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A study of the anion exchange behavior of certain divalent cations in sodium nitrite media

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A STUDY OF THE ANION EXCHANGE BEHAVIOR OF CERTAIN DIVALENT CATIONS IN SODIUM NITRITE MEDIA

by

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B.A. Montana State University, 1961

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1966

Approved by:

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Dean, Graduate School

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Date

ACKNOWLEDGMENT

The author expresses his appreciation to Dr. Wayne P. Van Meter for the guidance and counsel throughout the course of this investigation.

Special acknowledment is extended to my wife, Virginia, for her sincere encouragement and understanding.

FOREWORD

This work was undertaken to determine the elution behavior of certain divalent cations on a strong base quaternary amine ion exchange resin employing sodium nitrite solutions as the eluant ranging in concentration from 10^{-4} to 8M.

These data were then used to predict possible separations and to elucidate the nature of the anionic species adsorbing on the resin.

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A Study of the Anion Exchange Behavior of Certain Divalent Cations in Sodium Nitrite Media. (32 pp.)

Director: Dr. Wayne P. Van Meter

The elution constants for divalent Co, Mn, Ni, Cu, Zn and Pb were determined by the method of Kraus and Moore on a strong base quaternary amine ion exchange resin using sodium nitrite solution as eluant ranging in concentration from 10^{-4} to 8M. Precursory studies were also made with divalent Cd and UO_2.

The results are expressed in terms of the elution constant E, which is defined by the equation

$$E = \frac{dA}{V}$$

where d is the distance in cm. which the concentration maximum of the band traveled through a column of cross sectional area A in cm.^{2}, when a volume of V ml of eluant has passed through the column.

All the elements studied were found to adsorb on the resin to some extent, with the possible exception of Ni, and therefore were forming anionic species. The order of decreasing affinity of the elements for the resin at an eluant concentration at which the element starts adsorbing is $Cd \approx Cu > Pb > Zn > UO_2 > Co > Mn > Ni$.

All possible binary separations were effected except the Mn-Ni, Cd-Cu, and the UO_2-Zn mixtures. Several three component and four component separations were also effected.

The charges on the anionic species were determined. In all cases the adsorbing ion appears to have a charge of minus one. In addition to this species, there appeared to be another species formed at intermediate nitrite concentrations. The nature of this species, if present, can only be speculated upon.

TABLE OF CONTENTS

PAGE

INTRODUCTION

Ion exchange processes first proved their versatility as a separation technique with the separation of the rare earth elements (11, 28, 57, 58, 60). This technique has revolutionized separation schemes for the elements in the ease of the process, the time involved, and the high purity of the separated product. In addition, many investigators have separated other traditionally difficult combinations such as the Zr-Hf and Nb-Ta mixtures (22, 33, 34, 35, 36).

Kraus and Moore in the United States initiated studies on the elution behavior of the more common transition and representative elements.

Since their work separating Co from Ni using hydrochloric acid as eluant (37), many investigators have used this eluant either alone (6, 8, 26, 38, 40, 41, 42, 43, 46, 47, 53, 54, 59, 61, 62), or in combination with other substances to separate a great number of the elements and many of the heavier representative elements. Of particular usefulness is the constant hydrochloric acid-variable hydrofluoric acid eluant which is capable of separating virtually every combination of transition elements possible (22, 33, 34, 35, 36, 39, 50). In addition to this hydrochloric acid based eluant, other investigators have studied the elution properties of these metals using phosphoric acid (10, 13, 21), nitric acid (21, 30, 45), ethylenediamine tetracetic acid (23, 48, 49, 55), sulfuric acid (21), hydrobromic acid (14), hydroiodic acid (24, 25), and other miscellaneous and non-aqueous media as eluants (1, 2, 9, 27, 30, 45, 51).

The application of the ion exchange technique is not limited to the separation potential, but has been extended to investigate the nature of the species adsorbing in the resin. Many systems have been studied using both cation and anion exchange resins (3, 4, 5, 7, 16, 17, 18, 19, 20, 32, 42, 44, 51, 56). Cation and anion exchangers can be useful in elucidating the charges of cationic and anionic species, respectively.

EXPERIMENTAL PROCEDURE

The experimental procedure used in this study is based on that developed by Kraus and Moore. (34).

Apparatus

Columns: The columns used for the determination of the elution constants were constructed from pyrex glass tubing. The internal diameter of these columns was 0.49 cm. in all cases, and the length varied depending on the element being studied. Columns 13 cm. in length were used when studying strongly adsorbed colorless species, while 60 cm. columns were used for the weakly adsorbed species. The lengths of the columns for the colored bands were immaterial since the bands were not eluted from the columns.

The columns were constructed with an enlarged section at the top in order to facilitate the attachment of a burette for eluant volume measurement. The flow rate through the columns was regulated by a Hoke needle valve fitted with a capillary tip.

The columns used for the separations (see p. 16) were sections of burettes. The internal diameter was 1.0 cm. and the length 13.5 cm.

Resin: The resin used in the experiment was Dowex 1-X8, a quaternary amine strong base anion exchange resin of 8% cross-linkage in the nitrite form. The resin as purchased was in the chloride form and was converted to the nitrite form first by static treatment in a strong solution of sodium nitrite and then by additional conditioning on the column. The resin was added to the column in a slurry and backwashed three times to insure a uniform resin bed. The fine resin particles which settled slower were removed after each backwash to further insure the uniformity of the resin bed.

GENERAL PROCEDURE

The resin in the chloride form was converted to the nitrite form (see p. 3). The resin was added to the column in a slurry and backwashed three times to obtain a uniform resin bed. The finer resin particles were removed after each backwashing by removing the solution containing the slower settling fines above the settled resin bed.

The flow rate of eluant through the columns was maintained at 0.5 cm. per minute which was the value used by Kraus and Moore and was found to be suitable for these studies. The equivalent volume flow rate was determined by eluting a nonadsorbed cation, such as Ba, through the resin bed. The volume required to elute the concentration maximum of this cation was the interstitial volume in the resin. The interstitial volume for a 0.5 cm. length of resin bed is the desired volume flow rate per minute. Corrections were made for the dead space in the needle valve and below the resin bed in the column.

The dead volume below the resin bed and in the valve was determined by eluting a strong cobalt solution which is colored and easily observed through the resin bed. The volume required to elute the breakthrough of this colored solution from the resin bed through the needle valve was considered to be the dead volume.

