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ELUENT AND LIGAND EFFECTS IN CATION CHROMATOGRAPHY

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Eluent and ligand effects in

cation chromatography

by

Gregory James Sevenich

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Analytical Chemistry

Approved:

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For the Graduate College

Iowa State University
Ames, Iowa

1985

TABLE OF CONTENTS

DEDICATION

This work is dedicated to my wife and parents.

Without their guidance, strength, love, and support
these pages might still be blank.

GENERAL INTRODUCTION

The use of cation-exchange resins for separating metal cations has become quite popular and has seen extensive use involving characterization of complex samples. A wide variety of eluting conditions with different combinations of organic solvents, different eluting cations, and complexing ligands have been studied. Separations previously required relatively long periods of time and complex sample manipulation through classical separation methods. The effluent was monitored in a discontinuous fashion by taking fractions and analyzing each separately. The result from the separation is a plot of concentration of analyte versus elution volume.

Automation of the original gravity-flow ion-exchange columns to a forced-flow system with automatic detection greatly advanced the power and speed of metal determinations. Smaller sample sizes could be used and automated detection methods significantly reduced the amount of operator time spent monitoring the separation. Results were recorded in an analog fashion.

Even with the advances in liquid chromatographic instrumentation, the technology of resin synthesis lagged significantly and was generally considered a "black art". Extensive heterogeneity of resin composition, even in the

same bead, was significant. Most columns were poorly packed with resins that had relatively large particles covering a broad range of sizes. Column efficiency was not well-understood and was severely lacking.

The exchange capacity of most commercial cation exchange resins was relatively high (2-5 meq per gram) and required high buffer concentrations to elute most cations. Use of gradient elution speeded up the elution process, but a number of separations could still take up to an hour or more. Ion-exchange groups were located throughout the whole of the bead which have poor exchange kinetics for the rapid separations.

Modern ion-exchange chromatography results from significant advances in the field of polymer synthesis. The synthesis of small, spherical resin particles and increased homogeneity of the particles have greatly improved the quality of separations.

Rapid separations can be obtained by employing resins of lower exchange capacity with the exchange groups located on the outermost surface of the resin. Surface functionality provides better kinetics of the ion-exchange process by minimizing particle diffusion. The concentration of eluent necessary to elute the cations was proportionately lower. From this premise arose the field of chromatography commonly referred to as Ion Chromatography. The growth of Ion

Chromatography has been extremely rapid, mostly in the area of anion separations. Separations of cations on low-capacity resins have been studied to a very limited extent. The nature of the exchange process on low-capacity gel resins has received surprisingly little attention with most work focused on applications.

The major objective of this work was to expand the single-column Ion Chromatographic system for cations. The studies are centered around low-capacity sulfonated gel resins which are necessary for modern single-column Ion Chromatography using conductivity detection. Reproducible sulfonation of these gel resins is studied as is the location of exchange groups. Possible side reactions are also discussed.

Efforts are made to describe the equilibria and selectivity of this system in terms derived from the simple equilibrium expression of the ion-exchange process. Effects of eluting cations and resin capacity are also examined.

The effects that complexing agents added to the eluent have on cation retention are discussed. Parameters of the system such as eluent cation concentration, complexing agent concentration, and pH dependency are also examined.

The final section is an applications method for speciation and determination of iron. This study resulted from work in previous sections.

EXPLANATION OF DISSERTATION FORMAT

This dissertation is divided into four sections. The order of their appearance represents a logical order of investigation for cation chromatography. In fact, the true chronological order is quite different due to circumstances not under the control of the author. The order presented here and the division maintains good continuity of thought. Although each section is interrelated to the other, each may stand independently.

Section III through the work with EDTA represents a published paper which has been expanded somewhat for more rigorous analysis of the system. The other sections have not been published as of yet. Several of the introductions seem somewhat redundant because each section is self-contained. References made to tables, figures, and literature refer to the section at hand.

All work presented here was performed under the watchful eye and guidance of Dr. J. S. Fritz.

SECTION I. PREPARATION OF LOW-CAPACITY

SURFACE-SULFONATED GEL RESINS

INTRODUCTION

Purpose

Sulfonated cation exchange resins have been used successfully for some time in the separation of almost all combinations of metals from each other (e.g., 1,2,3,4). The most commonly used cation-exchange resin is the sulfonated poly(styrene-divinylbenzene) copolymer. Commercial versions of this resin typically have been functionalized to give the maximum capacity possible for the resin (ca. 2 - 5 meq per gram). Separations with the sulfonated resin were typically run in gravity flow columns with the effluent collected in fractions. Each fraction was analyzed for the metal of interest and the resulting data were presented graphically in a "digital" fashion. The practicality of these separation systems was limited by the long times and high concentration of eluting buffer necessary to achieve the desired separations.

Chromatographic systems using pumps to force the effluent through the ion-exchange columns and the use of detectors that could continuously and automatically monitor the effluent significantly decreased typical analysis times.

An additional method of speeding up the elution process is to use ion-exchange resins of a lower exchange capacity.

A simplified version of the ion-exchange equilibrium expression is given by equation 1.

$$Res\text{-}E + M \rightleftharpoons Res\text{-}M + E \tag{1}$$

This equilibium expression can be written in the form of equation 2.

$$K = \frac{[Res\text{-}M]\ [E]}{[E]\ [Res\text{-}M]} \tag{2}$$

With less than 1% of the exchange sites occupied by the analyte cation (given as M) and assuming the ratio of the amount of cation on the resin to the amount of cation in the mobile phase to be constant, a decrease in the resin capacity will subsequently decrease the concentration of the eluent cation (given as E) necessary to elute the analyte cation from the column. Lowering the cation-exchange capacity can notably decrease the elution time of most cations from hours (or even days) to a matter of minutes.

General resin design for ion-exchange chromatography has been discussed by several authors (5,6,7). Hansen and Gilbert (8,9) expanded the Gleuckauf equation to reflect diffusion of ionic species into the resin matrix of a pellicular or "pellicular-type" of chromatographic bead and found a maximum functionalization depth to be 5-15% of the total particle diameter as optimum for favorable exchange

kinetics. Hamilton, Bogue, and Anderson (10) have shown the
Gleukauf equation (an explicit description of
chromatographic diffusion) to be essentially the same as the
more popular van Deemter equation (an implicit description
of chromatographic diffusion).

Controlled sulfonation of poly(styrene-divinylbenzene)
neutral resin to give "pellicular-like" support is, at best,
difficult. Wiley and co-workers (11,12,13) determined rates
and activation energies for sulfonation of commercial
poly(styrene-divinylbenzene) and found them to be about
three times that of analogous dialkyl benzenes. Reaction
rates for sulfonation of resins prepared from pure
divinylbenzene isomers are slower than the commercial grade
of divinylbenzene and at different rates between the
individual isomers. Sulfonation of polymer beads typically
proceeds relatively slowly unless promoted by addition of a
catalyst (usually a silver salt) or heat. The reaction can
then become very rapid and hard to control. Reaction rates
vary easily for two similar types of resin (e.g., the same
crosslinking and bead size) polymerized under slightly
different conditions (e.g., different temperature or
agitation rate). Variation between batches of the same
resin is not unusual. Different divinylbenzene isomers are
also known to polymerize at different rates producing
localized regions of higher crosslinking in the resin beads

as the polymerization commences. Variations between individual beads in the same polymerization and sulfonation batch have even been observed (14,15).

Reproducible sulfonation of gel resins, at least within the same polymerization batch, appears to depend very strongly on stringent control of the resin preparation, reaction conditions, and reagents used in the sulfonation.

The major objective of this study is to determine which factors must be controlled to obtain a surface-sulfonated cation-exchange resin in a reproducible fashion. A well-defined resin of known composition and favorable ion-exchange kinetics is desired. This resin is to be used in the study of the equilibrium and selectivity behavior of very low capacity cation exchange resins for application in single-column ion chromatography systems.

Literature Survey

Ion-exchange has seen a long period of application for the separation and isolation of various ions. Despite its versatility, the largest application of ion-exchange is in demineralization and purification of water. Helfferich (16) and Inczédy (17) claim the earliest documented application of ion-exchange was by Moses in 3000 B. C. where the Waters of Marah were purified by throwing pieces of wood into the

water. The exchange was credited to the carboxylic acid groups on the oxidized cellulose of the wood.

Spotty accounts of possible ion-exchange processes have been noted in the literature, but the actual description of the process as one of ion-exchange has been credited to the collaboration of Thompson (18) and Way (19,20). They found animal urine to become clear, free of ammonium ions, and of increased acidity after being passed through a container of soil. They also found magnesium and calcium taken up by the soil and replaced by sodium and potassium. This early account of ion-exchange was explained on the basis of the presence of certain silicates of aluminum in the soils. These silicates were later identified by Eichorn (21) as zeolites.

The relatively low exchange capacity and acid sensitivity of natural and the first synthetic silicate based ion-exchangers forced a search for more inert and stable exchangers of higher capacity.

The first organic based cation-exchanger, a sulfite cellulose, was discovered by Kullegren (22). Copper ions were readily taken up by this material and subsequently eluted with acid.

The first synthetic polymer based ion-exchange resin was demonstrated in 1935 by Adams and Holmes (23). This cation-exchange material had phenolic functionality and was

prepared by condensation polymerization of phenol with formaldehyde. The actual production of this type of polymer, generally referred to as "Bakelite" polymers, may be traced to work by von Bayer in 1872 (24).

The first synthetic poly(styrene-divinylbenzene) copolymer with sulfonic acid functionality was prepared by D'Alelio (25) in 1944. This resin was prepared by polymerization of sulfonated polystyrene with divinylbenzene.

Much effort has been put into the study of the behavior of fully sulfonated poly(styrene-divinylbenzene) copolymers. This exchanger has demonstrated greater popularity and versatility than most other cation-exchange materials. About 30 years ago, an increased emphasis had been directed towards sulfonated resins of lower capacities.

Boyd et al. (26) prepared resins of reduced capacity through desulfonation of high-capacity material by acid hydrolysis at elevated temperatures (180-200°C). A homogeneous product was anticipated on the premise that desulfonation was a random process and would occur equally throughout the whole of the resin bead. As it turned out, the resins suffered noticeable structural damage through breakdown of the crosslinking under the desulfonation conditions.

Pepper (27) proposed that the sulfonation of neutral

poly(styrene-divinylbenzene) copolymer beads proceeded in a "layer-by-layer" fashion and could be stopped at any particular "layer" giving a partially sulfonated bead with a low capacity and a known depth of functionality. From this concept, Pepper (28) prepared the first superficially sulfonated polymer beads. Parrish (29) also prepared surface sulfonated beads and gave a brief example of their utility.

Freeman and Aiyar (30) claimed production of homogeneously sulfonated resin beads having a fraction of the maximum possible capacity of the resin. The process involved the use of dilute sulfuric acid in nitromethane as the sulfonating medium. Sulfonation by this method took about 40 to 60 days.

The surface sulfonation of poly(styrene-divinylbenzene) beads with crosslinking ranging from 0.5 to 8% divinylbenzene was studied by Small (31,32). Examination of the sulfonation depth of a resin bead in terms of optimum separation of several inorganic cations was subsequently studied by Stevens and Small (33,34). These resins were used for the chromatographic separation of simple cations in what is now know as Dual-Column Ion Chromatography.

Skafi and Lieser (35,36,37) studied the chromatographic behavior and distribution ratios of superficially sulfonated cation-exchange resins and found the effect of particle

diffusion on band broadening greatly reduced. The speed with which most separations could be accomplished was significantly reduced while the relative selectivities of the cations were unchanged when compared to higher capacity resins.

Fritz and Story (38,39) prepared several low-capacity sulfonated macroreticular resins for rapid separation of various metal ions. The selectivity of these resins was different from that of conventional microreticular (gel) resins.

Low-capacity resins have been prepared specifically for use in Single-Column Ion Chromatography by Fritz, Gjerde, and Becker (40). The resin used in the separations was a 3:2 blend of neutral resin with low-capacity sulfonated resin giving a final capacity of about 8 μeq per gram. Very good efficiency was demonstrated in separation of the alkali metals and alkaline earths.

Hajós and Inczédy (41) thoroughly investigated the effects of time and temperature on the sulfonation of 8% DVB crosslinked gel resins. Resins with capacities ranging from 7 to 500 μeq per gram were prepared from unswollen beads. The lack of swelling gave sulfonation only on the outer surface of the beads by slowing the diffusion of sulfuric acid into the resin matrix. Surface-sulfonation was confirmed by X-ray fluorescence analysis of the bead cross-

sections. It was found the temperature for the reaction mixture had a greater effect on the final capacity than did the time of reaction. Distinct capacity-time curves were obtained for various reaction temperatures with good reproducibility between batches under the same conditions.

Other types of liquid chromatographic supports with sulfonic acid groups have also been prepared. A low-capacity anion exchange support for use in Dual-Column Ion Chromatography of anions was prepared by agglomeration of aminated latex particles on a highly sulfonated gel resin (42). Wimberly (43) noticed the permanence of such a support was severely lacking and found enough free sulfonic acid groups present to give fair separations of various cations. Papanu et al. (44) developed a cation-exchange support analogous to the afore mentioned low-capacity agglomerated anion exchange material. In this case, a sulfonated latex is agglomerated onto an aminated support bead.

Battaerd (45) and Battaerd and Sivdak (46) prepared a superficially-sulfonated bead by graft-polymerization of a sulfonated α-olefin onto a poly-olefin core bead.

