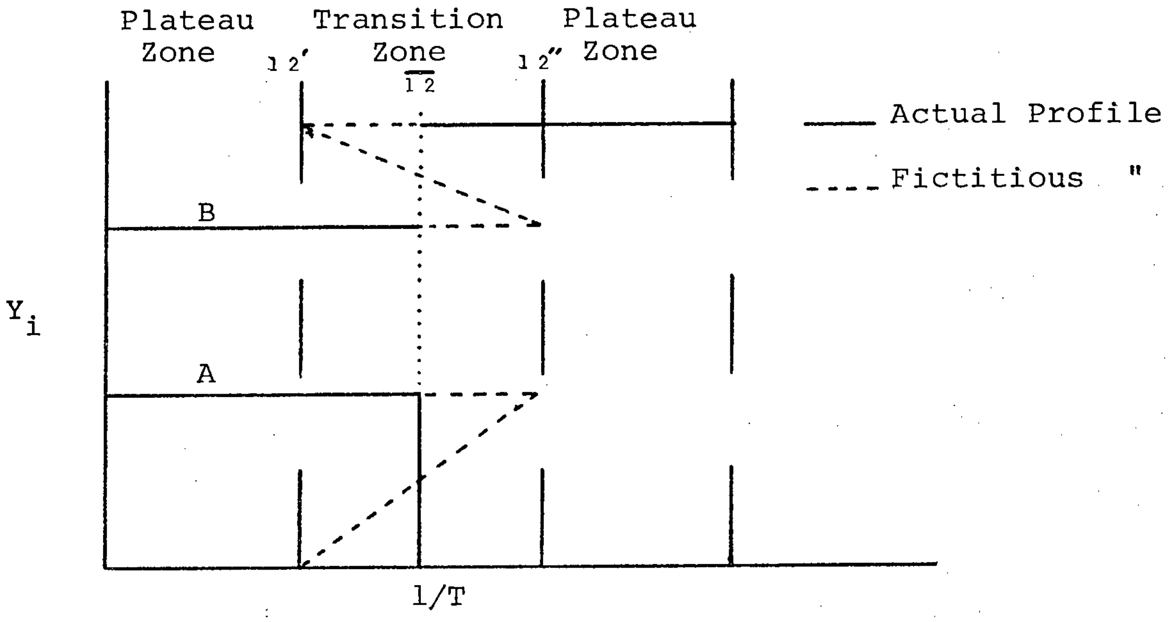


Figure 2.5

The overall profile for a multicomponent system can thus be evaluated in this manner. This then enables the evaluation of the corresponding liquid compositions and can be used with the evaluated 'T' value to calculate the volume of solution that can be passed through a given ion exchange bed of given capacity before breakthrough of any particular component occurs.

2.5 THEORETICAL PREDICTION OF THE SEPARATION OF CATIONS ON A CATION EXCHANGER

The separation of various ions in ion-exchange can be enhanced by the use of complexing agents. These complexing agents change the distribution coefficient of the particular ion for the resin under consideration. The distribution coefficient, D_M, is defined as the ratio of the concentration of the ion in the resin phase to the concentration of the ion in the aqueous phase

$$D_M = \frac{[M]_R}{[M]_{aq}} \tag{2.25}$$

By the use of suitable complexing agents under certain conditions, high efficiency separations of ions which are not normally separable can be achieved.

The theory outlined below was used to determine the optimum conditions under which the relevant separations would best be conducted.

Consider the ion exchange reaction:

$$2RA + M^{2+} \rightleftharpoons R_2M + 2A^+ \tag{2.26}$$

where A^+ - monovalent cation, usually the cation associated with the salt of the complexing agent;

M^{2+}- divalent metal cation.

The equilibrium coefficient for the above reaction can be expressed as:

$$\bar{K} = \frac{[M]_R}{[M]_{aq}} \frac{[A^+]_{aq}}{[A^+]_R} \tag{2.27}$$

where [ ] - concentrations expressed as moles/litre; then

$$D_M = \frac{[M]_R}{[M]_{aq}} = K\left(\frac{[R_2A]}{[A^+]}\right)^2 . \tag{2.28}$$

If we assume that $R_2A = Q$, the total capacity of the resin, then

$$D_M = \bar{K} \left[\frac{Q}{[A^+]}\right]^2$$

and

$$\log D_M = \log \bar{K}Q^2 - 2 \log [A^+]. \tag{2.29}$$

If complexing agents are now added to the system (the complexing agents chosen are usually the salts of organic acids, e.g. sodium oxalate, ammonium citrate) the equilibrium constant of the reaction expressed in equation (2.27) will no longer be valid. A new constant, the conditional constant for the system under consideration, is then defined [29],

$$K_{M'L'} = \bar{K}_{ML}/\alpha_M\alpha_L \tag{2.30}$$

where [30], $\alpha = [M']/[M]$

$[M']$ - concentration of a metal complex

$[M]$ - concentration of uncomplexed metal

α - a measure of the effect of side reaction on the main reaction being considered and is a function of the equilibrium constants of the side reactions.

α_M - side reactions of the metal with other ligands
α_L - side reactions of the ligand with other ions in the system (usually H^+).

If L forms various complexes with the metal M then

$$\alpha_{M(L)} = \frac{[M']}{[M]} = \frac{([M] + [MA] + [MA_2] + \ldots + [MA_n])}{[M]}$$

$$= 1 + [A]\beta_1 + [A]^2\beta_2 + \ldots + [A]^n\beta_n \qquad (2.31)$$

where β_n - stability products [31], i.e. for

$$M + nL \rightleftharpoons ML_n$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n} = \prod_{i=1}^{n} K_i \qquad (2.32)$$

If we now include in equation (2.29) the effect of complexation reactions, a new distribution coefficient modified for the conditional constant is obtained [32],

$$\log D_M = \log K \cdot Q^2 - \log \alpha_M - 2 \log [A] \qquad (2.33)$$

and for metal complexation with more than one ligand, equation (2.33) becomes

$$\log D_M = \log K \cdot Q^2 - \log \alpha_{M(L)} - \log \alpha_{M(B)} - \ldots$$

$$- 2 \log [A^+] \qquad (2.34)$$

If L forms complexes with other compounds, it becomes necessary to determine the conditional stability constants that apply.

Since $\beta_1 = K$ and $\beta_n = \Pi K_n$

we require all the $K_1' = K_1/\alpha_{L(H)}$ to $K_n' = K_n/\alpha_{L(H)}$. Incorporating these into equation (2.30) to evaluate $\alpha_{M(L)}$ we obtain

$$\alpha_{M(L)} = 1 + \frac{L}{\alpha_{L(H)}}\beta_1 + \left[\frac{L}{\alpha_{L(H)}}\right]^2\beta_2 + \dots + \left[\frac{L}{\alpha_{L(H)}}\right]^n\beta_n \qquad (2.35)$$

and

$$\alpha_{M(B)} = 1 + \frac{B}{\alpha_{B(Y)}}\beta_1 + \left[\frac{B}{\alpha_{B(Y)}}\right]^2\beta_2 + \dots + \left[\frac{B}{\alpha_{B(Y)}}\right]^n\beta_n \qquad (2.36)$$

If the log D_M values for various metals are now evaluated under different conditions, and the ratio of the D_M values are determined as a function of one of the variables in the system (pH, complexing agent concentration) a maximum or minimum can be obtained. This point then indicates the optimum conditions at which to perform the particular separation of the two metals.

CHAPTER 3

APPARATUS AND EXPERIMENTAL TECHNIQUE

3.1 DESCRIPTION OF EQUIPMENT

3.11 Ion Exchange Column

The apparatus used in this study (Figure 3.1) consisted of an all glass column with a 3 cm internal diameter [33] and height of 25 cm. Fused into the bottom of the column was a sintered glass disc of Porosity 0. Below the disc, the column tapered to an outlet of 0,6 cm I.D.

Attached to the top of the column by means of a rubber stopper, was a 250ml separating funnel used to contain the feed solution to the column. The flowrate of solution from the column was controlled by means of a clamp connected to rubber tubing which was attached to the column outlet.

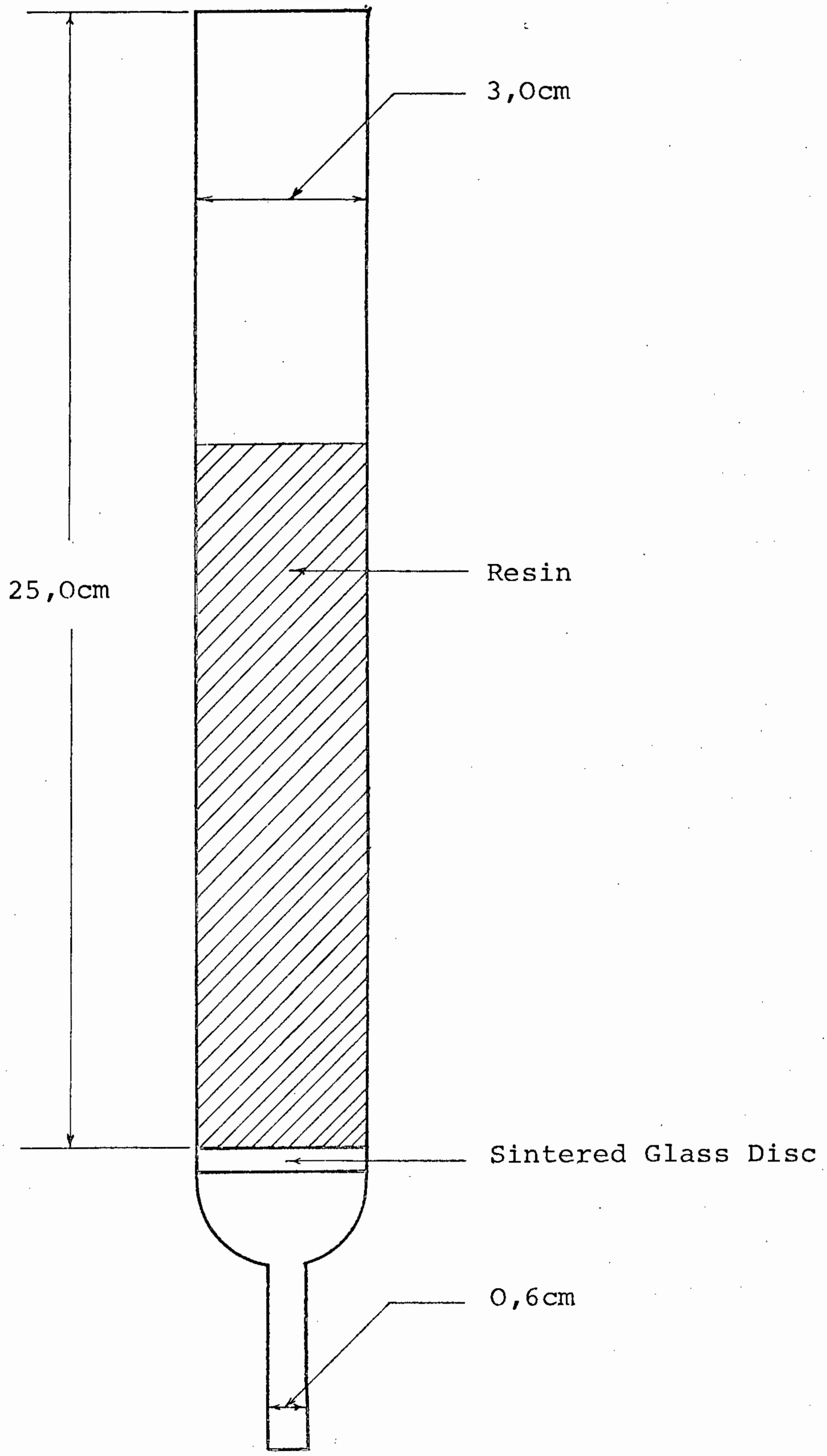
When large feed volumes were treated, the separating flask was connected to a 25 litre polythene feed tank by means of rubber tubing. When more than one column was used in series, the separating flasks on the second and third columns were dispensed with and the connection made by rubber tubing. Each of the succeeding columns was then fitted with a rubber stopper through which passed a 0,6 cm I.D. glass tube to which the connecting tube was attached. The flowrate was then controlled by means of a clamp attached to the outlet of the last column in the series.

During regeneration after a series operation, the columns were disconnected and separately regenerated using the separating funnel to hold the regenerant solution.

3.2 OPERATING CONDITIONS

3.21 Resin Type and Preparation

The cation resin used in this work was Amberlite IR-120, and the anion resin Amberlite IRA-400, both obtainable as



ION EXCHANGE COLUMN

FIGURE 3.1

Analytical Reagent grade. The properties of each one are outlined in Table 3.1.

The volume of resin used in each column (100ml) was determined by slurrying the beads into a column half filled with water until the resin level reached a predetermined mark on the column.

The cation resin was then regenerated with 1 bed volume (100ml) of 20 wt% H_2SO_4. The acid regenerant was followed by 2 B.V. (bed volumes) of distilled water rinse. The anion resin, initially in the Cl^- form, was regenerated with a 15 wt% NaOH solution (1 B.V. of feed) followed by 2 B.V. of distilled water rinse. In the case of the anion column, the regeneration was repeated before the resin was considered ready for use.

TABLE 3.1

PROPERTIES OF RESINS

Resin	Particle Size (mesh)	Functional Group	Ionic Form	% cross-linkage	Exchange Capacity (meg/ml)
IR-120	16-50	$-SO_3^-$	H^+	8	1,9
IRA-400	16-50	$-N(CH_3)_3^+$	Cl^-	8	1,4

3.22 Operating Flowrates

The flowrates used during the experimental work are those recommended by the resin manufacturers [34] and are summarised in Table 3.2. No attempt was made to optimise the flowrates for the particular conditions under which the runs were conducted.

Other workers (Goldblatt [35] and Tallmadge [36]) have used different flowrates from those used in this study, but have themselves not attempted to optimise these flowrates.

Due to the dilute nature of the waste stream and also the fact that it contains mostly divalent metal ions, the flowrate of this stream to a strong acid column could in all probability be increased without any effect on the occurrence of breakthrough. Similarly, the water wash flowrate could be increased without any ill-effects.

TABLE 3.2

FLOWRATES OF SOLUTIONS

Flowrate (B.V./min)	Feed	Elution of Metals	Acid Regen.	Water Wash	Caustic Regen.
Cation Column	0,15	0,1	0,1	0,1	-
Anion Column	0,15	-	0,1	0,1	0,1

3.23 Feed Solutions

Feed solutions were prepared for each run in question. The sulphate salts (A.R. grade) of the metals Copper, Iron, Nickel and Zinc were used in the preparation of the feed. The tests carried out on chrome and cyanide necessitated the use of the sodium salts of both the above. The metal cyanide salts were not used, as any industrial waste would contain the complexed cyanide after a reaction between the metal and free cyanide. The metal-cyanide reaction was given time to equilibrate prior to using the solution.

The concentrations of the various feed solutions varied from run to run and are given in Appendix A with the results obtained for each run.

3.24 Backwashing of Bed

The major purpose of backwashing a resin bed, as outlined by Kunin [37], is to remove any traces of suspended or colloidal matter that may be trapped within the bed. If this material is permitted to accumulate, channeling within the column is likely to occur.

Since the feed to the bed in all the experimental runs was synthetically produced, it was felt that backwashing of the bed was not necessary. Where precipitation of any materials did occur (usually due to an insoluble hydroxide precipitate of the metal) this was removed by a final acid regeneration step.

In order to remove any fine material which may have originated from resin bead fracture during column operation, the resin was washed out of the column into a large beaker. The resin within the beaker was then rinsed with distilled water and the clear liquor, containing the fine particles in suspension, was decanted; after which the resin was again slurried into the column.

This wash procedure was undertaken after every 5-6 runs, each run consisting of a loading, a regeneration and a wash step.

3.25 Column Behaviour during Loading.

During the loading operations on the freshly regenerated resin, certain effects were noticed. The bed shrinkage which occurred during the loading of the feed solution onto the hydrogen form of the resin, was usually between 10% and 20%.

A marked colour change also occurred within the bed. Initially the cation resin was a dark yellow orange colour, but this changed to a mottled green at the wavefront of the loading solution. The colour change was sufficiently sharp to give a good indication of when breakthrough of the feed solution was about to occur.

Initial loading of a new resin resulted in a darkening at the wavefront and not a complete colour change. The latter only occurred on resin that had been used in successive cycles.

3.26 Column Behaviour during Elution

The elution of the cation column and separation of the metals required a number of different steps (Chapter 4). The initial step on the loaded column, was the addition of an NH_3 solution. During the feeding of this solution, certain dramatic colour changes were noticed within the bed. The initially green beads changed to a dark yellow merging to blue and eventually ending as a dark blue-black colour. The temperature of the bed at the NH_3 wavefront increased noticeably although all operations were carried out at ambient temperature.

During the elution of the metals, each displayed a distinctive colour as it emerged from the column. The Cu elution, in the form of an NH_3 complex, was a deep blue in colour. The Fe solution complexed with citric acid was dark yellow, whilst the Ni solution was turquoise and Zn effluent showed no colour.

In each of the above cases, the colour of each solution tails off at the end of that particular metal's elution giving a good indication of when to change the feed composition in order to elute off the following metal.

The final regeneration of the bed with 20% H_2SO_4, prior to the start of the next cycle, causes a further 2% to 5% bed shrinkage. After successive regenerations with this concentrated acid, it was noticed that some of the resin beads had started to fracture and their colour had changed from an initial orange/brown to yellow.

The fracture could have been caused by heat effects during NH_3 addition or the high regenerant acid concentration. The former can be overcome by starting off with a dilute NH_3 feed initially.

3.3 METHODS OF ANALYSIS

3.31 Analysis of Metals

The analysis of the metals Cu, Fe, Ni, Zn, Cr and Na was carried out on a Varian Techtron Model 1000 Atomic Absorption apparatus. Standard solutions of the various metals were prepared, the concentration range of the standards being dependent on the sensitivity of the apparatus for the particular metal (Appendix F).

The analysis was carried out by calibrating the A.A. apparatus with standard solutions of the metals to be analysed. The samples to be tested were then aspirated and the concentration of each metal determined by comparison with the particular calibration curve.

The wavelengths and burner conditions at which each of the metals was detected are outlined in Appendix F together with the theory on which the technique is based.

3.32 Determination of pH

All pH determinations were carried out with a Beckman Zeromatic Model SS3 pH meter. This contains a calomel reference electrode and a glass electrode.

The meter was calibrated to pH 7 using Beckman pH buffer solution prior to the measurement of any pH.

3.33 Determination of Ammonia

Ammonia was determined volumetrically by titration with 0,02N H_2SO_4 solution using a Kjehldal indicator [38]. This indicator was prepared by mixing volumetrically in a 2:1 ratio a solution containing 0,2% methyl red in 95% ethanol with a solution containing 0,2% methylene blue in 95% ethanol.

3.34 Determination of Cyanide

Free and complexed cyanide was determined volumetrically by titration with 0,01N $AgNO_3$ using Rhodanine as indicator. The preparation of the sample, as outlined in Methods of Analysis, by prior digestion and distillation of the cyanide is necessary to breakdown the complexed cyanide before titration. A complete outline of the analytical procedure can be found in Appendix F.

CHAPTER 4

DISCUSSION OF RESULTS

4.1 PARAMETER DEFINITION AND DISCUSSION

During treatment of a mixed electroplating waste, the metal cations are loaded onto the cation ion exchange column. In order to achieve a separation of the metals loaded onto the ion exchange resin, various elution conditions were tried.

Some measure of comparison of the efficiency of elution was then necessary, in order to relate the effectiveness of one set of elution conditions for a certain metal or column loading, to that of another.

The criteria upon which these elution efficiencies and separation techniques are based are the following:

(a) Percentage Purity - this is a ratio of the concentration of the metal under consideration to the total metal in the effluent sample expressed as a percentage. This criterion determines the effectiveness of the elution technique at producing an effluent containing a good separation of the metal that is being eluted.

(b) Cumulative Percentage - this criterion determines the amount of eluant required to elute a certain percentage of the metal loaded. The parameter is defined as the mass of metal eluted after any particular volume of eluant has passed through the resin, to the total mass of metal loaded onto the column expressed as a percentage.

(c) Elution Efficiency - the ratio of the concentration of the metal in the effluent at a particular time to the concentration of the metal loaded onto the column. This criterion is necessary to compare the elution curves of different runs where different loadings of the resin occur. The higher the metal loading on the column, the greater the metal concentration in the effluent under a certain set of conditions. This ratio then normalizes the elution curve.

The three criteria outlined above are sufficient to determine the overall efficiency of an elution condition. The ideal elution conditions for any particular metal loaded onto the column are

(a) the purity must be 100% for all samples during the elution;

(b) the cumulative percentage should rise steeply to give 100% elution of the metal with a minimum of eluant and at the high purity;

(c) the elution efficiency must be greater than 1.

The results obtained, will be analysed in terms of the above parameters in order to determine the optimum conditions for the elution of each metal.

4.2 SEPARATION AND ELUTION OF COPPER

4.21 Elution with sulphuric acid

The separation of copper, from the other metals loaded onto the column, was first attempted by trying to utilise the natural selectivity of the resin for each of the metals.

This entailed loading the resin with the metals followed by a selective elution with H_2SO_4. This acid was chosen for the particular elution, as most of the metals in the waste that would normally be treated are metal sulphates. These metal salts are the ones generally put into the plating baths [39].

As can be seen from the graph of the particular run (Appendix C) the elution efficiency and cumulative percentage for the elution with H_2SO_4 is exceptionally good, but the ability of the elutant to achieve separation is poor. This is understandable if one considers the selectivity coefficients [40] of the metals copper, iron, nickel, zinc. Due to the relative selectivity of each being so close, no appreciable separation was anticipated for operation in any equipment other than a chromatographic column with this elution technique.

Successful separation of the metals Cu, Fe, Ni and Zn loaded onto a strong acid resin has been achieved by elution with HCl [41]. The elution sequence, however, required the HCl concentration to be 8,5M. Elution resulted from the formation of the Cl^- complexes of the metals which are anionic and no longer held by the cation resin.

4.22 Elution with Acetone and Ammonia

The separation efficiency in the elution of two metal ions on an ion exchanger can be markedly altered by changing the medium in which the separation is attempted. The use of non-aqueous media for the elution conditions causes a change in the swelling of the resin [42] and consequently the diffusion coefficients of the particular metal ions.

The results obtained using acetone (Run No.6) show a slight improvement in the elution efficiency of copper as opposed to that of iron and zinc. The overall purity of the copper was still, however, only 80%.

Acetone was not combined with H_2SO_4 as an eluting medium, as it was felt that the eventual recovery of acetone would present an extra problem in the overall process. Good results had been achieved in the separation of these metals using HCl and methanol on an anion resin [43]. The elution feed in this case though was 60% methanol and 40% 3,5M HCl. In the system envisaged for waste treatment, this would just add another pollutant that would require removal.

After the acetone feed had been passed through the column loaded with copper, iron and zinc, with very little separation and elution resulting, a concentrated ammonia feed (12,5N) was used as the eluent. Ammonia was used in order to achieve the desired separation, as it has the necessary physical properties of acetone [44] (an ability to change the hydrated ionic radius of the loaded cation) together with the ability to form complexes to a greater or lesser degree with the metals loaded onto the column.

The results of the pure NH_3 feed showed a marked increase in the ability to elute off pure Cu (89% pure) but still at a very low cumulative percentage (3,1%). In order to improve the cumulative percentage it was decided to follow the NH_3 feed by a water wash. This, it was hoped, would lower the pH and improve the elution of the Cu from the resin as it was felt that the NH_3 itself was only providing the cupra-ammonium complex but was not able to elute this complex off the resin.

In Run No.7 (Appendix A) this elution technique was tried, but no improvement in elution efficiency resulted although the percentage purity did rise to 95%. A reduction of NH_3 feed concentration from 12,5M to 6,25M resulted in an improved elution efficiency from which it was concluded that greater ionisation of the NH_3 had occurred at the lower pH with consequent better elution. The water wash showed that its eluting ability was not that of an H^+ ion but rather that of a medium where the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

could be influenced to achieve better elution.

4.23 Elution of Copper with Sodium and Ammonia

The previous copper elutions showed that some degree of separation could be achieved with the use of ammonia as elutant. The efficiency of elution for the runs was, however, not very high. In order to improve this efficiency and maintain the separation, Na^+ was tried as a co-elutant with NH_3.

In elution sequence (f) of Run No.7 (Appendix A) a solution of Na^+ and NH_3 was fed to a column previously loaded with Cu and Fe and having had a prior 12,5M NH_3 feed. The results of this run show extremely good separation occurring (99%) at high elution efficiencies. The cumulative copper elution after one litre of elutant feed was 55,5%.

The importance of adding NH_3 prior to the Na^+ feed was outlined in Run No.8. A feed containing 1,0N Na^+ and 12,5M NH_3 was passed through a bed loaded with Cu and Fe. The result was a heavy hydroxide precipitate within the bed with consequent flow disruption. All effluent samples contained precipitated iron. This indicates the necessity of first adding NH_3 to the column to condition it and form the necessary cupra-ammonium complexes prior to elution with the Na^+ feed.

Run No.9 (Appendix A) showed that a decrease in concentration of the initial NH_3 feed stream had no affect on the subsequent Cu elution and separation. The purity of the samples was again 99% whilst the cumulative Cu elution after 900ml of 1,0N Na^+ feed was 49,5%. The change in NH_3 concentration was from 12,5M to 3,3M. No iron precipitation occurred within either the bed or the effluent samples under the reduced NH_3 feed concentration.

A mixed Na^+ - NH_3 feed was thus shown to be effective in the separation of Cu from Fe provided an NH_3 feed was introduced to the loaded column prior to the elutant feed. Another metal, Zn, was now introduced to the mixture to determine the effectiveness of the above eluting technique with a column loaded with three metals.

As can be seen in the results of Run No.11 (Appendix A) there is a marked decrease in the purity of the Cu eluted, the amount of Fe in the samples being approximately the same as in the two metal case, but the Zn concentration very much higher. After one litre of feed, the Cu purity had dropped to 73% whilst the cumulative Cu elution was 91%.

Consideration was then given to deciding whether Na^+ was, in fact, the ideal eluting agent. As NH_3 had to be added to the column, the addition of Na^+ was in actual fact an extra contaminant in the recovered sample over and above NH_3 - NH_4^+. Furthermore, difficulty was experienced in preparing sufficiently concentrated Na_2SO_4 solutions due to precipitation of the material. These factors all suggested a change of eluting material from Na^+ to NH_4^+.

4.24 Elution of Copper with Ammonium ion and Ammonia

The first two runs in this series of elutions showed that a maximum NH_4^+ concentration existed above which no further improvement in separation occurred. At an NH_4^+ concentration of 2,25N, the column, initially loaded with Cu and Fe, became clogged with Fe precipitate. This NH_4^+ concentration was, however, less than the maximum Na^+ concentration used previously and showed that NH_4^+ was a considerably stronger eluting agent than Na^+. This was to be expected if one considers the relative selectivities of the two ions [45].

The maximum NH_4^+ concentration acceptable for the separation of Cu from Fe was found to be 0,75N (Run No.14, Appendix A). This resulted in an average Cu purity of 80,6%. If, however, more than two metals were initially loaded onto the column, an NH_4^+ concentration of 0,625N (Effluent Conc. vs Volume, Run No.15 Appendix B and Copper Elution Curves, Run No.15, Appendix C) the average Cu purity decreased to 76,3% due not to Fe elution but rather to Zn elution, this being the third metal loaded onto the column. This necessitated the experimental work being directed towards finding the optimum conditions for the separation and elution of Cu from a column loaded with all the metals under consideration, viz. Cu, Fe, Ni, Zn.