After the resin bed had been conditioned with the appropriate concentration of sodium nitrite, 0.1 ml. of a solution containing 3 mg of metal ion in the same concentration of sodium nitrite as the eluant to be used was allowed to seep into the resin bed a drop at a time in order to avoid wetting the walls of the column above the bed and prevent apparent band tailing. The flow rate through the column during this step was slower than 0.5 cm. per minute to aid in the formation of a more nearly ideal band. The bed was then covered with a piece of glass wool to prevent disturbing the resin bed. A small increment of eluant was added to the column several times and allowed to seep in, insuring that all of the metal ion was in the bed. Any bubbles trapped in the glass wool were dislodged, and the 50 ml. burette used to deliver the eluant was then attached to the column. The stopcock of the burette was opened slowly at first to allow for pressure adjustments and then the volume in the burette was adjusted to 50 ml. The level of the eluant in the small reservoir at the head of the column was noted. The volume flow through the resin bed was adjusted to correspond to the desired linear flow rate. This required calibrating the drop size which was done prior to a run. A correction was made for any difference in level of the eluant in the reservoir at the end of each run. The burette was used only when volumes greater than 20 mls. were required to elute the band. Otherwise, all volumes of eluant were pippetted onto the column.

The distance d which a given band concentration maximum migrated for a given volume V of eluant was determined by two methods. The distance which the colored bands traveled was measured while they were still on the column. The colorless bands were eluted from the column and detected by chemical methods. The following describes the two methods broken down according to the elements involved.

Cu-Pb-Co These three elements form intensely colored complexes in sodium nitrite media which are easy to observe on the column. The color of the complexes are copper—green, lead—yellow, and cobalt—salmon pink. The distance of migration was measured with a ruler graduated in millimeters. The distance measured was from the original center of the band to the center of the migrated band. Measurements were taken until the d and V values were of sufficient magnitude to yield reproducible values of the elution constant. The elution behavior of Co becomes complex at intermediate and high nitrite concentrations ($>.5M$). The band is observed to stain the resin a dark brown. This phenomenon is interpreted to be the oxidation of Co^{+2} to Co^{+3}, as would be predicted from the known behavior of Co^{+2}(28). This rate of oxidation increases with increasing sodium nitrite concentration and at 4M the oxidation is complete before any Co can be eluted from the column. This conversion appears to be irreversible since the Co^{+3} stain cannot be eluted from the column with H_2O.

Co^{+2} does form, however, a complex in the plus two oxidation state which is salmon pink and which does adsorb to the anion exchange resin. The values of E as shown on page 20 are for this complex. Note that these values only go to 4M because of the above mentioned behavior.

However, the elution behavior of Cu and Pb appears to be uncomplicated. These elements form well defined bands which do not smear or tail except for Cu at extremely low nitrite concentrations. This property of the Cu complex interfered with several separations (see p. 16).

Cd-Ni-Zn-Mn-UO_2 These elements form colorless or weakly colored complexes and therefore had to be eluted from the column and detected by chemical reagents. The chemicals used for the detection of these elements ranged from sodium sulfide for all but UO_2 to relatively specific or sensitive organic reagents such as dimethylgloxime for nickel and potassium ferrocyanide for UO_2 and Zn.

When an element was unadsorbed or only slightly adsorbed, each individual drop was collected and tested on a spot test plate. The more strongly adsorbed species were also eluted, but larger fractions were collected for testing.

The concentration maximum was determined visually by following the increase of the precipitate or intensity of the color test through its maximum and taking an average of the more concentrated test spots.

In addition to the column technique, the adsorption characteristics of Cd, Zn and Ag by the anion exchange resin were studied using the batch or equilibrium method of Kraus and Moore (40). This method was used because these elements were difficult to detect because of their large affinity for the resin.

The resin was dried in a vacuum desiccator after being converted to the nitrite form. Upon drying, the resin turned a brown red. One hundred milligrams of dry resin were allowed to equilibrate with 50 ml of a particular sodium nitrite solution containing the element to be studied at such a concentration that 10% of the resin exchange sites would be occupied if the entire concentration of the element was adsorbed as the monovalent anionic complex. The mixture was agitated periodically for three days. The solution in contact with the resin was then analyzed by atomic absorption spectroscopy.

The apparent unintelligible data obtained by these experiments can be explained by resin decomposition.

The first indication that the resin had decomposed was the change in color upon desiccation. This color change is in contrast to that of the resin in the chloride form. Addition of the nitrite solutions to this resin appeared to break up the resin into extremely fine particles. The resin did not regain its normal yellow color when treated with strong sodium nitrite solution. The silver complex underwent reduction on the resin even when the equilibrium was allowed to take place in the dark. The final evidence indication resin deterioration was the unintelligible data obtained for Zn and Cd.

INTERPRETATION AND DISCUSSION OF RESULTS

The results of the investigation reveal that all of the cations studied formed anionic complexes to some extent with the nitrite ion, with the possible exception of Ni.

The relative affinity of the resin for these complexes varies from element to element and appreciably with the sodium nitrite concentration. The order of decreasing affinity for the resin at intermediate sodium nitrite concentration is Cd Cu Pb UO_2 Zn Co Mn Ni.

Cd, Cu, Pb and UO_2 are grouped as having very similar strong affinities for the resin. Zn and Co have intermediate affinities while Ni and Mn show very weak adsorption.

The results of the study are described in terms of the elution constant E which is defined by the equation

$$E = \frac{dA}{V} \tag{1}$$

where d is the distance in cm. which a concentration maximum of a band on the resin bed travels when V milliliters of eluant have passed through a column of A cross sectional area in square centimeters. The elution constant is related to the distribution coefficient of the metal between the resin and interstitial volume in the resin bed by the equation

$$D = \frac{1}{E} - i \tag{2}$$

where i is the fractional interstitial volume in the bed.

For small values of E the equation may be reduced to

$$D = \frac{1}{E}. \tag{3}$$

Information concerning the ionic species in equilibrium with the resin can be obtained by the following line of reasoning which was developed by Kraus and Moore. (34).

Assume that the adsorption equilibrium of an ion A^{-n} can be represented by the equation

$$(4) \qquad nRNO_2 + A^{-n} \rightleftharpoons R_nA + nNO_2^-$$

where R represents the resin. The mass action constant for the above equation is represented by

$$(5) \qquad K_{A^{-n}} = \frac{[R_nA]\;(NO_2^-)^n\;\gamma^n_{NO_2^-}}{[RNO_2]^n(A^{-n})\;\gamma_{A^{-n}}}$$

where brackets indicate activities, parentheses concentrations and the activity coefficient of the ion given as subscript. For dilute solutions the following simplifications

$$(6) \qquad [R_nA] = \alpha\,(A^{-n})_r$$

and $[RNO_2]^n$ = a constant

will be assumed where α is a proportionality constant and $(A^{-n})_r$ the concentration of A^{-n} in the resin. Combining equations (2), (3), (5) and (6) and defining

$$(7) \qquad D_{A^{-n}} = \frac{(A^{-n})_r}{(A^{-n})}$$

one obtains

$$(8) \qquad D_A{}^{-n} = K^*_{A^{-n}}\,\frac{\gamma_{A^{-n}}}{\gamma^n_{NO_2^-}}\,\frac{1}{(NO_2^-)^n} = \frac{1 - Ei}{E} = \frac{1}{E^*} \approx \frac{1}{E}$$

where $K^*{}_{A^{-n}} = \dfrac{K_{A^{-n}}[RNO_2]^n}{\alpha}$

is a proportionality constant. Thus, neglecting the activity coefficient ratio, a plot of log E^x (or log E for small values of E) versus log

(NO_2^-) for a single species in a dilute solution has a slope equal to the charge n of the ion. For two ions of different charge, two straight lines will result which cross at some sodium nitrite concentration designated P.