Kirkland (47) impregnated a porous fluoro-polymer bead with a sulfonated fluoro-polymer giving a pellicular-type of ion-exchanger. Along the same lines, Siergiej and Danielson (48) sulfonated a Kel-F polymeric bead with chlorosulfonic

acid after modification of the bead by introduction of
phenyl groups onto the surface of the bead.

Horvath et al. (49) polymerized a coating of stryene and
commercial divinylbenzene into a poly(styrene-
divinylbenzene) coating on glass beads. They then
sulfonated the polymer layer to give a pellicular ion-
exchange support.

The chemical modification of silica particles to
introduce surface functionality onto the surface is outlined
by several authors (7,50,51). Sulfonic acid groups are
introduced by first chlorinating the surface of the silica
with thionyl chloride then introducing benzyl groups by
reaction with benzyl lithium. The aromatic rings are then
sulfonated with sulfuric acid or chlorosulfonic acid.
Limited stability of the silica support has precluded its
use for separating inorganic cations with traditional
eluents.

Several investigators found dynamically or permanently
adsorbed alkylsulfonates and alkylsulfates to be quite
effective in separation of ions on reverse-phase columns
(52,53,54,55). Debate over the exact mechanism of
separation (true ion-exchange, ion-pair, polar modification
of the surface, or a combination of all three) persists.
Control of the amount of alkyl anion present allows elution
behavior similar to low-capacity bonded phase systems.

RESIN DESIGN

Kinetic Considerations

The exchange kinetics of cation and anion exchange for column and batch systems has been described by Boyd, Adamson, and Meyers (56) as a process involving three major steps.

1. Diffusion of the cation through the external solution up to the resin surface.

2. Diffusion of the particle through the resin matrix structure (particle diffusion).

3. Ion-exchange at the resin site.

The exchange at the sulfonic acid resin sites is generally very rapid. Thus, this factor (step 3) may be neglected in determining the kinetics of exchange.

Diffusion of the cation through the external solution (step 1) is controlled mostly by the conditions set for the specific separation system. The ionic character and the concentration of the mobile phase have a direct effect on the cation diffusion rate. A decrease in the total distance a cation must migrate to the surface of a resin bead is readily accomplished in column separations by decreasing the size of the resin beads. As this contribution of kinetics

to the exchange process is reduced, there is also an increase in the efficiency of the column itself.

The major contribution to ion-exchange kinetics is the rate of diffusion of the cation through the resin matrix to the internal exchange sites. This diffusion process depends on two main characteristics of the resin matrix. The first is the physical size and general structure of the resin pores. Obviously, larger pores with fewer bends and terminating channels easily permit the hydrated cations to pass through the resin matrix. Smaller pores formed into twisting channels create a labryrinth laden with stagnant pockets or sinks that may trap ions quite effectively. The effective pore size varies with the differences in polarity between the mobile phase and the resin matrix. The Nernst potential from the bulk solution to the surface of the bead is relatively high for a hydrophobic resin structure in an ionic mobile phase. This high potential is the result of the tightening of the water structure about the surface of the resin beads making it almost impervious to ions.

As the surface polarity is increased, as occurs during sulfonation, the water structure loosens and is closer to the resin surface. The net result is a lowering of the Nernst potential at the resin surface and a closer possible approach to the resin surface by cations. The expansion of the water structure also widens the effective pore diameter

throughout the functionalized portions of the resin making
it easier for ions to negotiate the resin matrix.

The second characteristic is concerned with the depth of
functionalization in the resin bead and the resulting
distance a cation can travel within the bead. The
contribution of band spreading resulting from the stationary
phase, H_s, is given by equation 3.

$$H_s = \frac{QRS^2V}{D_s} \tag{3}$$

where: Q   depends on the physical shape of the
            stationary phase
R = a constant and depends on the diffusion rate
            of the solute in the mobile phase
S = the depth of the stationary phase
D_s = diffusion coefficient of the solute in the
            stationary phase
V = mobile phase flow velocity

It is apparent that greater depths of functionalization
lead to slower overall kinetics and significant loss of
column efficiency.

Optimization of exchange kinetics for rapid separation
systems require a carefully designed resin because the
largest contributing factor is typically diffusion of
cations through the resin matrix (particle diffusion). The
ideal ion-exchange would have surface functionalization with
a high density of exchange groups located on the outermost
surface. Porosity should be located only in the area of the

exchange groups while a rigid structure would make up the non-functionalized regions of the resin. Particle diffusion would be greatly reduced in this design and exchange would depend primarily on the film diffusion (5,9,57). Superficially functionalized chromatographic phases with essentially impenetrable cores also have these basic properties.

Choice of Sulfonating Conditions

A meaningful study of an ion-exchange system requires a resin of known composition. Mixed and non-reproducible functionality of a resin may lead to unpredictable exchange behavior and completely invalidate any data. To obtain a mono-functional resin of known composition requires the use of reagents that give the required product and known by-products. Control of the reaction rate is also a necessity.

Sulfonated cation-exchange resins have traditionally been prepared through direct reaction with one of several sulfonating reagents. Poly(styrene-divinylbenzene) based resins are aromatic in character and sulfonation of this material is analogous to sulfonation of alkyl aromatic compounds. Sulfonation of aromatic compounds involves the replacement of a carbon-bonded hydrogen atom with a sulfo-group. Replacing a nitrogen-bonded hydrogen atom

(sulfamation) or oxygen-bonded hydrogen atom (sulfation) may
also be readily accomplished, but will not be covered here.

The basic reagent in the sulfonation reaction is sulfur
trioxide. All other sulfonating reagents can be regarded
simply as compounds formed by reaction of a suitable
nucleophile with sulfur trioxide. Under the proper
conditions, each type of sulfonating reagent can act as a
carrier of sulfur trioxide in the sulfonation process.

One of the most thoroughly studied sulfonating agents of
aromatic compounds is pure sulfur trioxide. Sulfur trioxide
is highly reactive and is commonly diluted with inert
compounds such as sulfur dioxide for gas phase reactions and
nitromethane or other inert organic solvents for liquid
phase reactions. Products of sulfonation include aryl
monosulfonic acid, aryl sulfonic anhydride, and diaryl
sulfone. In excess reagent, aryl disulfonic acid and sulfo
diaryl sulfone are also produced. Sulfone production
increases with sulfur trioxide composition and reaction
temperature (58). Sulfur trioxide exists primarily as a gas
and is somewhat difficult to handle under normal laboratory
conditions.

Sulfonation with fuming sulfuric acid leads to a variety
of compounds such as mono- and di-sulfonic acids, sulfonic
anhydride, sulfones, and sulfonated sulfones. Lower
concentrations of sulfur trioxide lead to increased

production of the sulfonic acid while higher concentrations lead to greater production of the other products. Goldstein and Schmuckler (59) have demonstrated that using nitromethane as a swelling agent and diluent prevents formation of sulfones and sulfone bridges in the resin. Nitromethane complexes with the free sulfur trioxide preventing formation of sulfone bridges and generation of pyrosulfonic acids. This complex also penetrates the polymer matrix relatively easily and promotes rapid, homogeneous sulfonation. Oleum is highly reactive and previous kinetic studies on aromatic compounds were limited to strongly deactivated reactants containing sulfo, nitro, and trimethylamino groups.

Halosulfonic acids are stable up to their boiling points then tend to decompose into sulfur trioxide and the corresponding mineral acid. Water is readily absorbed by the halosulfonic acids leading to ionization followed by hydrolysis. The final products are sulfuric acid and the respective mineral acid. As with oleum and pure sulfur trioxide, a variety of sulfonation products can be obtained. These reaction products include mono-sulfonic acid, sulfonyl halides, and sulfones. The exact yield of each depends strongly on the reaction conditions. Nitromethane does not effectively block formation of sulfones or pyrosulfonic acid within the resin when sulfonating with halosulfonic acids.

Concentrated aqueous sulfuric acid has been shown to
give mono-benzene sulfonic acid as the only product in
sulfonation reactions with benzene (60).

Pepper (28) proposed on the basis of calculations of
capacity and bead density that resins sulfonated in
concentrated sulfuric acid had mono-sulfonic acid
functionality. Hart and Janssen (61) showed sulfonated
polystyrene and poly(p-styrene sulfonic acid) were identical
in structure. Only under rigorous sulfonating conditions
are di-sulfonic acids produced with aqueous sulfuric acid.
In many cases, these rigorous conditions may resemble
sulfonation with oleum. From activation energy data of
Wiley and Venkatachalan (11) for sulfonation of various pure
divinylbenzene crosslinked polymers and known mechanisms of
electrophilic aromatic substitution, it appears reasonable
to presume sulfonation functionality only occurs in the para
position on the styrene contributed aromatic rings.
However, most commercial resins are crosslinked with
divinylbenzene containing from 50 to 60% of the meta isomer
and a small fraction (~ 5%) of the para isomer. The balance
is made up of assorted alkyl aromatic compounds, ethyl
styrene, and polymerization inhibitors. The polymeric bead
resulting from such a reaction mixture would obviously be
lacking in homogeneity and give a myriad of mixed products.
Even though a single isomeric composition of a sulfonated

resin would not be expected, the probable control of ring

functionality to a single, known group per each aromatic

ring makes concentrated aqueous sulfuric acid a more

desirable sulfonating reagent than the previously mentioned

reagents.

The composition of concentrated sulfuric acid is

relatively complex. Gillespie (62) found concentrated

(100%) sulfuric acid to contain the species $H_3SO_4^+$, HSO_4^-,

$HS_2O_7^-$, and H_3O^+. Gillespie and Robinson (63) found H_2SO_4,

$H_3O^+ \cdot H_2SO_4$, HSO_4^-, and the possible ion-pair of $H_3O \cdot HSO_4^-$ to

exist with increased aqueous composition. The presence of

the ion-pair $H_3O^+ \cdot H_2O$ was also proposed in 70-90% sulfuric

acid (64). The actual amount of each species present may

vary significantly with slight changes in overall percent

composition of water in the reaction mixture (65).

Several precise mechanisms for sulfonation of aromatic

compounds have been proposed based on data from benzene and

other simple aromatic compounds. Elaborate discussions of

the proposed mechanism may be found elsewhere (60,66,67).

All of these mechanisms involve electrophilic attack of the

aromatic ring by the sulfonating reagent (e.g., SO_3, HSO_3^+,

$SO_3(H_2SO_4)$, $H_2S_2O_7$, etc.) in the first step forming somewhat

stable intermediate. Extraction of the original aromatic

hydrogen by a Lewis base (e.g., HSO_4^-, H_2SO_4, etc.) occurs

in the second step which is usually considered the slow step

of the reaction. The mechanism is generally considered to be an S_E2 type. No particular electrophilic sulfonating species predominates over any other under all circumstances and the exact reaction pathway appears to depend strongly on the current reaction conditions and the exact species present. Despite the unsure path taken in sulfonation, the resulting product is still presumed to be the mono-sulfonated aromatic ring.

Surface Functionalization

Sulfonations of most commercial resins have typically been done to obtain a maximum capacity. Some studies of capacity with varied reaction conditions have been performed. The general consensus has found sulfonation is a rapid "run-away" reaction once started and control is difficult. The limiting step in the process of resin sulfonation seems to be the initial contact of the sulfonating agent with the resin surface and the subsequent penetration into the bead.

Gel resins are hydrophobic in nature and typically have very small pores (6-30 Å). Penetration of these pores is difficult for highly polar compounds such as sulfuric acid. As mentioned previously, sulfonation with sulfuric acid initially occurs at the outermost surface of the bead. As

the resin matrix slowly becomes more functionalized and
increases in polarity, the sulfonation proceeds "layer-by-
layer" inward toward the center or the resin bead. In the
first stages of the functionalization, a pellicular bead is
formed with a hydrophobic core and a very hydrophilic,
sulfonated outer layer. The radius of the core decreases as
the reaction proceeds. Stevens and Small (33,34) calculated
the sulfonated depth of the beads versus capacity assuming
no differences with crosslinking and complete sulfonation of
each "layer" before proceeding to the next "layer". The
pellicular nature of a non-swollen, partially sulfonated
resin bead was proven by Hajós and Inczédy (41). A
Secondary Electron Microscopic Image of a low-capacity resin
bead showed a response for sulfur (as the sulfonic acid
group) at the surface of the bead with no response extending
into the core of the bead. Similar work by Jeřábek (68)
gave the same basic results with a non-swollen resin. He
also showed a very broad distribution of sulfur throughout
the whole of a resin bead that was swollen in
ethylenedichloride prior to reaction.

Obviously, the kinetics of sulfonation are controlled by
the rate of contact of the resin with the sulfuric acid. In
a heterogeneous mixture, the outermost surface of the resin
should sulfonate fairly rapidly. Sulfonation of the inner
bead will then commence with a sudden increase in the

reaction rate. This increased reaction rate results from penetration of the partially sulfonated bead by the sulfuric acid aided by the increased polarity of the resin bead. At this point, the reaction is independent of particle diffusion of the sulfuric acid. Subsequent sulfonation of the interior of the resin bead becomes dependent on the rate of diffusion of the reactants and products through the resin bead itself.

The temperature of the system has a dramatic effect on the diffusion through the resin and requires careful control. Support of this is also found in the work of Hajós and Inczédy (41). Curves of reaction time versus capacity versus reaction time at various temperatures show an immediate but small gain in capacity obtained with little increase in time. A steep rise in capacity is then obtained, and the curve slowly levels to a maximum value. Significant differences in reaction rate are found with temperature differences. It was also shown that pre-swelling the resin with methylene chloride before reaction increases the resulting capacity from 3 to 10 times depending on the reaction time. Pre-swelling increased the pore structure and subsequently the accessibility of sulfuric acid to enter the bead. As a result, a significantly higher capacity was obtained and control of the sulfonating reaction was lost. At the same time, the

cations must diffuse well into the resin matrix to reach the exchange sites, greatly increasing particle diffusion control of the exchange process.