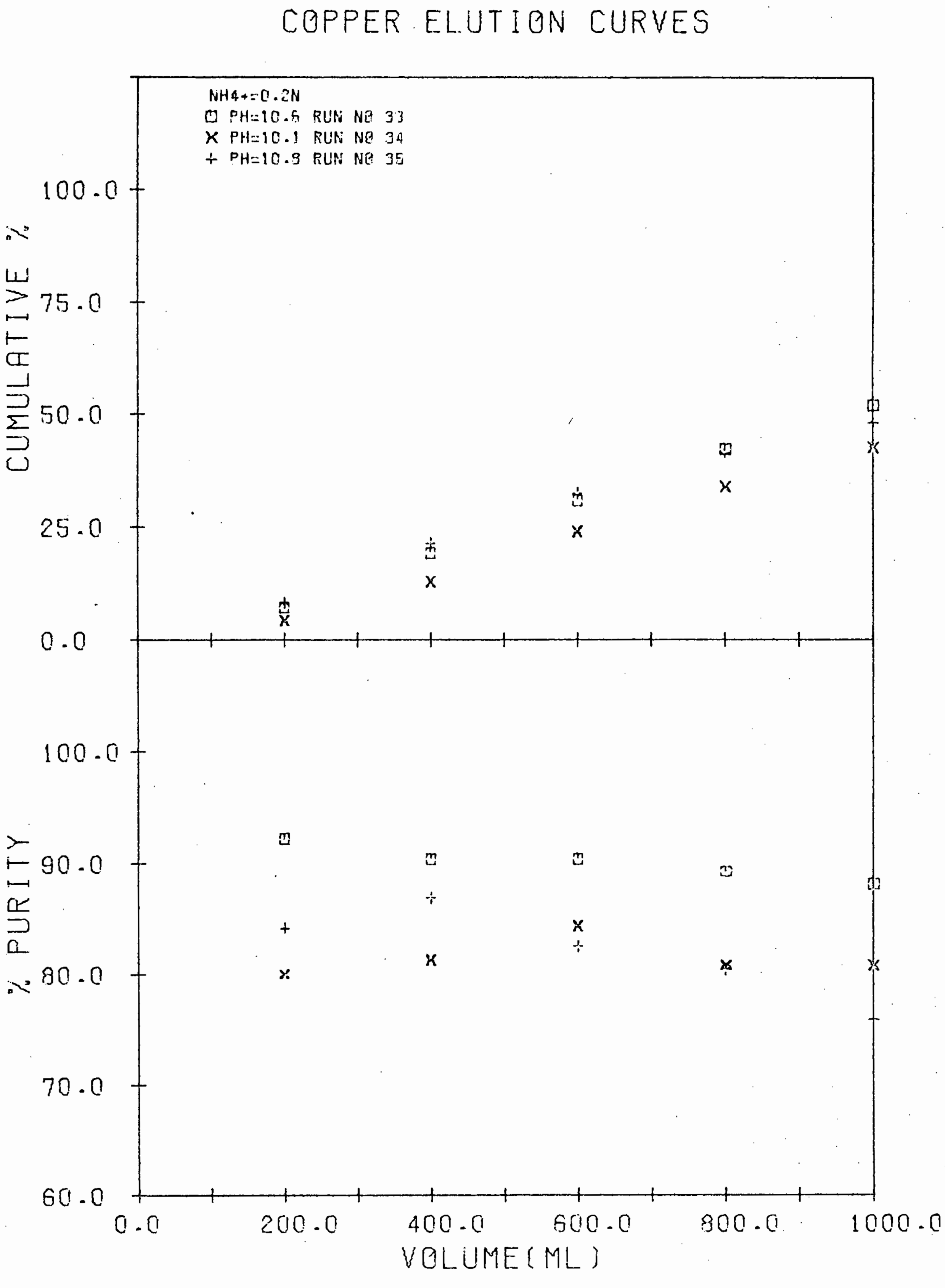
The two parameters that could be varied in the determination of the optimum conditions were

(A) the pH of the feed;
(B) the NH_4^+ concentration in the feed.

(A) Effect of changing pH of feed.

The results shown (Figure 4.1) indicate that the feed pH, at constant NH_4^+ concentration, has virtually no effect on the actual elution of the Cu. The cumulative percentage curves for the three cases showed just about identical slopes, the only difference being the throughput volume at which the Cu first starts appearing in the effluent.

FIGURE 4.1


COPPER ELUTION CURVES
NH4+=0.2N
□ PH=10.6 RUN NO 33
X PH=10.1 RUN NO 34
+ PH=10.9 RUN NO 35
CUMULATIVE %
100.0
75.0
50.0
25.0
0.0
% PURITY
100.0
90.0
80.0
70.0
60.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

This latter is a function of the total volume of liquid above the resin bed in the column. This volume has to be displaced by the elution feed before metal elution is observed, and as this volume was not held constant for consecutive runs a discrepancy in metal appearance resulted.

The fact that the rate of Cu elution is effectively constant under different pH conditions shows that NH_3 itself (used to produce and maintain the desired feed stream pH) plays no part in the elution of the Cu, but merely provides the necessary complexing conditions to achieve successful separation of the loaded metals.

The purity of the samples appears from the results (Figure 4.1), to be somewhat dependent on the pH at which the elution occurs. Here there appears to be an optimum pH at 10,6, for the average purity after 50% Cu elution varies according to pH (Table 4.1).

TABLE 4.1

Average % Purity for 50% Cu elution	88	81	82
pH	10,6	10,8	10,1
NH_4^+ concentration = 0,20N			

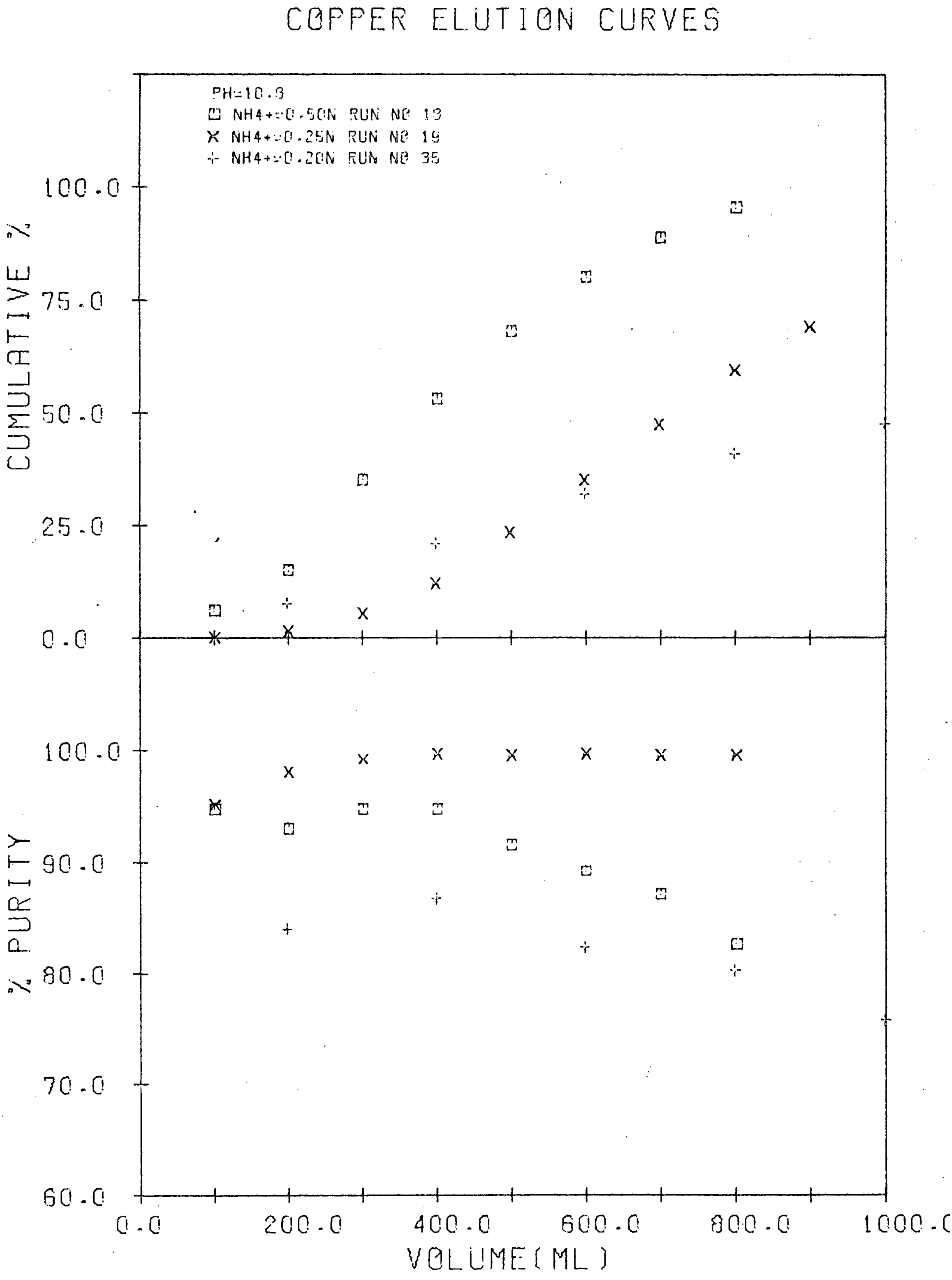
(B) Effect of changing NH_4^+ concentration in the feed.

The results of the elutions at constant pH but varying NH_4^+ concentrations (Figure 4.2) show clearly the effect of the eluting ability of NH_4^+. The rate of elution of Cu from the loaded column depends on the NH_4^+ concentration. The greater the concentration of the latter the greater the percentage elution after a specific volume of feed has passed through the column (Table 4.2).

TABLE 4.2

Volume of feed required for 50% Cu elution	1000ml	700ml	380ml
NH_4^+ concentration	0,2	0,25	0,5
pH = 10,8			

FIGURE 4.2


COPPER ELUTION CURVES
PH=10.8
□ NH4+=0.50N RUN NO 18
X NH4+=0.25N RUN NO 19
+ NH4+=0.20N RUN NO 35
CUMULATIVE %
100.0
75.0
50.0
25.0
0.0
% PURITY
100.0
90.0
80.0
70.0
60.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

The merit of changing the NH_4^+ concentration and consequently the purity of the sample (Figure 4.2) can really only be measured in terms of an economic balance. The general percentage purity vs volume curves all show a maximum purity at about 30% Cu elution. The rate of decline of the curve then depends on the run conditions. At high NH_4^+ concentrations, the rate of decline is very rapid (Figure 3, Appendix C) whilst a decrease in the relevant concentration results in a slower change of purity of the sample. This percentage purity must, however, be related to the cumulative percentage elution to obtain meaningful results.

TABLE 4.3

% Purity at 30% Cu Elution	95	99	89
% Purity at 60% Cu Elution	93	99	88
NH_4^+ concentration	0,5	0,25N	0,2
pH = 10,8			

As can be seen from Tables 4.2 and 4.3, although the percentage purity for 0,5N NH_4^+ concentration shows a faster drop than any of the others, the volume of feed required to achieve the relevant cumulative percentage elution is more than half that required for either of the other two sets of conditions.

The effect of changing the pH of the eluting feed shows that running at high pH conditions, i.e. above pH - 10,8, as was done for Runs 14, 15, 16, 17 (Appendix A) does not result in any improvement in cumulative percentage elution but in fact is really wasteful of NH_3. The high pH runs (Figures 1, 2, 3, Appendix C) were carried out in order to prevent Fe precipitation within the resin bed, but as was shown by the later results (Figure 4.1) that lower NH_3 concentrations (lower pH) achieve the same result.

Kawabuchi et al [46] have shown that the separation of Cu, Fe, Ni, Zn is possible when using a feed of 0,2M

$(NH_4)_2SO_4$ and 0,025M H_2SO_4. In order to assess the effect of eluting Cu with NH_4^+ under acidic conditions, a 0,15N NH_4^+ feed at pH 2,56 was introduced to the loaded column. The results indicate (Figure 4, Appendix C) that no successful separation was achieved. The Effluent Concentration vs Volume curve (Figure 3, Appendix B) shows that all the metals are eluted together.

4.3 SEPARATION AND ELUTION OF NICKEL

4.31 Elution with Ammonium ion and Ammonia

After the successful separation and elution of Cu by utilising its ability to form complexes with NH_3, the same technique was tried with Ni. This metal also forms a similar complex having properties on the resin that were assumed the same as those of Cu [47]. In all cases, the Ni elution is presumed to take place after Cu elution. The column was always conditioned to the form it would be in after a Cu elution.

The two parameters, as for the elution of Cu, that were varied were

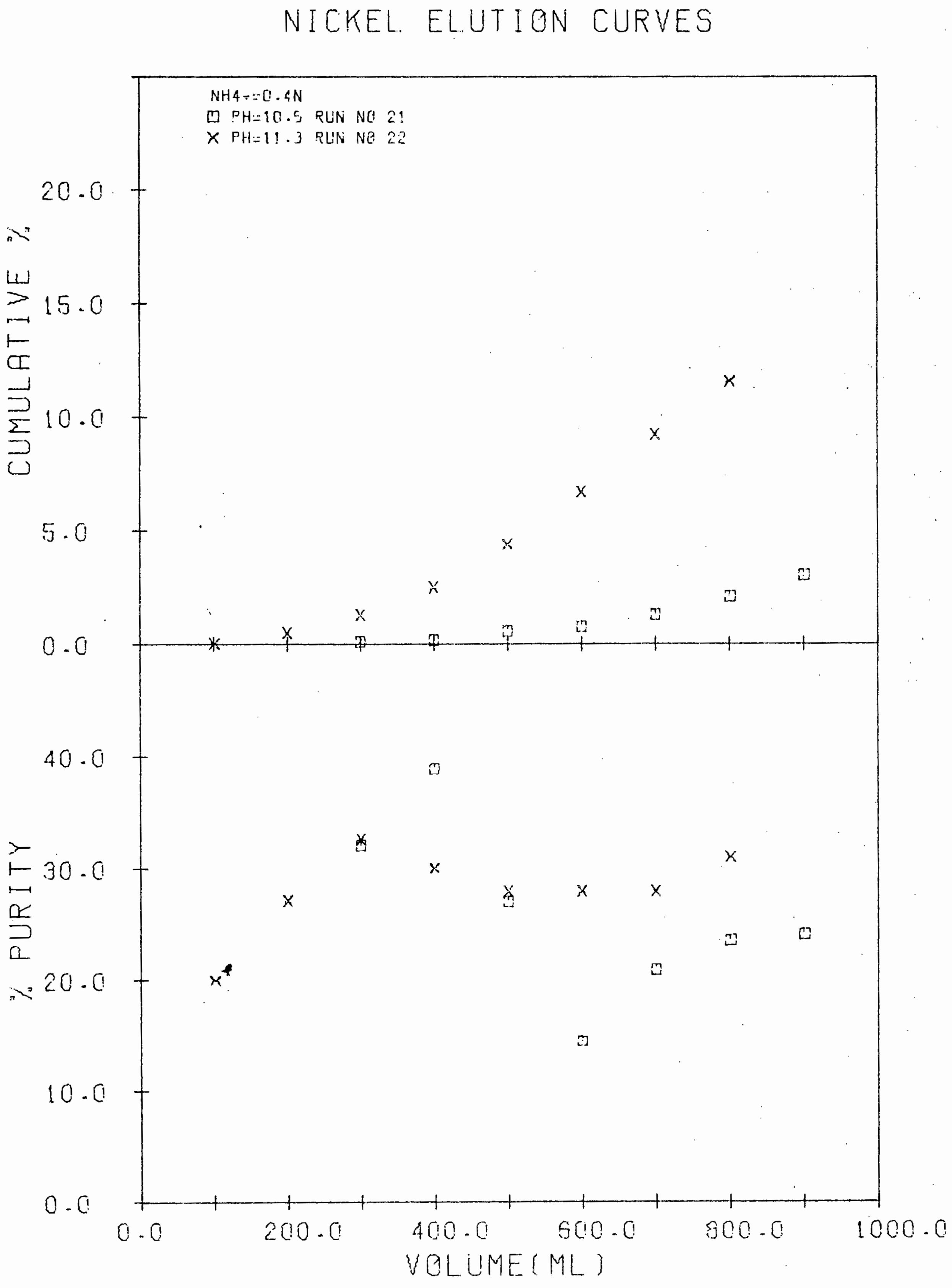
(A) the pH of the feed at constant NH^+ concentration;
(B) the concentration of NH_4^+ at constant pH.

(A) Effect of changing pH of feed.

The effect of changing the pH of the eluting feed had some influence on the rate of elution of the Ni from the loaded column (Figure 4.3). At the higher pH condition, the rate of elution was faster than the corresponding lower pH condition, but compared to the rate for Cu elution it was so slow as to be negligible. The increase in rate can only be due to the degree of complexation of the Ni. The Ni atom is capable of having 6 NH_3 molecules bonded to it as opposed to Cu's four [48]. The degree of ligand bonding affects the affinity of the complex for the resin and increases the ease of elution at higher NH_3 concentrations.

The percentage purity of the Ni eluted (Figure 4.3) does not change with a change in pH. The average purity lies somewhere between 20 - 40%, which is not satisfactory

FIGURE 4.3


NICKEL ELUTION CURVES
NH4+=0.4N
□ PH=10.5 RUN NO 21
X PH=11.3 RUN NO 22
CUMULATIVE %
20.0
15.0
10.0
5.0
0.0
% PURITY
40.0
30.0
20.0
10.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

if this method is to be used for the separation of Ni from Fe and Zn.

(B) Effect of changing NH_4^+ concentration in the feed.

A change in the NH_4^+ concentration gave the results anticipated for this parameter. As the NH_4^+ concentration controls the rate of elution, an increase in the concentration of this eluting material results in an increase in the rate of Ni elution (Figure 4.4). The low NH_4^+ concentrations cause virtually no Ni elution.

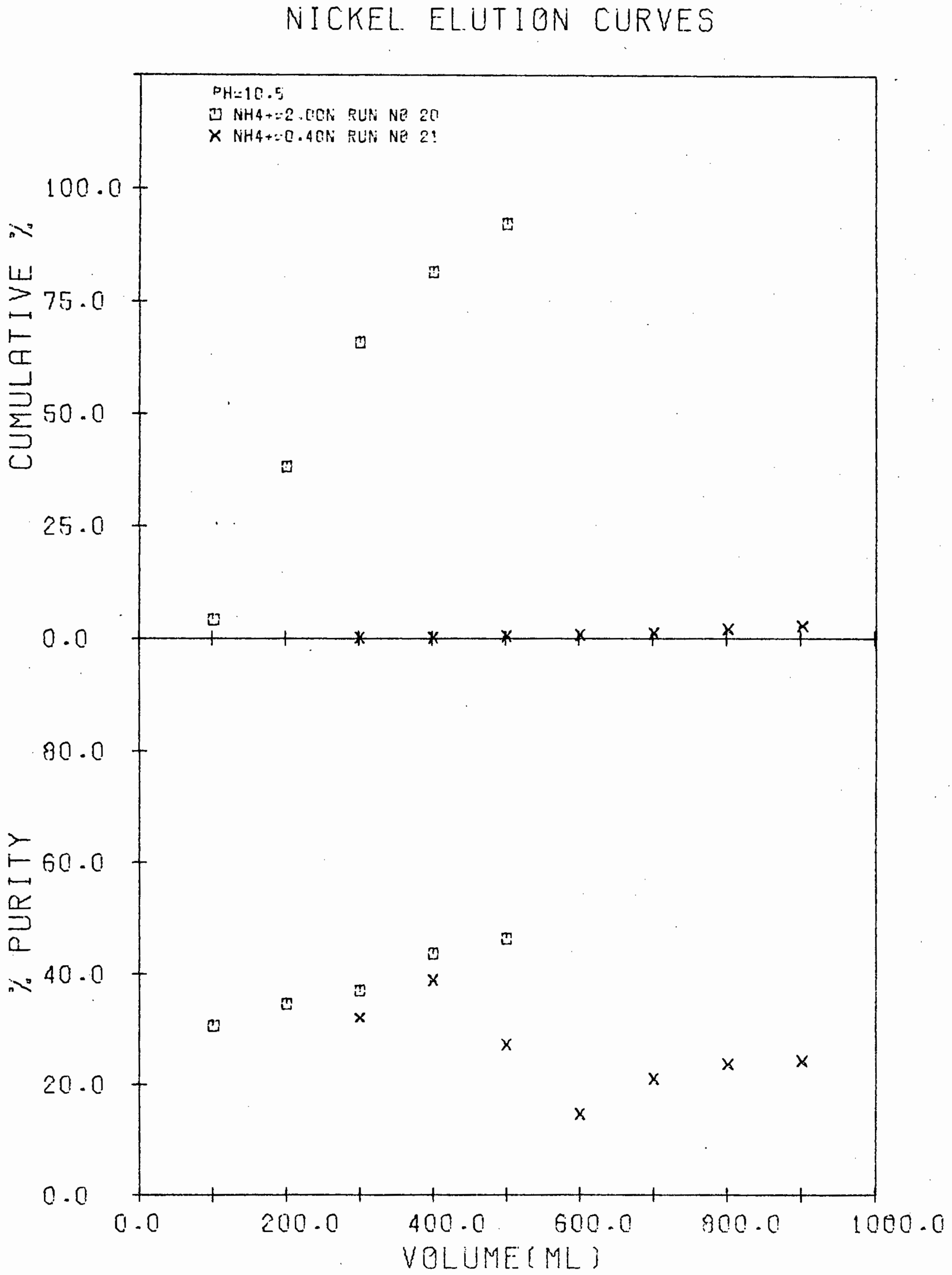
Although the rate of Ni elution at high elutant concentrations is high, the percentage purity of the samples is on average no different from that of the low elution rate curve (Figure 4.4). This indicates that the ability of the NH_4^+ ion to perform a separation of Ni from Fe and Zn is negligible, in fact, at an average Ni percentage purity of between 20 - 40% the NH_4^+ feed is not able to preferentially separate any of the three metals loaded. The Effluent Concentration vs Volume curve for Run No.20 (Figure 2, Appendix B) shows the virtually identical concentration of all three metals in the effluent, with no separation having occurred.

In order to achieve separation of Ni from Fe and Zn, it was decided to use EDTA (ethylene diamine tetra-acetic acid) as a complexing agent during the elution with NH_4^+. Successful separation on a chromatographic column with this technique had been achieved [49] using a 0,015M EDTA solution, adjusted to the required pH with NH_3. The results obtained for this experiment (Run No.25, Appendix A) are shown in Figure 5 (Appendix C) for the Ni elution.

As can be seen for the cumulative percentage curve, the rate of Ni elution was essentially constant although the percentage purity was only 30%. This is explained by noting that Ni is only being eluted by EDTA (hence constant cumulative percentage curve) and that Fe and Zn were eluted by the NH_4^+ in the feed.

Further experiments without NH_4^+ present, were not undertaken because the resulting Ni - EDTA complex formed

FIGURE 4.4


NICKEL ELUTION CURVES
PH=10.5
□ NH4+=2.00N RUN NØ 20
X NH4+=0.40N RUN NØ 21
CUMULATIVE %
100.0
75.0
50.0
25.0
0.0
% PURITY
80.0
60.0
40.0
20.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VØLUME(ML)

could not be broken under acidic conditions at a pH = 1. The cost of EDTA necessitated a recovery of this material, and due to the stability of the complex formed this could not be achieved.

4.32 Elution with Citric Acid and Ammonia

The attempted separation of Ni with NH_4^+ feed had shown this route to be inefficient, whilst the use of a complexing agent appeared to be better, the latter procedure was adopted for investigation. Citric acid was chosen for test as it had been successfully used by a number of workers for the separation of various rare earths [50,51,52]. The cost of this complexing agent is relatively low and the ability of the complexes to be broken by acidic conditions with consequent citric acid precipitation had been demonstrated [53,54].

The ability of citric acid to form complexes with Ni, Fe and Zn had also been utilised when a partial separation was achieved by eluting with acid after the relative complexes had been loaded onto an anion column [55], whilst the associated hydroxy acids [56,57] (malonic and tartaric) had been successfully used for metal separations.

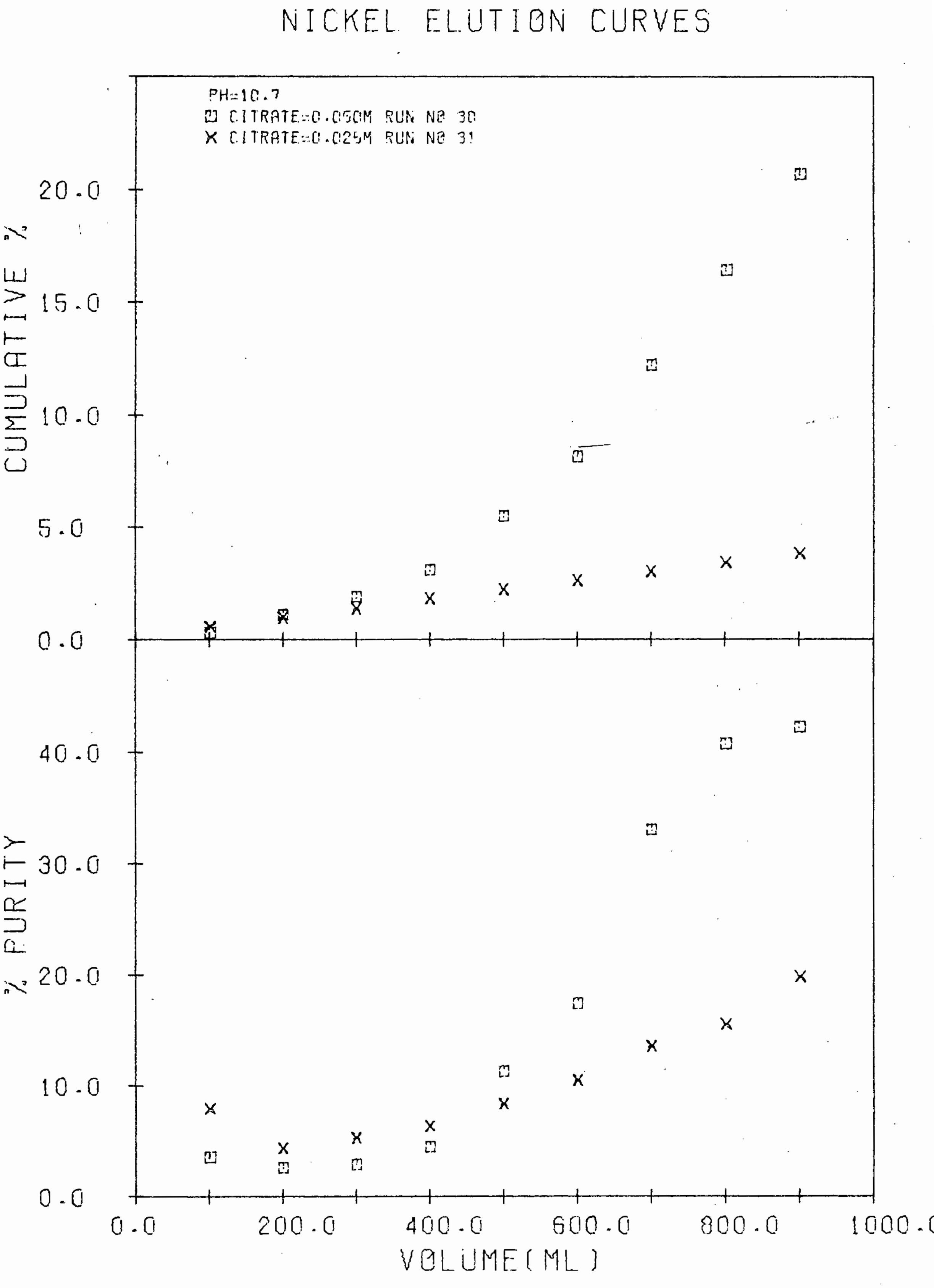
The experimental work conducted with citric acid as a complexing elutant involved determining the optimum conditions for the separation of nickel. The two parameters that were varied in this determination were

(a) the citric acid concentration in the eluting feed at constant pH;
(b) the pH of the eluting feed at constant citric acid concentration.