The analysis of the elution data as described above shows that in the cases where the element (complex) shows an appreciable affinity for the resin, the charge on the complex is approximately minus one (see p. 22). Difficulty arises, however, in interpreting the analysis of the data for Mn and Ni since these elements (complexes) adsorb only at very high eluant concentrations which yield very few points for analysis. In addition, only a small percent of the element is complexed. These factors make it difficult to determine whether or not the plot of these points represents the true slope of the charge of the species involved.

Of particular interest is the elution behavior of both Cu and Pb as the concentration of eluant increases. As can be seen from the plot of log E versus concentration of sodium nitrite (p. 21), the value of E decreases initially with an increase in nitrite concentration.

This behavior is due to the singly charged anion as determined by the analysis described on p. 10. The degree of formation of this species increases with increasing eluant concentration as would be predicted from the mass action expression for such a complex. This increase then of complex concentration permits more of the element to be available for adsorption at the exchange site in the resin and hence produces a decrease in the rate of migration of the element down the resin bed. At 1.5M and 0.5M sodium nitrite for Cu and Pb respectively, however, the plot of log E versus C passes through a minimum and begins to increase. There are several speculations which can be made concerning this change in elution behavior; these can be divided into two lines of reasoning.

The first approach to consider is the formation of a new complex. Examination of the log log plot of E versus C on p. 22 shows two straight lines intersecting. This could be caused by more than one species being in equilibrium with the resin, and it is necessary, then, to consider this possibility.

Kraus and Moore found that when an element forms more than one anionic complex, the singly charged complex has a greater affinity for the resin than the doubly charged species (35).

The explanation for this behavior can be interpreted from ion exchange theory. The bulkier the exchanging ion, the more difficult it is for it to enter the resin particle and the slower it will migrate through the resin to the exchange site. Since the migration into and through the resin particles is hindered by this increase in ion size, the exchange process is considered to be particle diffusion controlled (14).

There are several possible species which can be postulated that are bulkier than the proposed singly charged trinitrometalo-complex. These two elements are known to form complexes containing four ligands (29). It is necessary to consider the possibility of the formation of a doubly charged anion. Since more than one species may be in equilibrium with the resin, the mathematical treatment mentioned on pages 9 and 10 will not yield a straight line corresponding to the slope of the new ion since it alone is not entirely responsible for the adsorption.

The analysis will, however, yield a straight line which will intercept at a concentration P at which the second species starts to form. Evidence in favor of the doubly charged species can be seen at high nitrite concentration beyond the maximum where the slope is again negative and could represent the complete formation to the doubly charged anion. There is, however, another species which can be proposed that has a greater bulk than the singly charged species. At higher eluant concentrations the odor of NO_2-like gases can be detected above the solution which represents the decomposition of the nitrite ion into NO and NO_2.

This former decomposition product could complex with species I, the trinitrometalocomplex, thus forming a bulkier singly charged complex which would adsorb to a lesser degree than species I (29). Again, at higher concentrations this species could be converted to the doubly charged species.

A second line of reasoning for the change in the elution behavior is based on the possible non-validity of the assumption made in the derivation of equation (8), p. 10, that the activity coefficient ratio remains constant. A change in this parameter could have an effect on the elution behavior and could account for the observed maximum mentioned previously.

Not completely unrelated to all of the above reasoning is the fact that as the eluant concentration increases, the resin shrinks. When this happens, the channels in the resin, through which the anions must travel in order to reach the exchange site, contract, and this phenomenon has the same effect as that of increasing the bulk of the anionic species. That this may be the case is evidenced by the fact that in the eluant concentration range at which the elution behavior for these elements changes, considerable shrinkage of the resin bed is first observed.

If the above assumption is correct, then the rate of elution should increase gradually as the channels in the resin gradually shrink. The plot of log E versus C for these elements shows this to be the case. If a doubly charged anionic species is formed at very high eluant concentration, then the rate of elution should increase even further as predicted by the above discussion. Since this does not happen C probably indicates that no double charged anionic species is formed. Additional evidence against the formation of a doubly charged anionic species is presented in a paper by Kossiakoff and Sickman in which the Cu-NO_2^- system was studied by a colorimetric method to determine the number of complex species formed. No evidence of a double charged species was found even in saturated sodium nitrite solutions (31).

The data for Co and Zn, although incomplete (see p. 20), indicate that these two cations behave much like Cu and Pb in sodium nitrite medium on anion exchange resin. The plots of log E versus C show that the rate of elution is leveling off and is approaching the point of discontinuity previously mentioned as P. One would therefore predict that these cations do behave like those mentioned above and form only singly charged complexes in sodium nitrite media.

The data on the elution behavior of Cd, although very incomplete, shed some light on the affinity of Cd for the nitrite ion. Its behavior is probably similar to that of Cu and Pb.

The elution behavior of the UO_2 complex is such that the complex is unadsorbed at 0.5M $NaNO_2$, but has an E value less than 0.1 in 0.3M $NaNO_2$.

A comparison of the elution characteristics for these elements in HCl (37), HBr (14), and $NaNO_2$ media, although incomplete, indicates a trend in the preference of anion exchange resins for the elements in their anionic complex form. This trend in preference is also directly related to the strength of the complex. These trends are shown below for the previously mentioned systems.

The order of decreasing preference which an anion exchange resin possesses for these anionic-metal complexes can be presented in at least two ways.

The first is the order of increasing complex formation as determined by the eluant concentration at which the species is first adsorbed by the resin. The lower the eluant concentration at which this happens, the higher the element is in the sequence. The second method of classifying these elements with respect to their affinities by the resin is based on the maximum affinity which the resin has for the element (complex) at the optimum eluant concentration. The sequences are as follows:

HCl
$Zn > Cu > Co > Mn > Ni$ - Order of complex formation
$Zn > Co > Cu > Mn > Ni$ - Maximum affinity

$NaNO_2$	Cu > Zn > Co > Mn > Ni	- Order of complex formation
	Cu > Zn > Co > Mn > Ni	- Maximum affinity
HBr	Zn > Cu > Co > Ni	- Order of complex formation

Although the investigation of the HBr system was not carried out for the entire range of eluant concentrations possible and because the elution behavior of Co could not be determined at very high sodium nitrite concentration, the best sequence for comparing the trend in complex formation is the order of first occurrence of complex formation. These are shown above as the first sequence listed for each eluant. It can be seen that other than the difference in order of Cu and Zn in the HCl-HBr eluants from that of the $NaNO_2$ system, the sequences are identical.