Choice of Starting Polymer

Ideally, a resin having functional groups on the outermost surface of the beads is preferred. If the resin happens to have functionality in the core of the bead, the depth of the groups should be as shallow as possible with sufficient porosity in the matrix of the resin to permit rapid diffusion of cations to the exchange site. Very small resin beads are desired to give a closely packed resin bed with minimum dead volume in the column.

Rigid, highly crosslinked beads with large physical pores would be desirable for design of a highly efficient resin. XAD-2 resin has these general properties and was studied by Fritz and Story (38,39). The XAD resins are made up of non-porous, highly crosslinked (ca. 35% divinylbenzene) microspheres which form a rigid interconnected structure. The porosity of this material is primarily located in the space between the microspheres. This material is rigid, has high mechanical stability and is hardly affected by swelling. However, the resin beads do fracture readily into irregularly shaped particles and a

significant amount of fine material under moderate agitation
and elevated temperatures (69). These conditions are common
in typical sulfonation processes. Macroreticular beads such
as the XAD resins are not readily available in useful
particle sizes and shapes for high-performance work.

Stevens and Small (33,34) have demonstrated that a
maximum performance for surface sulfonated resins is
realized with 2% crosslinking. Such a low degree of
crosslinking permits rapid diffusion of cations through the
sulfonated matrix of the resin. The hydrophobic core acts
to limit the depth of penetration by the cations reducing
particle diffusion.

Higher crosslinked gel resins were chosen in this study
as a result of the above work which is protected to some
degree by patents (31,33). The mechanical strength of gel
resins increases with degree of crosslinking and should
provide added stability and reduce the "spongy" character of
the gel bead. This is desirable for higher flow rates which
tend to compress the resin bed and restrict flow except at
high pressures.

Gel resins are very stable under normal sulfonation
procedures and at higher crosslinking (~ 5% divinylbenzene
or greater) resist changes in swelling quite well except
with drastic changes in eluent composition.

The sulfonation process was studied for 4% crosslinked

gel resin. This material appeared to have a fairly narrow distribution of particle sizes. Determining a method to reproducibly sulfonate the neutral material was the main objective of this work and the trends applied to the sulfonation of high-quality "mono-disperse" beads. The choice of crosslinking for further studies was decided on the basis of which material might be most beneficial to current separation methods. The 12% crosslinked material was chosen because of its rigid structure and it was believed to give a truely surface-sulfonated resin bead.

EXPERIMENTAL

Resins Used

The neutral resins were obtained from Benson Co. (Reno, NE) and included crosslinking of 4, 6.5, and 12% with particle size ranges of 12-17, 12-16, and 12-16 μm, respectively.

Residual polymeric starting materials were present in the resins as noted by the clumping of the resin beads and the distinct styrene-like odor. These impurities were removed by Soxhlet extraction (70). The procedure involved three extraction periods of 24 hours each with the sequence of solvents being methanol, acetonitrile, then diethyl ether. The extracting solvents were all reagent grade and used as received.

Sulfonation Procedure

Sulfonations were done in a jacketed reaction vessel formed by encasing a 250 mL round bottom flask in a 500 mL round bottom flask. Inlet and outlet ports were provided for attachment to a circulating bath. The reaction vessel was manufactured in the Iowa State University glassblowing shop.

A measured amount (usually 25 mL) of reagent grade, concentrated (96%) sulfuric acid along with a Teflon coated stir bar were placed in the reaction vessel. The sulfuric acid was brought to within ± 0.1°C of the desired reaction temperature and monitored with a thermometer placed directly into the sulfuric acid. The reaction vessel was continuously purged with dry, high purity (99.99%) helium throughout the whole reaction procedure. A weighed and appropriately prepared portion of the resin to be sulfonated was transferred to the reaction vessel at time zero. The resin was dispersed into the sulfuric acid by increasing the stirring rate. The reaction was quenched by VERY SLOW addition of room temperature water to the reaction vessel. The resin was collected by suction filtration in a crucible and rinsed thoroughly with water then with methanol and allowed to dry overnight at 60°C.

Capacity Determination

Capacities of cation exchange resins are traditionally determined by direct titration of the hydrogen ion released by the resin with standard base. Alternately, the acidic groups are neutralized with a known excess of base and the excess base back-titrated with standard acid solution. These titrations are performed in excess electrolyte (e.g.,

0.5 M NaCl) to ensure total release of hydrogen ion from the resin and suppress the Donnan effect (71). This method has limited use for resins of low capacity (< 0.1 meq per gram) because of the very small amount of titrant used and the large amount of resin needed to give reliable results.

Hajós and Inczédy (72) devised a simple and reliable method for determination of exchange capacity for cation-exchange materials. Constant-current coulometry was used to directly titrate the acidic groups in the resin. Hydroxide ions were generated in an electrolyte of 0.5 M potassium bromide. The titration was followed with a pH meter and the end-point inflection taken directly from a strip chart recording of the titration. Advantages of this method include its sensitivity to both low- and high-capacity materials and the ability to differentiate between acidic exchange groups. Despite its simplicity, efforts to construct a similar system here were hindered by an old and very unstable coulometric source.

The method of choice for capacity determination involves placing the resin in the lithium form, displacement of the exchanged lithium with excess potassium, and determination of the displaced lithium by atomic absorption spectroscopy.

The desired amount of resin was weighed and transferred to a gravity column. Glass wool was used as a bed support at the base of the column and a small plug of glass wool was

placed at the top of the resin bed to prevent disturbances of the resin bed with addition of reagents. The column was rinsed with about 100 mL of distilled-deionized water then placed in the lithium form by passing a large excess of lithium (about 10 mL of 2.0 M lithium chloride solution) through the column. The column was again rinsed with about 100 mL of distilled-deionized water to remove any excess lithium not bound by the column. The bound lithium is displaced by passing a measured aliquot of potassium chloride solution through the column into a volumetric flask. Enough potassium chloride solution was used to displace all of the lithium and be present in the effluent at a concentration appropriate to act as an ionization buffer for determination of lithium by atomic absorption. Again, the column was rinsed with about 100 mL of distilled-deionized water to insure removal of residual potassium and lithium. Analyses were performed as per analysis instructions in the operating manual. All capacity determinations were made in duplicate and the results were typically within 2% of each other. Photomicrographs of a sample of resin recovered after a capacity determination showed the presence of a significant amount of glass wool. The diameter of a strand of glass wool is quite close to that of the resin beads. The two were very difficult to separate rendering the resin essentially useless.

RESULTS AND DISCUSSION

Poor reproducibility in capacities was found when dry
samples of resin were sulfonated under identical conditions.
The disparity of results was due to agglomeration of the
resin particles. These chunks of resin did not allow all
the resin to come into intimate contact with the sulfuric
acid when added to the reaction vessel. Some of these
agglomerations remained intact for most of the reaction
time. Much better reproducibility (< 5%) was obtained when
the resin clumps were physically broken apart to give a
loose, powder-like material prior to sulfonation. Some
agglomeration of the resin and slow dispersion into the
sulfuric acid was still observed. Bulk resin capacity was
studied as a function of time and gave fairly linear results
for the dry material with capacities slightly higher than
expected. The results are summarized in Table I and Figure
1.

The same type of resin sulfonated by the supplier under
very similar conditions (73) gave lower bulk capacities of
about 0.017, 0.032, and 0.056 meq per gram for reaction
times of 15, 30, and 60 minutes respectively. The raw
polymers were not extracted prior to sulfonation and
apparently had excess polymeric reactants and short chained
monomers trapped in the resin matrix. These impurities

Table I. Effect of reaction time on sulfonation[a] of 4%
          crosslinked gel resin

Reaction Time[b]	Capacity[c]
10	0.070
20	0.095
30	0.124
40	0.147
50	0.205
60	0.266
90	0.364
120	0.510
180	0.656
1440	4.90

[a]Reaction of 0.25 grams at 90°C.

[b]Units of minutes.

[c]Units of meq per gram.

Figure 1. Plot of bulk resin capacity versus reaction time. Material is 4%
           divinylbenzene crosslinked gel resin reacted in concentrated sulfuric
           acid at 90°C under an inert atmosphere. Resin was introduced into
           the reaction vessel as cleaned, dry beads
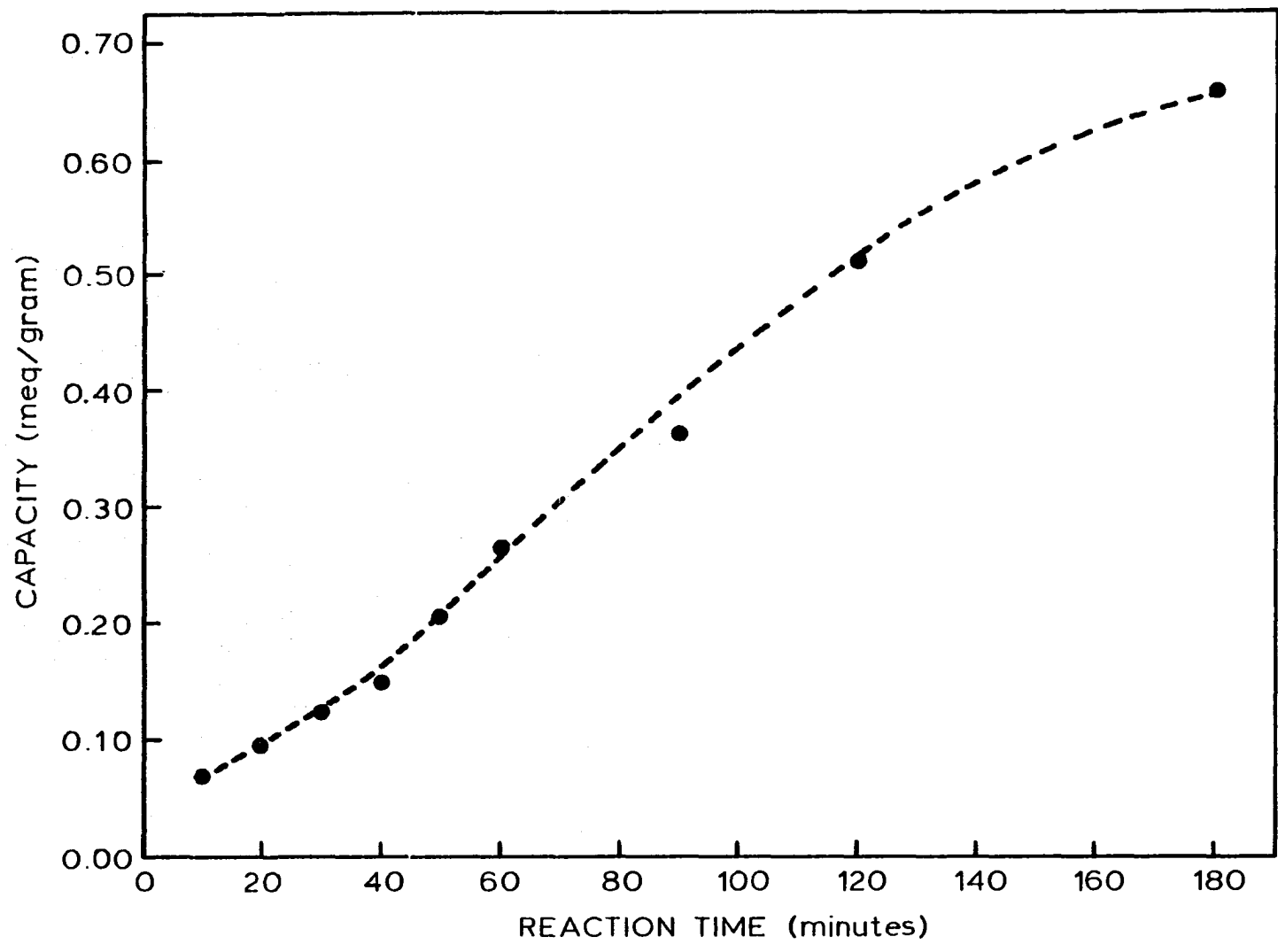
would be sulfonated along with the resin bead. The
resulting sulfonated by-products were removed when the resin
was washed after the reaction or slowly bled from the resin
with use. Washes of distilled-deionized water did appear as
though they contained some "surfactant" material possibly
washed from the resin.

The problem of wetting the surface of the resin and
dispersing the resin in the sulfuric acid appeared to be the
main factor in achieving a reproducible capacity. Several
surface wetting agents and dispersion techniques were
surveyed with questionable results (74). Although the
quantitative nature of the work is questionable, the
relative effects on capacity did show reasonable behavior
for a number of wetting agents. Methanol, acetic acid,
acetic anhydride all behaved similarly. Dimethyl sulfoxide
swelled the resin and produced resin of high capacity (ca. 2
meq per gram) (75). Acetonitrile also caused swelling in
the resin and gave higher capacities. The final procedure
involved mechanical and ultrasonic dispersion of the
particles in a wetting agent, passing the resin slurry
through a small 325 mesh sieve, then removal of as much of
the wetting agent as possible by suction filtration. The
resin was then sulfonated.

Methanol is generally considered an inhibitor to
sulfonation because it can react with sulfuric acid to give

dimethylsulfate, a highly toxic mutagen and suspected carcinogen. This compound is only produced in very small, if not trace, amounts. Dimethylsulfate decomposes in water at a moderate rate. Proper precautions and common sense are expected when using this procedure.

