

CHROMATOGRAPHY OF THE ALKALINE EARTHS
ON CHELATING ION EXCHANGE RESINS

by

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A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1962

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May 1, 1962

Typed by Eloise Allison

TABLE OF CONTENTS

Chapter	Page
I INTRODUCTION	1
II SURVEY OF PREVIOUS WORK	3
III PREPARATION OF RESINS	5
IV COLUMN ABSORPTION STUDIES	10
Buffer and Standards Preparation . .	10
Description of Equipment	11
Methods of Analysis	13
General Experimental Procedure . . .	14
Initial Testing of Resins	15
Absorption Characteristics of 8-Quinolinol Resin	16
Absorption Characteristics of O-aminophenol Resin	20
Summary	33
V SUMMARY AND CONCLUSIONS	34
BIBLIOGRAPHY	36

LIST OF TABLES

Table	Page
I Barium on 8-Quinolinol	18
II Determination of Total Hardness by Flame Analysis and Versene Titration	31
III Separation of Calcium and Magnesium at Different Volume Ratios	32

LIST OF FIGURES

Figure		
1 Elution of Alkaline Earths from 8-Quinolinol Resin at pH 9		19
2 Elution of Strontium Ions from O-aminophenol Resin		22
3 Elution of Barium Ions from O-aminophenol Resin		23
4 Elution of Calcium Ions from O-aminophenol Resin		24
5 Elution of Magnesium Ions from O-aminophenol Resin		25
6 Elution of Alkaline Earths from O-aminophenol Resin at pH 5		26

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CHAPTER I

INTRODUCTION

Ion exchange resins have been applied to analytical chemistry for many years. Some of their first applications were in the separation of ionic from nonionic materials and in concentrating ions. The solutions were passed through a column packed with an ion exchange resin and the ions were absorbed by the resin. By the use of a suitable elutriant such as a strong acid or base, the ions could be eluted. Resins were developed for the absorption of either cations or anions.

In general the strength with which ions were held depended mostly on the charge, with higher charged ions being more strongly held. The size of the solvated ion also had some influence.

To effect the separation of similarly bound ions, two methods are commonly employed. The first consists of complexing one to change the sign of its charge. Since the ions must be selectively complexed, this will have limited applications. The second method is to use an elutriant that will tend to replace or complex one ion and not another. These include the mineral acids, salt solutions, organic solvents, and complexing agents including

chelating agents. Most of these show only slight selectivity and consequently require long columns. The chelating agents on the other hand are frequently highly selective but have the disadvantage of often being only slightly soluble in aqueous solutions.

If the chelating agents are chemically incorporated onto the resin, advantage can be taken of their properties to absorb and desorb metal ions selectively. Furthermore, columns can be regenerated for reuse. Two criteria are necessary in this respect. The chelate must have a structure capable of resin formation and it must be stable enough to withstand polymerization. Since chelate complexes are formed only with polyvalent ions these resins will not absorb the alkali metal ions.

The purpose of this project was to test some of the properties and develop some applications of certain chelating ion exchange resins. Specifically, the experiments dealt with resins using 8-quinolinol and o-aminophenol incorporated on a sodium hydroxide formaldehyde resin. Applications were limited to investigations of the alkaline earth metals.

CHAPTER II

SURVEY OF PREVIOUS WORK

Abundant literature is available on the general use and specific applications of conventional ion exchange resins. The general theory and basic types are discussed by Kunin and Myers (4), by Samuelson (8) and by Kitchener (3).

The literature on chelating ion exchange resins is very limited. In 1952 Gregor and co-workers (2) published a paper dealing with them. He used m-phenylenediglycine as the chelating agent for most of his work. He made studies of the absorption characteristics at various pH levels with a number of divalent metal ions. He also made a resin using o-aminophenol and made a few tests on it with cobalt, ferrous iron, and nickel. He found that all ion absorption was reversible and could be desorbed by 1 M. HCl. He further found that the resin was unaffected by several hundred cycles.

Several more resins including resorcinol, resacetophenone, β -resorcyclic acid, o-aminophenol, and 8-quinolinol as the chelating groups were developed by Pennington (6, 7). Resorcinol although not a chelate does form a chelate structure in the resin. The

o-aminophenol resin here apparently had considerably greater capacity than in Gregor's work. This probably is the consequence of the physical structure. Somewhat different methods of polymerization were used. Pennington studied the absorption of various divalent ions; namely, copper, cobalt, iron, nickel, calcium, and magnesium at various pH levels. He further studied the chromatography of copper, nickel, and cobalt on 8-quinolinol resin. Copper and cobalt were satisfactorily separated, but nickel appeared in both eluates.

In 1959 (1) Dow Chemical Company announced a commercial chelating resin, Dowex A-1. The chelating agent is iminodiacetate. It is incorporated on a styrene-divinyl benzene copolymer. Its recommended uses are the concentration and separation of small amounts of heavy metals from alkali and alkaline earth solutions, the separation of alkaline earths from strong alkali solutions and the separation of nickel from cobalt or copper. Other applications are being developed.

CHAPTER III

PREPARATION OF RESINS

The recipes for the preparation of the resins were taken from Pennington (6, p. 21-24).

1. 8-quinolinol resin

8-quinolinol	29.0 ml. (0.20 mol.)
(Eastman white label)	
Water	100 ml.
Sodium hydroxide, 6 N. .	30 ml. (0.18 mol.)
solution (Mallinkrodt reagent)	
Formaldehyde	40 ml. (0.50 mol.)
(Van Waters & Rogers U.S.P.-N.F)	
Resorcinol (Paragon . .	22.0 g. (0.20 mol.)
Testing Laboratory)	

The resorcinol was dissolved in a beaker in the sodium hydroxide and water. The 8-quinolinol was stirred into this. Special effort was needed to get all the lumps broken up. This solution was left at room temperature for one and one-half hours with no noticeable change. The formaldehyde was added and allowed to set. No change was observed after three hours. It was placed on the steam bath and started to jell in 20 minutes, becoming quite firm in 35 minutes. It was then broken up into chunks and dried in an oven for four hours at 105°-110° C. At this

time it was ground up and dried overnight in the oven. The resin was ground in a mortar to pass through a 20 mesh sieve. The sample was screened into 20-40, 40-60, and finer than 60 mesh portions. The resin produced appeared black but was actually a very dark red.

A second batch was made similar to the one described. The results were essentially the same.

2. O-aminophenol resin

O-aminophenol	21.8 g. (.20 mol.)
(Eastman Practical)	
Sodium hydroxide	50 ml. (.30 mol.)
Water	100 ml.
Formaldehyde, 37%	40 ml. (.50 mol.)