SEPARATION PROCEDURES

Examination of the plots of log E versus sodium nitrite concentration reveals that many binary and possibly some multiple separations should be possible.

Binary Separations—

In general, at low concentrations of sodium nitrite, Cd, Cu and Pb should be easily separated from Mn, Ni, Co, Zn and UO_2. These various separations are shown on p. 22 and p. 23. At intermediate sodium nitrite concentration, Zn is easily separated from Co, Mn and Ni, while at still higher nitrite concentrations, Co is separated from Mn and Ni. Because of their similar elution characteristics, Mn and Ni could not be separated on the column used in the above separations. However, using 6M sodium nitrite, these two elements should be separable on a very long column.

The separation of Pb and Cu was tried at 10^{-3} and 5×10^{-3}M sodium nitrite. In each instance only partial separations were effected due to the smearing of the Cu band. This smearing occurs only at low nitrite concentrations. Separation of these two elements was possible, however, at 5M eluant where the ratio of the elution constants $\frac{E_{Pb}}{E_{Cu}}$ is about 10 (see p. 25).

Ternary Mixtures—

Several three-component mixtures were resolved into the components using the same columns which were used for the binary separations. In general these mixtures contained one element from each of the three broad groups mentioned on p. 9. The weakly adsorbed species was eluted with 0.5M sodium nitrite, the intermediate adsorbed species with 5×10^{-2}M while the strongly adsorbed species was eluted with water.

Quaternary Mixture—

Only one four-component mixture was resolved into its components, although several others could be by substitution of various weakly adsorbed elements one for another. The order of eluant strength is similar to that for the three component mixtures, except that after Zn was eluted, 0.5M eluant was required to elute Pb. Water was used to elute the strongly adsorbed Cu band.

The rate of desorption of a complex from the resin using water as the eluant was shown to be proportional to the elution constant for that element. The quantity of water required to elute these strongly adsorbed complexes ranged from 30 to 60 column volumes depending upon the element being eluted. The concentration of sodium nitrite in the resin bed changes drastically after the first column volume of water has eluted through the bed. When five column volumes have passed through the bed, the concentration of sodium nitrite is below that required to cause complex formation. The additional column volumes required for the complete removal of the elements from the resin bed indicate that the environment within the resin polymer network changed only slowly. This behavior is in agreement with previous findings that the preferred ions are readily taken up by the resin, but only slowly released.

Precautions

Several precautions must be taken when using sodium nitrite as the eluant for these cations. The Co^{+2} ion is not quantitatively eluted from the resin bed at moderate and strong sodium nitrite concentrations since it is probably oxidized to the Co^{+3} state which irreversibly stains the resin. This element can only be separated from the elements which adsorb strongly in dilute sodium nitrite.

The other phenomenon which requires attention when separations are to be made involving manganese, is the formation of a precipitate due to hydrolysis of this cation in neutral and alkaline media. The precipitate is visually observed after about three or four hours. Therefore, the nitrite should not be added to a solution containing these ions until the separation is to be effected.

SUMMARY

The investigation of the elution behavior of Cd, Co, Cu, Pb, Mn, Ni, Zn, and UO_2^{++} in sodium nitrite media on an ion exchange resin has revealed that all of the elements were adsorbed by the resin to some extent with the possible exception of Ni, thus indicating the formation of anionic species. The relative affinity of the resin for the complexes at the concentration at which they first start adsorbing is $Cd \approx Cu > Pb > Zn > UO_2 > Co > Mn > Ni$.

Analysis of the elution data for Cu, Pb, Zn, Co, Mn and Ni showed that in all cases except for possibly Mn and Ni, the primary adsorbing species is the singly charged anionic complex.

The elution behavior of Cu and Pb, though complicated, can be interpreted as adsorption by the singly charged anionic complex at low nitrite concentrations, while at higher concentrations this complex behavior is probably due to a decrease in the rate of exchange. The phenomenon responsible for the decrease in rate of exchange inside the resin polymer network at high nitrite concentration is due to the contraction of the network accompanied by a decrease of free solvent in this network and the probable formation of a bulkier nitrosyl trinitrometalocomplex. These processes decrease the rate of exchange within the resin and result in an increase in the elution constant E.

Many separations were predicted from the elution data. All predicted separations were effected, including binary, ternary and quaternary mixtures.

TABLE I

Elution Constants of Divalent Cations in $NaNO_2$ Media

Molarity $NaNO_2$	Co	Cu	Pb	Mn	Ni	Zn
5×10^{-4}	—	0.554	2.60	—	—	—
2×10^{-3}	—	0.348	1.0	—	—	—
1×10^{-2}	—	0.073	0.370	—	—	0.90
1×10^{-1}	2.60	0.050	0.070	3.42	3.46	0.60
2×10^{-1}	2.18	—	—	2.77	—	—
3×10^{-1}	—	0.019	0.044	—	—	—
5×10^{-1}	—	—	—	—	2.39	0.12
6×10^{-1}	—	0.014	0.045	2.29	—	—
1	1.04	0.012	0.048	1.89	2.12	0.054
1.5	—	0.012	—	—	—	—
2.0	0.47	0.013	0.064	1.29	1.54	0.024
3.0	0.22	0.012	0.078	0.86	—	—
4.0	0.18	0.011	—	0.56	1.13	—
5.0	—	0.011	0.095	—	—	—
6.0	—	0.010	0.092	0.284	0.95	—
7.0	—	—	—	—	—	—
8.0	—	0.009	0.081	—	0.94	—