Elimination of the methanol before reaction was tried by first wetting the resin with methanol then rinsing with room temperature sulfuric acid to displace the methanol. A slightly lower capacity was obtained compared to wetting with just methanol (Table II). The lower capacity apparently results from the viscous, and relatively non-reactive, sulfuric acid inhibiting physical penetration of the resin matrix. Not until the sulfuric acid is heated by the surrounding hot sulfuric acid can the reaction proceed at a comparable rate. The viscosity of sulfuric acid decreases by about 3.5 times when heated from 20°C to 60°C. The net result is a shorter reaction time.

Of the wetting agents examined, methanol is preferred because of its relatively low toxicity and its ease in handling. The small amount of methanol present when the resin is added to the hot reaction mixture immediately volatilizes and is swept out in the inert gas stream. This is confirmed by a short burst of vapor issuing from the reaction vessel when the resin is added. The resulting capacity as a function of reaction time is shown in Table II

Table II. Sulfonation[a] of surface wetted 4% crosslinked gel
resin as a function of time

Reaction Time[b]	Wetting Agent	Capacity[c]
30	$MeOH/H_2SO_4$	0.036_9
30	MeOH	0.044_4
45	MeOH	0.056_2
60	MeOH	0.080_3

[a] 0.25 grams of resin at 90 °C.

[b] Units of minutes.

[c] Units of meq per gram.

and showed generally linear behavior.

Sulfonation is usually performed in dehydrating conditions. Small amounts of water in sulfuric acid can inhibit the sulfonation of a resin. The effect of introducing a dehydrating agent into the reaction mixture was examined. Introduction of P_2O_5 into the reaction mixture at 50 °C gave a capacity approaching the maximum sulfonation possible for the resin. The capacity was comparable to those of a resin sulfonated at 90 °C for 30 minutes after preswelling the resin in ethylene chloride (Table III). It is obvious that the amount of water has a distinct effect on the reaction and might serve as a useful method in controlling the sulfonation reaction. Effects of other mild yet dehydrating conditions were tried and decided to be highly inclusive (74).

Two other gel resins of higher crosslinkiing were briefly examined. Resins of 6.5 and 12% crosslinking were each sulfonated in 30, 60, and 90 minute batches at 80 °C. For comparison, the 4% crosslinked material was also sulfonated under these same conditions. These data are summarized in Table IV and illustrated in Figure 2.

In general, the structure of polymeric resin beads may resemble one of two basic structural models. The first considers the medium as two phases consisting of the interstitial pore phases of the polymer and its interstitial

Table III. Effect of swelling and dehydrating agents on
            sulfonation of 4% crosslinked gel resin

Conditions	Temperature	Time[a]	Capacity[b]
Dry Resin	90 °C	30	0.124
Swelled[c]	90 °C	30	4.39
Dehydrating[d]	50 °C	30	3.91
Dry Resin	90 °C	1440	4.90

[a]Units of minutes.

[b]Units of meq per gram.

[c]0.5 g swelled in 30 mL ethylene chloride for 24 hours prior to reaction.

[d]0.25 g reacted in solution of 25 mL H_2SO_4 and 5.0 g P_2O_5.

Table IV. Capacity[a] of surface sulfonation resins with respect to reaction time for 4, 6.5, and 12% Divinyl-benzene crosslinked gel resins at 80°C

Crosslinking (% DVB)	Reaction Time (minutes) 30	60	90
4	33.0	49.5	87.7
6.5	11.8	22.2	46.8
12	6.1	13.8	24.9

[a]Units of µeq per gram of dry resin.

Figure 2.   Effect of reaction time on bulk capacity of gel
            resin for different degrees of crosslinking.
            Each sample was reacted in co:~entrated sulfuric
            acid at 80 °C under an inert atr əsphere.   Resins
            were wetted with methanol prior to reaction

CAPACITY (microeq/gram)

REACTION TIME (minutes)

● – 4%
▲ – 6.5%
■ – 12%

45
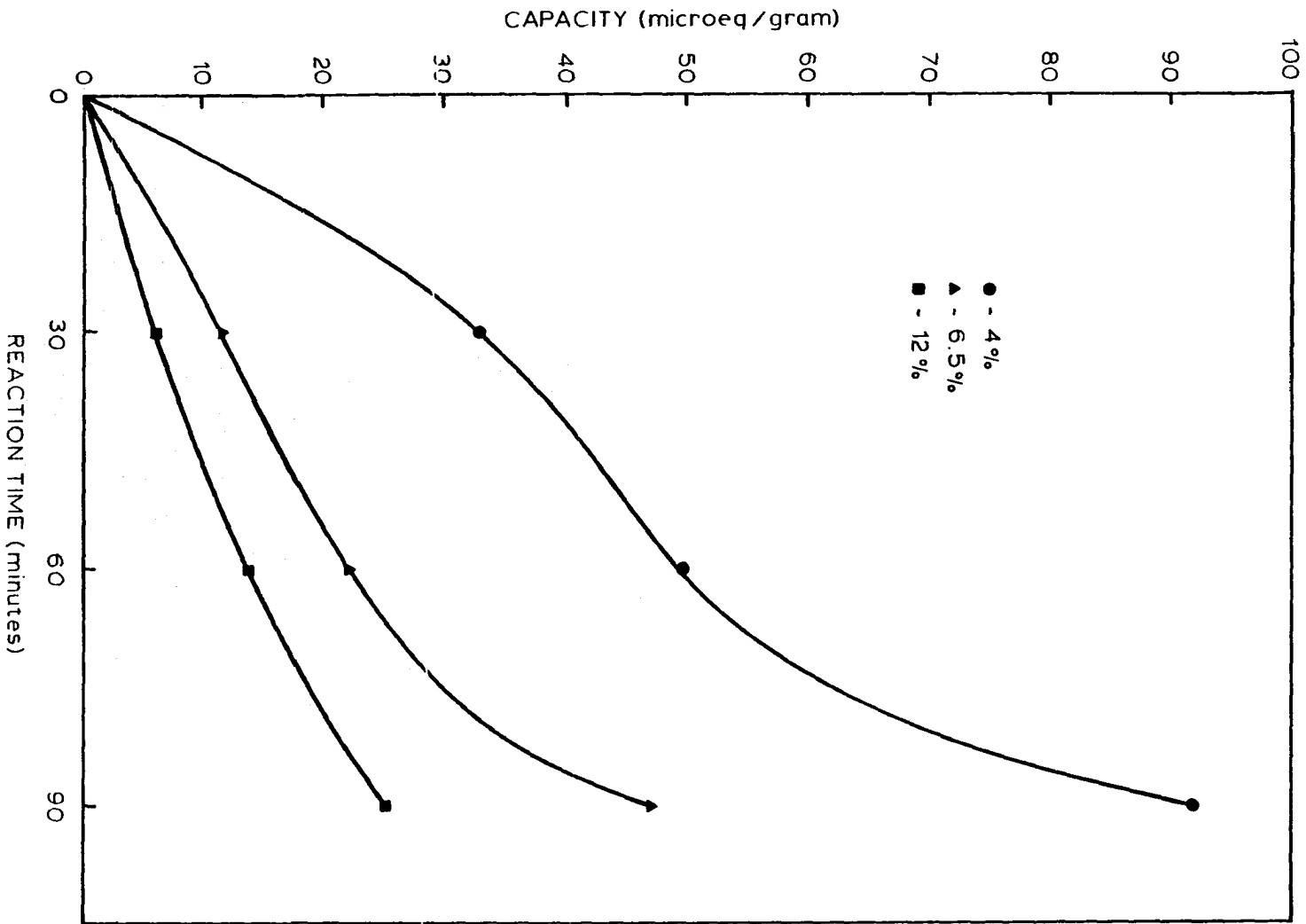
framework. The second type considers the resin as a single homogeneous phase whose nature is analogous to an organic electrolyte solution. Diffusion processes differ between these two models and are affected significantly by the details of the resin matrix structure.

In models of the first type, diffusion is considered to take place solely in the pores while the framework is totally inaccessible. Also, the diffusion path is laden with obstructions and the resin provides a tortuous path with numerous "dead-end" pores. Diffusion in this type of structure is limited by the mechanical or "frictional" resistance in the pores of the polymeric matrix. These characteristics are commonly found in the rigid macroreticular media. This medium is defined by a very rigid framework of high crosslinking and well-defined pores throughout the whole of the particle.

The model of the homogeneous medium considers the resin framework to be very loose allowing free diffusion throughout the whole of the matrix. Diffusion in the homogeneous model is considered to be retarded by the "excluded-volume" (i.e., the regions occupied by the organic matrix), but this does not make the path any more tortuous or add additional "frictional" resistance to the diffusion process. Resins following this model are those of very low crosslinking and might be described as having a "gelatin-

like" structure with no distinctly defined pores.

Of course, there exists an infinite number of possible intermediate structures. In the case of gel resins, these two extremes cover most general situations. There does exist an intermediate region where the structure of the resin is neither absolutely gelatinous nor completely rigid. These characteristics are found in resins with crosslinking between about 6 and 8 percent. In this "grey region", the resin has intermediate structural qualities between the microreticular and the macroreticular materials. The pores in this region are not well-defined and are referred to as "pseudo-pores".

As mentioned previously, the degree of sulfonation under the same conditions gives capacities in the order: 4% > 6.5% > 12%.

The 4% crosslinked material readily behaves as expected and has essentially the second type of structure, a loose gelatinous type of material. Diffusion of the sulfuric acid into the resin and products out of the resin is relatively rapid and meet with a minimum of resistance.

The more highly crosslinked resins have fewer of the more reactive "styrene" sites per unit depth into the bead. These resins also have less flexibility of the framework and tend to resist swelling of the pores necessary to accommodate the new sulfonic acid groups.

Both the 6.5% and the 12% materials behave as expected. The trend of increased crosslinking giving a decreased capacity follows work by Pepper (28) with high capacity resins and crosslinking up to 33%.

The only peculiarity of the curves (in Figure 2) lies in the close proximity of the capacity-time curve for the 6.5% crosslinked gel to that of the 12% crosslinked gel. If the 6.5% material had a "pseudo-pore" structure, then that curve would resemble the 4% curve a little more. Just from the information of sulfonation data presented here, it appears the 6.5% crosslinked gel resin has a pore structure more rigid than expected and closer to that of the 12% crosslinked material.

The sulfonation depth of the 6.5% and 12% crosslinked gel beads is estimated to be less than 100 Å from the work by Stevens and Small (33,34). For the size of resin beads employed here, this is less than 0.1% of the diameter of the bead itself. For the 4% crosslinked gel resin, the depth is estimated to be about 175 Å which is about 0.2% of the resin bead diameter. In both cases, this well represents a truly superficially sulfonated "pellicular-type" bead.

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SECTION II. METAL ION SELECTIVITY ON LOW-CAPACITY

SURFACE-SULFONATED GEL RESINS

INTRODUCTION

Ever since the process of ion-exchange was defined as such by Way in 1852 (1), notable efforts have been made to try to determine the precise mechanism involved in the exchange process and what effects cause different selectivities between ions.

The earliest efforts to describe the phenomenon of selectivity were the result of empirical equations constructed to fit the extensive supply of ion-exchange data. More discrete models and an expanded understanding of the physical factors affecting the exchange process developed with the advances in synthetic polymers. Improved technology of resin synthesis provided increased control of the basic properties of the exchangers such as porosity, crosslinking, bead size, and other basic structural parameters.

Several models have been proposed by a number of workers to explain selectivity of ion exchangers. Some of the more popular models are described in a latter part of this section. Additional models are covered quite well by Helfferich (2). Typical models follow either a mechanistic or thermodynamic approach on a microscopic or molecular level. Each model has its merits and, after close examination, the differences seem more a question of

semantics than absolute correctness. In many cases, the models actually complement each other.

Determination of distribution coefficients for ion-exchange resins is quite easy and readily performed with a minimum expense and with common laboratory equipment. The convenience and relative ease of the procedures involved have aided in the generation of "scads" of data for nearly every conceivable combination of ion-exchanger, solvent system (both organic and aqueous), and solute (e.g., 3). In many applications, it is more convenient to refer to distribution data than it is to actually consider the mechanism beyond a qualitative description. More intricate studies were left to the theoretical chemist.

Pepper (4) is believed to be the first to prepare and use low-capacity superficially-sulfonated resins. He outlined the advantages of increased speed and dilute eluting solution to obtain separations in a fraction of the time normally required. A very small amount of work has since been done in examining the behavior of low-capacity resins compared to the conventional, high-capacity resins.

Superficially sulfonated beads were prepared and examined for their selectivity by Skafi and Lieser (5,6,7). They examined the equilibrium and kinetic behavior of these resins and found vast improvements in the kinetics over fully sulfonated resins with no change in relative

selectivity. Unfortunately, only a limited number of radiochemically active cations were studied and few data were given.

Fritz and Story (8) examined superficially-sulfonated macroreticular resins and emphasized the effect of capacity on the selectivity. The data illustrate logistical factors of the exchange sites which affect selectivity of cations. For a given capacity, the data suggest good correlation to derivations of equilibration expressions.

In 1975, Small, Stevens, and Bauman (9) devised an ingenious separation method for simple anions with conductivity detection. An analogous system was devised for cations. The system is referred to as dual-column ion chromatography. An alternate and less complex instrument for anions was invented by Gjerde et al. (10,11) and is referred to as Single-Column Ion Chromatography. The system for cations was developed somewhat later (12). Each system is described quite thoroughly in a text by Fritz et al. (13). Both cation systems employ low-capacity, surface-sulfonated resins, which is important to their basic operation.