The ingredients were stirred together. A small amount of a sticky gumlike residue was formed at the bottom. It weighed about one gram and was discarded. During the stirring the sides of the beaker were rinsed down with a total of about 15 ml. of water. The solution was placed in the oven at 85° C. A scum formed in one and one-half hours. In another one and one-half hours this was dry on top. It was stirred in and again the beaker was rinsed down with about 5 ml. of water. After seven more hours in the oven the scum was again stirred in, producing a jell. This was placed in a warm oven overnight with the heat

turned off. It hardened very slowly. The chunks were frequently broken up to hasten the process and to facilitate grinding. The material was separated into two beakers and dried overnight in the oven at 85° C. The resin was rather hard, and it was quite difficult to grind. It was screened into 20-40, 40-60, and finer than 60 mesh portions.

A second batch was prepared doubling all constituents except water. To hasten the hardening and drying, only 180 ml. of water were used. As before, a small gumlike mass was formed. This weighed 1.5 g. A total of 28 hours in the oven was required to produce the final dry resin. Again, the resin was hard to grind. The resin was black in color.

The resins were next washed. The method and results were similar to those obtained by Pennington (6, p. 21-24). The washing consisted first of washing with water and decanting. When the wash waters had only a slight brown color, the resins were placed on several sheets of filter paper in a buchner funnel. Then they were washed alternately with 0.1 M. HCl and 0.1 M. NaOH, rinsing with water after each.

Pennington found that a slight brown color persisted in the 0.1 M. NaOH wash water. Upon acidification this

coagulated. It was decided to run a washing continuously and determine if possible how long this color would persist. Whereas Pennington washed his in a column for two to three days, these were washed approximately six weeks. A total of 45 liters of 0.1 M. NaOH was used without washing out all color. Subsequent tests indicated that the absorption properties had been destroyed.

The resins used in the experimental work were washed in columns by reverse flow. The 8-quinolinol resin was washed with water for a few hours, with 0.1 M. NaOH for three days, again with water for one day, with 0.1 M. HCl for three days, and finally with water until nearly neutral. A second batch was washed two days with 0.1 M. NaOH, 6 hours with water, 12 hours with 0.1 M. HCl, and finally with water until neutral. The flow rate for washing was from 1-3 ml. per minute.

The o-aminophenol resin was washed as above. A total of 10 liters each of 0.1 M. NaOH, H₂O, and 0.1 M. HCl were used, followed by water until neutral.

Several attempts were made to produce other resins. Arsenazo (3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid) and TTA (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) have benzene ring structures and could conceivably form chelate resins.

Arsenazo was mixed with NaOH, formaldehyde, and resorcinol and heated at 80° C. A jell formed in 24 hours and dried in another 24. This was ground up. The wash water was very intensely colored and never became clear. The resin became progressively softer and finally became almost gelatinous. This probably stemmed from the high solubility of arsenazo in water. No further work was done on it.

TTA was treated like Arsenazo except that the initial dissolution was in acetone, and alcoholic KOH was added instead of aqueous NaOH. The reaction was vigorous and produced a soft gummy mass in the solution which was not removed. It was placed on the steam bath for a few hours. The gum had now become very hard. When placed in an oven at 80° overnight, the solution also formed a hard substance. The combined residue was very tough but was ground up. It was washed in a column with water for several hours. In testing its properties copper was not absorbed at a pH of 8, and therefore the material was discarded. It is possible that these chelates could be co-polymerized in other ways or on different polymers.

CHAPTER IV

COLUMN ABSORPTION STUDIES

Buffer and Standards Preparation

A series of buffers was made up for pH ranges from two to ten. In order to avoid interferences as much as possible, buffers were made of ammonium acetate and either hydrochloric acid or potassium hydroxide. For every liter of solution, 100 ml. of 2.5 M. ammonium acetate were used with sufficient 0.1 M. HCl or 0.1 M. KOH to bring the pH to the desired level, using a pH meter. To avoid unnecessary repetition, a solution buffered at a pH of 2, for example, will be termed merely pH 2 buffer.

Similarly, buffers were made of solutions of cupric chloride, magnesium chloride, barium chloride, strontium chloride, and calcium chloride. These solutions were all 0.010 M. in metal ion and were made as follows. Magnesium metal was dissolved in HCl using a slight excess of acid. Barium chloride dihydrate was dissolved in water which was slightly acidic in HCl. Strontium chloride and calcium chloride were made by dissolving their respective carbonates in HCl. The selections for primary standards were made according to recommendations by Sandell (9). The correct amount was weighed out in each case to give 250 ml. of

0.50 M. solutions. To make the standard metal ion buffer solutions, 20 ml. were pipetted out and added in each liter of solution to make the solutions 0.010 M.

Throughout the remainder of this paper whenever a standard metal solution is added to a column, it will be 0.01 M. The concentration will, therefore, not always be repeated.

Description of Equipment

Several columns were made of glass tubing. They had an inside diameter of 12 mm. and were about 30 cm. long. The tubing was sealed to a glass crucible which had a coarse sintered glass disc sealed in it. This disc, however, would clog up and was replaced with a glass wool plug. Subsequent columns were constricted to hold the glass wool in place.

To control the flow rate, the tips were fitted with short lengths ($1\frac{1}{2}$ ") of latex tubing and fitted with screw clamps. Short glass tips were fitted into the tubing.

The resin was soaked in water for several hours and added to the columns. Enough was added so that the resin height came to exactly 12 cm. This length was increased to 24 cm. in later runs. Another piece of glass wool was tamped on top of the resin.

When resin beds of 12 cm. were used, the columns were long enough so that the desired quantities of solution could be added directly into the column. This set-up needed close attention to keep from running dry, especially during the elution. In the 24 cm. bed the column had to be modified. A side arm of 6 mm. glass tubing was sealed in about 2 cm. above the level of the resin. This was connected by a latex tube to a leveling flask. All solutions were added directly into this flask. By stoppering the column the leveling flask could be raised or lowered to make slight changes in the flow rate. Whenever a metal ion was added to the flask, it was carefully rinsed with a minimum of buffer of equal pH. This usually required two to three ml.

Before the addition of metal ion the columns were buffered to the desired pH. In the 12 cm. bed column, 100 ml. of buffer were sufficient except for pH 9 when 200 ml. were necessary. The 24 cm. bed also required 200 ml. The buffering was done by reverse flow. The tubing from the leveling flasks was attached to the bottom of the column and the solution drained through the side arm.

Aliquots were taken starting immediately upon the addition of metal ion. Obviously, the first few milliliters were part of the solution used to buffer the column.

This was done since no convenient way was available to indicate when the metal ion buffer first appeared in the eluant. The column when drained gave 8 ml. This then is an approximation of the volume of resin buffer in the first aliquot.

Throughout most of the study, the aliquots were taken in 25 ml. volumetric flasks. When more precision was required, 10 ml. flasks were used. After the method was established, the first aliquot was 250 ml.