The results shown in Figure 4.5 for the elution of Ni from the loaded column at two different citric acid concentrations (0,025M and 0,05M) show the effect of a change in this parameter.

The rate of elution as shown in the cumulative percentage vs volume curve is as would be expected in that the higher concentration of citric acid results in a faster rate

FIGURE 4.5


NICKEL ELUTION CURVES
PH=10.7
☐ CITRATE=0.050M RUN NO 30
X CITRATE=0.025M RUN NO 31
CUMULATIVE %
0.0
5.0
10.0
15.0
20.0
% PURITY
0.0
10.0
20.0
30.0
40.0
0.0
200.0
400.0
600.0
800.0
1000.
VOLUME(ML)

of elution. The percentage purity of the eluted Ni shows a result contrary to expectation. The higher concentration feed results in the average purity of the samples being higher. The only conclusion that can be drawn from this is that there is some optimum citric acid concentration that will achieve a maximum purity of eluted Ni, at a reasonably good rate of elution.

The effect of a pH change was determined by conducting the elution of Ni from the loaded column at a pH = 9,8 whilst the citric acid concentration was kept constant at the previously determined value of 0,05M. The results of the lower pH feed are contrasted to the previous run in Figure 4.6. The results show the dramatic effect of reducing the pH. The rate of elution of Ni is significantly increased by the change as well as the purity of the eluted sample. The reason for this change is due to the complexing ability of citric acid with Ni under these pH conditions (Section 2.5). The decrease in pH resulted in a three-fold increase in the rate of elution whilst producing a six-fold increase in the average purity of the eluted samples (Table 4.4).

In order to determine the effect of increasing the citric acid concentration at the optimum pH, a feed of 0,1M citric acid at pH = 9,8 was tried as an eluent. The results (Figure 4.7) show an anomaly, in that the higher feed concentration does not result in a higher elution rate (contrary to the results in Figure 4.5).

Another unexpected result is that at the higher feed concentration, the percentage purity shows a significant decrease. The only conclusion that can be drawn from this anomaly is that when the citric acid concentration is greater than a certain fixed amount, the excess over and above that used for Ni elution, is utilised for the elution of the other metals loaded on the column. This indicates that a certain maximum rate of elution of the metal under optimum conditions is possible, and that any change in these conditions will not improve the rate of elution, but will lower the purity of the metal eluted.

FIGURE 4.6

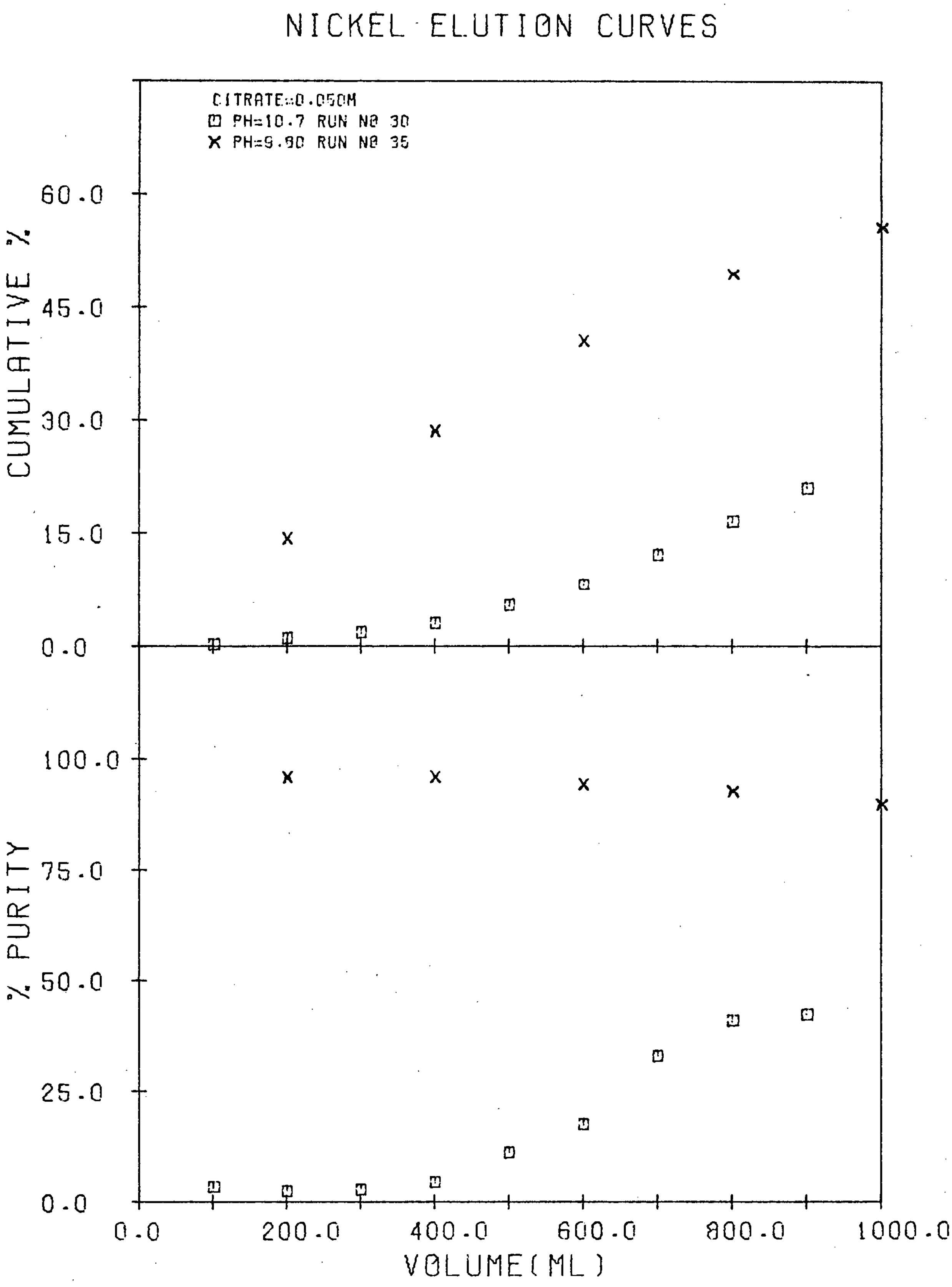
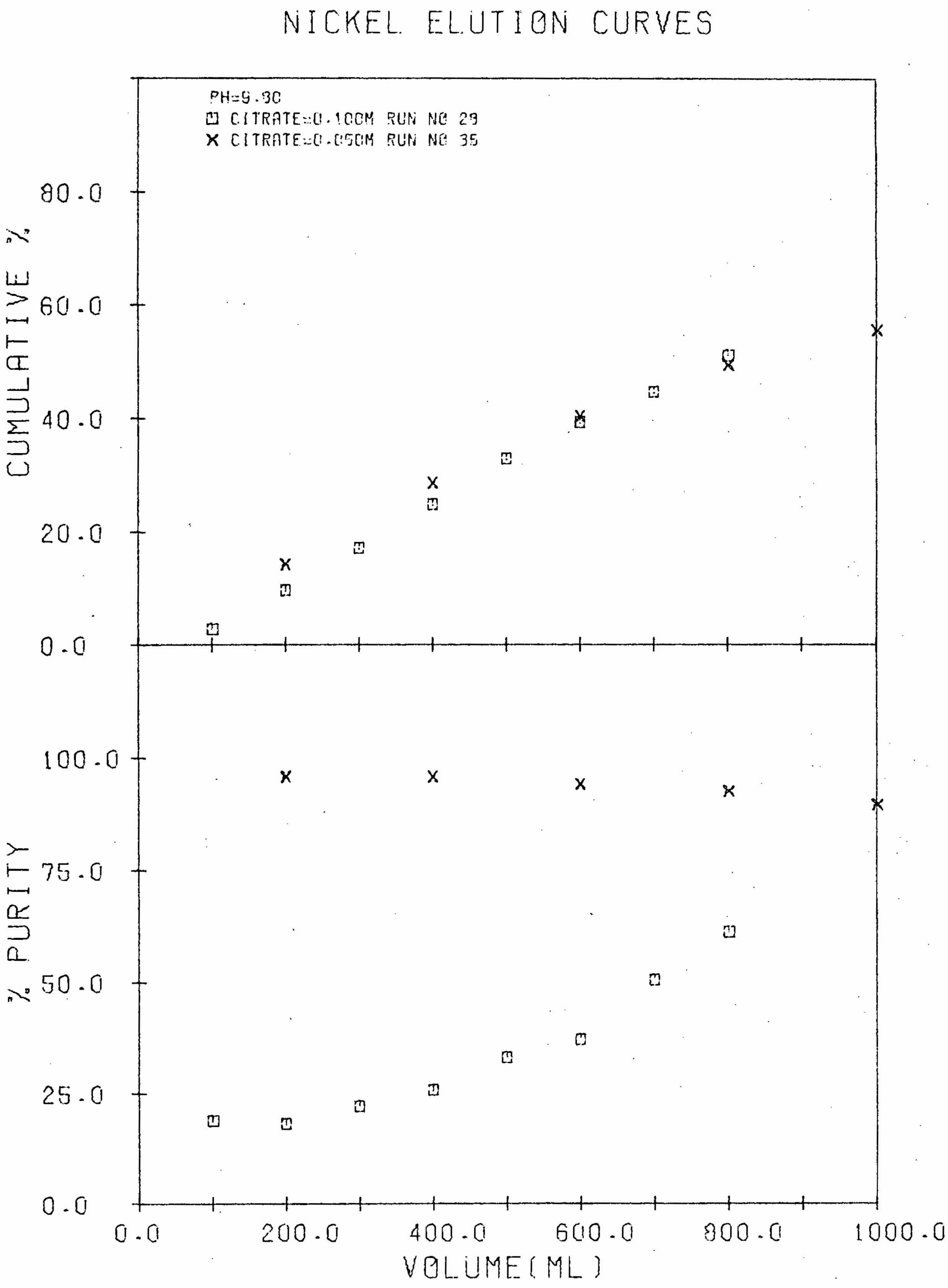

NICKEL ELUTION CURVES
CITRATE=0.050M
□ PH=10.7 RUN NO 30
X PH=9.90 RUN NO 35
CUMULATIVE %
60.0
45.0
30.0
15.0
0.0
% PURITY
100.0
75.0
50.0
25.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

FIGURE 4.7


NICKEL ELUTION CURVES
PH=9.30
⊡ CITRATE=0.100M RUN NO 29
X CITRATE=0.050M RUN NO 35
CUMULATIVE %
80.0
60.0
40.0
20.0
0.0
% PURITY
100.0
75.0
50.0
25.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

The elution data for Ni is summarised in Table 4.4 which shows distinctly that the best elution conditions appear to be a pH of 9,8 and a citric acid concentration of 0,05M.

Conditions	Cumulative % Eluted				Average % Purity			
Citric acid conc.	0,025M	0,05M	0,05M	0,10M	0,025M	0,05M	0,05M	0,1M
pH	10,7	10,7	9,8	9,8	10,7	10,7	9,8	9,8
After 400 ml of feed	3,5	6,1	29	25	5,9	3,3	96	21
After 800 ml of feed	6,8	16,1	50	51	8,8	14,5	95	33

TABLE 4.4

4.4 SEPARATION AND ELUTION OF IRON

4.41 Elution with Citric acid and Ammonia

Based on the results obtained for the successful elution of Ni with the above feed, this technique was tried for the elution of Fe. The results showed that two completely different sets of conditions were necessary in order to separate and elute ferrous and ferric iron from the resin. This section will deal with the elution of Fe^{3+}, which experiment showed, was eluted before the elution of Ni. The elution of Fe^{3+} before Ni was essential to obtain pure samples of either due to the greater complexing ability of the Fe^{3+} ion as opposed to the Ni^{2+} ion (Section 2.5).

The results for the elution of Fe^{3+} at a citric acid concentration of 0,025M (Figure 4.8) but different pH conditions show that the higher pH (pH = 10,7) produces a higher average purity of sample. The effect on the elution rate when changing the pH at constant citric acid concentrations is negligible.

Changing the latter concentration at pH = 10,7 (Figure 4.9) shows a better elution rate for the 0,05M acid concentration as compared to the 0,025M acid concentration. The

FIGURE 4.8

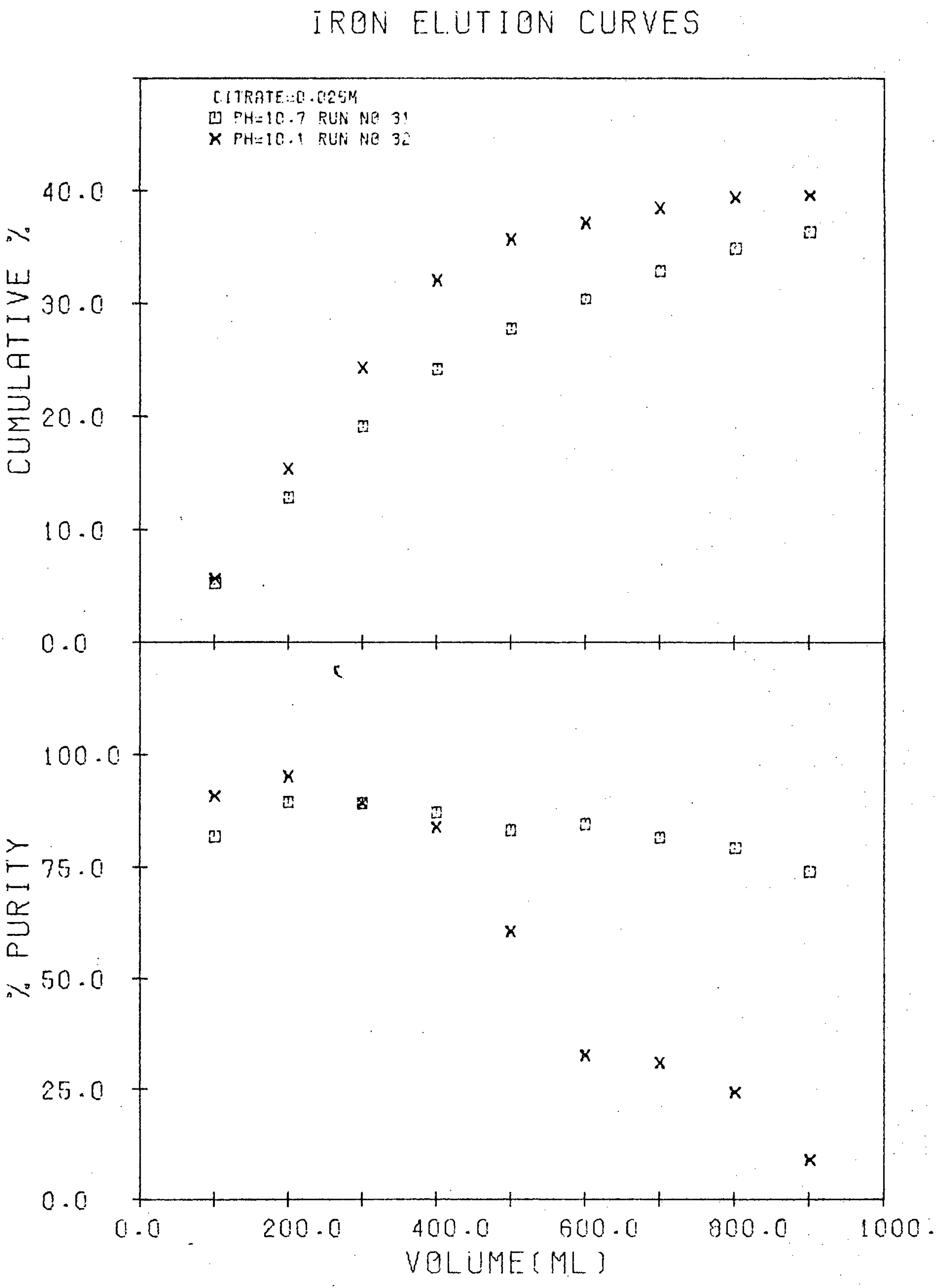
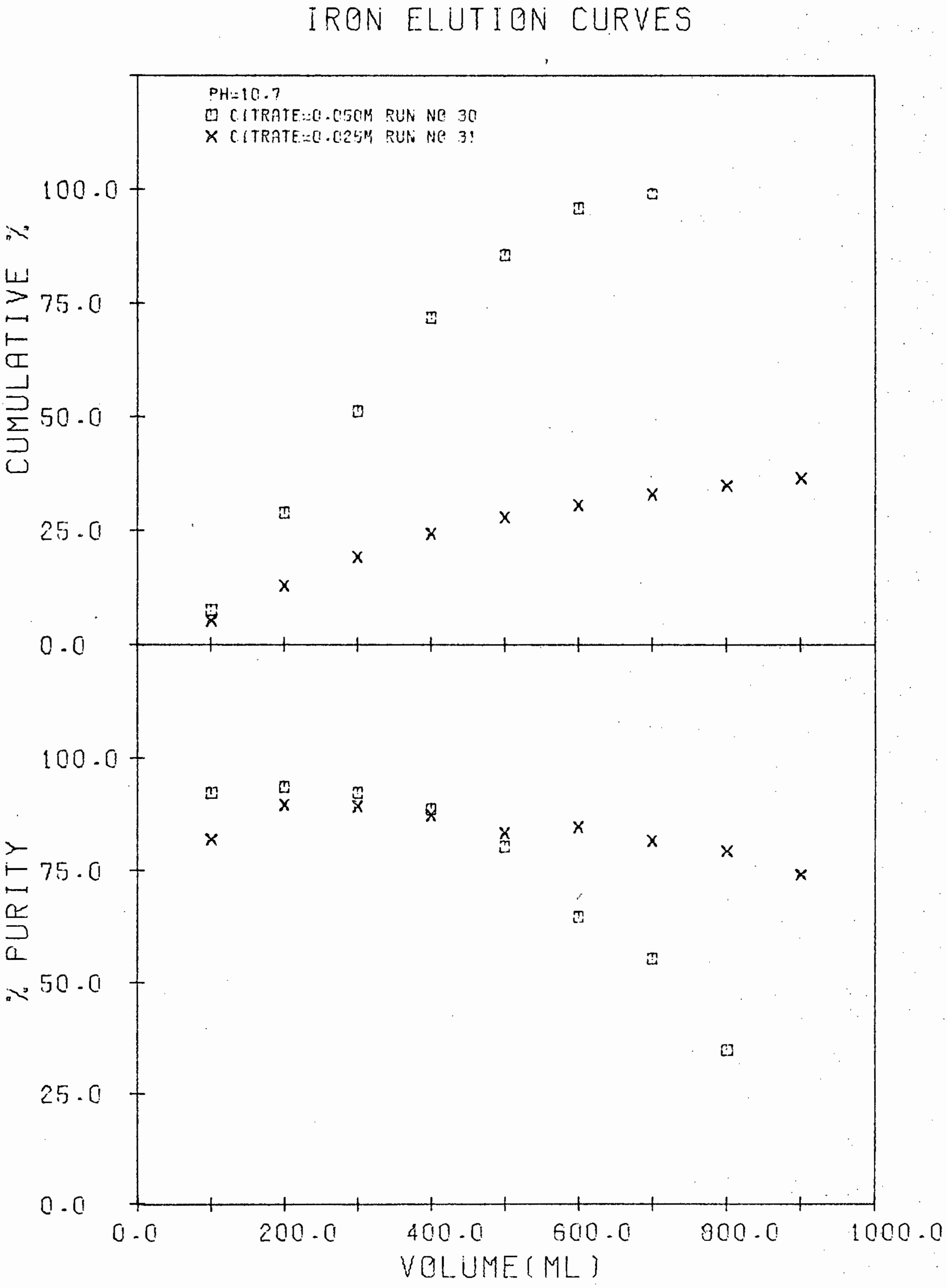

IRON ELUTION CURVES
CITRATE=0.025M
□ PH=10.7 RUN NO 31
X PH=10.1 RUN NO 32
CUMULATIVE %
0.0
10.0
20.0
30.0
40.0
% PURITY
0.0
25.0
50.0
75.0
100.0
0.0
200.0
400.0
600.0
800.0
1000.
VOLUME(ML)

FIGURE 4.9


IRON ELUTION CURVES
PH=10.7
□ CITRATE=0.050M RUN NO 30
X CITRATE=0.025M RUN NO 31
CUMULATIVE %
100.0
75.0
50.0
25.0
0.0
% PURITY
100.0
75.0
50.0
25.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

samples show an improved purity for a greater cumulative percentage eluted at the higher citric acid concentration.

The results for this set of runs show that 0,05M citric acid is the preferred concentration, but that a higher pH condition (which was not investigated due to the economic implications of NH_3 addition) might result in an even better purity sample. The average percentage purity of the highest pH run was 89% for the elution of 80% of the Fe^{3+} loaded onto the column.

The conditions for the elution of Fe^{2+} from the column using citric acid were not determined, because Zn elution occurred before Fe^{2+}. The latter could then be eluted during the regeneration of the column using a 20% H_2SO_4 regenerant solution.

4.5 SEPARATION AND ELUTION OF ZINC

4.51 Elution with Citric acid and Ammonia

The optimum conditions for the elution of Zn from the resin were determined by eluting the metal from the loaded column under two different citric acid concentrations at a constant pH (Figure 4.10). The results for these runs show that increased rate of elution is achieved with the higher acid concentration, whilst the percentage purity of the samples is just as random for both cases.

Although the rate of elution is increased for the one condition, it is still so low (6% cumulative elution after 800 ml of feed) as to be almost negligible.

Another set of runs was conducted in order to determine the effect of a pH change at constant citric acid concentration. The results obtained (Figure 4.11) show very vividly how both the rate of elution and the percentage purity of the samples is affected by a decrease in pH from 10,7.

As the pH is decreased, so the degree of Zn complexation increases and consequently the rate at which Zn elution

FIGURE 4.10

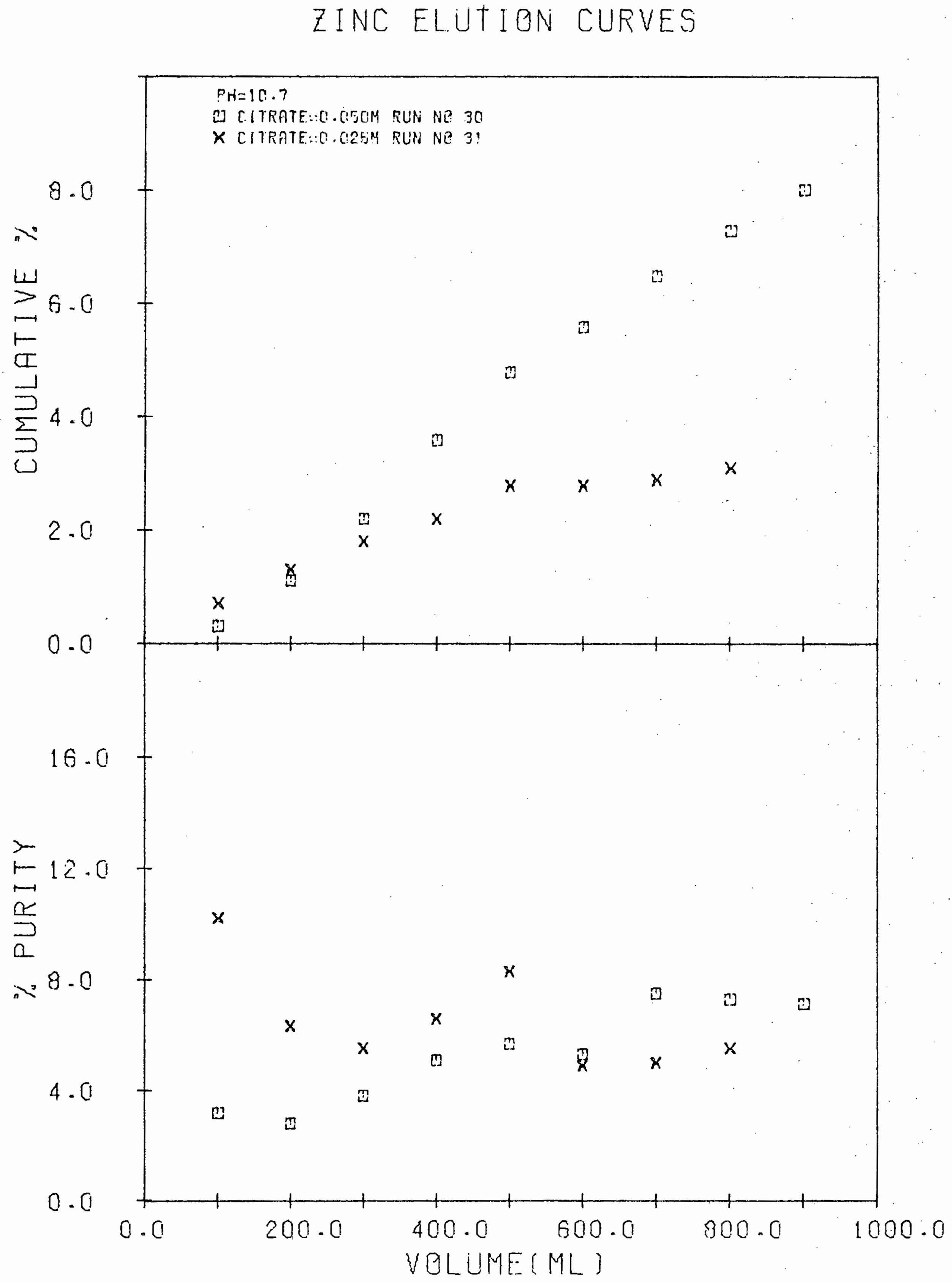
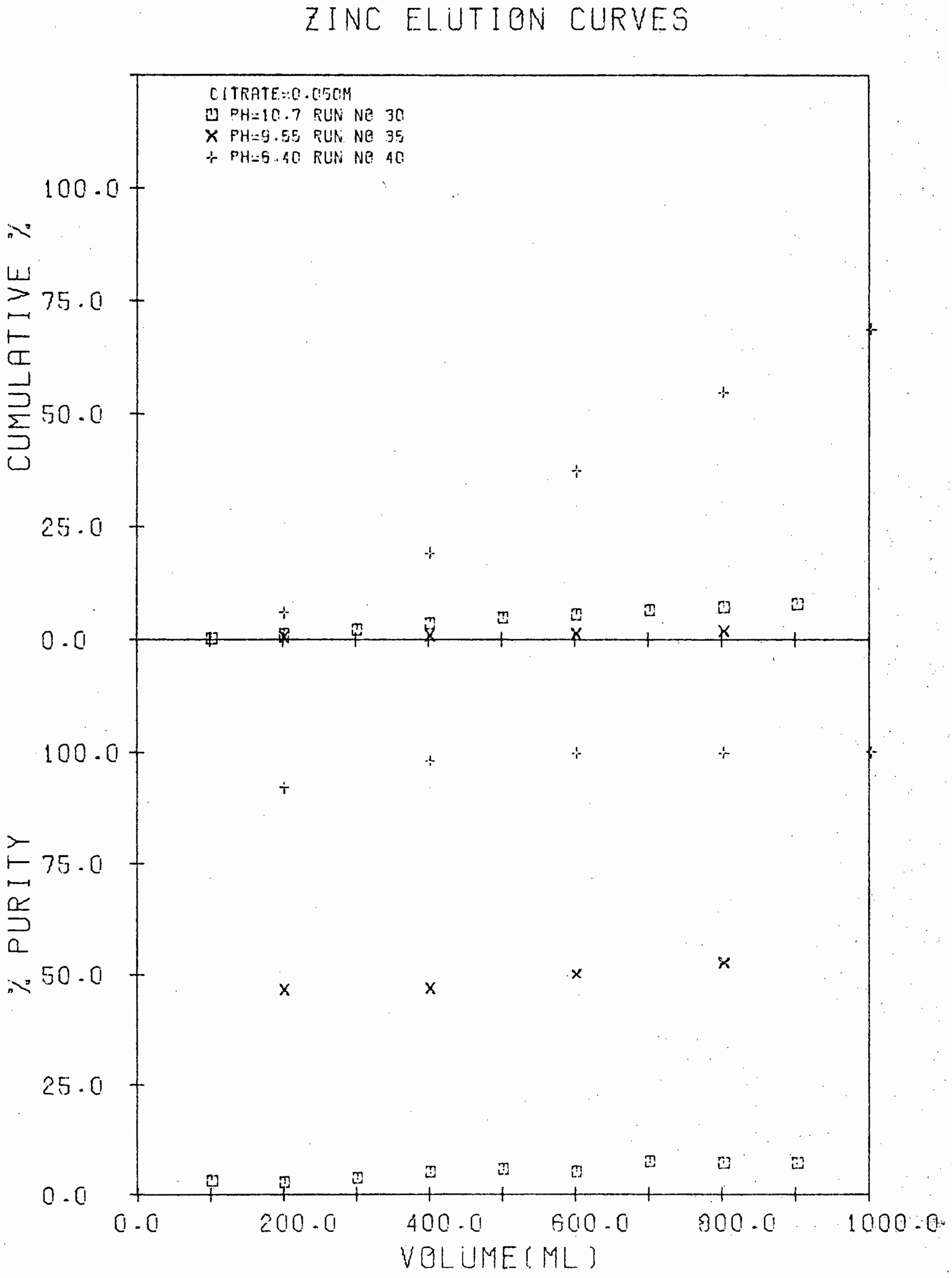

ZINC ELUTION CURVES
PH=10.7
⊡ CITRATE=0.050M RUN NO 30
X CITRATE=0.025M RUN NO 31
CUMULATIVE %
8.0
6.0
4.0
2.0
0.0
% PURITY
16.0
12.0
8.0
4.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

FIGURE 4.11


ZINC ELUTION CURVES
CITRATE=0.050M
□ PH=10.7 RUN NO 30
× PH=9.55 RUN NO 35
+ PH=6.40 RUN NO 40
CUMULATIVE %
100.0
75.0
50.0
25.0
0.0
% PURITY
100.0
75.0
50.0
25.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

occurs. The maximum rate was obtained at the lowest pH used for the elution - pH = 6,4.