Despite the immense popularity of ion chromatography, little has been published on the basic selectivity imposed by the low-capacity resins. Most work has been seemingly directed by intuition with no attempt at theoretical

correlation. To exploit cation chromatography to its limits, there must be a more basic understanding of the system, in particular the resins. Therefore, a need exists to define the basic behavior of surface-sulfonated resins and provide more insight into the mechanism associated with the exchange process. The behavior of these resins may not be assumed to be exactly the same as fully sulfonated resins because, as discussed in Section I, the surface-sulfonated resin is more sensitive to the imperfections of the beads. Work in this section focuses on the basic exchange behavior of surface-sulfonated resins and some comparison is made to fully sulfonated resins.

THEORETICAL CONSIDERATIONS

Exchange Equilibria

The behavior of ion-exchange systems can generally be described by examination of the equilibrium expression for the exchange process. Ion-exchange is typically illustrated by the equation:

$$y\bar{E} + xM \rightleftharpoons yE + x\bar{M} \tag{1}$$
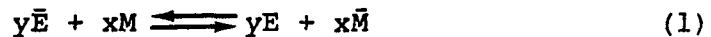
where x and y represent the absolute values of the charges of counter-ions E (the eluent cation) and M (the metal cation), respectively, and barred terms represent species in the resin phase.

Ions exchanged by the resin sites are commonly referred to as counter-ions as their charges are "counter" or opposite to that of the exchange site. Co-ions refer to the ions of opposite charge which accompany the counter-ion in order to maintain electroselectivity. In cation-exchange, cations are considered counter-ions while the anions are referred to as co-ions.

A complete description of the phenomenon of exchange involves the use of the thermodynamic equilibrium constant, $K°_E^M$, and is written for the exchange as equation 2.

$$K \circ {}^M_E = \frac{\alpha^{-Y}_E \, \bar{\alpha}^X_M}{\bar{\alpha}^{-Y}_E \, \alpha^X_M} \tag{2}$$

where α represents the thermodynamic activity of the respective species in the appropriate phase. The thermodynamic activities take into account the ion-exchange and all other forms of sorption and desorption of the solvents and electrolytes which necessarily accompany the whole process. The thermodynamic equilibrium constant is a temperature dependent, integral quantity defining the whole surface of the ion-exchange isotherm. Even though the thermodynamic approach is considered to be correct and universal, it suffers from rigorous and abstract terms which are not readily defined in practical terms. In most cases, these quantities cannot be obtained through independent measurement or predicted without non-thermodynamic assumptions. For example, activities of the ions resulting from various interactions that are known to exist in the resin phase can not be readily defined in common terms nor are they measurable by available means. The interdependent equilibria of the system also prevent accurate measurements.

For all practical purposes, there is a need to describe the ion-exchange process in terms of readily measured or fundamental information about the system at hand. As more restrictions are placed on the model, the system approaches the theoretical description. At the same time, the model

becomes so strictly defined that it loses its thermodynamic

description and the pertinent relations obtained are valid

only by specific systems which truly or very closely

represent that model.

Carefully control of the experimental parameters limits

the equilibria to what may be an experimental "best-guess"

of "accurate" ion-exchange (i.e., the process of ion

adsorption by the resin is only through actual ion-exchange

at the resin sites). This allows the examination of a small

portion of the whole ion-exchange isotherm. By eliminating

the effects of electrolyte adsorption of the resin, ion-

pairing, and other competing equilibria, the thermodynamic

equilibrium constant may be written in terms of a

selectivity coefficient using activities.

$$K^{*M}_E = \frac{\{E\}^Y\{\bar{M}\}^X}{\{\bar{E}\}^Y\{M\}^X} \tag{3}$$

The activities of the respective species in solution and

the resin phase are represented by braces and are different

from the "true" thermodynamic activities. It is more

correct to use activities instead of concentrations since a

more "true" estimate of the system is considered, especially

at higher concentrations of ions.

The selectivity coefficient represents the relative

affinity of the resin sites for ion M over ion E. If K^{*M}_E

is greater than unity, then ion M will be preferred by the
resin over ion E. If K_E^{*M} is less than unity, then the
converse holds true. In the rare cases where K_E^{*M} is equal
to unity, the resin would show no preference between the two
ions.

Typically, the selectivity coefficient varies with the
relative fraction of each counter-ion present in the
exchange system. In the case of tracer amounts of one
counter-ion with another counter-ion present in significant
excess, several simplifying assumptions are made (14).

1) The relative distribution of both counter-ions
between the resin and the external solution will
remain essentially constant.

2) The number of resin exchange sites occupied by
the tracer ion is relatively small and may be
considered negligible compared to the counter-
ion in excess.

3) The amount of tracer counter-ion in solution is
very small and may be considered negligible when
compared to the amount of counter-ion in excess.

4) The eluting ion (in large excess) exists as a
fully dissociated electrolyte.

Under these assumptions, the portion of the ion-exchange
isotherm under consideration is near the origin and is
relatively short. This range is considered essentially
linear and readily adaptable to exchange equilibria in
column separations, provided an equilibrium or "near-
equilibrium" state is reached (15). Lack of linearity in

this region suggests bifunctionality of the resin (14).

From ion exchange performed in batch or column operations, there are several useful expressions which are useful in describing tracer exchange and are readily applied here.

The amount of tracer ion taken up by the resin and the amount left in solution are commonly expressed as a ratio and referred to as the mass distribution coefficient, D_m. For M as the tracer ion:

$$D_m = \frac{\bar{M}}{M} \qquad (4)$$

If the distribution of the ion is expressed in terms of concentration, the ratio is called the concentration distribution coefficient, D_c.

$$D_c = \frac{\{\bar{M}\}}{\{M\}} \qquad (5)$$

In forced flow systems, the mass distribution coefficient, D_m, can be expressed as the adjusted retention volume for the ion, V', divided by the void volume of the column, V_c. This term is also called the capacity factor, k', and under constant flow rate can be described in terms of the adjusted retention time, t', and the dead time of the chromatographic column, t_c.

$$k' = \frac{t'}{t_c} = \frac{V'}{V_c} = D_m = \frac{\bar{M}}{M} \qquad (6)$$

The concentration distribution coefficient is related to the mass distribution coefficient by the ratio of the mobile phase volume in the chromatographic column to the mass of resin in the column, M_{res} (equation 7).

$$D_c = \frac{D_m V_c}{M_{res}}$$ (7)

The total ion-exchange capacity of a resin is equal to the number of available exchange sites per unit mass of resin and is commonly referred to in terms of molal concentration (meq per gram). For trace loading, where the tracer ion occupies less than about 1% of the total ion-exchange sites on the column, the resin capacity can be assumed to be equal to the activity of eluting ion occupying the resin ($\{\bar{E}\}$) multiplied by the absolute value of the valence of the eluent ion (x).

$$\text{Capacity} = |x| \; \{\bar{E}\}$$ (8)

Equations 4, 5, and 8 are substituted into equation 2 giving equation 9.

$$K^{*M}_E = \frac{D_c^x \; \{E\}^y}{(\text{Capacity}/|x|)^y}$$ (9)

This relationship between elution time of an ion and the

column parameters is more easily seen by taking the
logarithm of both sides and solving for the logarithm of D_c.

$$\log D_c = \frac{y}{x}\log(Capacity/|x|) - \frac{y}{x}\log\{E\}$$

$$- \frac{1}{x}\log K^{*M}_E \qquad (10)$$

The intuitively obvious results of changing resin
capacity and eluent concentration are now clearly
illustrated in quantitative terms, as is the role of K^{*M}_E.

If activities in solution are assumed to be unity and
concentrations are used instead, the selectivity coefficient
becomes an apparent selectivity coefficient, K'^M_E. In cases
of dilute eluent solutions, this assumption is valid and
equation 10 can be rewritten as:

$$\log D_c = \frac{y}{x}\log(Capacity/|x|) - \frac{y}{x}\log[E]$$

$$- \frac{1}{x}\log K'^M_E \qquad (11)$$

For a given system, the selectivity coefficient should
remain constant with reasonable variations in eluent
composition and resin capacity. As predicted by equation
11, the logarithm of retention for an ion should change in a
linear fashion with either the logarithm of the eluent
cation activity or the logarithm of the resin capacity for
the same chromatographic system.

A study of the elution behavior of certain ions with

varying eluent compositions would show decreasing eluent activities giving greater retention of the ions. Plotting the logarithm of the retention of the ion versus the logarithm of the eluent activity would give a straight line with a negative slope equal in magnitude to the ion charge divided by the eluent charge. Monovalent sample ions eluted with monovalent eluent ions would give a theoretical slope of -1, and divalent sample ions eluted with monovalent eluent ions, the theoretical slope would be -2. Some of these plots for different ions will intersect at different points indicating the two ions cannot be separated on that system under the same conditions.

The above derivations can be applied to both cation- and anion-exchange systems. It is important to note that the above derivations assume the only mechanism for counter-ion sorption is through ion-exchange of the ions with charge neutrality being maintained. The absence of ion-pairing and other competing equilibria is essential to maintain the model.

The effects of certain competing equilibria, such as addition of a complexing agent to the eluent, result in additional terms in equations 10 and 11. This situation is covered in Section III. Partial dissociation of the eluent ion as a weak acid or base would also be covered by such terms. An exception exists if the eluting counter-ion can

dissociate into more than one distinct eluting species. In
such cases, which are beyond the scope of this work, a more
complex derivation is necessary.

Application of this model to inorganic anion-exchangers
(16), low-capacity anion exchangers (11), fully sulfonated
cation exchange resins (17), and affinity chromatography at
ionogenic sites (18) has met with reasonable success.

Ion-Exchange Selectivity

When an ion-exchange resin having all of its exchange
sites occupied by counter-ion E is placed into contact with
a solution containing counter-ion M, an exchange of ions
between the solution and the resin takes place. When
equilibrium is reached, both the resin and the external
solution will contain counter-ions E and M. The preference
of the resin for E over M is easily and practically
illustrated by determining the distribution coefficient.

The exact processes involved in ion-exchange may be
described explicitly from a thermodynamic standpoint. The
thermodynamic approach is inherently abstract and generally
universal. This approach does not require a specific model
and is considered to be a "correct" representation of the
process. Early theories of this type were presented by
Kielland (19) in 1935 and later, a more rigorous approach by

Gaines and Thomas (20) in 1953. However, the thermodynamics give a minimum of useful information about the actual physical interactions causing differences in the exchange behavior between ions.

In most cases, the parameters of the thermodynamic approach cannot be determined by independent measurements nor can they be predicted without assumptions about the system which are non-thermodynamic in nature.

An alternate approach to prediction of ion-exchange behavior involves the proposal of models based on specific characteristics of the ion-exchanger. The more precise and complex a model becomes, the better it defines the properties and phenomenon of ion-exchange. The consequence of such a model is more useful and understandable data that can be obtained.

In a given model, information about the equilibrium of ion-exchangers can be obtained through several independent measures of the properties of the exchangers and the use of fundamental data of the system in terms of the solvent and solute species. As more restrictions are placed on the model, the system approaches the theoretical description. At the same time, the model becomes so strictly defined that it loses its thermodynamic description and pertinent relations obtained are specifically valid only by systems which are represented by that model. As a competent chemist

once mentioned, "Life is a series of compromises" (21).

Helfferich (2) describes the first models of ion-exchange system as simple interpretations of the ion-exchange system. Kielland (19) and Vanselow (22) treated ion-exchange materials as solid solutions of resinates. The concept of ion-exchangers as concentrated aqueous electrolytes with an imobilized ionic species was presented by Bauman and Eichhorn (23) in 1947.

In 1948, Gregor (24,25) introduced a macroscopic, semi-mechanistic theory on ion-exchange which had tremendous impact on the way ion-exchange systems were perceived. This model is based on the premise that the matrix of the ion-exchange resin behaves as a network of elastic springs with bound ions (the exchange groups) which are fully hydrated. The network is considered to consist of two basic parts, the crosslinked polyelectrolyte with the solvent making up the pores and the resin matrix crosslinking. According to Gregor, when an ion-exchange resin is put into contact with a solvent the bead tries to dissolve in the solvent and in the process takes up solvent and swells. The resistance of the crosslinking to the extension of the polymeric chains results in an elastic counter pressure. Equilibrium is attained when the counter pressure is equal to the residual osmotic pressure. The volume of the resin depends not only on the solvent occupying the pores, but also on the volume

of the hydrated counter-ion at the exchange sites. The
selectivity of the resin for counter-ion M over counter-ion
E is said to result from their difference in hydrated volume
of the ions and is illustrated in equation 12.

$$RT \ln K^{\circ M}_{E} = \Pi(|y|\bar{V}_E - |x|\bar{V}_M) \tag{12}$$

$\bar{V}_E$ and $\bar{V}_M$ are the hydrated volumes of the respective
counter-ions and Π is the swelling pressure of the resin.
R and T have their usual meanings in appropriate units.

Ions with smaller hydrated volumes would occupy less
pore volume and reduce the swelling pressure of the resin.
As a result of the reduced swelling pressure, the smaller
hydrated ion should be preferred by the resin.

This model provides a very simple illustration of
selectivity in terms of resin swelling. In most cases, the
model of Gregor (24,25) behaves quite well for medium to low
crosslinked resins (< 10% divinylbenzene). At higher
crosslinking and in unusual cases, the model fails to
predict selectivity crossovers or reversals.