Methods of Analysis

A Perkin-Elmer flame photometer was available and this permitted the direct analysis of the alkaline earths. Usually little interference was noted when analyzing in the presence of each other. The one exception was that strontium interfered in the determination of barium. Reproducibility was usually within five per cent. This means that when the readings taken for each aliquot were added together, they totaled within five per cent of the reading on the original sample added. The readings were always lower than calculated. This phenomenon is readily explained by the fact that the presence of HCl suppressed the readings. The last few aliquots were obtained, using HCl as the elutriant, and this fraction frequently

contained a major amount of the metal. The slightly lower readings then still justify the assumption of complete elution. Magnesium could only be determined to within about 15 per cent. Therefore, its behavior was established on a qualitative basis only by this method. In the later analysis of calcium and magnesium mixtures, calcium was determined by the above method. Total hardness was then run by a versene titration and the difference taken to be magnesium. For some unaccountable reason, an interference was present in this titration. The end point was not clear. This was remedied by the addition of a small amount of KCN. However, no theoretical justification for its use was proposed. It was proven that the interference was not linked with pH.

The recovery by this method was within 4 per cent. The analysis on the final runs of magnesium and calcium was done on a Beckman model B spectrophotometer with a flame attachment. The apparent accuracy was within about two per cent, based on total recovery.

General Experimental Procedure

The resins were treated as previously described. After the level of the metal solution that was pipetted into the leveling flask and the rinse solution reached the

top level of the resin, it was followed by the elutriant buffer. The amount of buffer added varied as was determined necessary. The buffer was always followed by HCl. The HCl removed all metal that remained absorbed. The resin was then washed with water until the pH was about 5. The column was then ready for the next run.

Initial Testing of Resins

Preliminary tests were made to see if the resins had any absorbing properties. Using a 12 cm. bed, the resins were buffered to a pH of 2. To each column were added 50 ml. of copper solution. Aliquots were taken starting immediately. The eluate consisted of 50 ml. of pH 2 buffer, 75 ml. each of 0.1 M. and 1.0 M. HCl. Each aliquot was 25 ml. The presence of copper was detected by adding ammonia and visually noting any blue color produced. If copper did not appear until after the HCl had been added, it was assumed that absorption had taken place. On the other hand, if copper appeared in the first or second aliquots, the absorption was considered too small to merit investigation.

The tests here indicated that those resins which had been washed for a very long time as previously described did not absorb to any detectable degree. The long washing

had obviously broken down the chelating structure.

A sample of 8-quinolinol resin was taken from batch I. This was the portion of the screenings passing through the No. 60 sieve. It was washed for three days with 0.1 M. NaOH, three days with 0.1 M. HCl with one day in water between and after the above steps. When tested with copper as above, absorption was indicated by the fact that copper did not appear in the eluate until 1 M. HCl was added. All subsequent 8-quinolinol resin tests were made on this resin.

Absorption Characteristics of 8-Quinolinol Resin

The absorption properties of 8-quinolinol resin were tested with barium, strontium, magnesium, and calcium. All resin beds were 12 cm. In each case a total of 50 ml. of metal ion solution was used. When two solutions were added simultaneously, 25 ml. of each were taken. Effluent aliquots were 25 ml. A total of 7 (and later 5) aliquots was thus taken. These were followed by 0.1 M. HCl until 2 more were obtained.

Barium and strontium were run at pH levels of 2, 4, 6, 8, and 9. Absorption dropped rapidly to negligible levels at pH 6 and below. Runs with calcium and magnesium were therefore made only at pH levels of 6, 8, and 9.

Table I gives the data obtained with barium above pH 4. This covers the range from zero to complete absorption. The flame readings for each aliquot were added and compared to the reference at 0.01 M. Since the added amount was 50 ml. and the aliquots taken were each 25 ml., the added total of the flame readings should be twice that of the reference. Whenever possible, the reference for 0.01 M. metal was set at 100. This table is representative of the type of data collected. This data can readily be graphed by plotting concentration vs. volume of eluate. Since graphical representation illustrates the elution patterns more clearly, it is used predominantly in subsequent data.

Analysis of the data showed similar elution patterns. At pH values of 2 and 4 all metal had been eluted by the third aliquot. Absorption was slight at pH 6, somewhat more at pH 8, and strong at pH 9. The absorption at pH of 8 and below, however, was not sufficient for practical consideration under these conditions of metal ion concentration and column length. The elution of the metals with HCl from the pH 9 buffered columns showed different elution patterns. This is illustrated in the graph of Figure 1. In order to determine if these elution patterns could be used for separations, long runs were made. At a

Table I. Barium on 8-Quinolinol

Aliquot No.	Run 1-I		Run 1-J		Run 1-K		Run 2-J	
	Elu- triant	Flame Read- ing on Eluate	Elu- triant	Flame Read- ing on Eluate	Elu- triant	Flame Read- ing on Eluate	Elu- triant	Flame Read- ing on Eluate
1	Buffer	22	Buffer	43	Buffer	12	Buffer	0
2	pH = 4	100	pH = 6	91	pH = 8	36.5	pH = 9	0
3	pH = 4	82	pH = 6	71	pH = 8	38	pH = 9	0
4	pH = 4	2	pH = 6	8	pH = 8	13.3	pH = 9	0
5	pH = 4	0	pH = 6	2	pH = 8	2	pH = 9	0
6	0.1 M.HCl	0	0.1 M.HCl	0	0.1 M.HCl	0	pH = 9	0
7	0.1 M.HCl	0	0.1 M.HCl	0	0.1 M.HCl	0	pH = 9	0
8							pH = 9	0
9							1.0 M.HCl	23
10							1.0 M.HCl	>100
Total		206		215		101.8		--
0.01 M Ba (for reference)		100		100		55.3		100
Per cent Recovery		103		107.5		92		--