The percentage purity curves show a trend completely analogous to the cumulative percentage curves. The lower the pH the higher the purity of the samples obtained, with an average percentage purity of 99% being attained at a feed pH = 6,4.

TABLE 4.5

COMPARISON OF ZINC ELUTION AFTER 800ml OF FEED

pH	10,7	9,55	6,4
Cumulative %	4	8	55
% Purity	7,0	53	99

The optimum conditions for the Zn elution and separation would appear to lie at a pH of 6,4 and a citric acid concentration of 0,05M (Table 4.5.)

4.6 ADSORPTION OF FREE AND COMPLEXED CYANIDES

The adsorption of CN^- on the strong base anion column used for the study presented certain problems. The affinity for the resin of free and complexed CN^- differs considerably in relation to that of OH^- and Cl^-.

The selectivity sequence for the resin used indicates that only OH^- is less selective than CN^- [58], and that this is only the case when the CN^- enters the resin as hydrocyanic acid.

Loading of a Cl^- form of the anion resin with a solution containing CN^- together with the metals Cu, Fe, Ni, Zn (Run No. 37, Appendix A) showed that a constant breakthrough of CN^- occurred. The CN^- concentration in the effluent from the column represented 25% of the feed concentration. This confirms the work of Kunin and McGarvey [58] but contradicts that of Inczedy [59] et al, who found breakthrough to be earlier when the resin was in the Cl^- form, but not to be immediate.

The metal cyanide complexes have been found more selective than most of the simple anions by most researchers [60,61,62], to the extent that poisoning of the anion resin occurs when these complexes are loaded.

The ability for complex cyanides to load onto the Cl^- form of the anion resin was found in Run No.37 (Appendix A) when a mixed feed was loaded onto the resin. A total of 75% of the CN^- fed was held by the resin, and all of this CN^- was presumed to be complexed with the metals in the feed.

When the corresponding feed to the above was loaded onto the OH^- form of the anion resin, no early breakthrough of CN^- occurred. The treated water had less than 0,5ppm CN^- after passing through the resin (Run No.38, Appendix A).

In order to successfully treat CN^- containing waters by this method, care must be taken to ensure that the breakthrough of CN^- (which will occur before that of any other ion) is detected as early as possible. A two column system, as outlined by Bellobono [63], for anion removal would in fact be more satisfactory, with both columns being regenerated when breakthrough of the next most selective ion (generally Cl) occurs in the first column. This will ensure that CN^- leakage and breakthrough in the treated water is eliminated.

4.7 ELUTION OF FREE AND COMPLEXED CYANIDES

The elution of free CN^- from the loaded column presents no problem. Tallmadge and Bellobono have found a 5% NaOH solution to be perfectly acceptable for this regeneration.

The results obtained in the elution of total CN^- from the resin showed that using a 15% NaOH solution, only 35% of CN^- loaded could be eluted. The non-eluted CN^- was presumed to be complexed with the metals.

In order to achieve elution of complex CN^-, Goldblatt found a 0,2N H_2SO_4 feed to be most effective, but required 30 bed volumes of feed to achieve 80% elution. Tallmadge obtained 100% elution using 13,8 bed volumes of 5 wt% H_2SO_4. The H_2SO_4 feed achieved elution by splitting the complex metal CN^- into a free cationic metal and free CN^- anion.

The results obtained using this method for complex CN^- elution showed that a 20 wt% H_2SO_4 feed (2,5 B.V.) followed by 2,5 B.V. of 15% NaOH achieved only a 57% elution of CN^- loaded onto the resin, an increase of 22% on the CN^- that is eluted only with NaOH.

Burstall et al found in his work that no one eluting agent was completely successful in the elution of all metal-complexes. Each complex required a different eluting technique and they found that 0,2N HCl would achieve better than 90% elution of Zn and Ni complexes, but less than 30% of Fe and Cu complexes, whilst acetone - HCl mixtures reversed this effect.

It appears from the experimental results obtained in this work and also that of other authors, that CN^- complexes cannot be effectively eluted from a strong base anion resin.

4.8 TREATMENT OF WATER CONTAINING CHROMATE

The efficiency of chromate removal on a strong base anion exchanger has been demonstrated by many workers in this field [64,65,66]. In the work reviewed, optimum loading conditions were found to be at a pH = 4-5, whilst elution of the resin was undertaken with either NaCl, NaOH or a mixture of the two [67,68,69]. The chromate solution was loaded onto a column in either the Cl^- or the OH^- form.

The experiments showed that the initial form of the anion column had no appreciable effect on the chromate breakthrough. Loading onto both the Cl^- and OH^- forms of the resin showed that after a fixed amount of Cr^{6+} had been loaded, the effluent concentrations of Cr^{6+} was 4,6ppm and 3,4ppm respectively.

The elution of the loaded chromate was undertaken by using either NaOH or H_2SO_4 as the eluting agent. The results obtained showed that either method was acceptable, but that the latter was advantageous where Cr recovery was required. The NaOH eluted the loaded Cr as a chromate whilst the H_2SO_4 in conjunction with the resin resulted in a reduction of the Cr from a hexavalent to a trivalent state. The latter form is easy to remove from the regenerant stream by raising the pH above 7, when the hydroxide compound formed precipitates.

Both elution methods give the same Cr recovery (>80% of the Cr loaded) and are thus equally efficient as eluting agents. The H_2SO_4 has the added advantage when Cr recovery is required.

4.9 PREDICTION OF OPTIMUM CONDITIONS FOR METAL SEPARATION USING CITRIC ACID

A computer program was developed to predict the optimum pH conditions at which to perform the separations of the metals loaded onto the cation column. The theory used in the program is that outlined in Section 2.5.

The distribution coefficient of the metal between the resin and the aqueous phase (D_M) was calculated at different pH's for a constant citric acid concentration of 0,05M. The effect of complexation with other ligands in the system (hydroxide, ammonia) was taken into account during the calculation of the distribution coefficient.

The results of the calculation of each metal (Cu, Fe^{2+}, Fe^{3+}, Zn) (Appendix G) show the effect of the complexing ability of the other ligands in the system. The effect of citrate complexation on each of the metals is constant above pH 6,50 (complete dissociation of citric acid occurs at this point) whilst the effect of NH_3 and OH^- complexation increases steadily with pH above pH 7,0.

All the metals, except Ni, show a constant distribution coefficient from pH 5,0 - 9,0 (Figure 4.12). In this pH range, the citrate complexing ability is totally utilised whilst that of NH_3 and OH^- does not influence the distribution.

FIGURE 4.12

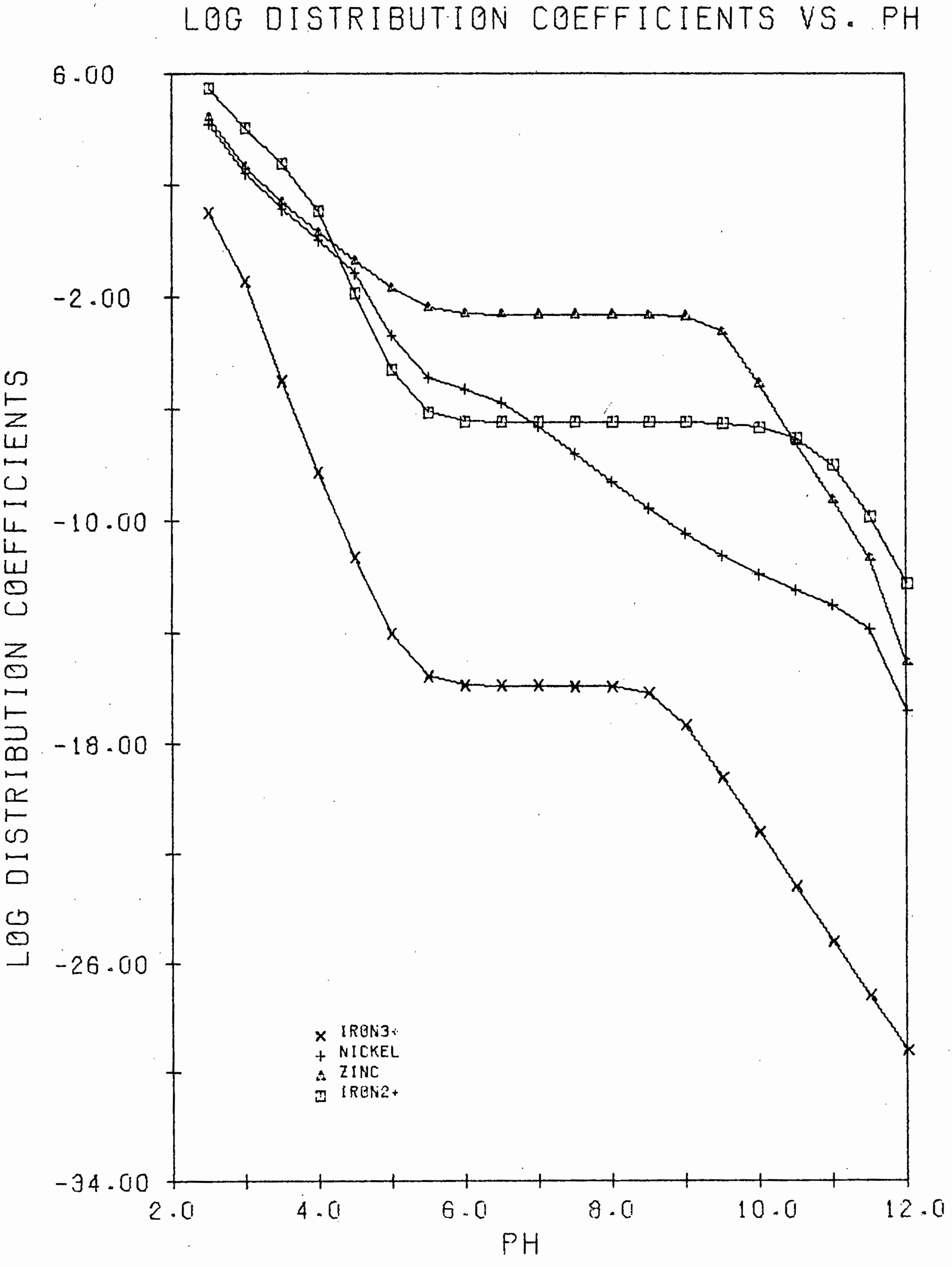
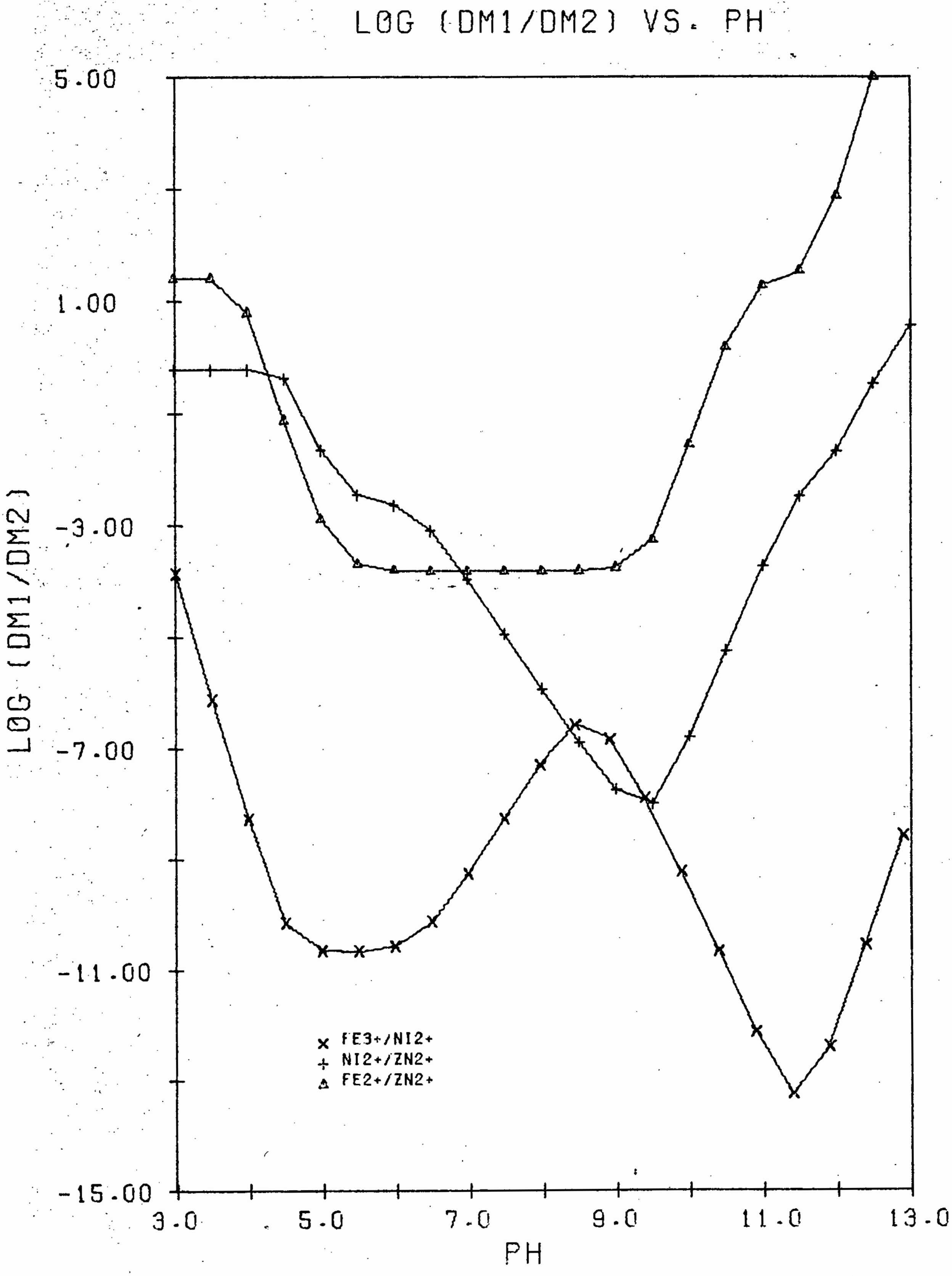

LOG DISTRIBUTION COEFFICIENTS VS. PH
6.00
-2.00
-10.00
-18.00
-26.00
-34.00
LOG DISTRIBUTION COEFFICIENTS
2.0
4.0
6.0
8.0
10.0
12.0
PH
× IRON3+
+ NICKEL
△ ZINC
⊡ IRON2+

FIGURE 4.13


LOG (DM1/DM2) VS. PH
LOG (DM1/DM2)
5.00
1.00
-3.00
-7.00
-11.00
-15.00
3.0
5.0
7.0
9.0
11.0
13.0
PH
× FE3+/NI2+
+ NI2+/ZN2+
△ FE2+/ZN2+

At pH > 9,0 a sharp increase in the distribution coefficient can be seen. The anomally with Ni can only be attributed to its greater ability to complex with NH_3, and thus a much earlier display of the NH_3-complex is shown.

The ratio's of the distribution coefficients at each pH was next calculated in order to determine either the maxima or minima of the ratio's. This indicates the optimum condition for separation (Section 2.5). The results obtained from the calculation (Table 5, Appendix G) are plotted in Figure 4.13.

The curves obtained, show a definite global minimum in each case. The relevant pH at the minimum obtained for each curve was then determined and compared with the experimentally determined pH for the separation.

The simulated results agree favourably with those found in practice as can be seen from Table 4.6.This would indicate that optimum conditions can be predicted for other organic acids. This has been demonstrated by Inczedy [70] using oxalic acid in the separation of Ni from Co.

4.10 PREDICTION OF BREAKTHROUGH CONDITIONS DURING COLUMN LOADING

The theory outlined in Section 2.4 was used in a mathematical simulation of the loading conditions of the strong acid cation exchanger. A computer program was written to sequentially calculate the composition profiles within the resin bed, assuming in all cases that the bed was initially in the hydrogen form prior to feed being introduced.

The input data necessary to calculate the profiles is listed in Table 4.7. The program was written in order to evaluate the conditions existing within the bed for a feed containing from two to six components, provided that the input data was introduced to obey the Alphabet Rule.

The point at which the composition of each component dropped to zero was calculated by taking the mean of the value at the beginning of the next plateau zone.

TABLE 4.6

COMPARISON OF OPTIMUM pH CONDITIONS FOR METAL SEPARATION

Component	Experimentally Determined pH	Calculated pH
Iron 3+	10,7	11,4
Nickel	9,8	9,8
Zinc	6,4	6-9

TABLE 4.7

```
                    FEED PARAMETERS
                    ---- ----------
COMPONENT     PPM   EQUIVALENT SELECTIVITY    CHARGE
                     FRACTION  COEFFICIENT
 NICKEL      100.0     .004         3.094      2.000
 COPPER      100.0     .018         3.031      2.000
  IRON       100.0     .016         2.756      2.000
  ZINC       100.0     .014         2.732      2.000
 SODIUM      100.0     .726         1.559      1.000
HYDROGEN     100.0     .223         1.000      1.000

     PH                        2.00
EXCHANGER CAPACITY             1.980  MEQ/ML
SOLUTION CONCENTRATION          .0449N
```

A typical plot of the concentration profiles obtained within the resin bed is shown in Figure 4.14. This plot only shows the plateau zones which exist, the transition zones occur where each step change in component concentration is indicated. As can be seen in Figure 4.14 and from the selectivity data in Table 4.7 the first component to drop to zero is the most selective component viz. Nickel. At the same point, an increase in the concentrations of all other components occurs, the greatest increase being that of the next most selective component, copper. Since the calculations were only performed for a loading operation, and as there was always hydrogen ion in the feed stream, no component composition rose from zero.

Table 4.8 shows how the composition of each of the components varies within a transition zone. As can be seen from the figures, the rate of increase in composition of each of the components is dependent upon their relative selectivities.

In order to determine the breakthrough volume of any of the components, it is only necessary to determine the throughput parameter 'T' at the point in the bed at which the particular component goes to zero. Since

$$T = \frac{C_o(V - v\varepsilon)}{vQ\rho} \qquad \text{(a)}$$

then by rearranging

$$V = \frac{TvQ\rho}{C_o} + v\varepsilon \qquad \text{(b)}$$

where V - volume of feed.
Thus, for a constant bed volume and specific feed conditions the breakthrough volume of any component can be determined.

The results obtained in the simulation studies, and those from the corresponding experimental results are summarised in Table 4.9. From the calculated and experimental breakthrough volumes, it can be seen that for certain of the

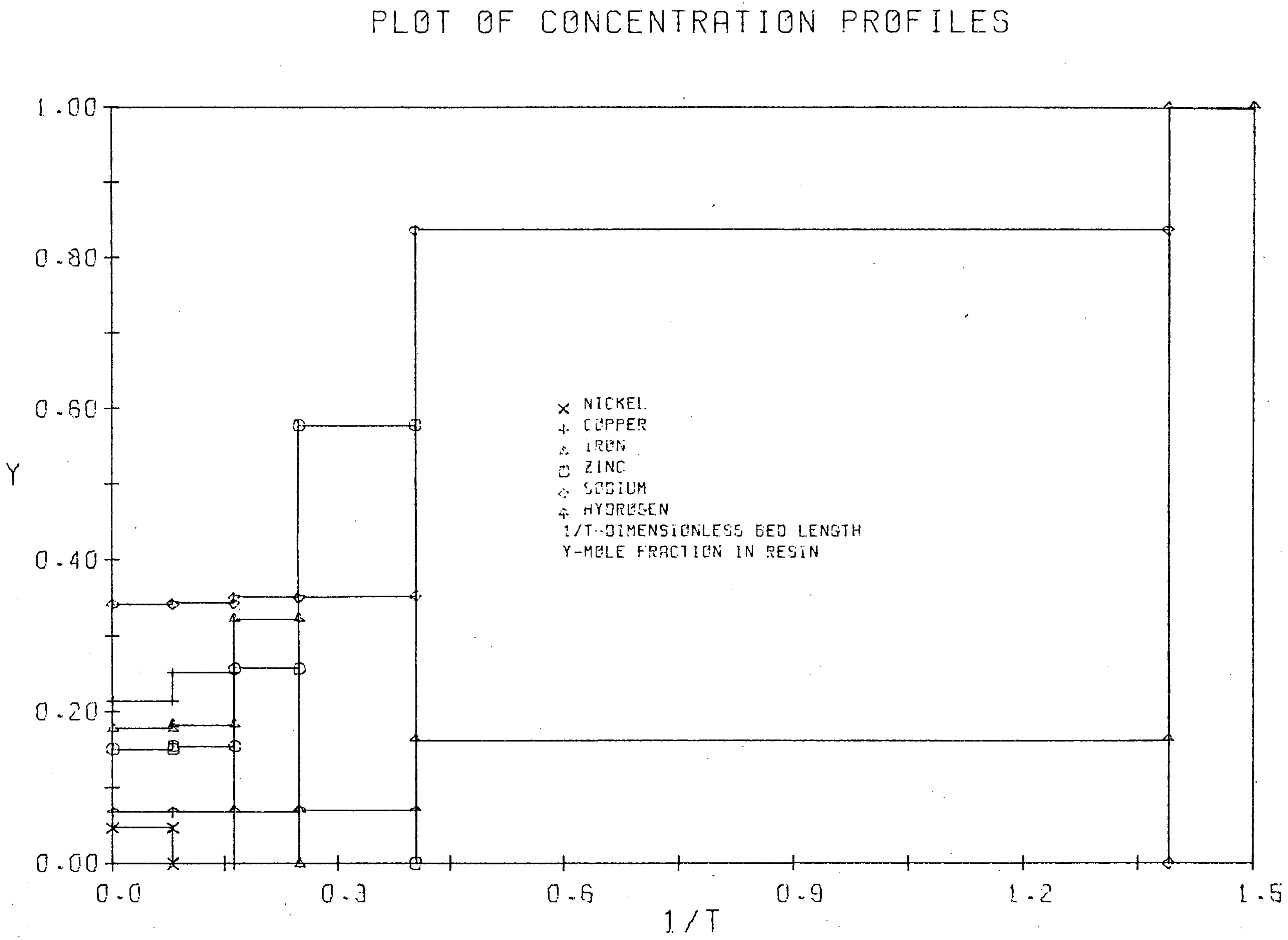

PLOT OF CONCENTRATION PROFILES
1.00
0.80
0.60
0.40
0.20
0.00
Y
0.0
0.3
0.6
0.9
1.2
1.5
1/T
× NICKEL
+ COPPER
△ IRON
□ ZINC
◇ SODIUM
⊕ HYDROGEN
1/T-DIMENSIONLESS BED LENGTH
Y-MOLE FRACTION IN RESIN

FIGURE 4.14

CONCENTRATION PROFILES IN THE BED

EQUIVALENT FRACTION IN THE LIQUID PHASE

NICKEL	COPPER	IRON	ZINC	SODIUM	HYDROGEN	ZONE NO.& TYPE
.0038	.0175	.0159	.0136	.7264	.2227	1ST PLATEAU
.0013	.0195	.0162	.0138	.7265	.2227	1ST TRANSITION
	.0205	.0164	.0139	.7265	.2227	2ND PLATEAU
	.0167	.0184	.0155	.7267	.2227	2ND TRANSITION
	.0130	.0205	.0170	.7268	.2228	2ND TRANSITION
	.0093	.0226	.0185	.7269	.2228	2ND TRANSITION
	.0057	.0246	.0200	.7270	.2228	2ND TRANSITION
	.0021	.0265	.0214	.7271	.2228	2ND TRANSITION
		.0277	.0223	.7272	.2228	3RD PLATEAU
		.0256	.0244	.7272	.2228	3RD TRANSITION
		.0234	.0266	.7272	.2228	3RD TRANSITION
		.0212	.0287	.7272	.2228	3RD TRANSITION
		.0191	.0309	.7272	.2228	3RD TRANSITION
		.0169	.0330	.7272	.2228	3RD TRANSITION
		.0148	.0352	.7272	.2228	3RD TRANSITION
		.0126	.0373	.7272	.2228	3RD TRANSITION
		.0105	.0395	.7272	.2228	3RD TRANSITION
		.0083	.0416	.7272	.2228	3RD TRANSITION
		.0062	.0438	.7272	.2228	3RD TRANSITION
		.0040	.0459	.7272	.2229	3RD TRANSITION
		.0019	.0480	.7272	.2229	3RD TRANSITION
			.0497	.7274	.2229	4TH PLATEAU
			.0129	.7584	.2287	4TH TRANSITION
			.0022	.7674	.2304	4TH TRANSITION
				.7692	.2308	5TH PLATEAU
				.5313	.4687	5TH TRANSITION
				.3339	.6661	5TH TRANSITION
				.1674	.8326	5TH TRANSITION
				.0251	.9749	5TH TRANSITION

TABLE 4.8

TABLE 4.9

BREAKTHROUGH VOLUME COMPARISON

Run	Breakthrough	Volume (ml)
No.	Experimental	Calculated
2	400	1050
3	200	740
6	12000	11500
17	350	288
25	600	510
29	600	490
39	3800	3230

runs the breakthrough volume of the least selective feed component can be predicted with considerable accuracy. The inability of the simulation to accurately predict the results for Run No.2, is due to the fact that the feed composition is extremely high. This would result in the non-attainment of equilibrium during the loading operations. Since the simulation relies on equilibrium being attained at every point within the exchanger bed, this explains the discrepancy. For dilute solutions the simulation and experimental loading agree.

The experimental loading results together with the full simulation results for the corresponding feed conditions are in Appendix D.

CHAPTER 5

CONCLUSIONS

This study has shown that a plating waste wash solution can be successfully treated to produce water of a sufficiently high quality to satisfy the specifications of any national water body.

The treated water can be disposed of into any local sewer or river without it endangering the ecology, or it can be reused in the plating operation for solution preparation. Due to the high quality of the treated water it is admirably suited to the latter operation.