The original model of Gregor (24,25) was almost purely
mechanistic in its description and made no allowance for the
other interactions possible within the exchange process.
Continued work by Lazare et al. (26) expanded the original
model to take into consideration the differences in

electrostatic attractions within the resin. An additional term was added to the right side of the selectivity equation (equation 12) which contains the ratio of activity coefficients for the ions in the resin phase. This additional term makes provision for interactions between the ion and the resin matrix to contribute to the selectivity. However, major emphasis was still placed on the hydration of the counter-ions. Modification of the model has made it relatively complex and somewhat difficult to apply. This model has found application mostly in swelling and electrolyte adsorption equilibria of membranes.

Rice and Harris (27) proposed a more intricate explanation of the mechanism involved in resin swelling. The resin matrix is viewed as an interconnected structure of rigid, "rod-like" chains each having an exchange group attached to it. Each counter-ion is considered to be "bound" to the exchange site and controlled by a mass-action type of constant different for each pair of counter-ions. Within the matrix, "unbound" counter-ions are presumed to be paired with a co-ion. This last statement seems to contradict the existence of a Donnon potential.

The model defined swelling as a balance between the electrical repulsion between the like charges of various "unbound" sites and the configurational entropy of the polymer network. The model was almost totally non-

mechanistic and little indication of factors controlling the binding constants was given. Also, no prediction of selectivity reversal could be made.

Katchalsky and Lifson (28) and Katchalsky (29) proposed a model very similar to that of Rice and Harris (27) somewhat earlier, but used a slightly different method of computation of electrostatic attraction. This model was restricted to weakly crosslinked resins and neglected ion-pair formation. Several other differences do exist and rather than expand on them here, the reader is directed to the original papers. Both the models of Rice and Harris and that of Katachalsky work to limited degree in resins of low crosslinking. The merit of both models lies in their approach to describing the ion-exchange system on a molecular scale.

Eisenman (30,31) proposed a theory based on two general types of energy interactions. When a monovalent counter-ion is brought into contact with a fixed exchange group on the resin from the bulk of a dilute solution, there will exist a electrostatic interaction between the two counter charges. There also exists the interaction of arranging the hydration sphere of the fixed charge to permit the counter-ion to obtain close approach or even contact. The overall process is viewed in terms of the net gain in free energy of the system.

Eisenman's model has been successful in prediction of selectivity of alkali metal cations for various type of exchange groups. It has also correctly predicted most selectivity reversals of the alkali metals on the basis of ionic radii. Application of this model becomes difficult for multivalent cations.

Reichenberg (32) proposed a mechanistic model on a molecular level based upon the environment immediately surrounding the exchange sites. Non-destructive desulfonation of a fully mono-sulfonated resin was performed and compared to a resin that was partly sulfonated. In a fully mono-sulfonated resin, all styrene and divinylbenzene rings should contain a single sulfonic acid group. The process of desulfonation under relatively mild conditions (to prevent breakage of crosslinking) was assumed to be indiscriminate and would randomly desulfonate both low- and highly-crosslinked regions of the resin.

Light sulfonation was presumed to mono-sulfonate only those more reactive aromatic rings, such as styrene and ethylbenzene moieties, in regions of low crosslinking. So, even though the total capacities of the two resins may be identical, the exchange sites of each were located in different environments which was assumed to cause variations in selectivity. Reichenberg stated the selectivities of the two resins were different. When both resins were fully

sulfonated, the differences in selectivity disappeared, supporting the effect of environment as a contributing factor of selectivity.

From a mechanistic view, Reichenberg also cited the importance of hydration of the ions (both counter-ions and the exchange sites), and swelling effects which may force "stripping" of hydrated layers of certain ions. Additional interactions of prime importance include various ion-ion interactions. These interactions include coulombic and hydration interactions, which arise from direct electrostatic interaction of the counter-ions and the exchange sites similar to the treatment of Eisenman (30,31). Second is the interaction caused by one ion inducing a dipole on a second ion, unsurprisingly referred to as ion-induced dipole interactions. Next is the interaction of the counter-ion with the fixed exchange sites. Instead of treating the fixed exchange sites as individual charged sites, they receive treatment as a network or system of point charges even though little is known of the actual distribution of such charges throughout the resin matrix. Finally, consideration should be given to overlapping of fixed group fields. When exchange sites are located closely enough certain affinity reversals may occur. This general result was seen by Story (33) and explained by a simpler model proposed by Pauley (34).

Diamond and Whitney (35) proposed another molecular level, semi-mechanistic description of ion-exchange based primarily on the solvation differences of the external solution and the ion-exchange site for the counter-ion. This model is very qualitative in nature and was provided with no real quantitative relationships. Despite this lack of quantitative description, the approach is very unique and intuitively sound.

Most models of ion-exchange are based strongly upon the mutual electrostatic attraction the fixed ion-exchange site and the counter-ion have of each other. Selectivity differences between various counter-ions are the result of differing values of free energy of the counter-ions in the exchange process. The model proposed by Diamond and Whitney (35) views the phenomenon of selectivity more as a result of the external solvent phase rejecting the counter-ion. If the counter-ion is readily hydrated, then it will partition into the external aqueous phase. If the counter-ion is poorly hydrated, it will prefer the resin phase where it is better "solvated". The distribution might be viewed as a choice of "a lesser of two evils" by the counter-ion.

The interactions in selectivity are those commonly considered in solvation of various compounds. Interaction of water with itself (water-water interactions) comprise the major concern of this model. At room temperature, water

forms a highly hydrogen-bonded network of molecules with relatively strong intermolecular forces. This tight water structure is considered to have a significant effect on the ion-exchange process because of its tendency to reject species which disturb it. Species which are hydrophilic, charged, or interact with the water molecules to a greater extent than the water-water interactions are accepted into the aqueous phase quite readily. Small ions which can fit snugly within the network of the water structure tend to reorient the water molecules immediately around the primary hydration layer and stabilize the network. Larger ions, and molecular species do not reorient the water molecules and force them outward, tightening the water structure and forcing rejection of the molecule by entropy effects.

Ion-water interactions result from the fact that ions carry a charge and as a result can orient the dipolar water molecules about themselves. The effective orientation of the water molecules depends on the size, charge, and electronic structure of the ions. In effect, the ions acts to delocalize its charge over a larger available volume resulting in a decrease in its electrostatic free energy.

Another interaction is between ions (ion-ion interactions) of like or opposite charge. Along with the consideration of immediate attraction or repulsions of ions are the higher multipole interactions such as ion-dipole,

dipole-dipole, ion-multipole, and others. These latter
interactions are typically of less importance than the
direct ion-ion interactions. The possibility of
transmitting ion-ion interactions through adjacent water
molecules also exists. More specifically, a cation can
polarize a water molecule which in turn promotes hydrogen
bonding to a neighboring anion.

Finally, ion-resin matrix interactions are apart from
the interaction of the counter-ion with the fixed ion-
exchange site are also possible. These interactions are
most prevalent for large ions that can act through
dispersive forces with the π-electrons in the aromatic
structure of common aryl-based resins. This type of
interaction does not play an important role in the exchange
of most common inorganic cations and small inorganic anions.

Additional factors described by Diamond and Whitney (35)
include effects of swelling, Donnon potential, and exclusion
(sieving effects). Although each of these effects plays an
important role in the nature of the exchange environment, of
themselves they are not considered influential of
selectivity.

Of the previously described models, those of Reichenberg
(32) and Diamond and Whitney (35) seem to consider the whole
process of selectivity in a complete manner. Even though
several of the interactions are considered minimal for

inorganic cation exchange, their inclusion adds universality to the model. Consideration of these interactions makes the models more readily applicable to the larger quaternary ammonium cations and most larger, easily polarizable anions. These larger ions are known to deviate severely from the models of Gregor (24,25), Eisenman (30,31), Rice and Harris (27), and others. The correlation of these theories to low-capacity anion exchange is summarized quite well by DuVal (36). Affinity reversals are also more readily predicted.

Of course, the models of Reichenberg (32) and of Diamond and Whitney (35) are strongly qualitative which leads to skepticism about their absolute quantitative validity. These models might best be approached as a description of new direction for future work in ion-exchange theory.

EXPERIMENTAL

Eluent Considerations

To examine the basic equilibria of ion-exchange, it is necessary to eliminate factors which may compete with the exchange process. In studying the exchange between the eluent cation and other metals, competition by complexation of the cations had to be eliminated. Even co-ions that are considered weakly complexing can affect the equilibrium. Perchlorate was chosen as the eluent co-ion in this study because it is not considered to form complexes and those complexes which do form are considered extremely weak (37) and easily broken in the presence of competing equilibria (38).

Other anions such as nitrate, chloride, and sulfate are much more reactive than perchlorate except under dehydrating conditions or in contact with strong reducing agents (39), neither of which are encountered here. These anions also tend to form relatively stable complexes or precipitate a number of cations causing obvious shifts in the cation-exchange equilibrium.

Perchloric acid is one of the strongest acids and is highly dissociated, even at concentrations up to 4 M (40). As a result, the dissociation equilibria can be considered

as negligible.

It is of prime importance to note the dangers of
perchloric acid and its tendency to form explosive organic
perchlorates or perchlorate salts. In relatively dilute
solutions, perchloric acid and metal perchlorates are
relatively stable and pose no particular hazard. In contact
with certain organic materials or reducing substances, the
potential of explosion or fire exists, especially if the
material is heated or allowed to dry. Generous dilution of
such mixtures with water minimizes the hazard potential.
Materials suspected to be hazards should be treated as
though they were and handled with care. It is imperative
that the experimenter familiarize himself with the potential
dangers and necessary precautions before undertaking any
experimental work with perchloric acid or perchlorates.
Texts (39,41) describing the chemistry and safe handling of
perchloric acid and perchlorates should be consulted.

Eluent Preparation

All eluents were prepared with Type I reagent grade
water obtained from a NANOpure II cartridge water
purification system (Barnstead Co., Boston, MD).

Concentrated reagent-grade perchloric acid (70%) was
used to prepare all perchloric acid eluents and adjustment

of pH of all other eluents. Individual perchloric acid eluents were prepared by dilution of appropriate aliquots of a perchloric acid stock solution. The eluent was filtered through a 0.45 μm membrane filter and degassed under suction with stirring. The exact concentration of perchloric acid in each eluent was determined by standardization against primary standard tris-hydroxymethylaminomethane using methyl red as an indicator (42). The concentration of hydrogen ion studied covered a relatively limited range. Concentrations of perchloric acid above 1.0 M could not be properly prepared for use as eluents and showed corrosive effects on the chromatograph.

Sodium and magnesium perchlorate eluents were prepared by dissolution of an appropriate amount of reagent grade sodium bicarbonate or reagent grade magnesium carbonate with perchloric acid, respectively. The salt was dissolved, diluted to near the final volume, and the pH adjusted to near 2.5. The eluent solution was then diluted to volume, mixed, the pH checked, and adjusted to 2.5 if necessary. Final pH adjustment was done with 1:1 perchloric acid and typically changed the final volume of the eluent by no more than 0.5%. Each eluent was then filtered through a 0.45 μm membrane filter and degassed under suction.

Ethylenediamine, pyridine, and aniline eluents were prepared from 0.100 M stock solutions. Ethylenediamine

stock solutions were prepared from reagent grade amine after
redistillation. Pyridine and aniline stock solutions were
prepared from freshly opened bottles of reagent grade
chemicals. Aniline required addition of perchloric acid to
aid in the dissolution of the free base. Dilution and pH
adjustment of the amine eluents was done in the same manner
as with the sodium and magnesium perchlorate eluents.

Cation-Exchange Resins

Cation-exchange resins used in this work were 12%
crosslinked poly(styrene-divinylbenzene) gel beads. The
bead diameter was 12-15 μm. These resins were those
prepared in Section I. The eluent studies were run with the
resin having a bulk cation-exchange capacity of 6.1 μeq per
gram. The more highly functionalized resins were used in
the capacity study.

Metal Ion Solutions

All metal solutions were prepared from highest purity
reagent grade salts available and appropriate amount of
perchloric acid added to the solutions to prevent
hydrolysis.

Rare Earths solutions were prepared from the oxides

obtained in purity of at least 99.99% (Dr. J. E. Powell,

Ames Laboratory, Ames, IA). Dissolution of each oxide was

with the appropriate acid.

The metal stock solutions typically 0.200 to 0.020 M

were kept at appropriately low pH values with perchloric

acid to prevent hydrolysis. Retention times were measured

from injections of 0.20 mM metal solutions. Type I reagent

grade water was used in all dilutions with addition of

enough perchloric acid to prevent hydrolysis.

Post-Column Reagents

Post-column color-forming reagents were chosen merely to

cover the various metal cations studied here. No attempt

was made to find optimum conditions for detecting all metal

ions because quantitation was not the prime purpose of the

study. The only exception is the study of a rapid

separation of magnesium and calcium which is discussed

later.

Pyridylazoresorcinol (PAR) was chosen as a general-

purpose color-forming reagent since it forms colors with

most metals of interest over a relatively wide pH range

(43). Solutions of PAR were prepared by weighing out 0.25 g

of the free acid and transferring it to a 2000 mL volumetric

flask with a minimum amount of water. Any large clumps were

physically broken up to aid in dissolution. Reagent grade ammonium hydroxide (670 mL) and a Teflon coated stirring bar were placed in the flask. The mixture was stirred at a high rate until all solids were dissolved and then diluted to volume. Just before use, the solution was filtered through a 0.45 μm membrane filter. A significant amount of particulate matter was removed from the solution by filtration. This material would normally clog the post-column reaction chamber or cause a high background. The pH of the effluent after mixing with equal volumes of 1.00 M perchloric acid did not go much below 9.6 and reached a maximum just above pH 10 with 0.100 M perchloric acid.