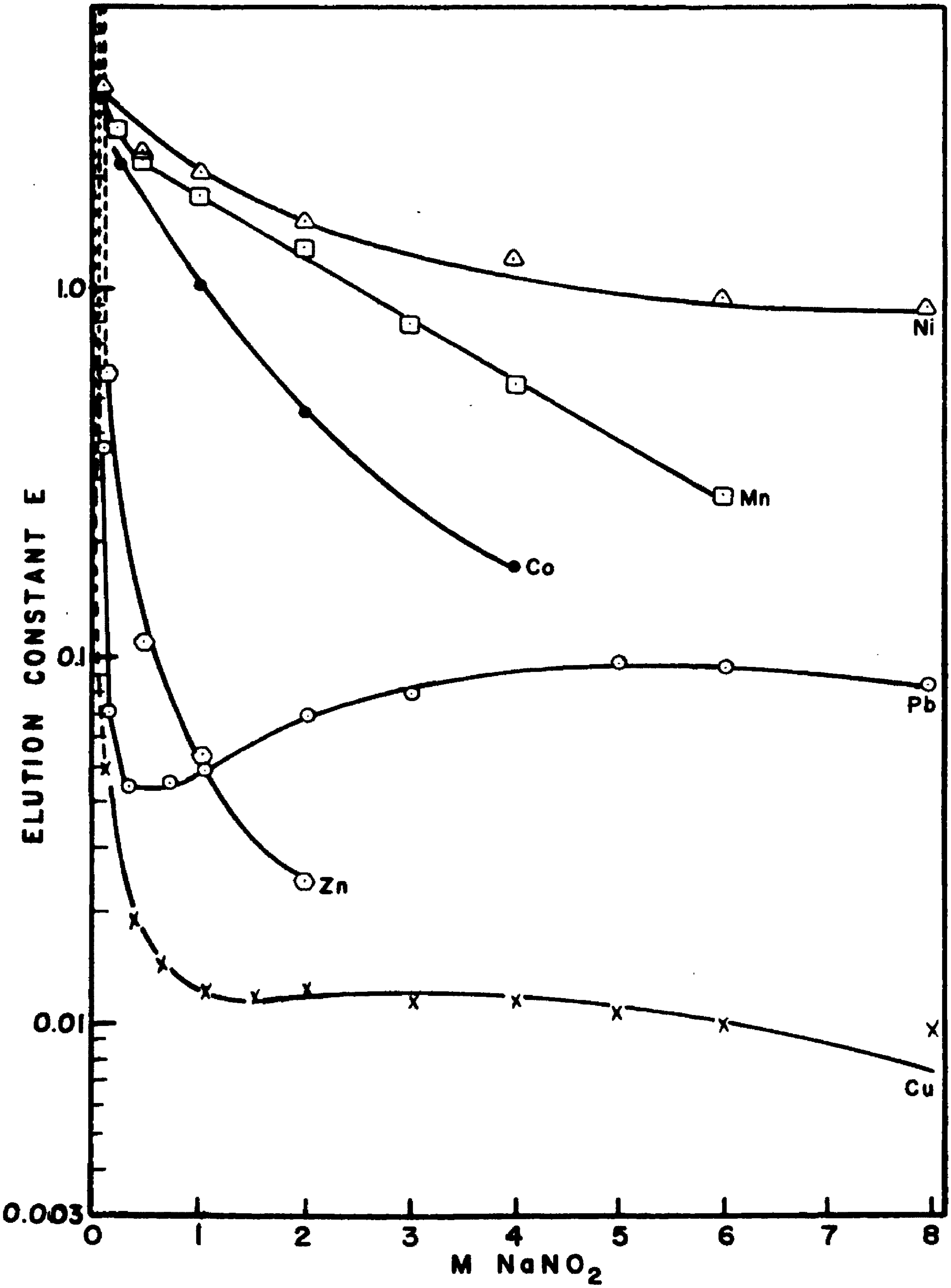


Figure I--Semilog Plots of Elution Constants Versus Eluant Concn.

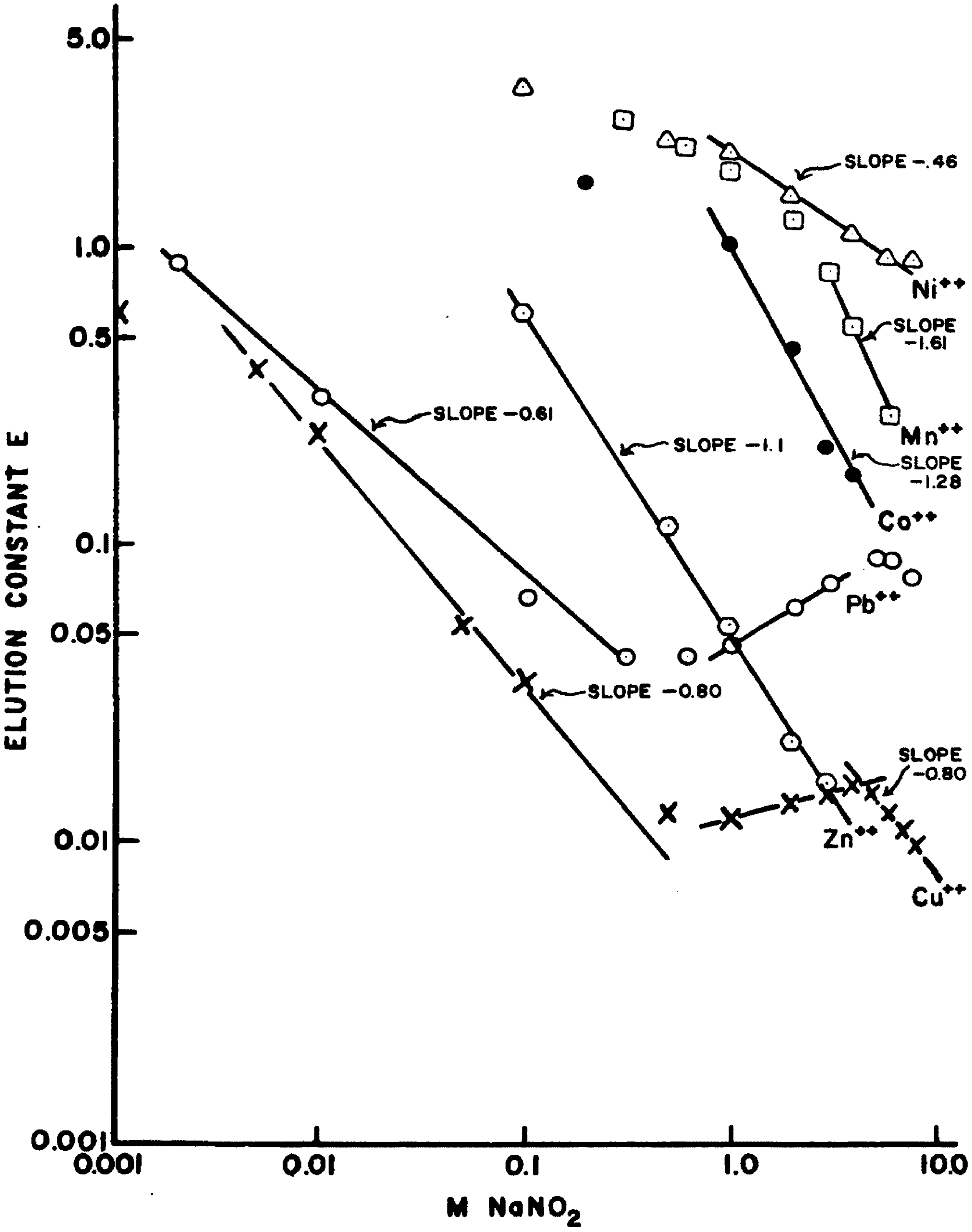


Figure II—Log Log Plots of Elution Constants Versus Eluant Concn.