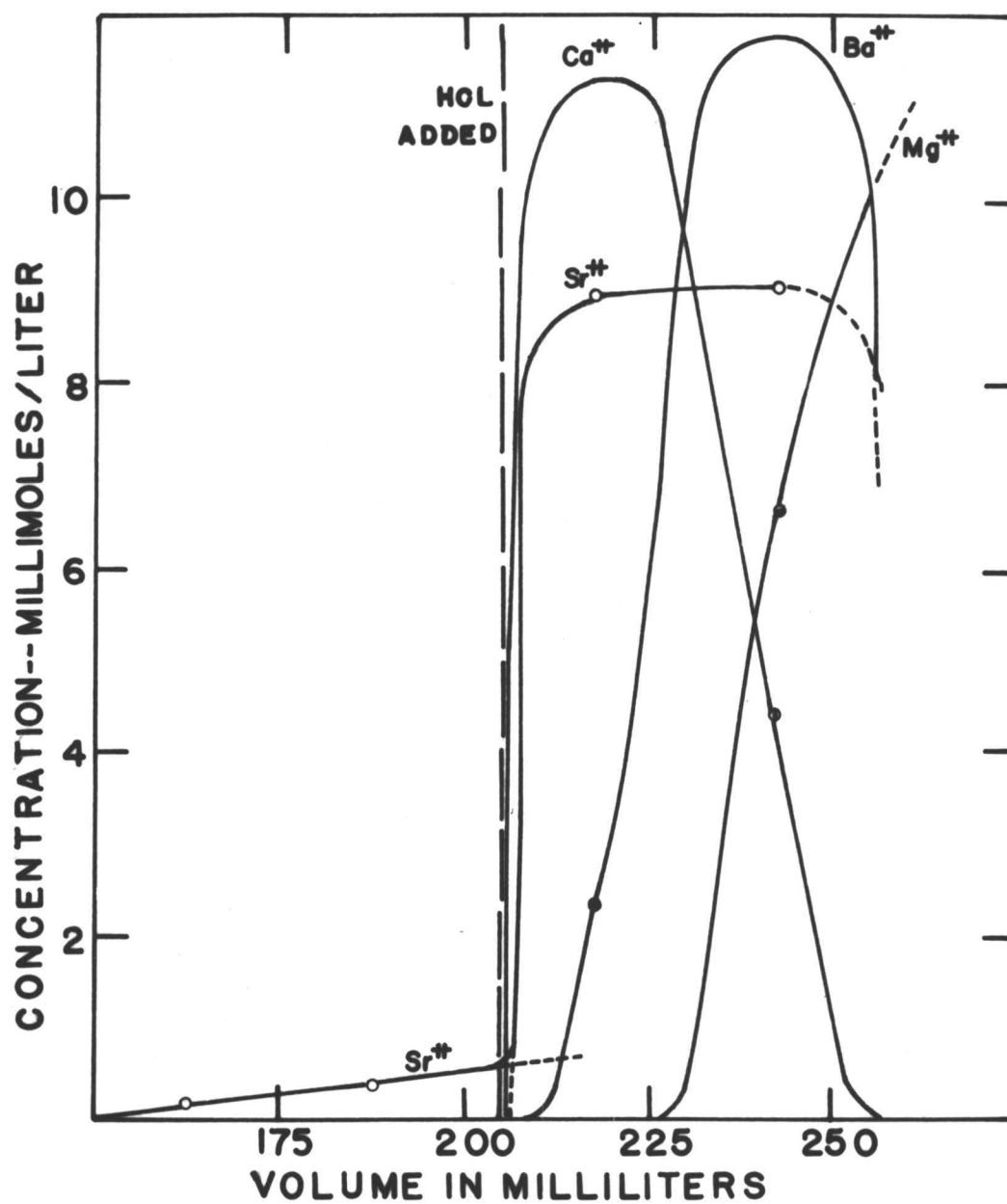


FIGURE 1. ELUTION OF THE ALKALINE EARTH METALS FROM 8-QUINOLINOL RESIN AT PH 9

pH of 9 a mixture of strontium and barium was added. The first 10 aliquots were taken at the same pH. This was followed by 5 aliquots at a pH of 8 and finally with 100 ml. of 1 M. HCl. Traces of barium and strontium appeared from the beginning. More appeared at a pH of 8. However, only about 20 per cent of the total added was eluted in the first 15 aliquots. The remainder came out with the acid. No appreciable separation was obtained.

A similar run was made with calcium and magnesium. These showed similar elution patterns with no obvious selectivity. Therefore, no further tests were made on this resin.

Absorption Characteristics of O-aminophenol Resin

Similar testing was simultaneously done on o-amino-phenol resin. This resin showed properties that could be utilized. As in the previous case, runs were made with strontium and barium at pH 2, 4, 6, and 8. Calcium and magnesium were run at pH 4, 6 and 8. With barium and strontium some absorption was observed at pH 4. However, about 90 per cent was eluted in the first 7 aliquots, i.e., before any HCl was added. At pH 6 small amounts of strontium appeared in all aliquots, but only a total of about 10 per cent was eluted in the first 7 aliquots.

Graphs for the elution patterns for strontium, barium, calcium and magnesium are shown in Figures 2, 3, 4 and 5, respectively. At pH 8 complete absorption took place and therefore no elution patterns occur.

Having demonstrated that absorption did take place at pH greater than four, the next step was to establish elution patterns for the several metals. To improve on the accuracy of the patterns, it was decided to collect 10 ml. sample aliquots and to double the length of the columns to 24 cm. The first two aliquots collected were 25 ml. each and were followed by 22 aliquots of 10 ml. each. Finally two more were taken of 25 ml. each. The columns were buffered and 50 ml. of sample added at pH 6. This was then eluted by a pH 5 buffer. The results are plotted in Figure 6. The volume of effluent is plotted versus concentration in the effluent.

Several things were indicated from these data. Magnesium was eluted most rapidly, followed by strontium, barium, and calcium in that order. Barium and strontium patterns were quite similar. However, later runs showed barium more strongly absorbed than here indicated. The most probable separation should be magnesium from calcium. The others had elution patterns that widely overlapped.