Elchuk and Cassidy (44) used PAR in a buffer solution 2.0 M in ammonium hydroxide and 1.0 M in ammonium acetate. This reagent solution provided a slightly more stable baseline and seemingly less pungent effluent. The buffered solution of PAR was prepared as the previous solution with the exception of adding less ammonium hydroxide and adding the ammonium acetate after complete dissolution of the PAR. If the ammonium acetate is added too early, the PAR is much more difficult to dissolve.

Arsenazo III has shown good sensitivity for a number of metal cations and was used as an alternative to PAR. 0.75 g of Arsenazo III and 136 g of hydrated sodium acetate were dissolved in 2-liters of Type I water and filtered. The pH

resulting from mixing of the perchloric acid eluents was relatively acidic (pH 2 - 4.5) and gave good sensitivity for metals such as strontium and barium.

Arsenazo I has been used for detection of alkaline earths, in particular, magnesium and calcium (45). The solutions of Arsenazo I were prepared in the same basic manner as the PAR solutions using 0.035 g of Arsenazo I and using a buffer of either 3.0 M ammonium hydroxide or 0.10 M trishydroxymethylaminomethane adjusted to pH 9.0.

Chrom Azurol S was chosen as a specific reagent for aluminum because of poor sensitivity demonstrated with the other reagents. For one-liter of solution, 0.05 g of the dye was dissolved with two moles of sodium acetate and 0.10 g of cetyltrimethyl-ammonium bromide. The solution was filtered prior to use.

Apparatus

Chromatograph

The instrument used in this work was constructed in a modular fashion from individual components. The pump was a model 396 Milton Roy Singlex pump (Riviera Beach, FL). The flow rate for all work was 1.0 mL per minute. The injection system consisted of a Rheodyne model 7010 injector (Rainin Instrument Co., Woburn, MA) fitted with a 20-µL sample loop.

Under highly acidic conditions (> 0.70 M $HClO_4$) the rotor

seal in the injector undergoes some decomposition causing

particles to break free from the rotor seal and clog the

frit at the top of the column. The polyimide rotor seal was

replaced with one made of Tefzel (part no. 7010-039-S,

Rainin Instrument Co.) alleviating the problem. A pressure

gauge (0-5000 psig) and coil-type pulse dampener (LiChroma

Damp, Norristown, PA) were placed off-line in a parallel

configuration between the pump and injector. A Swagelok

pressure relief valve (Cleveland, OH) set for 1200 psig. was

fitted between the pulse dampener and pressure gauge to

prevent system damage by excessively high pressures.

Chromatographic columns were constructed of thick-walled

glass and measured 25 cm long with a 2 mm i.d. (Rainin

Instrument Co.). These columns were packed by an upward

slurry packing method as described by Barron (46). The

resin was packed in an aqueous solution of ethylene glycol

(45% v/v) at about 2000 psig. After packing, the column was

rinsed by pumping distilled-deionized water through the

column and topped off with additional resin as necessary.

At least one hour of equilibration time with the eluent was

allowed before use. The chromatographic column was fitted

with a water jacket and thermostated at 25°C.

Post-column detection system

Detection of metal cations was by post-column derivatization with color-forming reagents. The reaction chamber was the same used by Elchuk and Cassidy (44) and was constructed from a stainless steel tee that had the ports drilled through through to accommodate 1/16" Teflon tubing. Lines for the chromatographic column and color-forming reagent to the reaction chamber were cut at 45° angles and fitted into the tee so the tubing faces fit flush against each other. The outlet line was cut square and fitted up against the other tubing. This arrangement provided direct impingement of the column effluent flow with the reagent flow. The resulting stream had to flow around the tubing in the tee to the outlet line to the detector. Apparently, intimate mixing of the effluent and reagent is accomplished in a minimum of dead-volume (est. 2-µL). Mixing chambers as devised by Sickafoose (47) were considered but provided no greater turbulence for larger mixing volumes.

Color-forming reagents were delivered to the mixing chamber with a chemically inert pump. Two separate pumps were tried with the system, a piston-type pump (Fluid Metering Inc., Oyster Bay, NY) and a peristaltic pump (Rainin instrument Co.). The peristaltic pump gave greater reproducibility of flow and was less prone to damage by the large concentration of buffer in the reagent solutions.

Pump pulsations were also of a higher frequency (ca. 10 Hz.) than the piston pump (1/3 Hz.) and were more easily filtered out by the active filter system of the detector. Pump pulsations were further reduced with a diaphram-type pulse dampener (Fluid Metering Inc.) and a home-made debubbling column. All lines in the post-column reagent delivery system were polypropylene, Teflon, or polyvinyl chloride. Waste effluent was diluted and properly disposed of.

The spectrophotometric detector was a Kratos model 783 scanning UV/VIS detector (Ramsey, NJ) and was equipped with a 12-μL flow cell. The temperature stabilization coil provided a back-pressure too high for the post-column reagent pumping system to safely handle so it was disconnected and replaced with a shorter length of Teflon tubing (0.3 mm i.d.). This reduced the back-pressure by about 25 psig and the dead volume of the detection system by about one-half.

RESULTS

Snyder and Kirkland (15) define the effects of varying sample size with elution time and separation of two closely eluting components. At very low concentrations of analyte, there is no change in retention time with sample size. The only difference between sample sizes for a given component is a proportionate change in peak height or area. This Brange is referred to as the linear elution isotherm. Higher sample concentrations may demonstrate a decrease in retention time for each compound and some loss of resolution. At even higher concentrations, this trend continues to give a total loss of resolution and horribly distorted peaks.

Such a trend is evident in the system used here. Figure 1 shows the effect of sample size on peak shape and resolution for injections of successively dilute samples of magnesium and calcium. The loss of resolution between the two peaks was more evident than the decreased retention time with higher sample concentration. Constant retention times were obtained for sample concentrations below about 1.0 mM.

Relative retention of metal cations with varying eluent concentration was studied for the 12% crosslinked gel resin. The capacity of this resin was 6.1 meq per gram. Eluent cations that were examined included hydrogen, sodium, and

Figure 1. Successive injections of magnesium and calcium solution.
Concentration of each 20-μL injection is (a) 10.0 mM, (b) 5.0 mM, (c)
1.0 mM, (d) 0.50 mM, and (e) 0.10 mM. Detection is with Arsenazo I
in 3.0 M ammonium hydroxide

(a)　　(b)　　(c)　　(d)　　(e)

TIME (seconds)
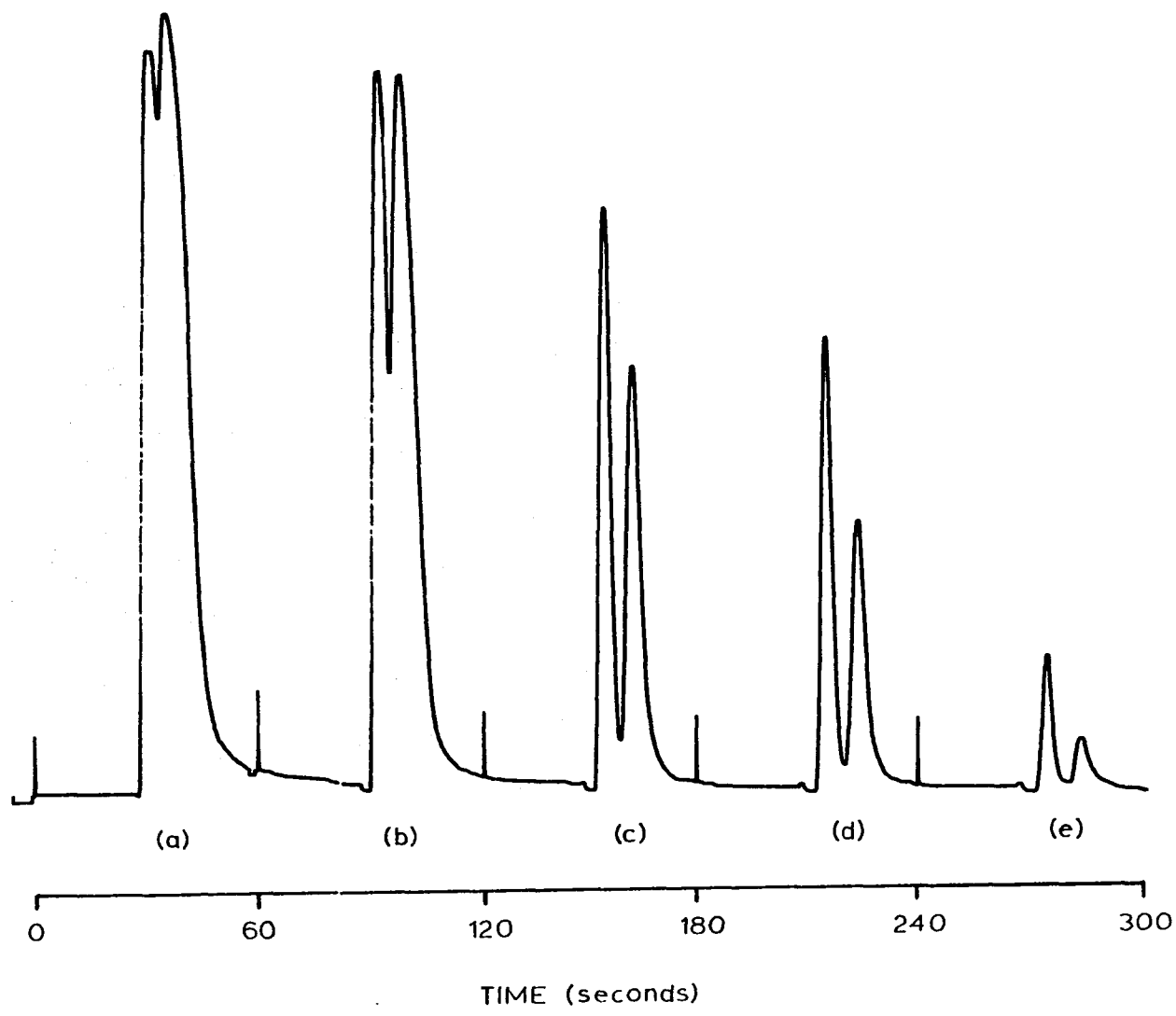
magnesium.

Adjusted retention times for metals using the perchloric acid eluent (Tables I and II) decreased with increasing acid concentration as predicted by mass-action expressions (equation 10). Elution with 1.0 M perchloric acid was quite rapid for divalent metals and retention times became difficult to measure. Metal ion peaks for eluent concentrations much below 0.10 M perchloric acid eluted very late and were lost in the baseline. As expected, elution generally followed valence of the cations with lower valence cations eluting first. Peaks for rare earth cations were relatively wide and somewhat tailed. This peak shape may very well have resulted from slow kinetics of the hydrogen ion displacing the trivalent rare earth cations from the sulfonic acid groups of the resin. The elution order followed decreasing atomic number as also reported by Surls and Choppin (48) with a similar system.

Aluminum(III), indium(III), lead(II), strontium(II), barium(II), and iron(III) eluted between most divalents and the rare earths. The later eluting divalent cations are known for their higher affinity for sulfonated resins and similar trends are reported by Strelow and Sondorp (49) who used AG50W-X8 in perchloric acid media.

Higher valence cations such as vanadium(IV), uranium(VI), and zirconium(IV) elute with most of the

Table I. Adjusted retention times (in minutes) for various cations using perchloric acid eluents. Conditions as described in the text

Cation	Perchloric Acid Concentration (molar)							
	1.00	0.850	0.750	0.600	0.500	0.400	0.250	0.100
Be(II)	0.05	0.09	0.12	0.15	0.19		0.92	2.27
Mg(II)	0.08	0.09	0.13	0.18	0.25	0.33	0.69	3.71
Ca(II)	0.16	0.20	0.28	0.48	0.73	1.12	2.96	10.6
Sr(II)	0.22	0.33	0.40	0.69	1.02	1.53	4.23	17.5
Ba(II)	0.50	0.64	0.75	1.35	1.95	3.28	7.80	-
V(IV)	0.04	0.05	0.06	0.08	0.14	0.20	0.45	2.59
Fe(II)	0.08	0.09	0.13	0.19	0.26	0.42	0.96	4.55
Hg(II)	0.08	0.09	0.15	0.21	0.34	0.49	1.48	5.79
Mn(II)	0.08	0.09	0.13	0.21	0.27	0.47	1.00	6.01
Zn(II)	0.06	0.09	0.15	0.23	0.35	0.48	1.26	6.27
Ni(II)	0.08	0.11	0.14	0.19	0.29	0.44	1.00	6.31
Cu(II)	0.08	0.11	0.16	0.24	0.30	0.48	1.58	6.35
U(VI)	0.08	0.11	0.14	0.20	0.33	0.49	1.74	6.35
Zr(IV)	0.07	0.10	0.12	0.19	0.32	0.47	0.99	6.59
Co(II)	0.10	0.11	0.14	0.19	0.24	0.52	1.00	6.71
Cd(II)	0.11	0.14	0.16	0.29	0.38	0.69	1.76	12.5
Pb(II)	0.60	0.81	0.94	1.48	2.35	3.65	14.1	49.5
Al(III)	0.34	0.50	0.79	1.46	2.61	4.90	21.3	-
V(III)	0.56	0.99	1.43	2.31	5.00	9.94	-	-
In(III)	0.57	1.05	1.51	2.89	5.24	9.82	31.6	-
Fe(III)	0.53	0.83	1.43	2.74	4.94	9.12	39.6	-
Bi(III)	4.33	6.49	10.5	15.8	26.6	66.9	-	-

Table II. Adjusted retention times (in minutes) for rare earth cations using perchloric acid eluents. Chromatographic conditions are described in the text

Cation	Perchloric Acid Concentration (molar)					
	1.000	0.850	0.750	0.600	0.500	0.400
Lu(III)	1.32	2.33	3.25	6.47	13.4	25.0
Yb(III)	1.45	2.55	3.55	7.00	14.2	26.0
Tm(III)	1.47	2.60	3.73	7.30	14.3	28.2
Y(III)	1.55	2.94	4.05	8.11	14.9	29.5
Er(III)	1.57	2.63	3.92	7.78	15.1	29.6
Ho(III)	1.66	2.78	4.25	8.27	16.3	31.4
Dy(III)	1.87	3.02	4.58	9.21	17.7	35.1
Gd(III)	2.42	4.16	6.18	12.2	23.6	45.2
Eu(III)	2.70	4.58	6.85	13.6	26.2	52.0
Sm(III)	2.99	5.63	7.64	15.0	29.4	57.4
Nd(III)	3.53	6.75	8.79	17.5	34.3	68.2
Pr(III)	3.70	7.04	9.19	18.6	35.3	70.4
Ce(III)	4.30	7.15	10.5	21.4	40.0	83.0
La(III)	4.79	7.74	11.8	23.7	46.4	92.9

divalent cations. In aqueous solution, these cations exist as divalent oxo-cations (VO^{2+}, UO_2^{2+}, and ZrO^{2+}) and rapid elution is not all that unusual. Other cations such as chromium(III), antimony(III), tin(IV), tellurium(III), titanium(IV), and thorium(IV) did not give peaks. Tin(IV) gave a precipitate when injected. Oxo-anions of metals (molybdate, MoO_4^-; and tungstate, WO_4^-) were not retained by the cation exchange resin under these conditions and were not studied further.