During the loading operation, the cation column loading characteristics were investigated in order to compare experimental breakthrough results with predicted figures. The prediction accuracy for the loading of dilute solutions is very good, and enables column scale-up to be performed more accurately.

The results obtained in this study indicate further that a strong acid ion exchange resin can be successfully utilised not only for the removal, but for the separation and recovery of metals in a relatively pure state. The separation can be achieved by the use of appropriate eluting agents (such as organic acids) under the correct conditions.

The optimum conditions at which to perform the required metal separations can be accurately predicted from a knowledge of the ion exchange resin properties and the relevant equilibrium data of the various organometallic complexes formed. This predictive technique allows the appropriate separation conditions to be determined without prolonged experimental work.

The anions present in the waste water investigated, viz. chromate, free and complexed cyanide, are all successfully loaded onto the strong base anion column. The anionic metal cyanides do, however, poison the resin. The elution requirements necessary to restore resin capacity are complicated and costly without being 100% successful.

The economic viability of the process outlined in this work is uncertain. An economic study (Appendix E) of a proposed treatment plant (Appendix E) indicates that the overall costs are comparable with present methods of treating this type of waste. It should be stressed that this proposed treatment technique does separate the pollutants for reuse whilst the present methods e.g. precipitation/ sedimentation, reverse osmosis and present ion exchange techniques do not.

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APPENDIX A

EFFLUENT CONCENTRATION VS VOLUME RESULTS

(A) CATION COLUMN REGENERATION

Run No.5

Loading: 4 litres of feed containing 50ppm of Cu, Fe and Zn respectively.

Regeneration: 3,58N H_2SO_4 passed through column.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn
50	18	20	1
100	1000	1077	313
150	2069	1623	667
200	1630	1304	583
250	1045	920	417
300	750	724	313
350	600	580	250
400	455	442	192
Mass of metal loaded (mg)	200	200	200

Run No.6

Loading: Feed containing 50ppm of Cu, Fe and Zn respectively.

Regeneration: (a) 200ml of acetone passed through column;
(b) 200ml of 12,5N NH_3 passed through column.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn
(a)	200	4,4	0,71	0,22
(b)	200	43,5	5,9	0,0

Run No.7

Loading: Feed to column contained 2500ppm of Cu and Fe respectively.

Regeneration: (a) 200ml of 12,5N NH_3 followed by 750ml of water acidified to pH = 5,8;
(b) 200ml of 12,5N NH_3 followed by 750ml of water acidified to pH = 5,8;
(c) 200ml of 12,5N NH_3 followed by 500ml of pure water;
(d) 750ml of 6,25N NH_3;
(e) 250ml of 3,125N NH_3;
(f) 1000ml of 2,18N Na^+ + 7,5N NH_3.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm)	
		Cu	Fe
(a)	200	13,3	1,8
	250	31,7	0,7
	500	11,3	0,4
	750	8,2	0,3
(b)	200	23,3	0,6
	250	25,0	0,7
	500	5,0	0,7
	750	2,7	0,3
(c)	200	23,5	0,6
	250	34,7	0,4
	500	13,5	1,0
(d)	250	35,0	0,7
	500	46,0	0,7
	750	42,8	0,6
(e)	250	41,0	1,2
(f)	250	591	2,96
	500	2227	1,48
	750	829	1,5
	1000	360	1,5

Run No.9

Loading: One litre of feed containing 2000ppm of Cu and Fe respectively.

Column Conditioning: 250ml of 3,3N NH_3.

Regeneration: (a) 800ml of feed containing 0,5N Na^+ as Na_2SO_4 + 6,66N NH_3;
(b) 500ml of 20% H_2SO_4.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe
(a)	200	463	4,8
	400	1967	4,8
	600	1359	1,0
	800	788	0,6
(b)	500	905	3966

Run No.10

Loading: One litre of feed containing 2000ppm Cu, Fe and Zn respectively.

Column Conditioning: 250ml of 3,3N NH_3.

Regeneration: (a) 200ml of 0,5N Na^+ + 6,7N NH_3;
(b) 200ml of 0,75N Na^+ + 3,3N NH_3;
(c) 200ml of 0,5N Na^+;
(d) 400ml of 1,0N Na^+ + 6,7N NH_3;
(e) 500ml of 20% H_2SO_4.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn
(a)	200	65	0,0	10
(b)	200	1185	6,3	178
(c)	200	1357	3,7	305
(d)	200	557	1,6	615
	400	350	0,5	538
(e)	500	616	6706	1895

Run No.11

Loading: Same as Run No.10.

Column Conditioning: 250ml of 3,3N NH_3.

Regeneration: (a) 600ml of 10,0N NH_3 + 0,25N Na^+;
(b) 400ml of 6,7N NH_3 + 0,5N Na^+;
(c) 200ml of 3,3N NH_3 + 0,75N Na^+;
(d) 600ml of 3,3N NH_3 + 1,5N Na^+.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm)		
		Cu	Fe	Zn
(a)	200	919	9	62
	400	1464	15	75
	600	1268	12	102
(b)	200	1430	8	234
	400	936	11	336
(c)	200	502	11	381
(d)	200	16	11	1027
	400	6	5	709
	600	5	4	575

Run No.14

Loading: One litre containing 2000ppm Cu, Fe and Zn respectively.

Column Conditioning: 250ml of 4,8N NH_3.

Regeneration: 250ml of 0,75N NH_4^+ + 6,25N NH_3.

Volume of Regenerant (ml)	Effluent Concentration (ppm)		
	Cu	Fe	Zn
50	56	0	0,5
100	1902	38	149
150	3500	142	516
200	3597	172	591
250	2361	155	391
Mass of metal loaded (mg)	1600	1980	1570

Run No.15

Loading: Same as Run No.14.

Column Conditioning: 200ml of 6,6N NH_3 (pH = 12,4)

Regeneration: 700ml of 0,625N NH_4^+ + 6,6N NH_3 (pH = 11,0).

Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn
100	1211	20	108
200	2367	62	341
300	2762	80	478
400	2218	80	481
500	1483	78	414
600	1088	72	561
700	721	70	446
Mass of Metal Loaded (mg)	1600	1980	1570

Run No.16

Loading: Same as Run No.14.

Column Conditioning: 200ml of 3,5N NH_3.

Regeneration: 900ml of 6,6N NH_3 + 0,325N NH_4^+ (pH = 11,2).

Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn
100	733	10	41
200	1867	24	104
300	2000	30	133
400	2133	35	141
500	1760	32	136
600	1587	30	155
700	1147	30	120
800	1147	37	160
900	680	37	56
Mass of Metal Loaded (mg)	1880	1300	1950

Run No.17

Loading: One litre of feed containing 2000ppm of Cu, Fe, Ni and Zn respectively.

Column Conditioning: 200ml of 6,6N NH_3.

Regeneration: 800ml of 0,75N NH_4^+ + 9,86N NH_3.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Ni	Zn
100	253	0	26	32
200	1840	64	218	267
300	1880	93		373
400	1506	98	246	347
500	1120	85	237	355
600	787	82	226	325
700	493	80	218	285
800	293	75	207	285
Mass of metal loaded (mg)	600	500	1000	1050

Run No.18

Loading: One litre of solution containing 2000ppm of Cu, Fe and Zn respectively.

Column Conditioning: 200ml of 3,29N NH_3.

Regeneration: 800ml of 0,5N NH_4^+ + 3,29N NH_3.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn
100	683	0	38
200	1000	0	75
300	2267	0	128
400	2000	0	113
500	1683	0	157
600	1333	0	162
700	983	0	145
800	733	0	154
Mass of metal loaded (mg)	1120	1400	1500

Run No.19

Loading: One litre of feed containing 1000ppm of Cu, Ni, Fe and Zn respectively.

Column Conditioning: 200ml of 3,91N NH_3.

Regeneration: (a) 900ml of 0,25N NH_4^+ + 2,94N NH_3;
(b) 900ml of 0,3N NH_4^+ + 2,94N NH_3;
(c) 1000ml of 0,375N NH_4^+ + 2,94N NH_3.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Ni	Zn
(a)	100	14	0	0	1
	200	146	0	0	3
	300	367	0	0	3
	400	700	0	0	2
	500	1083	0	0	4
	600	1133	0	0	3
	700	1183	0	0	5
	800	1167	0	0	5
	900	950	0	4	6
(b)	100	606	0	4	4
	200	446	0	7	6
	300	434	0	7	14
	400	343	0	11	11
	500	194	0	13	12
	600	125	0	16	12
	700	81	0	17	12
	800	50	0	20	17
	900	27	0	21	16
(c)	100	14	3	24	21
	200	12	4	40	32
	300	9	6	53	31
	400	6	7	89	36
	500	4	8	104	76
	600	0	8	110	51
	700	0	8	111	45
	800	0	8	121	55
	900	0	9	133	60
	1000	0	11	130	49

Run No.19

Loading: One litre of feed containing 1000ppm of Cu, Ni, Fe and Zn respectively.

Column Conditioning: 200ml of 3,91N NH_3.

Regeneration: (a) 900ml of 0,25N NH_4^+ + 2,94N NH_3;
(b) 900ml of 0,3N NH_4^+ + 2,94N NH_3;
(c) 1000ml of 0,375N NH_4^+ + 2,94N NH_3.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm)			
		Cu	Fe	Ni	Zn
(a)	100	14	0	0	1
	200	146	0	0	3
	300	367	0	0	3
	400	700	0	0	2
	500	1083	0	0	4
	600	1133	0	0	3
	700	1183	0	0	5
	800	1167	0	0	5
	900	950	0	4	6
(b)	100	606	0	4	4
	200	446	0	7	6
	300	434	0	7	14
	400	343	0	11	11
	500	194	0	13	12
	600	125	0	16	12
	700	81	0	17	12
	800	50	0	20	17
	900	27	0	21	16
(c)	100	14	3	24	21
	200	12	4	40	32
	300	9	6	53	31
	400	6	7	89	36
	500	4	8	104	76
	600	0	8	110	51
	700	0	8	111	45
	800	0	8	121	55
	900	0	9	133	60
	1000	0	11	130	49

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Ni	Zn
(d)	100	0	42	262	413
	200	0	64	838	1091
	300	0	20	210	109
	400	0	20	171	121
	500	0	11	190	155
	600	0	10	419	118
	700	0	8	324	125
	800	0	7	229	100
Mass of metal loaded (mg)		970	1000	1000	990

Run No.20

Loading: One litre of solution containing 1000ppm of Fe, Ni and Zn respectively.

Column Conditioning: 200ml of 2,94N NH_3.

Regeneration: 500ml of 2,0n NH_4^+ + 2,94N NH_3.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	507	415	433
200	3122	3390	3297
300	2302	2781	2473
400	1093	1562	917
Mass of metal loaded (mg)	994	1000	997

Run No.21

Loading: One litre of solution containing 1000ppm of Fe, Ni and Zn respectively.

Column Conditioning: 200ml of 1,174N NH_3.

Regeneration: 900ml of 0,4N NH_4^+ + 1,174N NH_3.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	0	0	0
200	0	0	0
300	11	8	8
400	14	14	8
500	45	34	47
600	97	24	46
700	155	45	15
800	243	80	17
900	281	99	31
Mass of metal loaded (mg)	1000	1000	1000

Run No.22

Loading: One litre of solution containing 1000ppm of Fe, Ni and Zn respectively.

Column Conditioning: 200ml of 5,87N NH_3.

Regeneration: 800ml of 0,4N NH_4^+ at pH = 11,3.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	7	2	1
200	70	41	40
300	136	79	27
400	210	116	61
500	320	173	127
600	393	217	166
700	404	236	206
800	334	231	180
Mass of metal loaded (mg)	930	940	930

Run No.23

Loading: Same as Run No.22.

Column Conditioning: 250ml of 2,94N NH_3.

Regeneration: 0,3N NH_4Cl at pH = 10,8.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	2	0	0
200	4	2	0
300	10	6	14
400	65	41	16
500	82	77	149
600	107	66	377
700	144	86	230
800	161	95	269
900	347	226	226
1000	753	428	207
Mass of metal loaded (mg)	995	999	998

Run No.24

Loading: One litre of solution containing 2000ppm of Ni and Zn respectively.

Column Conditioning: 200ml of 3,24N NH_3.

Regeneration: (a) 200ml of 12,96N NH_3;
(b) 200ml of 0,25N NH_4^+ + 9,72N NH_3;
(c) 200ml of 0,25N NH_4^+ + 3,24N NH_3 + 0,01M EDTA.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Ni	Zn
(a)	100	0	1
	200	0	1
(b)	100	153	107
	200	324	344
(c)	100	360	328
	200	666	369

Run No.25

Loading: One litre of solution containing 2000ppm of Fe, Ni and Zn respectively.

Column Conditioning: 200ml of 2,98N NH_3.

Regeneration: 900ml of 0,2N NH_4^+ + 0,01M EDTA + 2,98N NH_3.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	743	597	424
200	1143	548	323
300	1200	629	316
400	1286	597	287
500	1171	581	260
600	1057	581	234
700	1171	581	236
800	971	500	201
900	400	484	189
Mass of metal loaded (mg)	1370	1387	1379

Run No.26

Loading: One litre of solution containing 2000ppm Fe, Ni and Zn respectively.

Column Conditioning: 350ml of 1,85N NH_3.

Regeneration: 500ml of 0,25N NH_4^+ at pH = 10,1.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Zn	Ni
100	21	20	55
200	43	71	139
300	49	79	145
400	50	69	138
500	26	67	133

Run No.27

Loading: One litre of solution containing 2000ppm Fe, Ni and Zn respectively.

Column Conditioning: 350ml of 1,85N NH_3.

Regeneration: 400ml of 0,25N NH_4^+ at pH = 7,0.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Zn	Ni
100	21	20	51
200	58	59	188
300	41	49	191
400	10	34	165

Run No.28

Loading: One litre of solution containing 2000ppm Fe, Ni and Zn respectively.

Column Conditioning: 250ml of 2,95N NH_3.

Regeneration: 800ml of 0,1M Citric acid at pH = 9,8.

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	1636	391	58
200	3927	899	178
300	3291	989	166
400	2818	1029	156
500	2000	1058	133
600	1291	855	152
700	582	710	112
800	473	869	77
Mass of metal loaded (mg)	1327	1319	1620

Run No.29

Loading: One litre of solution containing 1000ppm Cu, Fe, Ni and Zn respectively.

Regeneration: 800ml of 0,15N NH_4^+ at pH = 2,65.

Volume of Regenerant (ml)	Effluent Concentration (ppm)			
	Cu	Fe	Ni	Zn
100	43	51	46	26
200	270	327	319	202
300	512	655	652	372
400	679	818	783	446
500	809	927	913	519
600	791	909	870	496
700	586	691	667	386
800	530	600	609	359
Mass of metal loaded (mg)	953	945	931	927

Run No.30

Loading: One litre of solution containing 2000ppm of Ni, Fe and Zn respectively.

Column Conditioning: 300ml of 1,08N NH_3.

Regeneration: 900ml of 0,05M Citric acid + 0,947N NH_3 (pH = 10,7).

Volume of Regenerant (ml)	Effluent Concentration (ppm)		
	Fe	Ni	Zn
100	1167	52	48
200	3333	110	119
300	3483	128	169
400	3200	193	217
500	2167	355	179
600	1583	426	129
700	917	610	138
800	400	638	119
900	350	667	112
Mass of metal loaded (mg)	1560	1603	1536

Run No.31

Loading: One litre of solution containing 2000ppm of Fe, Ni and Zn respectively.

Column Conditioning: 250ml of 1,296N NH_3.

Regeneration: 900ml of 0,025M Citric acid + 1,78N NH_3 (pH = 10,7).

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Zn	Ni
100	884	110	85
200	1304	92	63
300	1072	66	64
400	870	66	63
500	623	62	63
600	449	26	56
700	420	26	70
800	348	24	68
900	261	22	70
Mass of metal loaded (mg)	1710	1462	1535

Run No.32

Loading: One litre of solution containing 2000ppm of Fe, Ni and Zn respectively.

Column Conditioning: 250ml of 1,296N NH_3.

Regeneration: 900ml of 0,025M Citric acid + 0,484N NH_3 (pH = 10,1).

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	855	20	66
200	1464	20	53
300	1349	120	44
400	1174	167	59
500	551	310	48
600	217	423	26
700	188	400	22
800	145	437	15
900	43	423	18
Mass of metal loaded (mg)	1507	1600	1332

Run No.34

Loading: One litre of solution containing 1000ppm of Cu, Fe, Ni and Zn respectively.

Column Conditioning: 250ml of 1,296N NH .

Regeneration: (a) 1000ml of 0,2N NH^{+} at pH = 10,1;
(b) 1200ml of 0,025M Citric acid at pH = 11,1
(c) 1000ml of 0,5M Citric acid at pH = 10,9.

Regen.	Volume of Regenerant	Effluent Concentration (ppm)			
	(ml)	Cu	Fe	Ni	Zn
(a)	200	197	5	21	18
	400	387	1	41	38
	600	511	1	44	40
	800	387	0	43	39
	1000	393	0	44	39
(b)	200	433	3	40	16
	400	197	4	20	7
	600	197	3	21	8
	800	157	3	18	6
	1000	269	6	54	17
	1200	289	7	77	23
(c)	200	329	11	141	28
	400	269	11	183	54
	600	190	10	200	47
	800	164	20	174	37
	1000	151	14	217	42

Run No.35

Loading: One litre of solution containing 1000ppm of Cu, Fe, Ni and Zn respectively.

Column Conditioning: 250ml of 2,716N NH_3.

Regeneration: (a) 900ml of 0,2N NH_4^+ at pH = 10,8;
(b) 1000ml of 0,05M Citric acid at pH = 9,8;
(c) 800ml of 0,05M Citric acid at pH = 9,55.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Ni	Zn
(a)	100	374	0	32	29
	200	617	0	58	19
	300	504	0	50	44
	400	409	0	48	40
	500	304	0	47	38
	600	174	0	49	39
	700	104	0	50	39
	800	157	0	50	42
	900	122	0	50	47
(b)	100	183	3	314	34
	200	14	0	1289	27
	300	12	0	1289	28
	400	8	0	1058	27
	500	7	0	810	24
	600	8	0	562	25
	700	6	0	314	24
	800	6	0	165	26
	900	4	0	54	25
	1000	4	0	54	25
(c)	200	0	0	32	36
	400	0	0	23	42
	600	0	0	9	44
	800	0	0	6	41

Run No.40

Loading: One litre of solution containing 1000ppm of Cu, Fe, Ni and Zn respectively.

Column Conditioning: 250ml of 1,219N NH_3.

Regeneration: (a) 1000ml of 0,2N NH_3 at pH = 10,8;
(b) 1000ml of 0,05M Citric acid at pH = 9,8;
(c) 700ml of 0,05M Citric acid at pH = 6,4;
(d) 300ml of 20wt% H_2SO_4.

Regen.	Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Ni	Zn
(a)	100	300	-	8	40
	200	640	-	16	71
	300	720	-	16	76
	400	760	-	18	84
	500	680	-	19	88
	600	480	-	20	92
	700	240	-	40	120
	800	132	-	48	132
	900	60	-	48	124
	1000	37	-	57	124
(b)	100	14	20	192	100
	200	6	16	792	100
	300	4	4	880	76
	400	2	-	824	76
	500	0	-	720	72
	600	-	-	568	68
	700	-	-	424	68
	800	-	-	240	52
	900	-	-	160	60
	1000	-	-	94	44
(c)	100	-	-	99	1144
	200	-	-	51	2492
	300	-	-	6	3476
	400	-	-	2	3364
	500	-	-	0	2640
	600	-	-	-	2392
	700	-	-	-	504
(d)	100	-	31	-	20
	200	-	696	-	131
	300	-	1344	-	161
Mass of metal loaded (mg)		976	982	977	910

(B) ANION COLUMN LOADING AND REGENERATION

Run No.37

Loading: Feed containing 23ppm CN^- plus Cu, Fe, Ni and Zn.

Anion Column: Feed loaded onto resin in Cl^- form.

Effluent Concentration: 5,8ppm CN^-.

Run No.38

Loading: Feed containing 50ppm CN^- plus Cu, Fe, Ni and Zn.

Anion Column: Feed loaded onto resin in OH^- form.

Effluent Concentration: <0,5ppm CN^-.

Regeneration: (a) After 100mg of CN^- loaded, column regenerated with 15% NaOH.
(b) After further 100mg of CN^- loaded, column regenerated with (i) 20% H_2SO_4 and (ii) 15% NaOH.

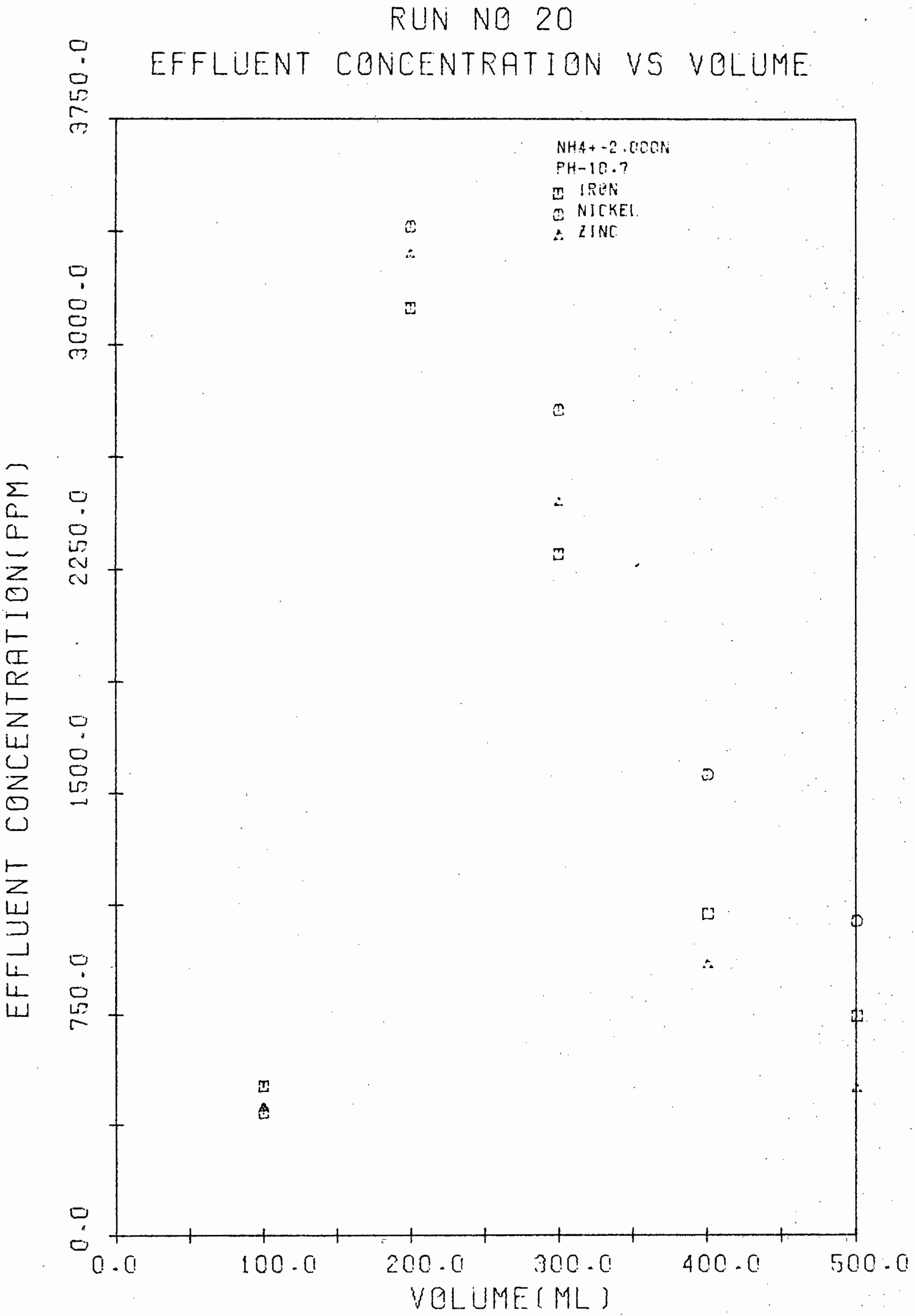
Regeneration Sequence	Mass of CN^- eluted (mg)
a	35,4
b	57,2

Run No.39

Loading: (a) Feed containing 200ppm Cr as the chromate onto Cl^- form of anion resin.
(b) Feed containing 200ppm Cr as the chromate onto OH^- form of anion resin.