In order to test conclusions reached from individual

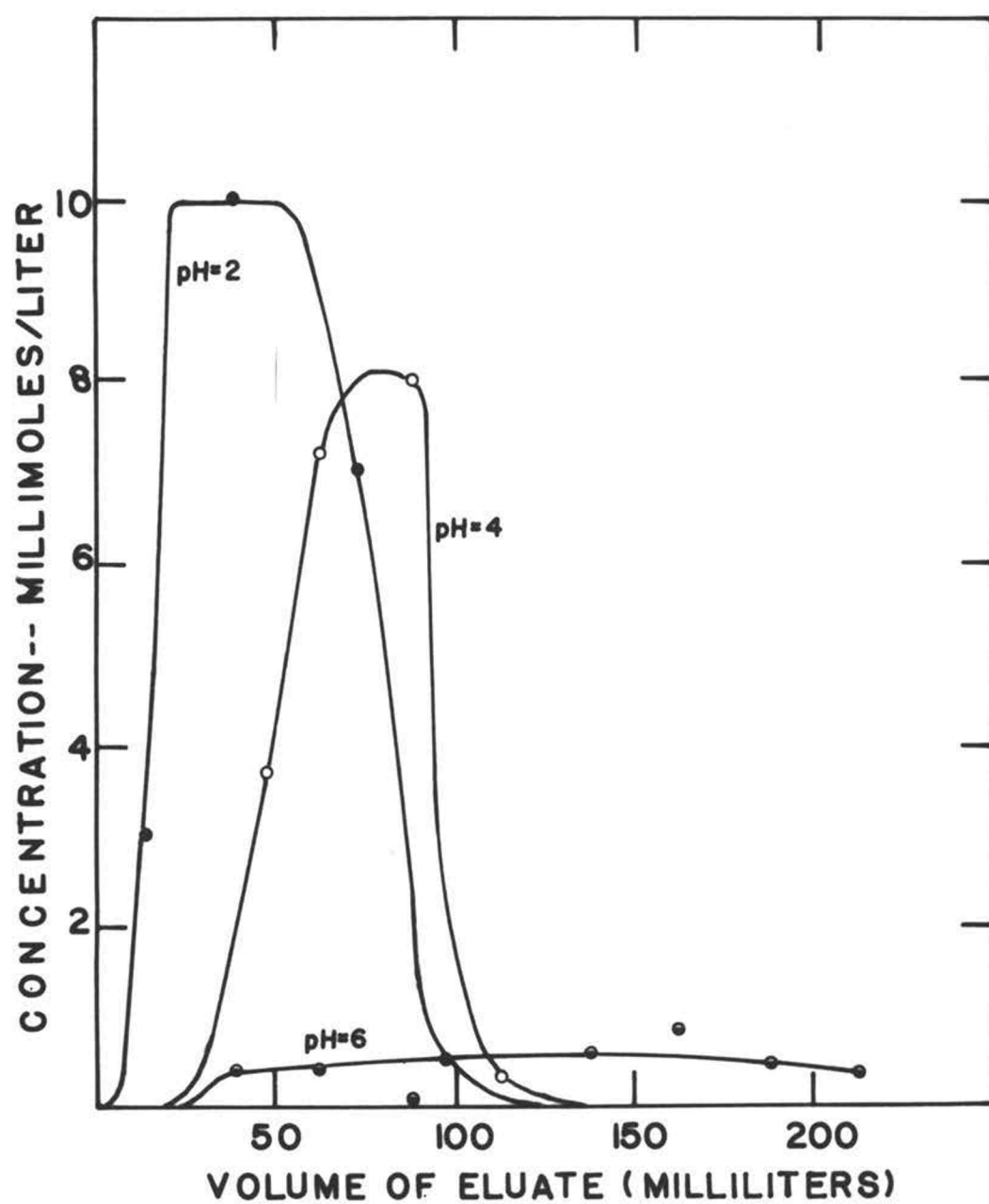


FIGURE 2 ELUTION OF Sr^{++} FROM
O-AMINOPHENOL RESIN

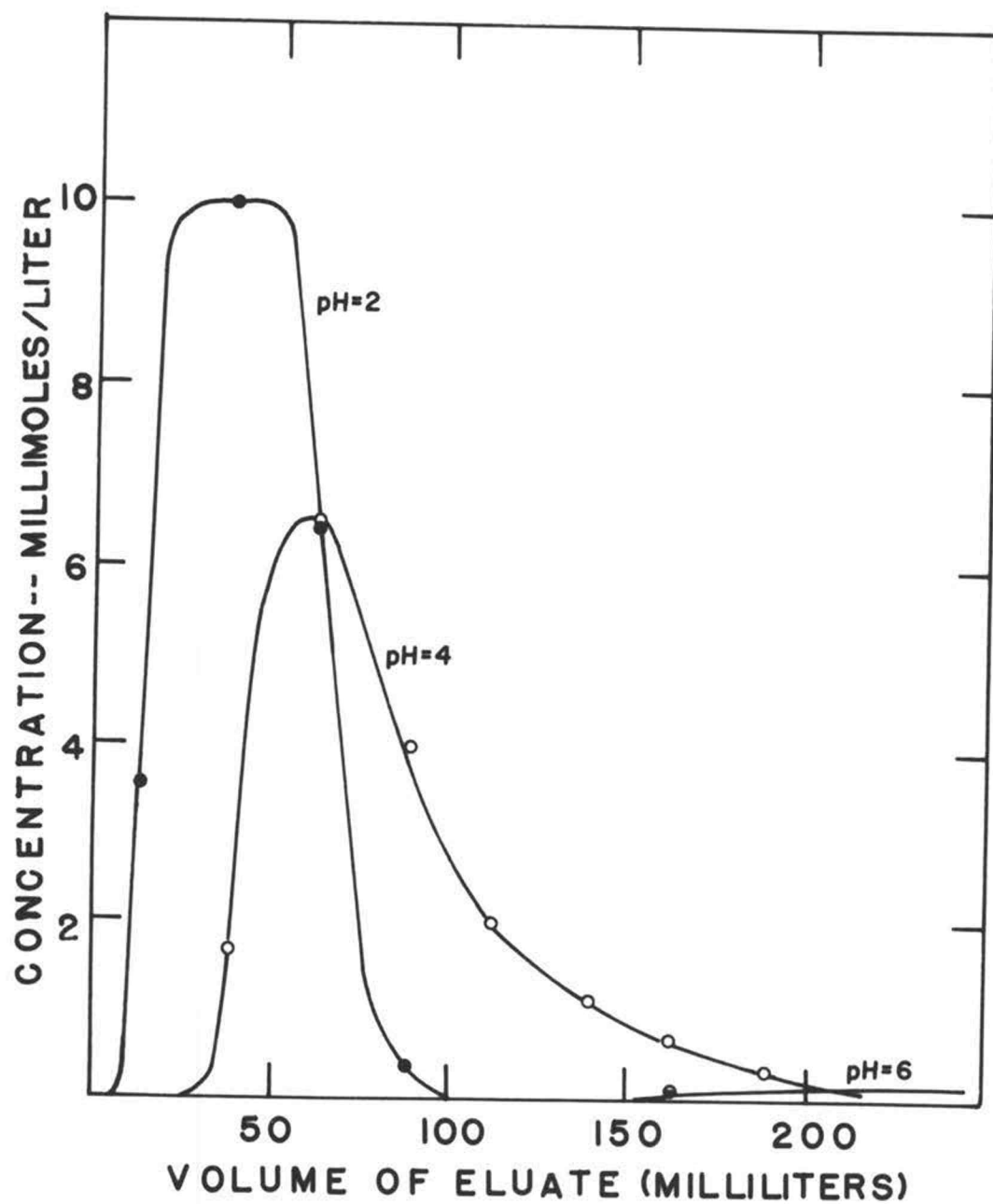


FIGURE 3 ELUTION OF Ba^{++} FROM
O-AMINOPHENOL RESIN

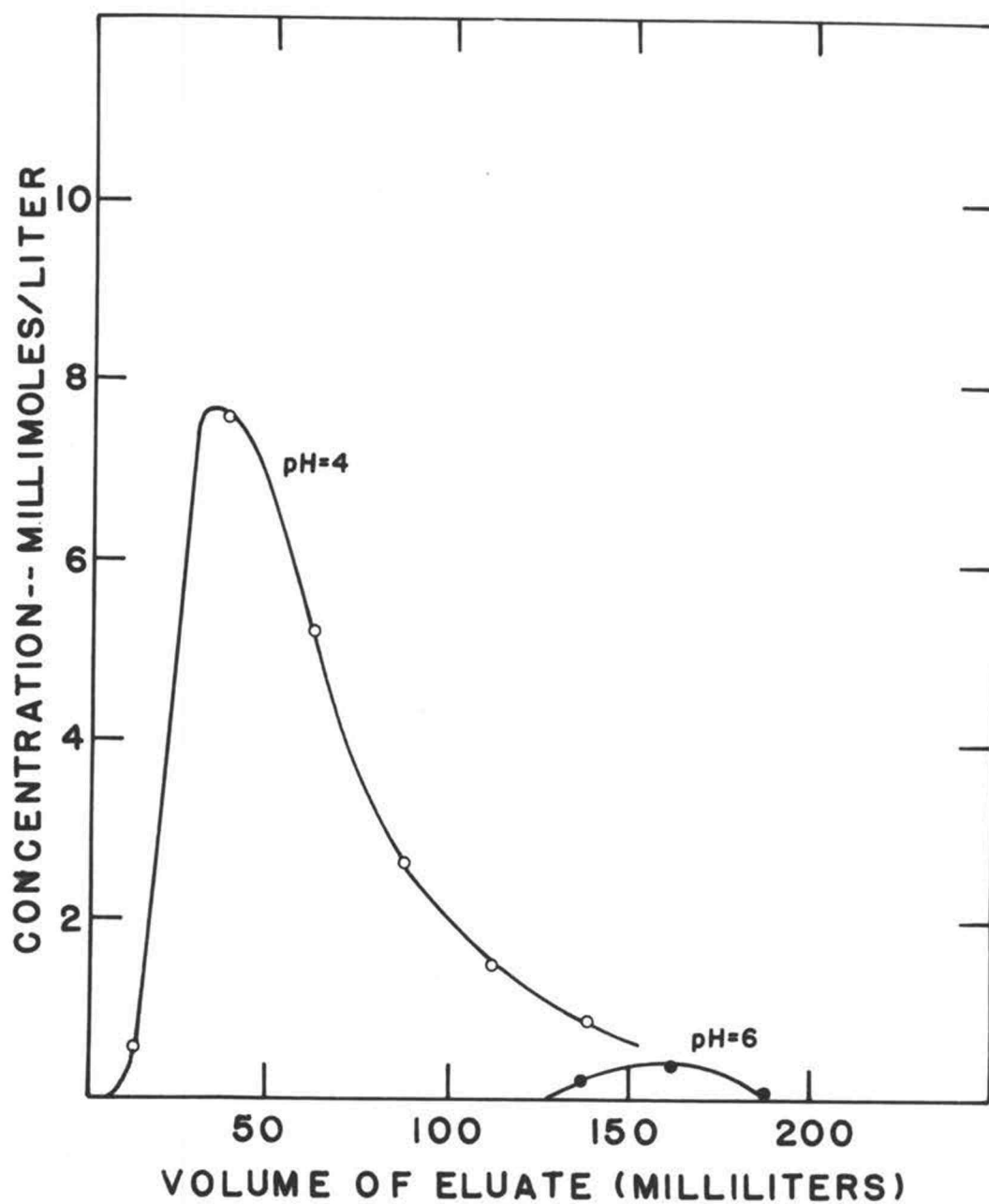


FIGURE 4 ELUTION OF Ca^{++} FROM
O-AMINOPHENOL RESIN

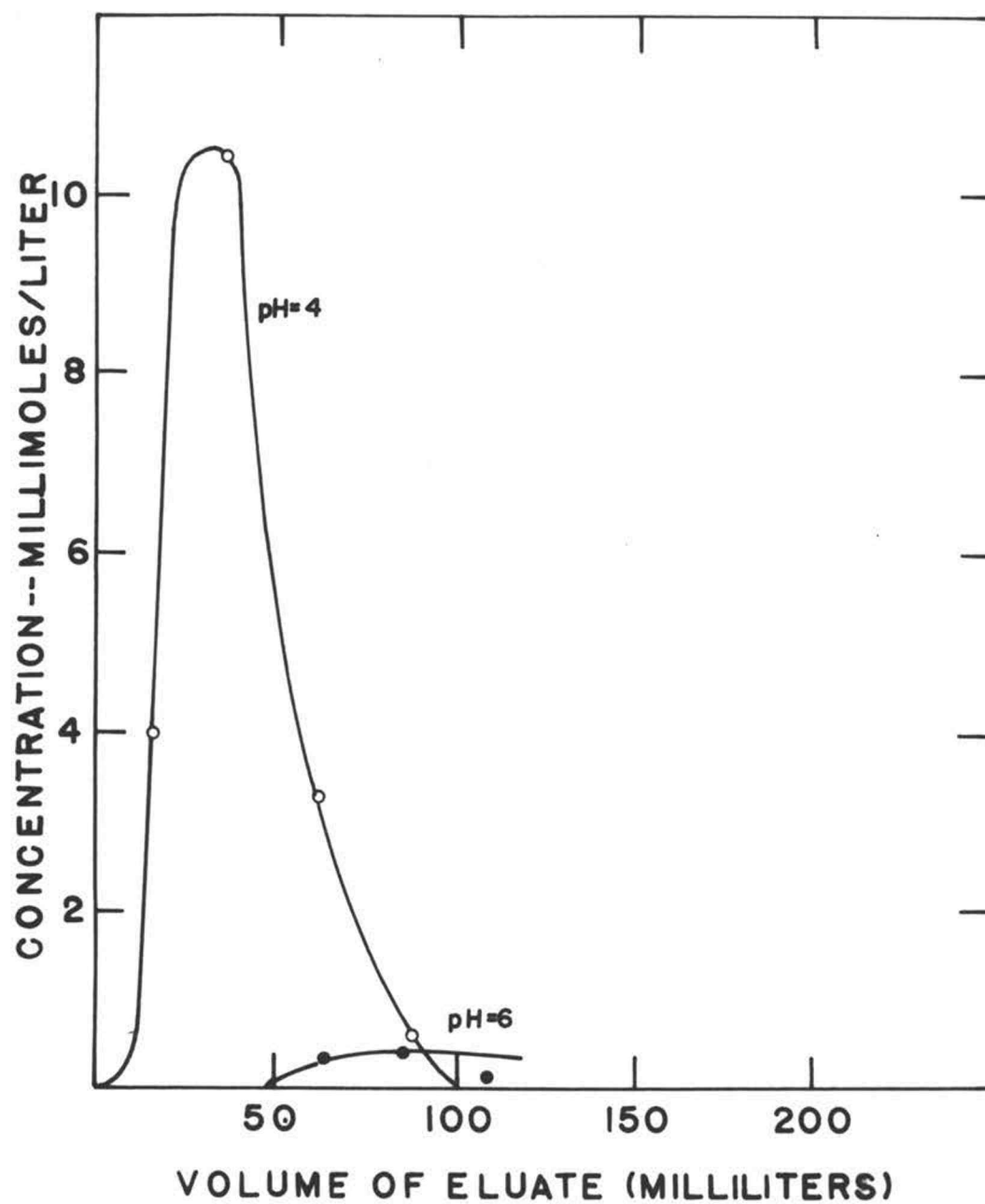


FIGURE 5 ELUTION OF Mg^{++} FROM
O-AMINOPHENOL RESIN

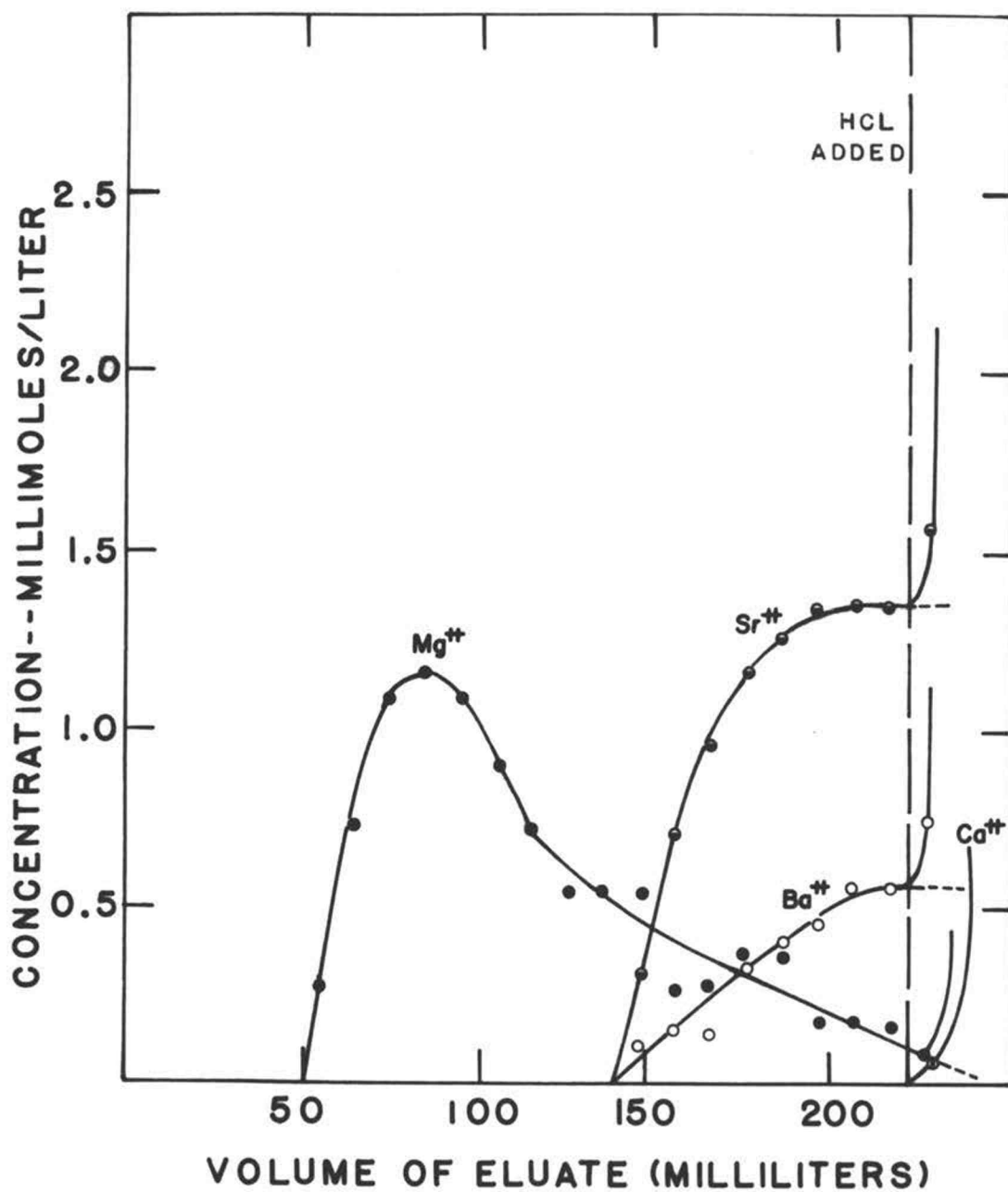


FIGURE 6 ELUTION OF THE ALKALINE EARTH METALS FROM O-AMINOPHENOL RESIN AT PH 5

elution patterns and from the total mixture above, the following combinations were run. A 25 ml. aliquot of each metal ion solution was used.

(a) Barium and Strontium

A mixture of barium and strontium yielded individual elution patterns that overlapped over a considerable portion. Exact patterns were not established because of the limits in the analysis. Strontium interfered strongly in the flame photometer determination of barium. Strontium appeared in definite measurable quantities when the barium was about two-thirds eluted.