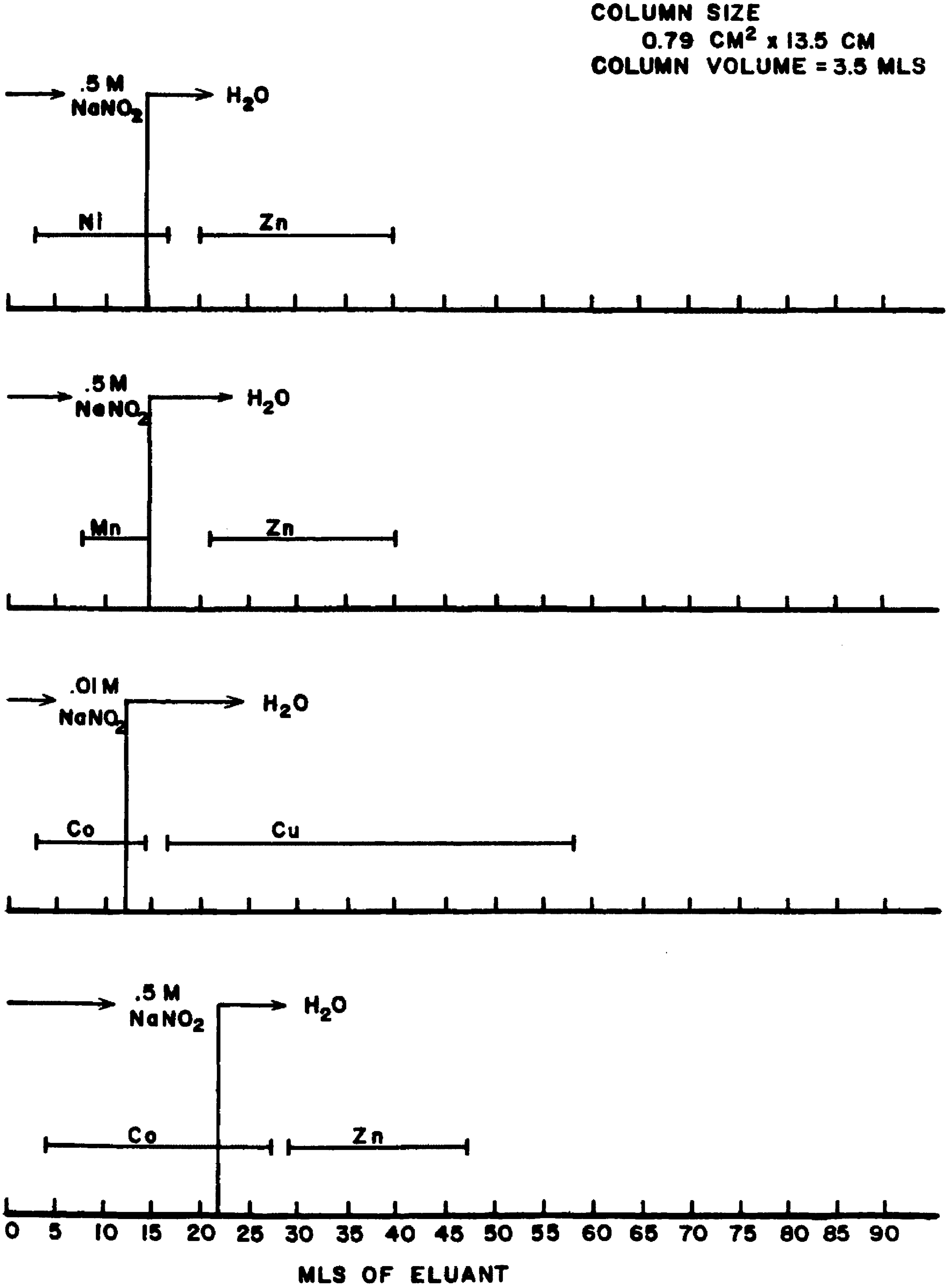


Figure III—Separation Schematics, Binary Mixtures

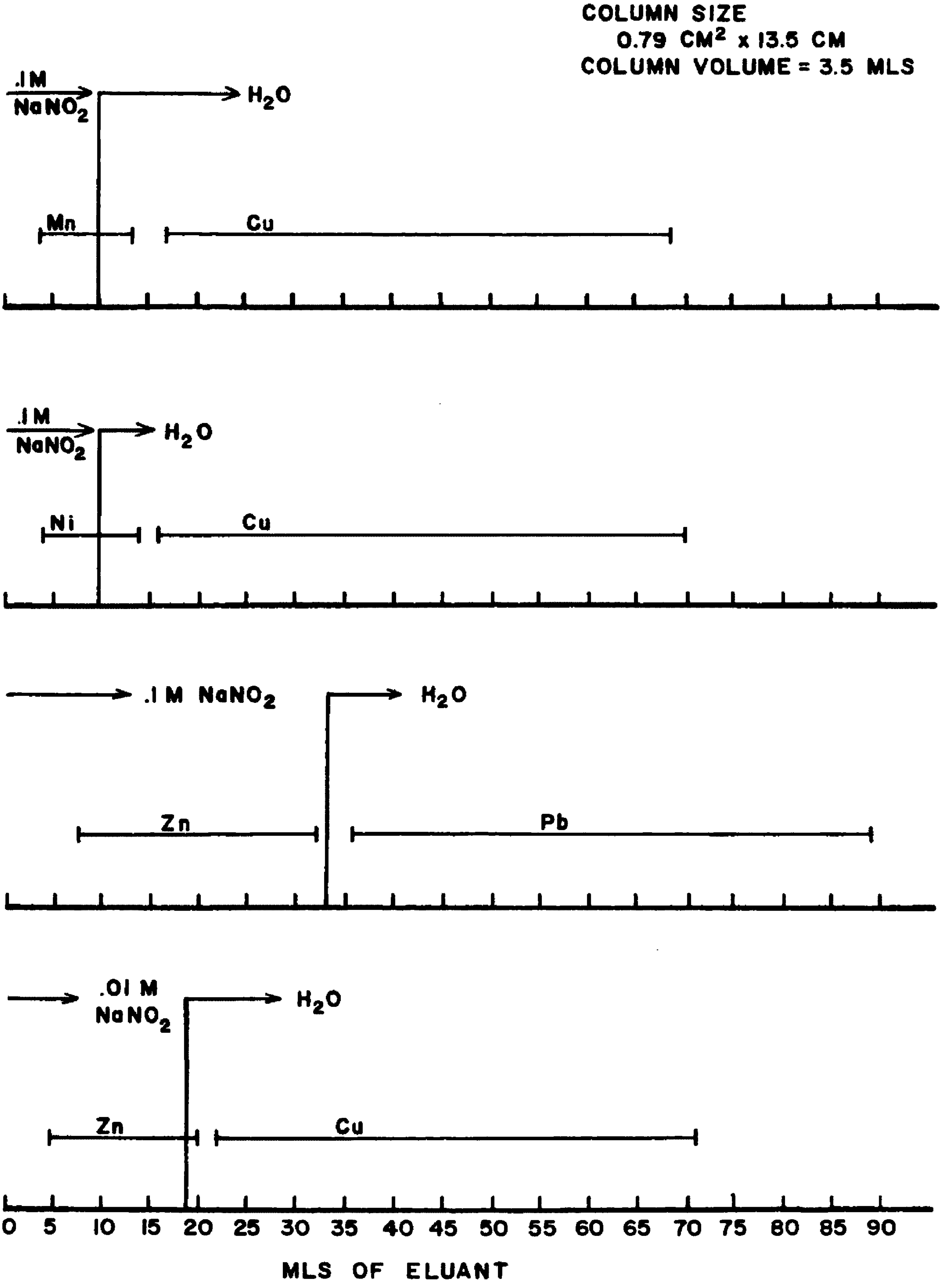