Loading	Volume (ml)	Effluent Concentration (ppm)
a	1000	0,0
	2000	0,0
	3000	4,6
b	1000	0,0
	2000	0,0
	3000	3,4

FIGURE B.2


RUN NO 20
EFFLUENT CONCENTRATION VS VOLUME
NH4+-2.000N
PH-10.7
IRON
NICKEL
ZINC
EFFLUENT CONCENTRATION(PPM)
0.0
750.0
1500.0
2250.0
3000.0
3750.0
0.0
100.0
200.0
300.0
400.0
500.0
VOLUME(ML)

APPENDIX B

EFFLUENT CONCENTRATION VERSUS VOLUME CURVES

FIGURE B.1

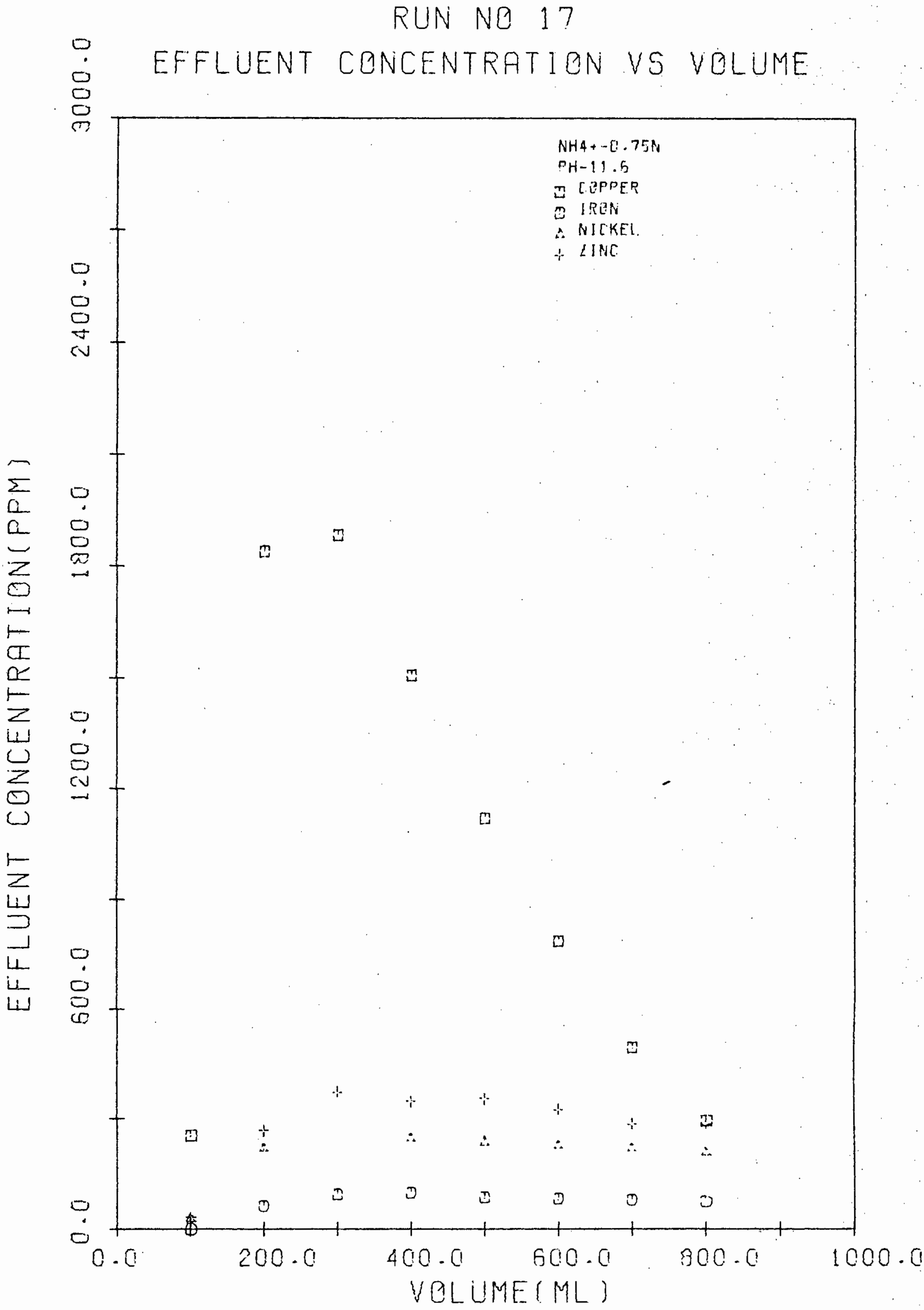


FIGURE B.3

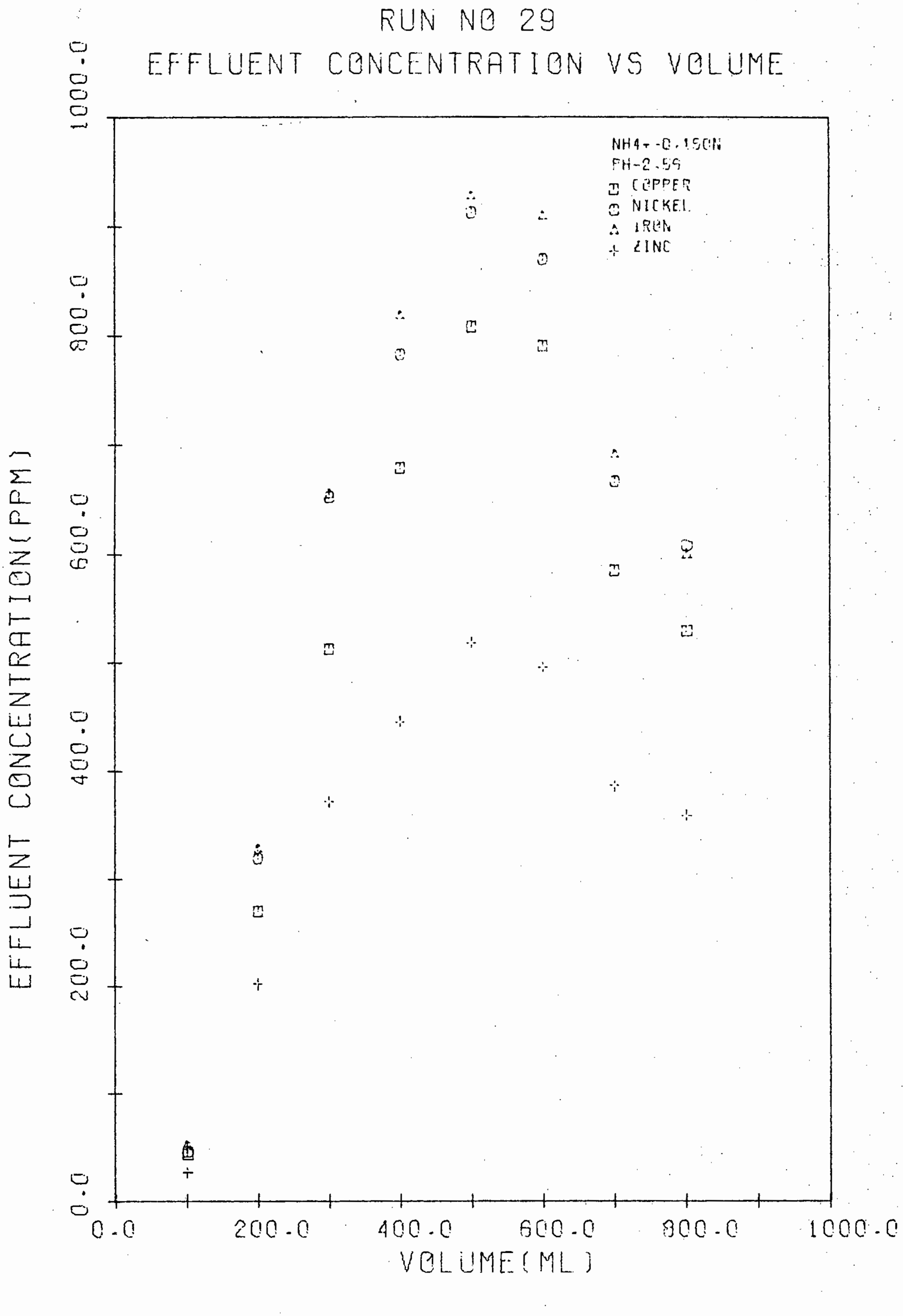

RUN NO 29
EFFLUENT CONCENTRATION VS VOLUME
NH4+-0.150N
PH-2.59
COPPER
NICKEL
IRON
ZINC
EFFLUENT CONCENTRATION(PPM)
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)
0.0
200.0
400.0
600.0
800.0
1000.0

FIGURE B.4

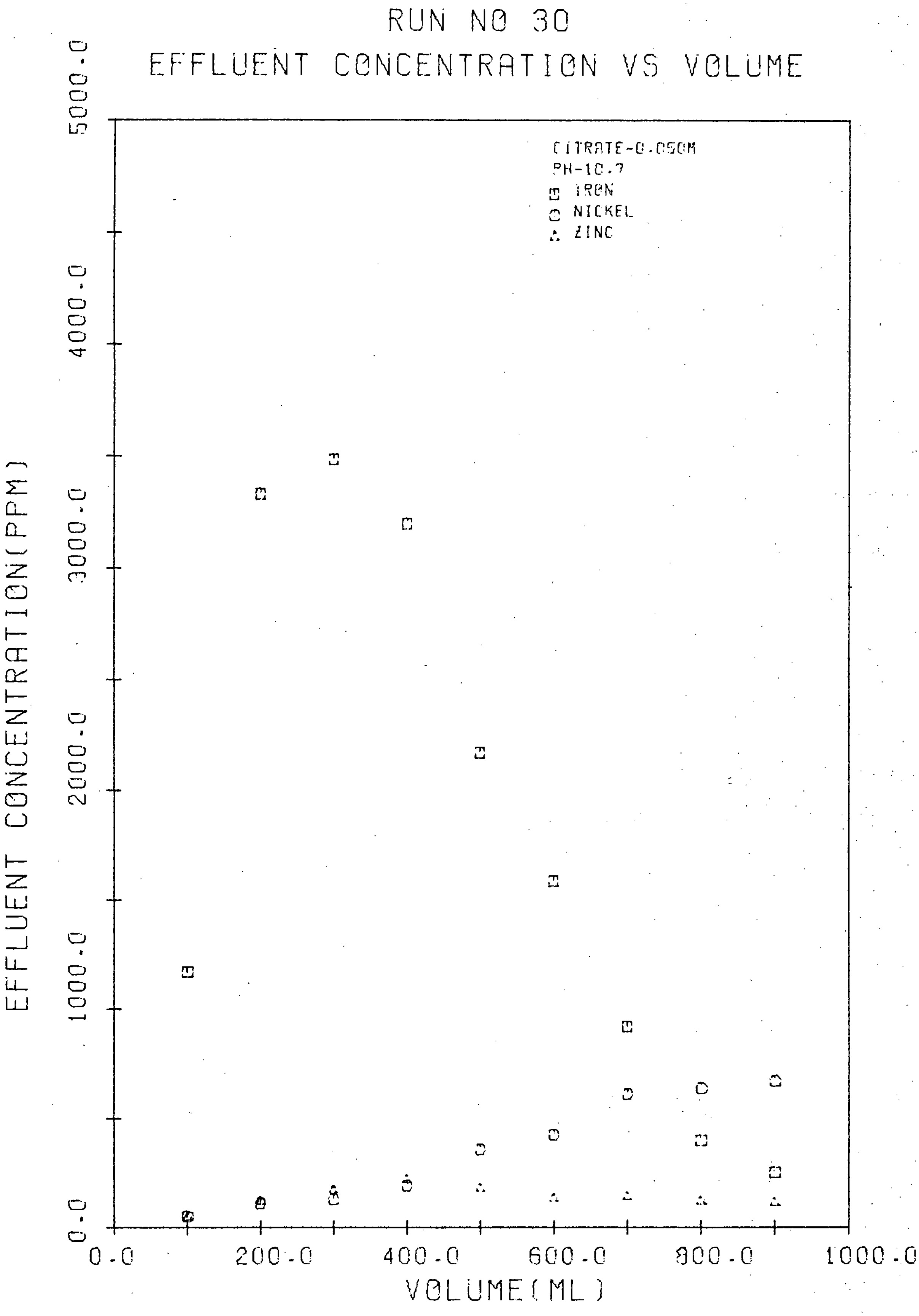
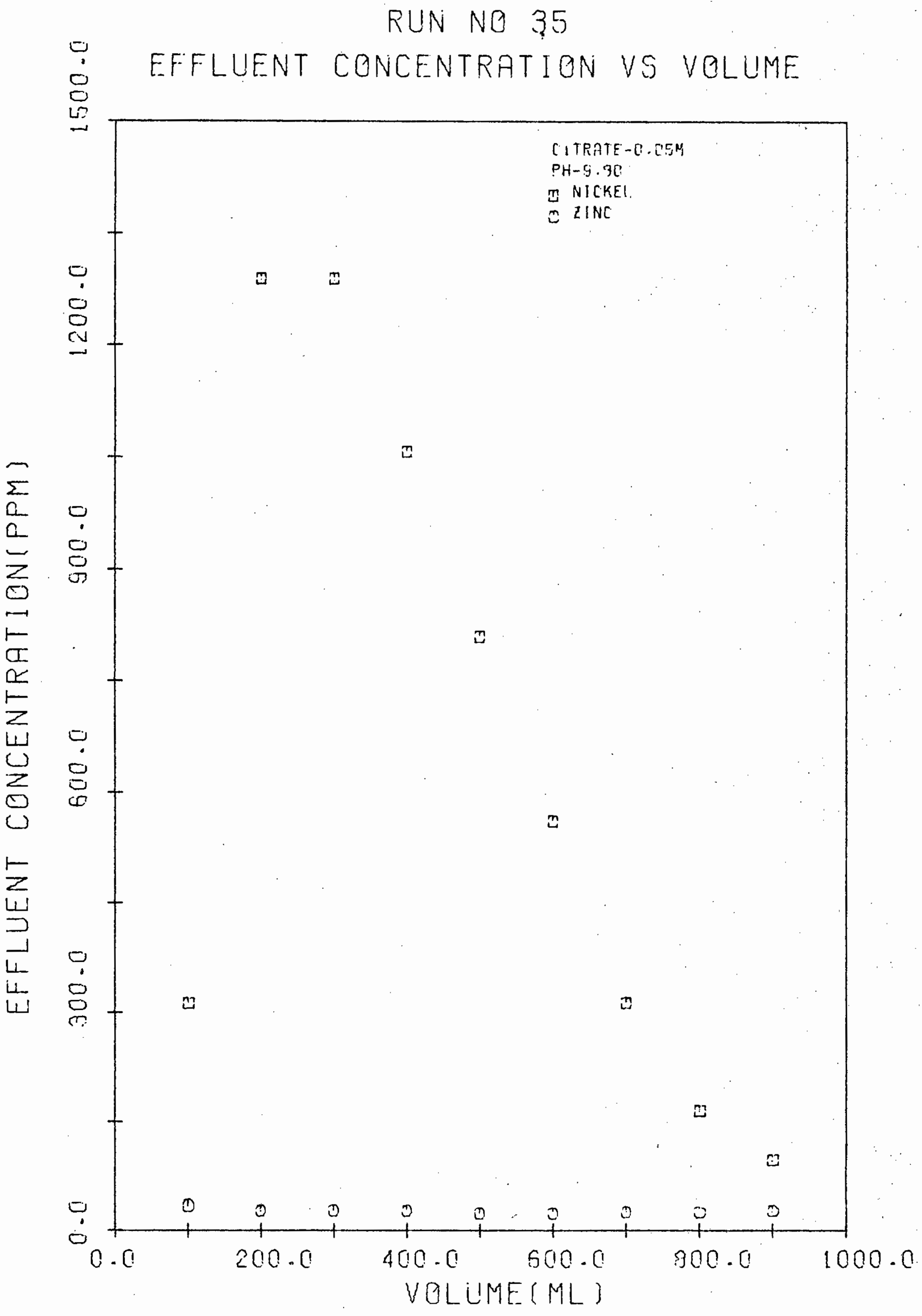

RUN NO 30
EFFLUENT CONCENTRATION VS VOLUME
CITRATE-0.050M
PH-10.7
⊡ IRON
○ NICKEL
△ ZINC
EFFLUENT CONCENTRATION(PPM)
0.0
1000.0
2000.0
3000.0
4000.0
5000.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

FIGURE B.5


RUN NO 35
EFFLUENT CONCENTRATION VS VOLUME
CITRATE-0.05M
PH-9.90
NICKEL
ZINC
EFFLUENT CONCENTRATION(PPM)
0.0
300.0
600.0
900.0
1200.0
1500.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)

RUN NO 40
EFFLUENT CONCENTRATION VS VOLUME

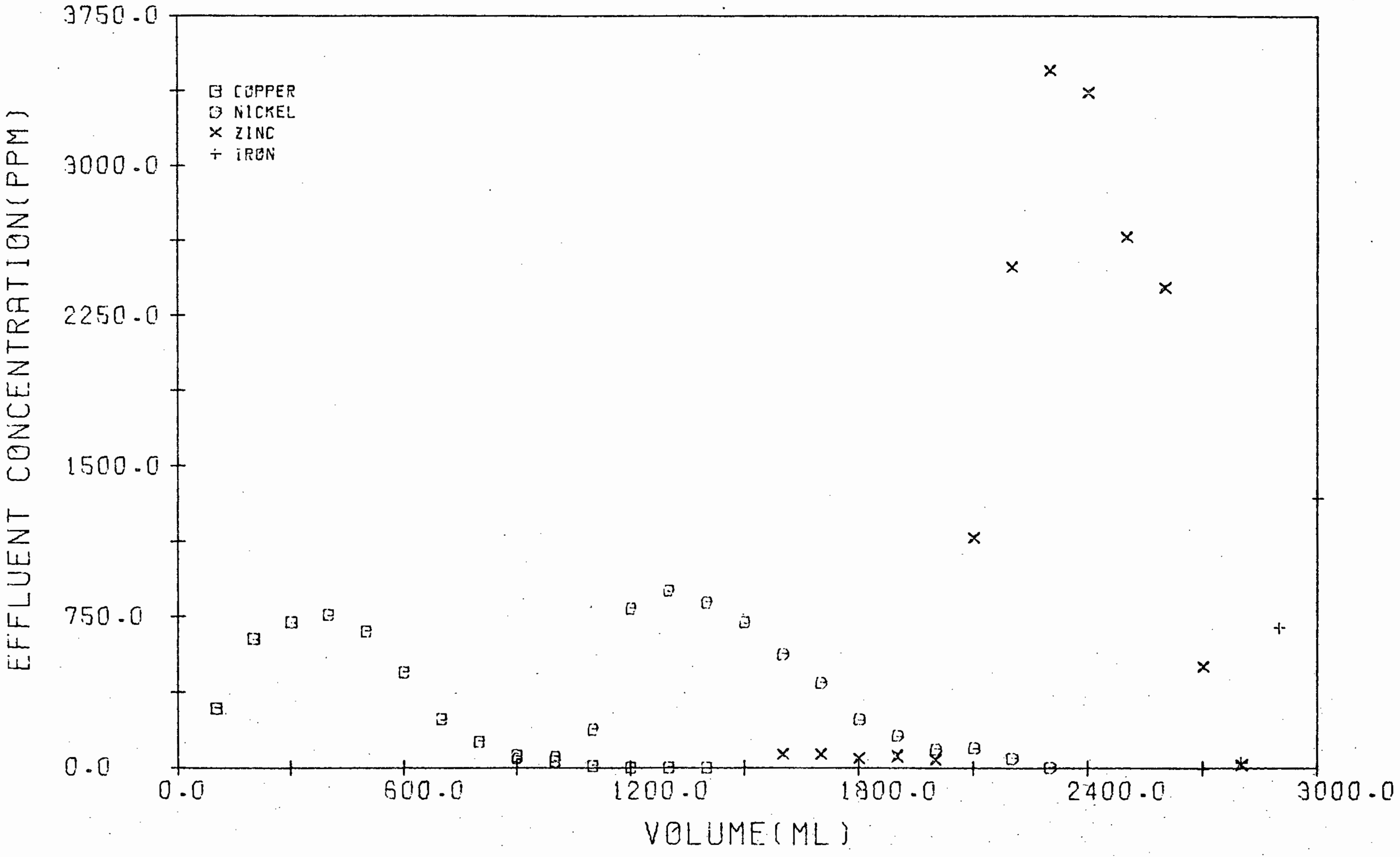


FIGURE B.6

APPENDIX C

ELUTION COMPARISON CURVES

FIGURE C.1

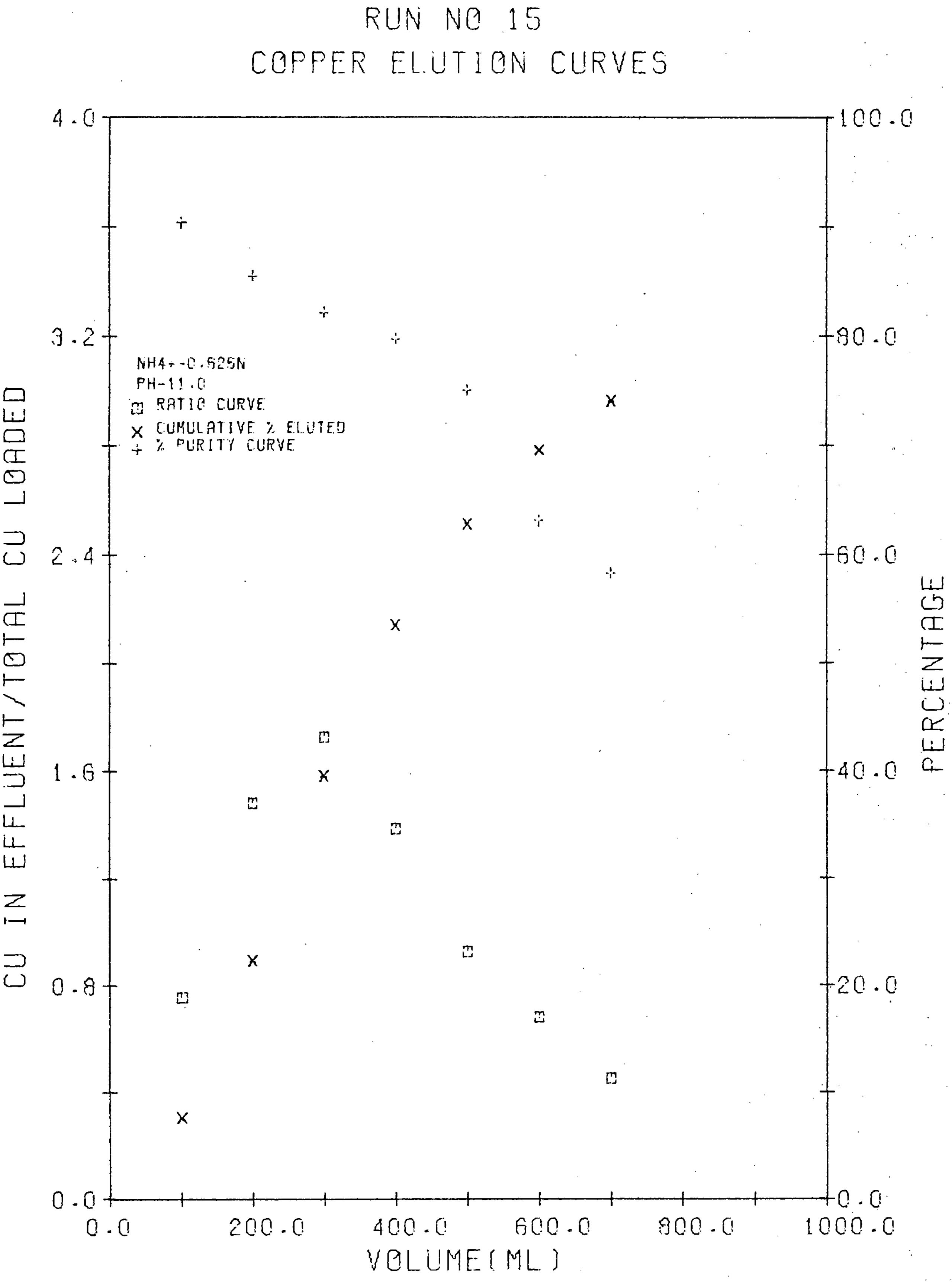


FIGURE C.2

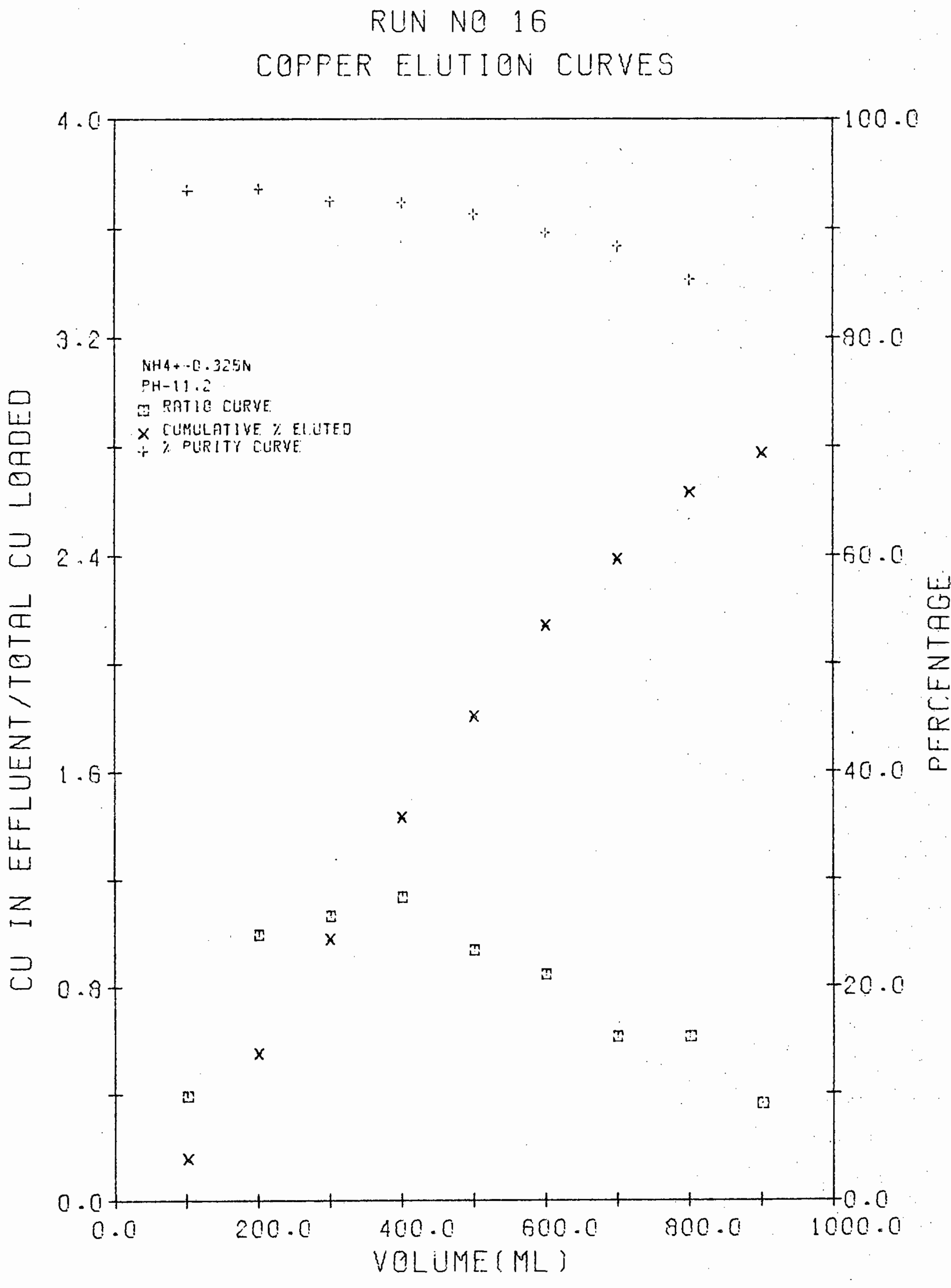

RUN NO 16
COPPER ELUTION CURVES
NH4+-0.325N
PH-11.2
⊡ RATIO CURVE
× CUMULATIVE % ELUTED
+ % PURITY CURVE
CU IN EFFLUENT/TOTAL CU LOADED
PERCENTAGE
VOLUME(ML)
0.0
0.8
1.6
2.4
3.2
4.0
0.0
20.0
40.0
60.0
80.0
100.0
0.0
200.0
400.0
600.0
800.0
1000.0

FIGURE C.3

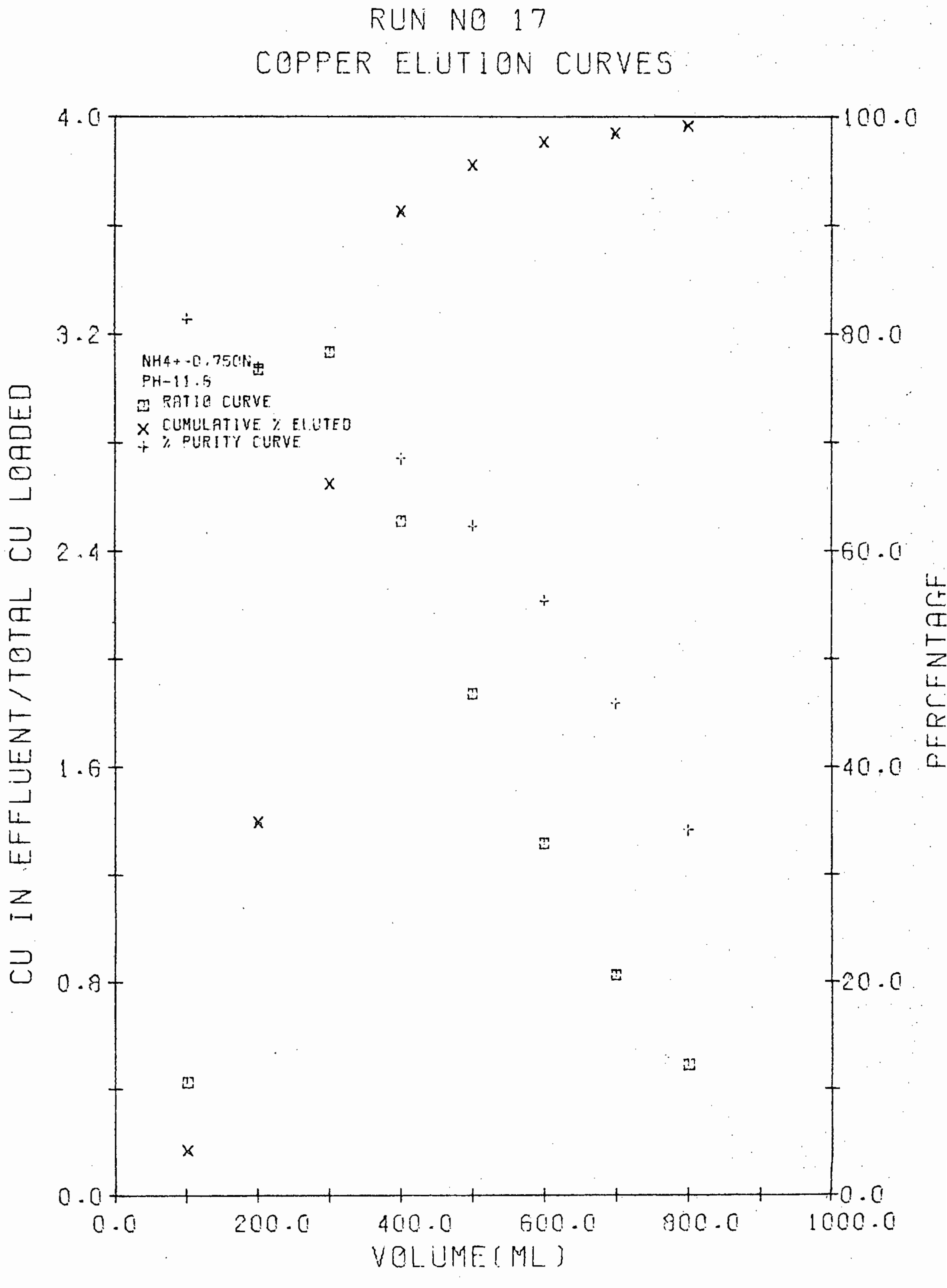

RUN NO 17
COPPER ELUTION CURVES
NH4+-0.750N
PH-11.5
RATIO CURVE
CUMULATIVE % ELUTED
% PURITY CURVE
CU IN EFFLUENT/TOTAL CU LOADED
4.0
3.2
2.4
1.6
0.8
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
VOLUME(ML)
100.0
80.0
60.0
40.0
20.0
0.0
PERCENTAGE