(b) Magnesium and Strontium

Runs with strontium and magnesium mixtures were made eluting with pH 5 and pH 6. Strontium is more strongly absorbed but at pH 5 strontium appeared when the magnesium was about 50 per cent eluted. At pH 6 the magnesium was not yet being eluted after 12 aliquots.

(c) Calcium and Strontium

Calcium and strontium (10 ml. each) were absorbed with about equal facility. At a pH 5 elution no separation was observed. Only slight amounts of each appeared after 600 ml. of buffer.

(d) Calcium and Barium

Calcium and barium were treated as the previous

mixture. The results showed barium was preferentially absorbed but not by a sufficient margin to effect separation under these conditions.

(e) Magnesium and Barium

Magnesium and barium were run as above but using a pH 4.5 buffer. By collecting 350 ml. at this pH, the magnesium was eluted and the barium absorbed. A versene titration showed that the first 350 ml. contained 98 per cent of the magnesium. The flame photometer detected no barium in this portion. When further eluted with 1 M. HCl, the flame photometer indicated 90 per cent barium recovery. Both of these results were within the accuracy of the methods used.

(f) Magnesium and Calcium

The calcium-magnesium separation seemed most probable and was the most extensively investigated system in this project. The results obtained here differed markedly from the data by Pennington (6, p. 68, 84). His data indicated no calcium absorption below pH 6 while magnesium absorption was still appreciable. The data gathered here indicated that at pH 5 calcium was strongly absorbed although the capacity of the resin had been greatly reduced. At pH 4 in a mixture of calcium and magnesium, calcium began to appear in the fourth aliquot. This means

that it appeared in the second aliquot after pH 4 buffer was added since 25 ml. each of pH 6 calcium and magnesium solution had been used to rinse the ions onto the column. However, only about 20 per cent of the calcium had been eluted by the end of aliquot 6.