Figure IV--Separation Schematics, Binary Mixtures

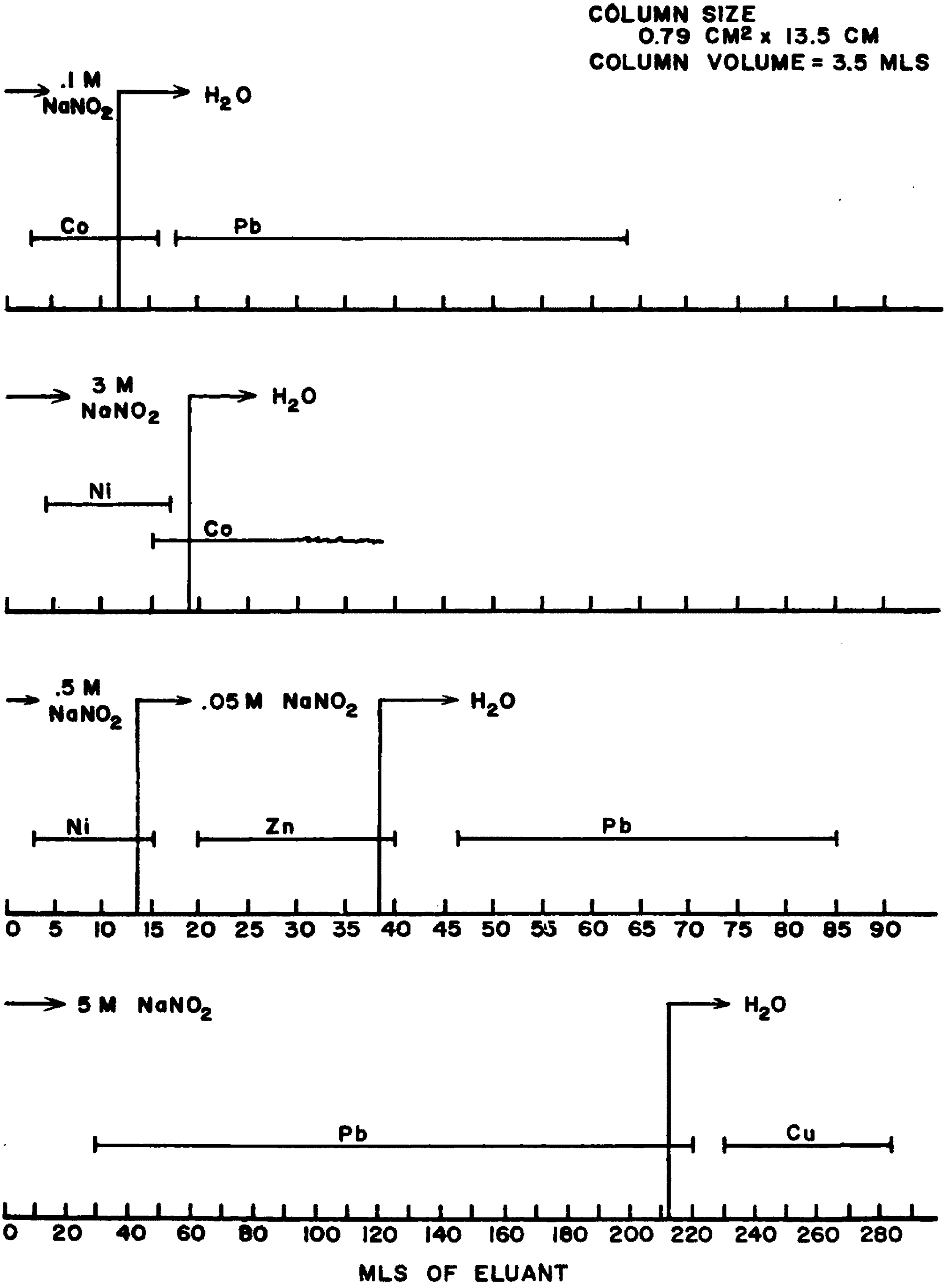
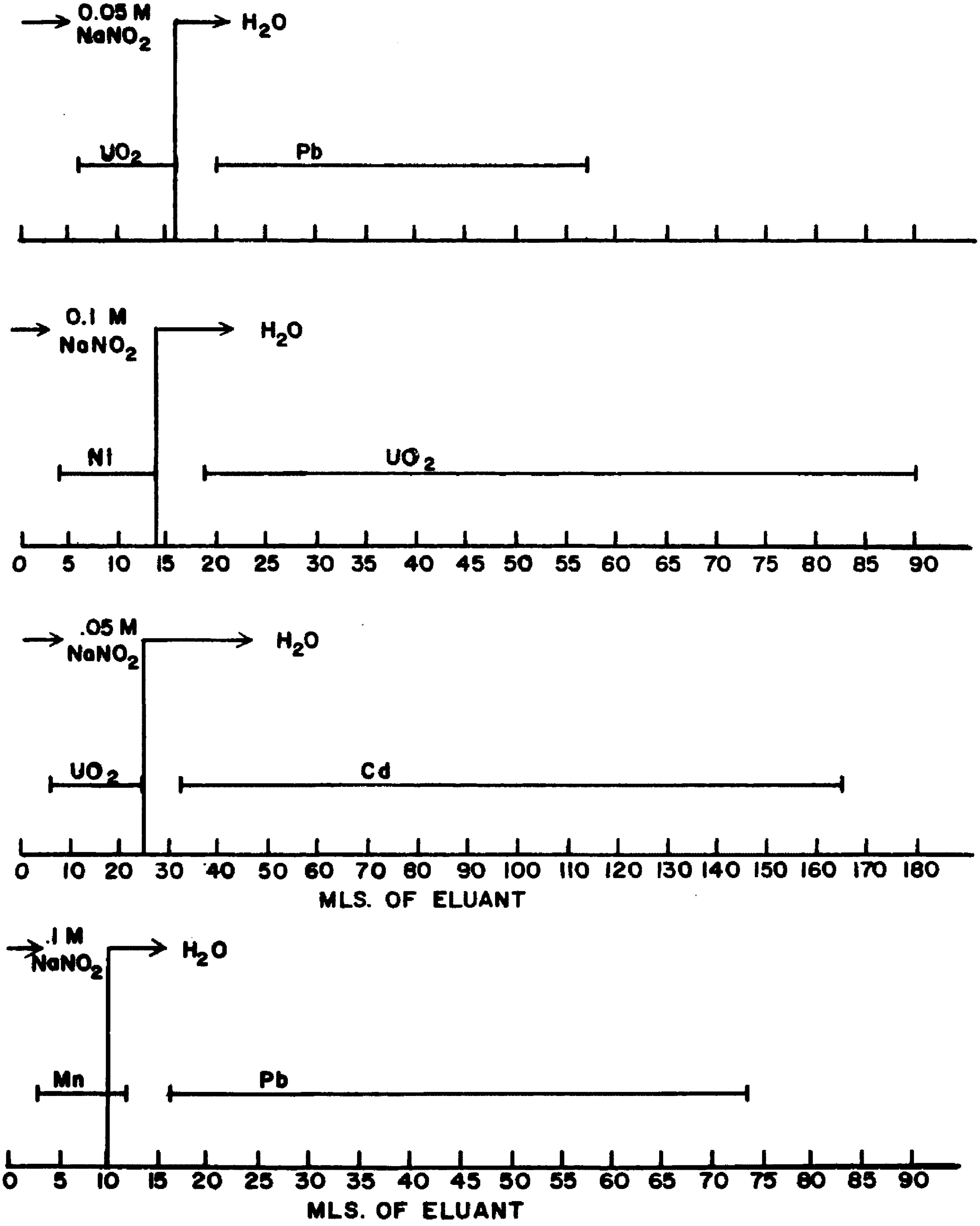