FIGURE C.4

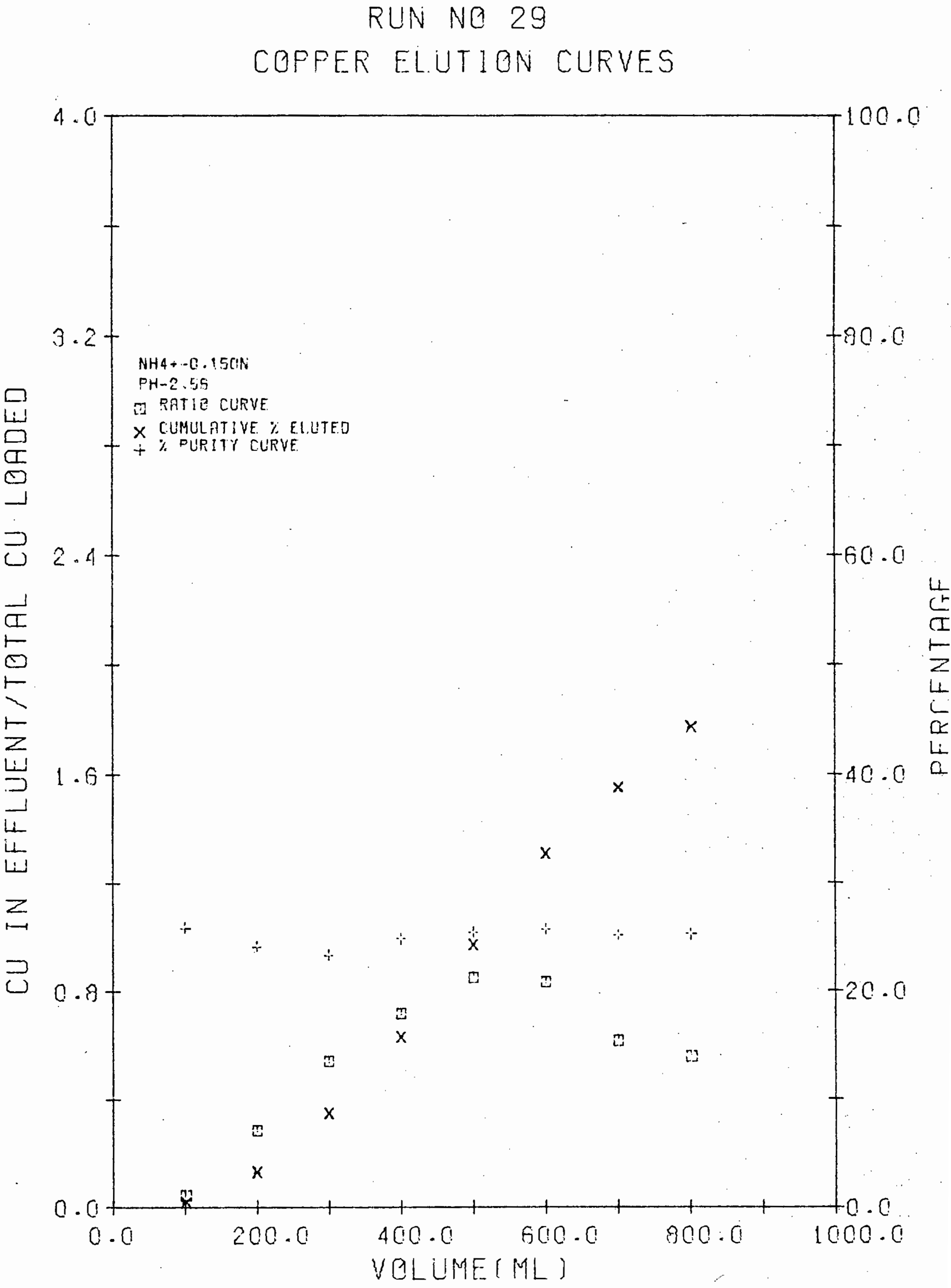

RUN NO 29
COPPER ELUTION CURVES
NH4+-0.150N
PH-2.55
□ RATIO CURVE
X CUMULATIVE % ELUTED
+ % PURITY CURVE
CU IN EFFLUENT/TOTAL CU LOADED
PERCENTAGE
VOLUME(ML)
4.0
3.2
2.4
1.6
0.8
0.0
100.0
80.0
60.0
40.0
20.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0

FIGURE C.5

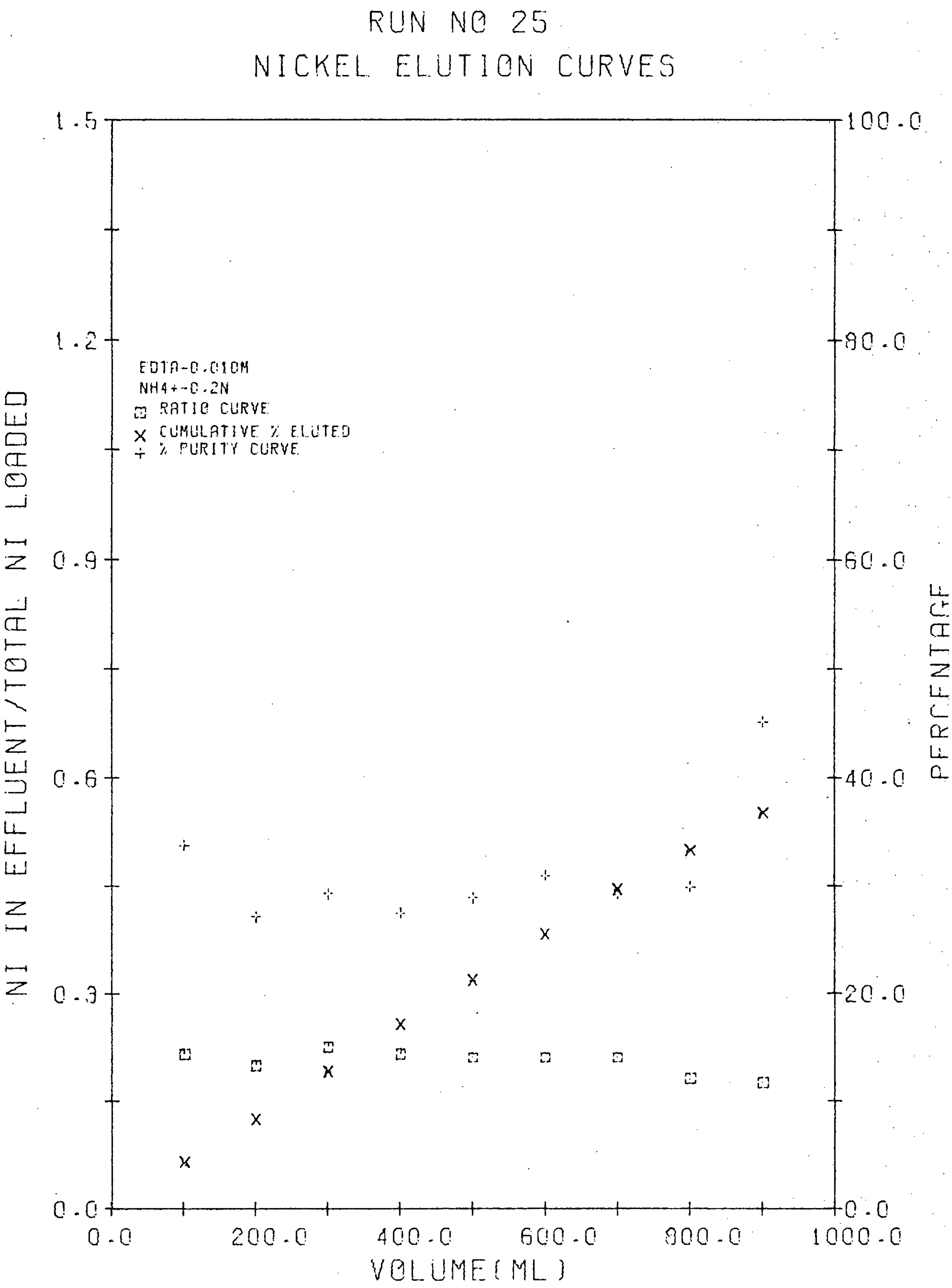
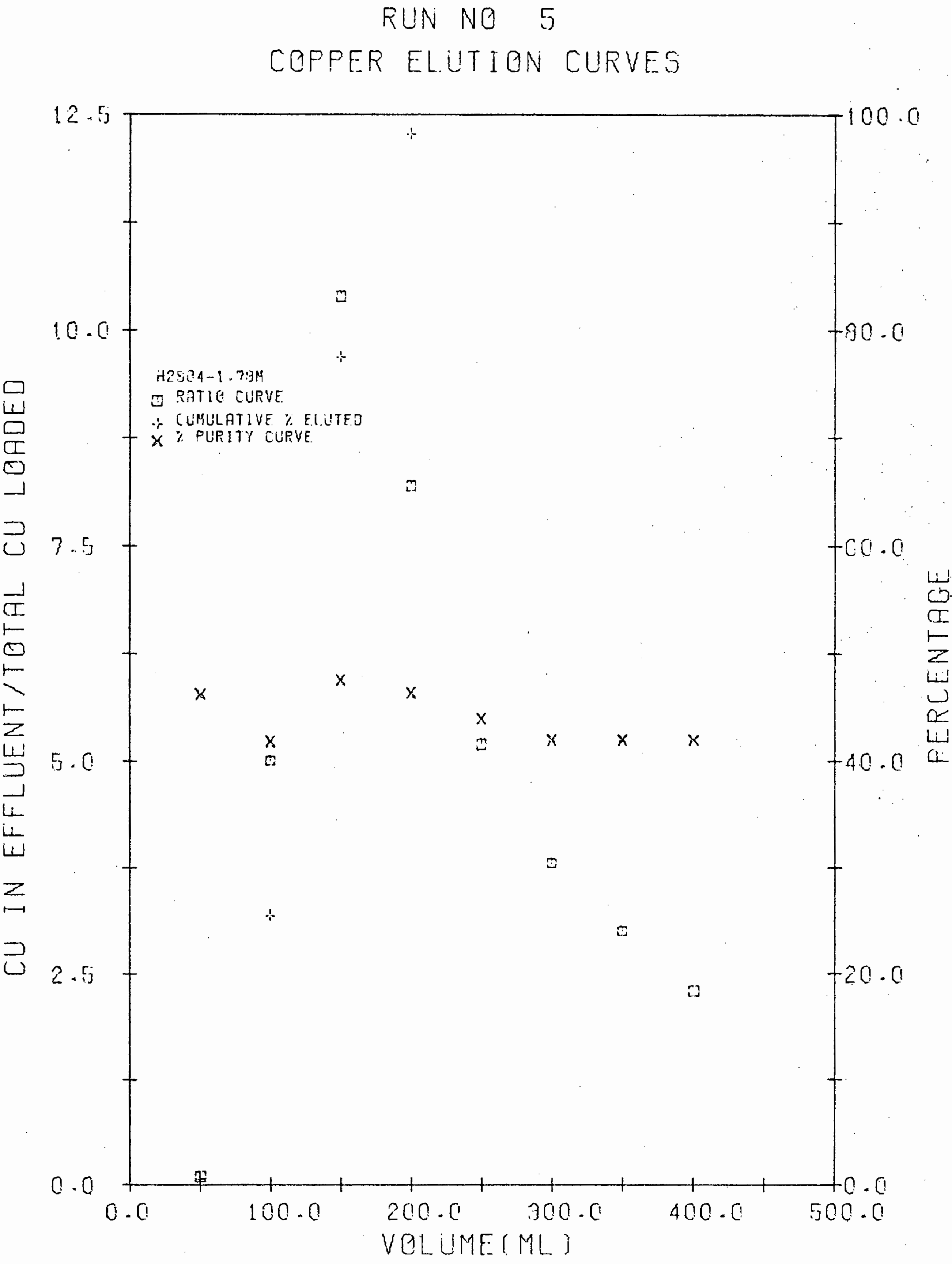

RUN NO 25
NICKEL ELUTION CURVES
EDTA-0.010M
NH4+-0.2N
□ RATIO CURVE
X CUMULATIVE % ELUTED
+ % PURITY CURVE
NI IN EFFLUENT/TOTAL NI LOADED
PERCENTAGE
VOLUME(ML)
0.0
0.3
0.6
0.9
1.2
1.5
0.0
20.0
40.0
60.0
80.0
100.0
0.0
200.0
400.0
600.0
800.0
1000.0

FIGURE C.6


RUN NO 5
COPPER ELUTION CURVES
H2SO4-1.78M
□ RATIO CURVE
+ CUMULATIVE % ELUTED
X % PURITY CURVE
CU IN EFFLUENT/TOTAL CU LOADED
PERCENTAGE
VOLUME(ML)
0.0
2.5
5.0
7.5
10.0
12.5
0.0
20.0
40.0
60.0
80.0
100.0
0.0
100.0
200.0
300.0
400.0
500.0

APPENDIX D

RESULTS OBTAINED IN COLUMN BREAKTHROUGH STUDIES

A. Actual Results

Run No.2

Feed Concentration: Fe - 2792,5ppm
Cu - 3177,0ppm
pH - 4,5

Volume of Regenerant (ml)	Effluent Concentration (ppm)	
	Cu	Fe
200	11,3	11,5
400	37,5	50,0
600	62,5	60,0
800	377	386
1000	1971	1732

Run No.3

Feed Concentration: Fe - 2792,5ppm
Cu - 3177,0ppm
pH - 0,9

Volume of Regenerant (ml)	Effluent Concentration (ppm)	
	Cu	Fe
200	372	227
400	1628	1477
600	2588	2386
800	3030	2614
1000	3933	3295

Run No.6

Feed Concentration: Cu - 50ppm
Fe - 50ppm
Zn - 50ppm
pH - 3,9

Volume of Regenerant	Effluent Concentration (ppm)		
(ml)	Cu	Fe	Zn
1000	0,0	0,0	0,0
2000	0,0	0,0	0,0
3000	0,0	0,0	0,0
.	.	.	.
.	.	.	.
.	.	.	.
8000	0,0	0,0	0,0
10000	0,0	0,0	0,0
12000	0,3	0,3	0,3
14000	0,4	0,4	0,6
16000	1,4	1,3	1,5
18000	3,2	3,0	3,0

Run No.17

Feed Concentration: Cu - 2000ppm
Fe - 2000ppm
Zn - 2000ppm
Ni - 2000ppm
pH - 2,0

Breakthrough occurred after 350ml of feed.

Run No.25

Feed Concentration: Ni - 2000ppm
Zn - 2000ppm
Fe - 2000ppm
pH - 2,0

Breakthrough occurred after 600ml of feed.

Run No.29

Feed Concentration: Cu - 1000ppm
Fe - 1000ppm
Ni - 1000ppm
Zn - 1000ppm
pH - 2,0

Breakthrough occurred after 600ml of feed.

Run No.39

Feed Concentration: Cu - 100ppm
Ni - 100ppm
Fe - 100ppm
Zn - 100ppm
pH - 2,0

Volume of Regenerant (ml)	Effluent Concentration (ppm) Cu	Fe	Zn	Ni
2500	0,0	0,4	0,3	0,2
4000	1,0	0,4	1,4	0,3

B. Simulated Results

```
                    FEED PARAMETERS
                    ---------------
COMPONENT     PPM   EQUIVALENT  SELECTIVITY   CHARGE
                     FRACTION   COEFFICIENT
 COPPER    3177.0      .500         3.031      2.000
  IRON     2793.0      .500         2.756      2.000
HYDROGEN      .0       .000         1.000      1.000

     PH                          4.50
EXCHANGER CAPACITY               1.980  MEQ/ML
SOLUTION CONCENTRATION            .2000N


                 CONCENTRATION PROFILES
                       IN THE BED

        EQUIVALENT  FRACTION  IN  THE  LIQUID  PHASE

COPPER     IRON    HYDROGEN   ZONE  NO.& TYPE
 .4999     .4999     .0002    1ST  PLATEAU
 .4501     .5498     .0002    1ST  TRANSITION
 .4007     .5992     .0002    1ST  TRANSITION
 .3517     .6481     .0002    1ST  TRANSITION
 .3032     .6966     .0002    1ST  TRANSITION
 .2552     .7446     .0002    1ST  TRANSITION
 .2076     .7922     .0002    1ST  TRANSITION
 .1605     .8393     .0002    1ST  TRANSITION
 .1138     .8861     .0002    1ST  TRANSITION
 .0675     .9323     .0002    1ST  TRANSITION
 .0216     .9782     .0002    1ST  TRANSITION
           .9998     .0002    2ND  PLATEAU
           .3295     .6705    2ND  TRANSITION
           .1091     .8909    2ND  TRANSITION
           .0377     .9623    2ND  TRANSITION
           .0112     .9888    2ND  TRANSITION


                  BREAKTHROUGH CONDITIONS
                  -----------------------

          FOR  THE  FOLLOWING  BED  PARAMETERS
             (A)  BED  VOLUME                          100.00  ML
             (B)  VOID  FRACTION                          .40
             (C)  EXCHANGER  CAPACITY                    1.98  MEQ/ML

        BREAKTHROUGH  OF    IRON    OCCURS  AFTER     1053.54  ML
```

```
                    FEED PARAMETERS
                    ---------------
COMPONENT    PPM   EQUIVALENT SELECTIVITY   CHARGE
                    FRACTION  COEFFICIENT
 COPPER    3177.0     .307          3.031       2.000
  IRON     2793.0     .307          2.756       2.000
HYDROGEN    125.9     .386          1.000       1.000

     PH                           .90
EXCHANGER CAPACITY              1.980  MEQ/ML
SOLUTION CONCENTRATION            .3259N


                 CONCENTRATION PROFILES
                      IN THE BED

        EQUIVALENT FRACTION IN THE LIQUID PHASE

COPPER     IRON    HYDROGEN   ZONE NO.& TYPE
 .3069     .3069     .3863    1ST PLATEAU
 .2722     .3413     .3865    1ST TRANSITION
 .2379     .3753     .3868    1ST TRANSITION
 .2040     .4090     .3870    1ST TRANSITION
 .1704     .4423     .3873    1ST TRANSITION
 .1372     .4752     .3875    1ST TRANSITION
 .1044     .5079     .3878    1ST TRANSITION
 .0718     .5402     .3880    1ST TRANSITION
 .0396     .5721     .3882    1ST TRANSITION
 .0078     .6037     .3885    1ST TRANSITION
           .6112     .3888    2ND PLATEAU
           .2395     .7605    2ND TRANSITION
           .0906     .9094    2ND TRANSITION
           .0314     .9686    2ND TRANSITION
           .0060     .9940    2ND TRANSITION


                 BREAKTHROUGH CONDITIONS
                 -----------------------

        FOR THE FOLLOWING BED PARAMETERS
            (A) BED VOLUME                              100.00  ML
            (B) VOID FRACTION                               .40
            (C) EXCHANGER CAPACITY                        1.98  MEQ/ML

        BREAKTHROUGH OF   IRON   OCCURS AFTER           741.19  ML
```

```
                 FEED PARAMETERS
                 ---------------
COMPONENT    PPM  EQUIVALENT SELECTIVITY  CHARGE
                   FRACTION  COEFFICIENT
 COPPER     50.0     .314        3.031     2.000
  IRON      50.0     .357        2.756     2.000
  ZINC      50.0     .305        2.732     2.000
HYDROGEN      .1     .025        1.000     1.000

     PH                      3.90
EXCHANGER CAPACITY           1.980  MEQ/ML
SOLUTION CONCENTRATION        .0050N


                 CONCENTRATION PROFILES
                      IN THE BED

      EQUIVALENT FRACTION IN THE LIQUID PHASE

COPPER    IRON     ZINC   HYDROGEN   ZONE NO.& TYPE
 .3135    .3567    .3047    .0251    1ST PLATEAU
 .2318    .4035    .3396    .0251    1ST TRANSITION
 .1515    .4495    .3739    .0251    1ST TRANSITION
 .0725    .4947    .4077    .0251    1ST TRANSITION
          .5362    .4387    .0251    2ND PLATEAU
          .4874    .4875    .0251    2ND TRANSITION
          .4386    .5362    .0251    2ND TRANSITION
          .3899    .5850    .0251    2ND TRANSITION
          .3413    .6336    .0251    2ND TRANSITION
          .2926    .6823    .0251    2ND TRANSITION
          .2440    .7309    .0251    2ND TRANSITION
          .1955    .7794    .0251    2ND TRANSITION
          .1470    .8279    .0251    2ND TRANSITION
          .0985    .8764    .0251    2ND TRANSITION
          .0501    .9248    .0251    2ND TRANSITION
                   .9748    .0252    3RD PLATEAU
                   .0178    .9822    3RD TRANSITION
                   .0034    .9966    3RD TRANSITION
                   .0010    .9990    3RD TRANSITION
                   .0003    .9997    3RD TRANSITION


                 BREAKTHROUGH CONDITIONS
                 -----------------------

      FOR THE FOLLOWING BED PARAMETERS
          (A) BED VOLUME                       100.00 ML
          (B) VOID FRACTION                       .40
          (C) EXCHANGER CAPACITY                 1.98 MEQ/ML

      BREAKTHROUGH OF   ZINC   OCCURS AFTER  11589.83 ML
```

```
                   FEED PARAMETERS
                   ---------------
COMPONENT    PPM   EQUIVALENT  SELECTIVITY   CHARGE
                    FRACTION   COEFFICIENT
  NICKEL    2000.0     .249         3.094      2.000
  COPPER    2000.0     .230         3.031      2.000
   IRON     2000.0     .261         2.756      2.000
   ZINC     2000.0     .223         2.732      2.000
HYDROGEN      10.0     .037         1.000      1.000

    PH                          2.00
EXCHANGER CAPACITY              1.980  MEQ/ML
SOLUTION CONCENTRATION           .2739N


                    CONCENTRATION PROFILES
                         IN THE BED

          EQUIVALENT FRACTION IN THE LIQUID PHASE

NICKEL   COPPER     IRON     ZINC   HYDROGEN  ZONE NO.& TYPE
 .2487    .2298    .2615    .2234    .0365    1ST PLATEAU
 .1938    .2758    .2666    .2274    .0365    1ST TRANSITION
 .1390    .3215    .2716    .2313    .0365    1ST TRANSITION
 .0846    .3670    .2766    .2353    .0365    1ST TRANSITION
 .0303    .4124    .2816    .2392    .0366    1ST TRANSITION
          .4372    .2846    .2416    .0366    2ND PLATEAU
          .3551    .3324    .2759    .0366    2ND TRANSITION
          .2743    .3794    .3096    .0367    2ND TRANSITION
          .1948    .4257    .3428    .0367    2ND TRANSITION
          .1167    .4712    .3754    .0368    2ND TRANSITION
          .0398    .5159    .4075    .0368    2ND TRANSITION
                   .5391    .4241    .0368    3RD PLATEAU
                   .4905    .4727    .0368    3RD TRANSITION
                   .4419    .5213    .0368    3RD TRANSITION
                   .3934    .5698    .0368    3RD TRANSITION
                   .3449    .6182    .0368    3RD TRANSITION
                   .2965    .6667    .0368    3RD TRANSITION
                   .2481    .7151    .0368    3RD TRANSITION
                   .1998    .7634    .0368    3RD TRANSITION
                   .1515    .8117    .0368    3RD TRANSITION
                   .1032    .8599    .0369    3RD TRANSITION
                   .0550    .9082    .0369    3RD TRANSITION
                   .0068    .9563    .0369    3RD TRANSITION
                            .9631    .0369    4TH PLATEAU
                            .3682    .6318    4TH TRANSITION
                            .1345    .8655    4TH TRANSITION
                            .0485    .9515    4TH TRANSITION
                            .0144    .9856    4TH TRANSITION


                   BREAKTHROUGH CONDITIONS
                   -----------------------

        FOR THE FOLLOWING BED PARAMETERS
            (A) BED VOLUME                              100.00  ML
            (B) VOID FRACTION                              .40
            (C) EXCHANGER CAPACITY                        1.98  MEQ/ML

      BREAKTHROUGH OF   ZINC    OCCURS AFTER      288.51  ML
```

```
                 FEED PARAMETERS
                 ---------------
COMPONENT    PPM   EQUIVALENT  SELECTIVITY   CHARGE
                    FRACTION   COEFFICIENT
  NICKEL   2000.0     .323          3.094      2.000
   IRON    2000.0     .340          2.756      2.000
   ZINC    2000.0     .290          2.732      2.000
HYDROGEN     10.0     .047          1.000      1.000

    .PH                         2.00
EXCHANGER CAPACITY              1.980 MEQ/ML
SOLUTION CONCENTRATION           .2109N


                  CONCENTRATION PROFILES
                      IN THE BED

       EQUIVALENT FRACTION IN THE LIQUID PHASE

NICKEL     IRON      ZINC   HYDROGEN   ZONE NO.& TYPE
 .3230    .3395     .2901    .0474     1ST PLATEAU
 .2421    .3854     .3250    .0475     1ST TRANSITION
 .1629    .4304     .3592    .0475     1ST TRANSITION
 .0852    .4745     .3927    .0476     1ST TRANSITION
 .0091    .5177     .4255    .0476     1ST TRANSITION
          .5228     .4295    .0477     2ND PLATEAU
          .4747     .4776    .0477     2ND TRANSITION
          .4267     .5256    .0477     2ND TRANSITION
          .3786     .5736    .0477     2ND TRANSITION
          .3307     .6216    .0477     2ND TRANSITION
          .2827     .6695    .0477     2ND TRANSITION
          .2349     .7174    .0477     2ND TRANSITION
          .1870     .7653    .0477     2ND TRANSITION
          .1392     .8131    .0477     2ND TRANSITION
          .0915     .8608    .0477     2ND TRANSITION
          .0437     .9085    .0477     2ND TRANSITION
                    .9522    .0478     3RD PLATEAU
                    .3222    .6778     3RD TRANSITION
                    .1089    .8911     3RD TRANSITION
                    .0379    .9621     3RD TRANSITION
                    .0111    .9889     3RD TRANSITION


                  BREAKTHROUGH CONDITIONS
                  -----------------------

      FOR THE FOLLOWING BED PARAMETERS
          (A) BED VOLUME                          100.00 ML
          (B) VOID FRACTION                          .40
          (C) EXCHANGER CAPACITY                    1.98 MEQ/ML

    BREAKTHROUGH OF   ZINC   OCCURS AFTER     512.78 ML
```

```
                    FEED PARAMETERS
                    ---------------
COMPONENT     PPM    EQUIVALENT SELECTIVITY   CHARGE
                       FRACTION  COEFFICIENT
 COPPER    2000.0      .306        3.031       2.000
  IRON     2000.0      .348        2.756       2.000
  ZINC     2000.0      .297        2.732       2.000
HYDROGEN     10.0      .049        1.000       1.000

     PH                          2.00
EXCHANGER CAPACITY               1.980 MEQ/ML
SOLUTION CONCENTRATION            .2058N


                    CONCENTRATION PROFILES
                         IN THE BED

           EQUIVALENT FRACTION IN THE LIQUID PHASE

COPPER     IRON      ZINC    HYDROGEN    ZONE NO.& TYPE
 .3059     .3481     .2974     .0486     1ST PLATEAU
 .2254     .3942     .3317     .0486     1ST TRANSITION
 .1464     .4394     .3655     .0487     1ST TRANSITION
 .0686     .4840     .3987     .0487     1ST TRANSITION
           .5232     .4280     .0488     2ND PLATEAU
           .4751     .4761     .0488     2ND TRANSITION
           .4271     .5241     .0488     2ND TRANSITION
           .3791     .5720     .0488     2ND TRANSITION
           .3312     .6199     .0488     2ND TRANSITION
           .2833     .6678     .0488     2ND TRANSITION
           .2355     .7156     .0488     2ND TRANSITION
           .1877     .7634     .0489     2ND TRANSITION
           .1400     .8112     .0489     2ND TRANSITION
           .0923     .8589     .0489     2ND TRANSITION
           .0446     .9066     .0489     2ND TRANSITION
                     .9511     .0489     3RD PLATEAU
                     .3179     .6821     3RD TRANSITION
                     .1067     .8933     3RD TRANSITION
                     .0370     .9630     3RD TRANSITION
                     .0108     .9892     3RD TRANSITION


                    BREAKTHROUGH CONDITIONS
                    -----------------------

          FOR THE FOLLOWING BED PARAMETERS
             (A) BED VOLUME                          100.00 ML
             (B) VOID FRACTION                          .40
             (C) EXCHANGER CAPACITY                    1.98 MEQ/ML

       BREAKTHROUGH OF    ZINC    OCCURS AFTER      545.19 ML
```

```
                  FEED PARAMETERS
                  ---------------
COMPONENT    PPM   EQUIVALENT SELECTIVITY   CHARGE
                    FRACTION  COEFFICIENT
 NICKEL     100.0     .147        3.094      2.000
 COPPER     100.0     .136        3.031      2.000
  IRON      100.0     .154        2.756      2.000
  ZINC      100.0     .132        2.732      2.000
HYDROGEN     10.0     .431        1.000      1.000

    PH                          2.00
EXCHANGER CAPACITY              1.980  MEQ/ML
SOLUTION CONCENTRATION           .0232N


                   CONCENTRATION PROFILES
                         IN THE BED

          EQUIVALENT FRACTION IN THE LIQUID PHASE

NICKEL   COPPER     IRON      ZINC   HYDROGEN   ZONE NO.& TYPE
 .1469    .1357    .1544     .1319    .4311     1ST PLATEAU
 .1135    .1636    .1575     .1343    .4312     1ST TRANSITION
 .0802    .1914    .1605     .1367    .4312     1ST TRANSITION
 .0471    .2190    .1636     .1391    .4312     1ST TRANSITION
 .0142    .2465    .1666     .1415    .4312     1ST TRANSITION
          .2577    .1680     .1426    .4317     2ND PLATEAU
          .2078    .1969     .1634    .4319     2ND TRANSITION
          .1587    .2255     .1838    .4320     2ND TRANSITION
          .1105    .2535     .2039    .4321     2ND TRANSITION
          .0631    .2810     .2237    .4322     2ND TRANSITION
          .0165    .3081     .2431    .4323     2ND TRANSITION
                   .3175     .2499    .4327     3RD PLATEAU
                   .2879     .2793    .4328     3RD TRANSITION
                   .2585     .3087    .4328     3RD TRANSITION
                   .2291     .3381    .4328     3RD TRANSITION
                   .1997     .3675    .4328     3RD TRANSITION
                   .1703     .3969    .4328     3RD TRANSITION
                   .1410     .4262    .4328     3RD TRANSITION
                   .1117     .4555    .4328     3RD TRANSITION
                   .0824     .4848    .4328     3RD TRANSITION
                   .0531     .5140    .4328     3RD TRANSITION
                   .0239     .5433    .4328     3RD TRANSITION
                             .5667    .4333     4TH PLATEAU
                             .0523    .9477     4TH TRANSITION
                             .0123    .9877     4TH TRANSITION
                             .0038    .9962     4TH TRANSITION
                             .0010    .9990     4TH TRANSITION


                   BREAKTHROUGH CONDITIONS
                   -----------------------

       FOR THE FOLLOWING BED PARAMETERS
           (A) BED VOLUME                           100.00  ML
           (B) VOID FRACTION                           .40
           (C) EXCHANGER CAPACITY                     1.98  MEQ/ML

    BREAKTHROUGH OF   ZINC    OCCURS AFTER   3230.26  ML
```