As illustrated in Figure 4, at pH 6 calcium appears in the eluant for a few aliquots and then no more is eluted until HCl is added. Since this is only about 10 per cent of the total amount added to the column, the implication seems to be that the amount added was in excess of the capacity of the resin under those conditions. At pH 6, 25 ml. of 0.01 M. calcium solution is too much for a 12 cm. column.

Consequently, the column was increased to 24 cm. In this separation the attempt was first made at pH 4 and pH 5. In the pH 4 run neither calcium nor magnesium was very strongly absorbed. At pH 5 the magnesium elution was rather slow. The calcium seemed to follow a pattern indicating a saturation condition despite the 24 cm. columns. The volume of calcium was then reduced to 10 ml. and a compromise pH of 4.5 was used. At this concentration and pH the calcium was selectively absorbed and the magnesium could be eluted. Since the flame methods were not very sensitive to magnesium, the analysis procedure was

modified to compensate for this. The aliquots were analyzed for calcium on the flame photometer and each aliquot was also titrated for total hardness with EDTA. The minimum detectable deviation on the photometer meter was about 0.5 scale division or about 2.5 per cent of the total calcium added. When an aliquot showed this reading, it was assumed that calcium was being eluted and it, with all subsequent aliquots, was analyzed for calcium. It was further assumed that the previous aliquots contained all the magnesium. Table II illustrates the results. It is based on the run described in the following paragraph where 10 ml. of calcium and 50 ml. of magnesium were added and eluted at pH 4.5. The minimum detectable calcium is indicated as appearing in eluant No. 4. However, with the inherent error of such small scale readings, an equal concentration could have gone undetected in eluant No. 3. If No. 3 is included with the calcium, the recoveries are very nearly complete. This overlap here is concerned with about 5 per cent of the total calcium but only about 0.6 per cent of the total hardness. Table III shows the exact percentage recoveries. As described in the following paragraph, this overlap can be substantially decreased.

A final series of runs was made in which the amount of calcium added was kept constant while the amount of

Table II. Determination of Total Hardness by
Flame Analysis and Versene Titration

Eluant No.	Elutrient buffer	Volume of collected aliquot	Flame read- ings (set for calcium)	Volume of versene (for total hardness)
1	pH 4.5	250 ml.	0	51.980
2	pH 4.5	100	0	3.024
3	pH 4.5	25	0	0.460
4	pH 4.5	25	0.5	0.450
5	1 N HCl	25	1	0.500
6	1 N HCl	25	42	9.545
7	1 N HCl	25	0	0.0
Total		475 ml.	43.5	65.949
Standards				
Ca	0.005 M.		54	
Ca	0.01	10 ml.		10.942
Mg	0.01	10 ml.		10.916
Mg	0.01	50 ml.		54.580
Theoretical total			43.2	65.522

Table III. Separation of Calcium and Magnesium at Different Volume Ratios

Run	Volume Used		Per cent recovery at					
			350 ml.		375 ml.		450 ml.	
	Ca ⁺⁺	Mg ⁺⁺	Mg ⁺⁺	Ca ⁺⁺	Mg ⁺⁺	Ca ⁺⁺	Mg ⁺⁺	Ca ⁺⁺
U	10	10	100.0	100.7				
V	10	25	99.7	103.2				
M	10	50	100.1	99.45	101.5	95.8		
N	10	100	97.5	125.0			100.0	99.9

magnesium was varied, including sample volumes of 10, 25, 50, and 100 ml. The results are tabulated in Table III. Up to 50 ml. or 0.5 millimole of magnesium, the elution was essentially complete after the total eluant volume was 350 ml. The greater volume required when 100 ml. of Mg was used stems directly from the fact that this sample like the others was added at pH 6; for, although the first 100 ml. were part of the collected eluant, they were actually not part of the elutriant. This effect should have appeared slightly at the 50 ml. sample level but did not appear to. It seems then that the concentration of the magnesium could vary considerably, but the volume should be kept below 50 ml.

The final run consisted of making two runs simultaneously. One consisted of 10 ml. of each solution, the

other was a check and contained only the magnesium. The first aliquot contained 250 ml. Four subsequent aliquots were then taken of 25 ml. each. These were analyzed for calcium on a Beckman model B spectrophotometer with flame attachment. The concentration of the calcium was at the lower limit of the instrument sensitivity, i.e., less than 1 ppm. However, the readings indicated that the amount of calcium in the first 350 ml. is about 0.5 per cent or less of the total amount added.

Summary

These experiments clearly demonstrate that at the levels indicated, magnesium can be separated from calcium by the use of o-aminophenol resin to within at least 99 per cent accuracy. The runs at the 10 ml. level were repeated on different but identical columns, on different days and at flow rates varying from about 1 ml. to 3 ml. per minute. The results were essentially identical. A total of 50 runs, 25 on each column, was made with this resin. Many of the calcium-magnesium runs were repeated, and the elution patterns were essentially the same throughout for any given conditions. This serves to indicate the stability of the resin and the reproducibility of the results.

CHAPTER V

SUMMARY AND CONCLUSIONS

The field of chelating ion exchange resin applications is still largely undeveloped. The stated application for the commercial chelating resins is primarily for the concentration of heavy or alkaline earth metals from concentrated alkali metal solutions. Only a few chromatographic-type separations have been developed.

It was the purpose of this project to test the reproducibility of the resin synthesis, to briefly attempt new combinations, and to investigate the applicability of these resins to the alkaline earths.

The resin preparation readily duplicated previously published (2, 6) results. This indicated that the resins could be prepared readily with consistent results.

An attempt was made to form a resin incorporating arsenazo. A resin formed, but upon washing it became progressively softer until gelatinous. The apparent reason was that the solubility of the arsenazo group was so great that water was adsorbed on the resin until the structure broke down.

In the chromatographic applications the 8-quinolinol resin showed appreciable absorption above pH 8. However, under the conditions of concentration and column length

used, separations seemed improbable. The o-aminophenol resin absorbed at pH values above 4. Some selective absorption was shown. At a pH of about 5 the order in which the alkaline earths were absorbed was magnesium, strontium, barium, calcium; in which calcium was the most strongly absorbed and magnesium the least. It appeared that magnesium could be separated from either barium or calcium by eluting the magnesium at pH 4.5.

The conditions for the calcium-magnesium separations were carefully determined. By washing the metals onto the column at a pH 6 or 7 and eluting with pH 4.5 buffer, the magnesium is eluted in 350 ml. For 24 cm. columns the total calcium used should be about .1 millimoles. The magnesium can be increased to at least 1.0 millimoles providing the total volume of metal solution added to the column is kept to about 50 ml.

As noted, these results differ from predictions based on the equilibrium studies of Pennington (6, p. 68). It is possible then that the demonstrated selectivity is due primarily to a kinetic rather than a thermodynamic phenomenon. Additional evidence would be needed to definitely prove this.

It is felt that in the field of chelating ion exchange chromatography lies the potential for separating other metals of similar chemical properties.

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