Figure V—Separation Schematics, Binary and Ternary Mixtures



COLUMN SIZE
0.79 CM^2 x 13.5 CM
COLUMN VOLUME = 3.5 MLS

Figure VI—Separation Schematics, Binary Mixtures

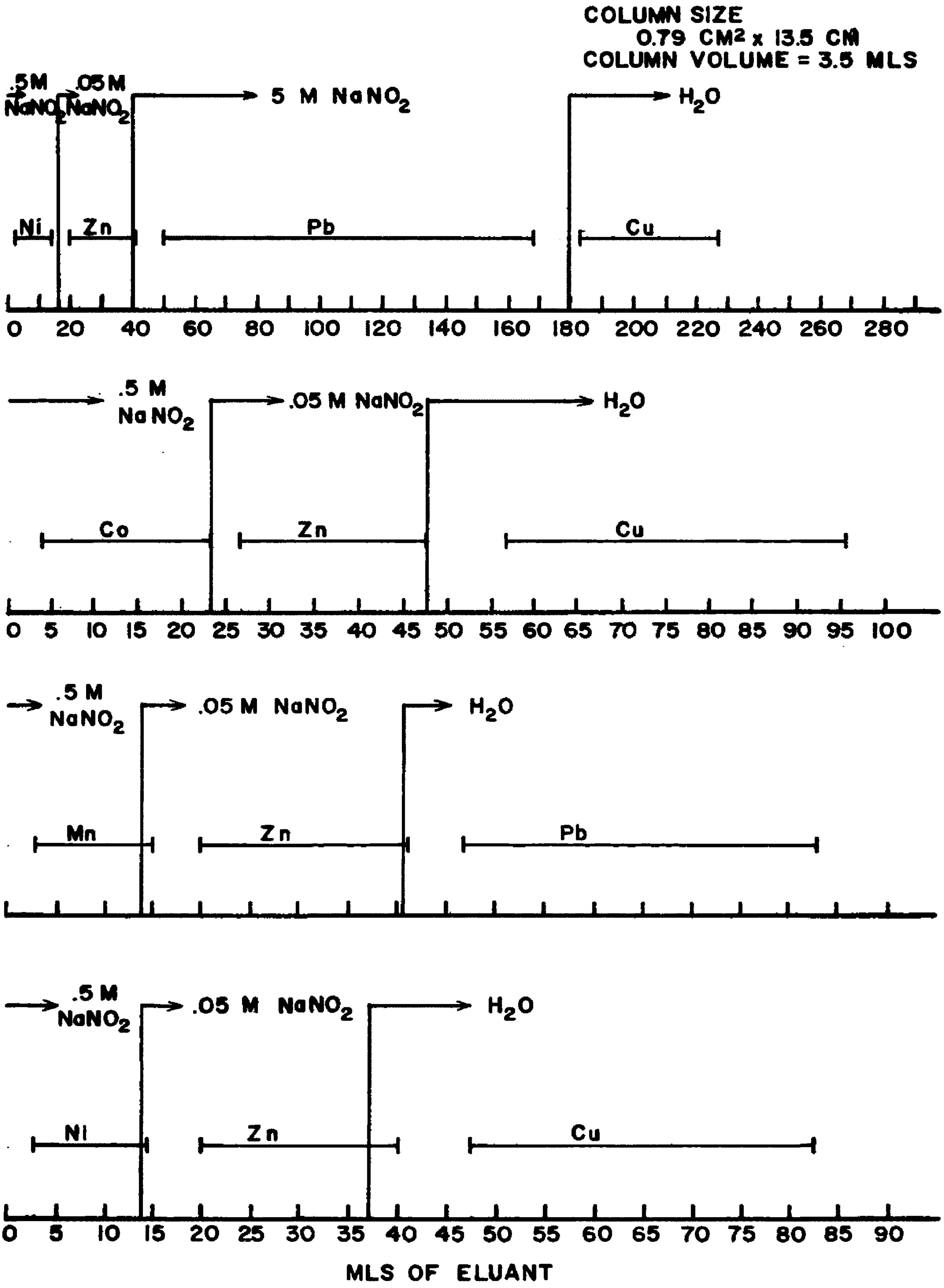


Figure VII--Separation Schematics, Ternary and Quaternary Mixtures

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