APPENDIX E

DISCUSSION OF PROPOSED TREATMENT PLANT

The proposed plant on which the economics are evaluated is outlined below. This plant would incorporate two ion exchange columns of a capacity dependent upon the volume of solution to be treated.

The operation of the treatment plant would involve all the steps necessary for the loading and subsequent separation of the metallic waste wash solution.

The loading of the anion and cation column would be a series operation in which the solution to be treated is passed through the cation column first. This avoids precipitation of metals if the column order were reversed. The acidified solution emanating from the column also assists the free CN^- uptake in the anion column in that it provides a better driving force for the reaction.

In the present layout the cation column on the regeneration cycle would allow the separated metals to pass straight to the respective plating tanks as make-up solution. This may, however, be changed to a holding tank where the solution can be further concentrated by solid addition to plating bath strength.

The effluent from the anion column would be passed to a holding tank that initially contains alkaline solution. During the acid regeneration of this column, the loaded chromate breaks down to the cationic chrome form which precipitates out on being neutralised in the holding tank. The chrome hydroxide formed is then removed for chrome recovery after which a cyanide oxidation treatment is followed by adding chlorine to the tank.

After cyanide treatment the tank can be limed to precipitate calcium sulphate. This is removed leaving a caustic salt solution which could be treated to recover sodium hydroxide and chlorine, both of which can then be reused in subsequent treatment.

In order to improve the economic viability of the treatment process, the separated metal solution can be further treated. This would include loading onto a cation column in the NH_4^+ form after the individual solutions had been acidified. Acidification of the respective solutions results in the citrate complexes being broken with consequent citric acid precipitation and recovery.

The effluent from the column loading operation which now contains only $(NH_4)_2SO_4$ could again be limed with resulting NH_3 recovery and $CaSO_4$ precipitation. The loaded columns are then regenerated with H_2SO_4 to give a further concentration step, and the eluted metals are recycled to the plating operation.

ECONOMIC EVALUATION OF PROPOSED TREATMENT PLANT

Basis of Calculation:

Plant costed to treat the following stream:

(a) Flowrate - 4000 litres/day

(b) Concentration -

Component	Concentration (ppm)
Cu	200
Ni	200
Zn	200
Fe	200
CN^-	250
Cr	200
pH	2,5

Assumptions:

(a) Resin Volume - resin requirements are such that capacity is sufficient to load a working days effluent.

(b) Association of Anions/Cations - toxic anions are not associated with toxic cations,

i.e. cation for CN^- and $CrO_4^{=}$ is Na^+

anion for Cu, Ni, Fe and Zn is $SO_4^{=}$.

(c) Resin and Equipment Cost - cost of resin and equipment is equal.

Resin Requirements

(a) Capacity of Resins -

Cation	Amberlite IR-120	1,90 equiv/litre
Anion	Amberlite IRA-400	1,40 equiv/litre [71]

(b) Resin Volume - the following resin equivalents are required to treat each metal.

Component	Equiv./day
Cu^{2+}	25,12
Ni^{2+}	28,16
Fe^{2+}	28,68
Zn^{2+}	24,52
Na^+ for CrO_4^{-2}	27,72
Na^+ for CN^-	35,72
	171,92

Cation resin capacity required: 200 equivalents

Cation resin volume required $= \frac{200}{1,90}$

$= 105$ litres

Anion resin volume required $= \frac{200}{1,40}$

$= 143$ litres

(c) Resin Costs

Cation resin density - 0,8 kilo/litre

Anion resin density - 0,7 kilo/litre

Cost of resins (i) Cation R0-97/kilo

(ii) Anion R3-52/kilo

Mass of Resin required (i) Cation 84 kg

(ii) Anion 100,1 kg

Total Cost (i) Cation R292

(ii) Anion R690

Chemical Costs

(a) Regeneration Chemicals.

NH_3 (15M)	R0-13/litre
H_2SO_4 (36N)	R0-17/litre
Citric acid	R0-73/kilo

(b) Cost of metals lost.

$CuSO_4$	R0-45/kilo
$FeSO_4$	Negligible
$NiSO_4$	R0-60/kilo
$ZnSO_4$	R0-26/kilo
$Cr_2(SO_4)_3$	R1-40/kilo

These costs are for industrial quantities as of 1.9.73 - Cape Town.

Regeneration Requirements

(a) Elution of Copper.

Feed Composition: pH = 10,8 NH_4^+ = 0,2N

Volume required: 10 bed volumes = 1050 litres

Chemicals required:

	Component	Volume (litres)	Cost
	H_2SO_4	5,8	R0-99
(i)	NH_3	100,0	R13-00
(ii)	NH_3	43,7	R5-46

(i) Required for production of $(NH_4)_2SO_4$

(ii) Required for resin conditioning prior to elution.

(b) Elution of Nickel.

Feed Composition: pH = 9,8 Citric acid = 0,05M

Volume required: 10 bed volumes = 1050 litres

Chemicals required:

Component	Quantity	Cost
Citric acid	11,1kg	R8-04
NH_3	38,8 litres	R4-85

(c) Elution of Zinc.

Feed Composition: pH = 6,4 Citric acid = 0,05M

Volume required: 10 bed volumes = 1050 litres

Chemicals required:

Component	Quantity	Cost
Citric acid	11,1kg	R8-04

(d) Final Regeneration.

Feed Composition: 20wt% H_2SO_4

Volume required: 2,5 bed volumes = 263 litres

Chemicals required: 29,5 litres of H_2SO_4; Cost - R5-00

(e) Anion Column Regeneration.

Feed Composition: (i) 10wt% H_2SO_4

(ii) 20% w/v NaOH .

Volume required: (i) and (ii) 2,5 bed volumes = 263 litres

Chemicals required:

Component	Quantity	Cost
H_2SO_4	15 litres	R2-50
NaOH	53kg	R9-50

Value of Recovered Metal Salts in Solution

Metal	Quantity (kg)	Value
Cu	3,144	R1-40
Ni	3,656	R2-20
Zn	3,536	R1-00
Cr	5,31	R7-45
		R12-00

Economic Balance

(a) Resin Costs - expected life of one year.

Cation R292/year = R0-97/day

Anion R690/year = R2-30/day

(b) Equipment - depreciated over 5 years.

Total Cost - R1000

= R200/year = R0-66/day.

(c) Total costs per day

Resin	R 3-30
Equipment	R 0-70
Regeneration	R57-40
	R61-40

APPENDIX F

METHODS OF ANALYSIS

(A) THEORY AND PROCEDURE IN ATOMIC ABSORPTION SPECTROSCOPY

The analytical method works by measuring the intensity of transmitted radiation of a particular wavelength. The transmission intensity, altered by the amount of radiation absorbed by the sample that is aspirated into the apparatus, is expressed mathematically by Beer's Law [72]:

$$I_t = I_o \, e^{-kc\ell}$$

I_t - intensity of transmitted radiation
I_o - intensity of incident radiation
k - absorption coefficient
c - concentration of absorbing atoms
ℓ - length of absorption path

For constant k and ℓ, the concentration of the absorbing atoms is proportional to the absorbence expressed as

$$\log_{10} \frac{I_o}{I_t} = \text{absorbence} \propto c$$

The experimental settings are summarised in Table F.1, whilst Figures F.1, F.2 show typical calibration curves obtained.

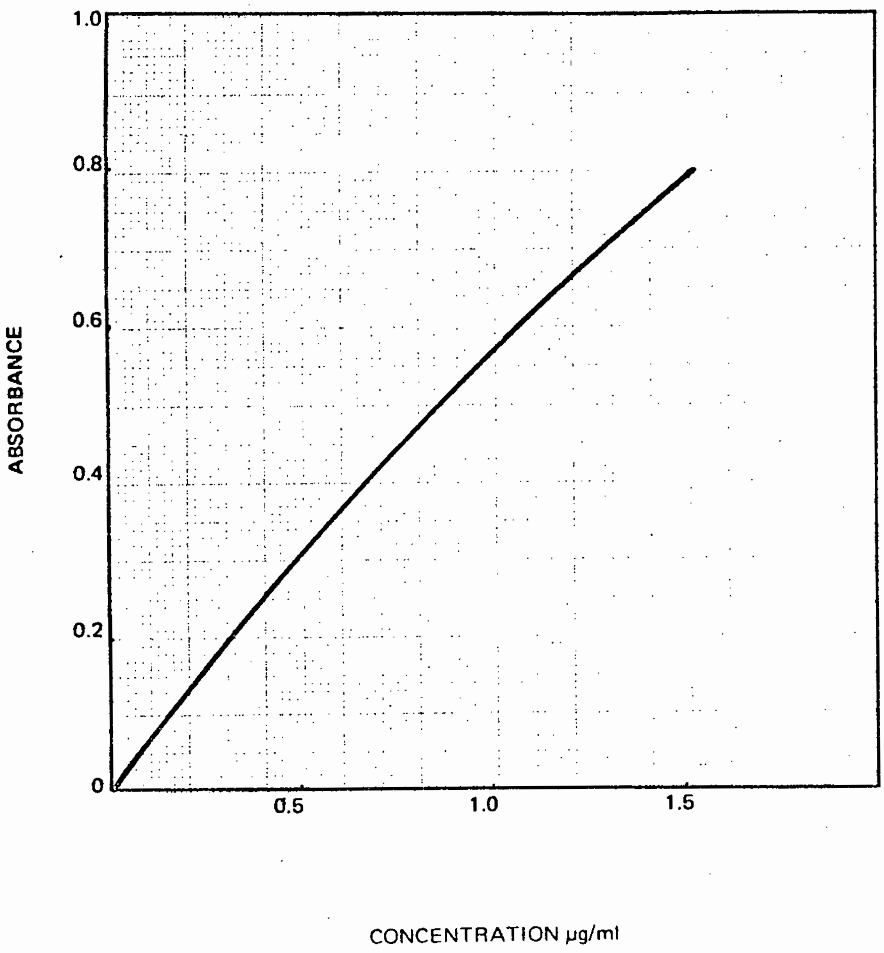
(B) ANALYSIS OF SOLUTIONS CONTAINING CYANIDE

(a) Distillation of sample

A sample of solution containing 10 to 15mg of CN^- to be analysed is placed in an all glass distillation apparatus, and diluted to 400ml. Ten ml of freshly prepared solution of 2% w/v $CuCl_2$ in 5N HCl is then added. The whole is distilled so that HCN gas is evolved and allowed to pass into

TABLE F.1

Metal	Wavelength (nm)	Lamp Current (mA)	Burner Fuel	Slit width	Support gas
Cu	324,8	3	Acetylene	0,2	Air
Fe	248,8	5	"	0,2	Air
Ni	232,0	5	"	0,2	Air
Zn	213,9	5	"	0,5	Air
Na	589,0	5	"	0,2	Air



ZINC CALIBRATION CURVE

FIGURE F.1

a beaker containing 2,5N NaOH. Distillation is continued until successive 40ml samples contain no further cyanide.

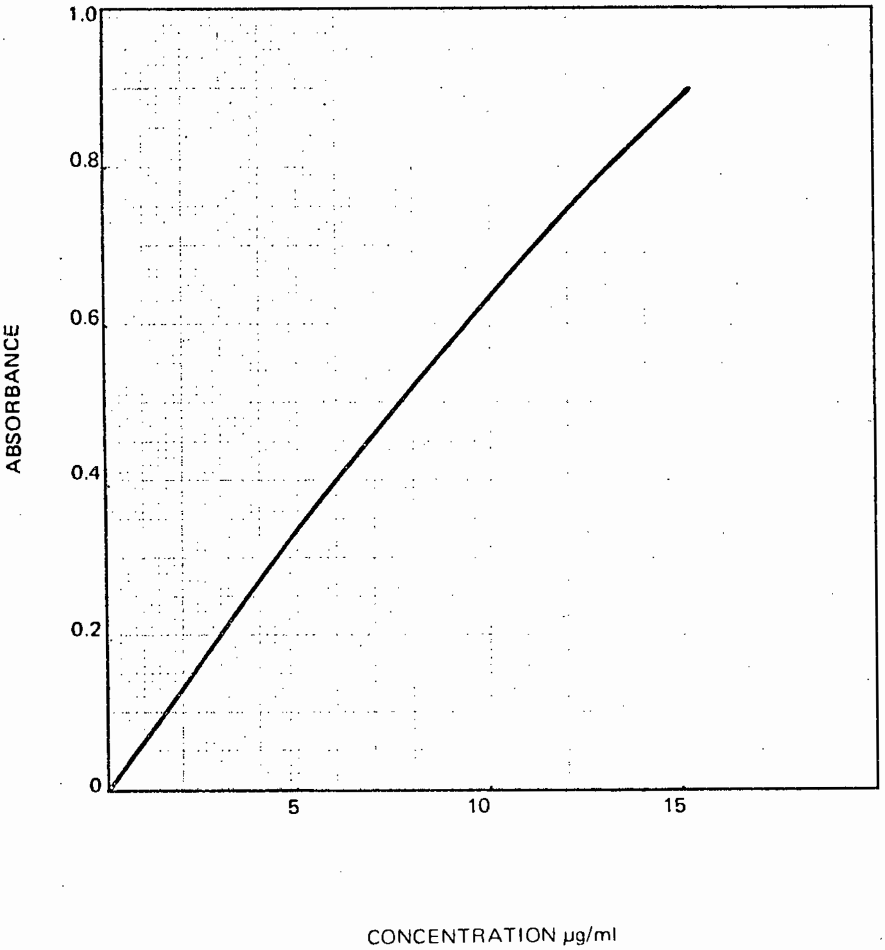
(b) Titration of Sample

The sample is titrated with 0,01N $AgNO_3$ solution using a 0,02% w/v solution of p-dimethylaminobenzylidene rhodanine in acetone as indicator. The end point is indicated by a permanent red colour.

(c) Determination of Result

$$1\text{ml } 0{,}01\text{N } AgNO_3 \equiv 0{,}52\text{mg of } CN^-$$

Test procedures on the method, using potassium ferrocyanide to make up standard solutions containing 50 and 100mg of CN^-, showed a 99% accuracy in both determinations.



COPPER CALIBRATION CURVE

FIGURE F.2

APPENDIX G

DISTRIBUTION COEFFICIENTS IN CITRIC ACID MEDIA

IRON3+

PH	LOG DM	LOG ALPHA CITRATE	LOG ALPHA NH3	LOG ALPHA OH
2.50	.97	4.78	.00	.00
3.00	-1.49	6.79	.00	.00
3.50	-5.04	10.24	.00	.00
4.00	-8.30	13.47	.00	.00
4.50	-11.36	16.52	.00	.00
5.00	-14.07	19.23	.00	.00
5.50	-15.58	20.74	.00	.00
6.00	-15.90	21.06	.00	.00
6.50	-15.94	21.09	.00	.00
7.00	-15.94	21.10	.00	.00
7.50	-15.95	21.10	.00	.00
8.00	-15.97	21.10	.00	.03
8.50	-16.21	21.10	.00	.26
9.00	-17.38	21.10	.00	1.44
9.50	-19.26	21.10	.00	3.31
10.00	-21.25	21.10	.00	5.30
10.50	-23.24	21.10	.00	7.30
11.00	-25.24	21.10	.00	9.30
11.50	-27.24	21.10	.00	11.30
12.00	-29.24	21.10	.00	13.29
12.50	-31.23	21.10	.00	15.28
13.00	-33.19	21.10	.00	17.25
13.50	-35.09	21.10	.00	19.14
14.00	-36.82	21.10	.00	20.88

TABLE G.1

NICKEL

PH	LOG DM	LOG ALPHA CITRATE	LOG ALPHA NH3	LOG ALPHA OH
2.50	4.16	1.59	.00	.00
3.00	2.40	2.90	.00	.00
3.50	1.11	4.08	.00	.00
4.00	.00	5.16	.00	.00
4.50	-1.18	6.33	.00	.00
5.00	-3.40	8.54	.00	.00
5.50	-4.90	10.04	.01	.00
6.00	-5.31	10.36	.10	.00
6.50	-5.79	10.39	.54	.00
7.00	-6.66	10.40	1.41	.00
7.50	-7.64	10.40	2.39	.00
8.00	-8.63	10.40	3.38	.00
8.50	-9.59	10.40	4.34	.00
9.00	-10.50	10.40	5.25	.00
9.50	-11.29	10.40	6.04	.00
10.00	-11.95	10.40	6.69	.00
10.50	-12.51	10.40	7.26	.00
11.00	-13.05	10.40	7.78	.01
11.50	-13.91	10.40	8.56	.10
12.00	-16.83	10.40	11.03	.54
12.50	-20.60	10.40	13.94	1.41
13.00	-24.53	10.40	16.91	2.38
13.50	-28.47	10.40	19.90	3.32
14.00	-32.33	10.40	22.89	4.19

TABLE G.2

****ZINC****

PH	LOG DM	LOG ALPHA CITRATE	LOG ALPHA NH3	LOG ALPHA OH
2.50	4.39	1.30	.00	.00
3.00	2.64	2.60	.00	.00
3.50	1.36	3.78	.00	.00
4.00	.25	4.86	.00	.00
4.50	-.78	5.87	.00	.00
5.00	-1.71	6.81	.00	.00
5.50	-2.42	7.52	.00	.00
6.00	-2.63	7.72	.00	.00
6.50	-2.66	7.75	.00	.00
7.00	-2.66	7.75	.00	.00
7.50	-2.66	7.75	.00	.00
8.00	-2.66	7.75	.00	.00
8.50	-2.67	7.75	.01	.00
9.00	-2.72	7.75	.06	.00
9.50	-3.26	7.75	.60	.00
10.00	-5.12	7.75	2.46	.00
10.50	-7.24	7.75	4.58	.00
11.00	-9.30	7.75	6.63	.04
11.50	-11.40	7.75	8.65	.09
12.00	-15.13	7.75	10.66	1.81
12.50	-20.10	7.75	12.66	4.78
13.00	-25.07	7.75	14.66	7.75
13.50	-30.10	7.75	16.66	10.78
14.00	-35.25	7.75	18.66	13.93

TABLE G.3

IRON2+

PH	LOG DM	LOG ALPHA CITRATE	LOG ALPHA NH3	LOG ALPHA OH
2.50	5.45	.25	.00	.00
3.00	4.02	1.22	.00	.00
3.50	2.75	2.39	.00	.00
4.00	1.02	4.09	.00	.00
4.50	-1.92	7.02	.00	.00
5.00	-4.63	9.73	.00	.00
5.50	-6.14	11.24	.00	.00
6.00	-6.46	11.56	.00	.00
6.50	-6.50	11.59	.00	.00
7.00	-6.50	11.60	.00	.00
7.50	-6.50	11.60	.00	.00
8.00	-6.50	11.60	.00	.00
8.50	-6.50	11.60	.00	.00
9.00	-6.51	11.60	.01	.00
9.50	-6.55	11.60	.05	.00
10.00	-6.70	11.60	.20	.00
10.50	-7.09	11.60	.59	.00
11.00	-8.05	11.60	1.54	.01
11.50	-9.89	11.60	3.31	.08
12.00	-12.27	11.60	5.30	.47
12.50	-15.11	11.60	7.30	1.31
13.00	-18.08	11.60	9.30	2.28
13.50	-21.02	11.60	11.30	3.22
14.00	-23.89	11.60	13.30	4.09

TABLE G.4

RATIO OF THE DISTRIBUTION COEFFICIENTS

LOG(DM1/DM2)

PH	IRON3+/NICKEL	NICKEL/ZINC	ZINC/IRON2+
2.50	-3.18	-.23	-1.06
3.00	-3.89	-.25	-1.38
3.50	-6.15	-.25	-1.39
4.00	-8.30	-.25	-.77
4.50	-10.18	-.40	1.14
5.00	-10.68	-1.68	2.92
5.50	-10.68	-2.48	3.72
6.00	-10.60	-2.68	3.83
6.50	-10.15	-3.13	3.84
7.00	-9.28	-4.00	3.84
7.50	-8.31	-4.98	3.84
8.00	-7.34	-5.97	3.84
8.50	-6.61	-6.93	3.84
9.00	-6.88	-7.77	3.79
9.50	-7.97	-8.03	3.29
10.00	-9.30	-6.82	1.57
10.50	-10.73	-5.27	-.15
11.00	-12.20	-3.75	-1.25
11.50	-13.33	-2.52	-1.51
12.00	-12.41	-1.70	-2.85
12.50	-10.62	-.50	-4.98
13.00	-8.66	.54	-6.99
13.50	-6.62	1.64	-9.08
14.00	-4.49	2.92	-11.36

TABLE G.5

APPENDIX H

CALCULATION METHOD FOR DETERMINING PERCENTAGE PURITY AND CUMULATIVE PERCENTAGE YIELD

Results of Run No.28

Volume of Regenerant (ml)	Effluent Concentration (ppm) Fe	Ni	Zn
100	1636	391	58
200	3927	899	178
300	3291	989	166
400	2818	1029	156
500	2000	1058	133
600	1291	855	152
700	581	710	112
800	473	869	77
Mass of metal on Resin Bed (mg)	1327	1319	1620

(a) Calculation of Percentage Purity.

The percentage purity of the particular metal in question is calculated by determining the percentage of that metal in the effluent sample related to the total metal content of the sample

$$\%\text{Fe in sample 1 above} = \frac{1636}{1636 + 391 + 58} \times \frac{100}{1}$$

$$= 78{,}5\%$$

$$\%\text{Ni in sample 1} = \frac{391}{1636 + 391 + 58} \times \frac{100}{1}$$

$$= 18{,}8\%$$

(b) Calculation of Cumulative Percentage Eluted.

The calculation of the elution percentage is carried out by determining the total mass of metal eluted after each sample and expressing this as a percentage of the mass of metal loaded onto the column for the run in question.

Concentration of Fe in sample 1 = 1636mg/ℓ

Volume of sample 1 = 100ml

$$\text{Mass of Fe in sample 1} = 1636\ \frac{\text{mg}}{\text{litre}} \times \frac{100}{1}\ \text{ml} \times \frac{1}{1000}\ \frac{\text{litre}}{\text{ml}}$$

$$= 163{,}6\text{mg}$$

Total Mass of Fe loaded = 1327mg

$$\text{Cumulative \%Fe in sample 1} = \frac{163{,}6}{1327} \times \frac{100}{1}$$

$$= 8{,}6\%$$

Concentration of Fe in sample 2 = 3927

Volume of sample 2 = 100ml

$$\text{Mass of Fe in sample 2} = 3927\ \frac{\text{mg}}{\text{litre}} \times \frac{1}{10}\ \text{litre}$$

$$= 392{,}7\text{mg}$$

Total Mass of Fe eluted after 200ml of elutant = Mass of Fe in 1 + Mass of Fe in 2 = 163,6 + 392,7

= 558,3

$$\text{Cumulative \%Fe up to sample 2} = \frac{558{,}3}{1327} \times \frac{100}{1}$$

$$= 30{,}0\%$$

The same procedure is used to determine the cumulative percentage of the other metals eluted for each sample.