Sodium perchlorate eluents were examined over the same basic concentration range as perchloric acid eluents (0.200 to 1.00 M). The same trends of decreasing retention time with increasing eluent concentration were found (Tables III and IV). Elution order of the rare earths and general elution by valence of the cations studied were also observed. The selectivity of sodium ion for sulfonic acid resins is known to be greater than hydrogen ion. In turn, a stronger eluting strength per equivalent is expected for sodium ion over hydrogen ion. This happens to be the case when compared on the same system. At the same time, lower selectivity between eluent and eluate cations is obtained using sodium perchlorate. Table V shows the separation factor (α_{Mg}^{Ca}) and calculated resolution (R_s) for magnesium and calcium cations with respect to eluent composition.

Table III. Adjusted retention times (in minutes) of various
cations using sodium perchlorate eluents.
Chromatographic conditions are described in the
text

Cation	Sodium Perchlorate Concentration (molar)				
	1.00	0.750	0.500	0.250	0.200
Be(II)	0.03	0.03	0.06		0.52
Mg(II)	0.03	0.05	0.09	0.36	0.61
Ca(II)	0.09	0.15	0.24	1.02	2.16
Sr(II)	0.14	0.25	0.48	1.79	2.93
Ba(II)	0.37	0.60	1.12	2.21	
V(IV)	0.07	0.08	0.68	0.47	1.19
Zn(II)	0.05	0.06	0.15	0.51	1.09
Ni(II)	0.03	0.07	0.13	0.54	1.20
Zr(IV)	0.06		0.15	0.64	1.34
Co(II)	0.04	0.08	0.10	0.62	1.38
Cu(II)	0.10	0.15	0.23	0.65	1.38
Hg(II)	0.05	0.09	0.18	0.55	1.46
Cd(II)	0.08	0.11	0.33	0.74	1.60
Mn(II)	0.08	0.10	0.13	0.60	1.71
Fe(II)	0.04	0.07	0.16	0.57	1.77
U(VI)	0.30	0.43	0.63	1.75	3.59
Al(III)		0.37	1.15		
Pb(II)	0.57	0.75	1.50		13.7
Fe(III)				21.9	
In(III)	1.65	2.48			

Table IV. Adjusted retention times (in minutes) of rare
          earth cations using sodium perchlorate eluents.
          Chromatographic conditions are described in the
          text

Cation	Sodium Perchlorate Concentration (molar)			
	1.00	0.750	0.500	0.250
Lu(III)	0.65	1.30	3.42	21.9
Yb(III)	0.68	1.42	3.61	31.0
Tm(III)	0.77	1.50	3.92	32.1
Y(III)	0.76	1.46	4.10	32.2
Er(III)	0.80	1.50	4.13	33.2
Ho(III)	0.82	1.64	4.43	33.6
Dy(III)	0.96	1.97	5.37	42.6
Tb(III)	1.06	2.04	5.61	44.0
Gd(III)	1.24	2.42	6.53	51.5
Eu(III)	1.38	2.72	7.28	57.5
Sm(III)	1.63	2.97	8.19	61.2
Nd(III)	1.55	3.09	8.34	65.2
Pr(III)	1.59	3.07	8.87	68.6
Ce(III)	1.69	3.38	10.1	73.1
La(III)	1.88	3.89	10.6	85.9

Table V.   Comparison of retention times, separation factor, and resolution data of magnesium and calcium using perchloric acid and sodium perchlorate eluents. Chromatographic conditions are described in the text

Eluent		Eluent Concentration (molar)			
		1.00	0.750	0.500	0.250
$HClO_4$	t_r' $(Mg)^a$	0.08	0.13	0.25	0.69
	t_r' $(Ca)^a$	0.16	0.28	0.73	2.96
	α_{Mg}^{Ca}	2.00	2.15	2.92	4.29
	R^s	0.53	1.11	1.60	1.90
$NaClO_4$	t_r' $(Mg)^a$	0.03	0.05	0.09	0.36
	t_r' $(Ca)^a$	0.09	0.15	0.24	1.02
	α_{Mg}^{Ca}	3.0	1.50	2.67	2.83
	R_s	0.23	0.28	0.32	1.15

[a] Units of minutes.

The low separation factors result from the reduced
difference in selectivity between eluent and eluate cations
going from hydrogen eluent to sodium eluent. The increase
in resolution is not as rapid as that in the separation
factor because of peak tailing.

Magnesium perchlorate was also examined for its eluting
behavior. Only a limited number of metal cations were tried
using this eluent. Concentrations from 10.0 mM down to 1.00
mM were studied and are summarized in Table VI. As
expected, its eluting strength was significantly greater
than the monovalent cations.

The relative eluting strength of several eluent cations
was examined. These eluents were all made up to give a
concentration of 2.0 meq of positive charge per liter of
eluent at pH 2.50. The eluent cations included aniline,
pyridine, ethylenediamine, p-phenylenediamine, and
magnesium. No peaks were obtained for aniline or pyridine
eluents while the other eluents gave well defined peaks.
The retention data for these eluents is listed in Table VII
with that for the perchloric acid and sodium eluents of near
comparable strength.

The effect of varying resin capacity for the 12%
crosslinked resin on retention time was studied and is
listed in Table VIII. Obvious trends of increasing
retention time with increased capacity are observed. The

Table VI. Adjusted retention times (in minutes) of various
cations for magnesium perchlorate eluent.
Chromatographic conditions are in the text

Cation	Magnesium Concentration (millimolar)			
	10.0	5.00	1.00	0.500
V(IV)	0.33	0.79	3.65	6.62
Zn(II)	0.68	1.38	6.47	12.3
Co(II)	0.77	1.53	7.02	12.6
Fe(II)	0.71	1.50	6.73	12.9
Ni(II)	0.72	1.53	6.93	13.2
Cu(II)	0.95	1.81	7.83	13.2
Zr(IV)	0.78	1.54	7.11	13.5
Hg(II)	0.74	1.56	7.21	13.7
Mn(II)	0.82	1.68	7.63	14.7
Cd(II)	0.51	1.25	7.81	16.5
U(VI)	1.38	2.92	10.9	18.9
Pb(II)	6.47	15.8	-	

Table VII. Adjusted retention times (in minutes) of various cations with cationic eluents. Chromatographic conditions are described in the text

Cation	$HClO_4$[a]	$NaClO_4$[b]	EnH_2^{2+}[c]	$PhenH_2^{2+}$[c]	$Mg(ClO_4)_2$[c]
			Eluent		
Ba(II)	7.80		6.93	8.80	
Be(II)	0.92	0.52	0.78		
Ca(II)	2.96	2.16	2.38	2.58	
Cd(II)	1.76	1.60	1.82	1.84	7.81
Co(II)	1.00	1.38	1.47	1.47	7.02
Cu(II)	1.58	1.38	1.22	1.79	7.83
Fe(II)	0.96	1.77	1.42	1.41	6.73
Hg(II)	0.99	1.46	1.37	1.56	7.21
Mg(II)	0.69	0.61	0.98	1.19	
Mn(II)	1.00	1.71	1.49	1.49	7.63
Ni(II)	1.00	1.20	1.46	1.49	6.93
Pb(II)	14.1	13.7	9.79	12.0	
Sr(II)	4.23	2.93	3.18	3.60	
U(VI)	1.74	3.59	3.09	2.98	10.9
V(IV)	0.45	0.47	1.04	1.10	3.65
Zn(II)	1.26	1.09	1.36	1.44	6.47
Zr(IV)	0.99	1.34	1.41	1.53	7.11

[a] Concentration of 0.250 M.

[b] Concentration of 0.100 M.

[c] Concentration of 1.00 mM, pH 2.5.

Table VIII. Adjusted retention times (in minutes) for various cations with resins of differing bulk capacities. Eluent is 0.750 M $HClO_4$. Other chromatographic conditions are described in the text

Cation	Resin Capacity (μeq per gram)		
	6.1	13.8	24.9
Be(II)	0.12	0.16	0.19
Mg(II)	0.13	0.16	0.32
Ca(II)	0.28	0.52	1.22
Ba(II)	0.75	2.50	-
V(IV)	0.06	0.20	0.40
Fe(II)	0.13	0.20	0.46
Zn(II)	0.15	0.21	0.42
Ni(II)	0.14	0.25	0.43
Cu(II)	0.16	0.23	0.47
Zr(IV)	0.12	0.20	0.51
Cd(II)	0.16	0.25	0.55
U(VI)	0.14	0.29	0.60
Mn(II)	0.13	0.33	0.63
Pb(II)	0.94	2.46	5.47
Fe(III)	1.43	2.81	5.42
In(III)	1.51	3.03	
Bi(III)	0.28	21.0	60.7
Lu(III)	3.25	7.88	17.5
Yb(III)	3.55	8.12	18.2
Tm(III)	3.73	8.80	19.0
Er(III)	3.92	9.32	21.0
Y(III)	4.05	9.56	21.2
Ho(III)	4.25	10.1	23.2
Dy(III)	4.58	12.1	27.4
Tb(III)	5.22	13.2	32.2
Gd(III)	6.18	15.6	36.2
Eu(III)	6.85	17.5	41.7
Sm(III)	7.64	19.5	47.4
Nd(III)	8.79	22.3	52.6
Pr(III)	9.19	24.2	56.9
Ce(III)	10.5	28.0	61.7
La(III)	11.8	33.7	85.2

most drastic increases are seen with the trivalent cations.
The increases of retention time appear to be somewhat
proportional to increases in resin capacity.

DISCUSSION

Eluent Effects

To determine the correlation of the experimental data to the basic theoretical description of the exchange process (equation 10), it is first necessary to calculate the distribution coefficient from retention data using equation 7.

In calculations using high-capacity resins that are sulfonated throughout the whole bead, the weight of the resin (M_{res}) is taken as the total weight of resin contained within the column. In the case of the surface-sulfonated resins, the active portion of the resin in the column comprises a small fraction of the total amount of resin in the column. Calculations from the ratio of capacities of the surface-sulfonated and fully-sulfonated beads and density data for the two show that less than about 0.5% of the total bead is sulfonated. For a 25 cm x 2 mm i.d. column packed with resin (ca. 0.75 g) having a bulk capacity of 6.1 μeq per gram only about 1 mg of the resin is sulfonated. If the assumptions are made that the divinylbenzene groups of the resin do not become sulfonated (as discussed in section I) and the sulfonation proceeds through a "layer-by-layer" mechanism (50), one finds that

the capacity of the active layer is near that of the fully
sulfonated resin (ca. 4-5 meq per gram).

Therefore, the weight of "active" resin in the column
should be used. This makes sense since the core of the
superficially-sulfonated beads are impervious to ions (a
result of their hydrophobic nature) and play no significant
part in the exchange process. This adjustment in no way
affects the slopes of lines from the logarithm of the
retention versus the logarithm of the eluent ion activity.
A change in the intercept is noticed and is merely the
result of including constant parameters. Correcting the
resin mass results in distribution coefficients somewhat
larger than generally expected.

For the perchloric acid eluents, the values of the
concentration distribution coefficients (Tables IX and X)
were plotted as the logarithms against the logarithm of the
eluent activity. These data are summarized in Tables XI and
XII. Plots of data for several cations are illustrated in
Figures 2 and 3. The slopes match fairly well with those
predicted. In a few cases, the slopes deviated from the
theoretical values. Correlation coefficients showed
generally good linear relations as is supported by the
graphs.

One easily explained deviation is that of bismuth(III).
In aqueous solution, even with pHs as low as 1.0, bismuth is

Table IX. Concentration distribution coefficients for various cations using perchloric acid eluents. Chromatographic conditions are described in the text

	Perchloric Acid Concentration (molar)							
Cation	1.00	0.850	0.750	0.600	0.500	0.400	0.250	0.100
Be(II)	48	87	117	146	185		897	2215
Mg(II)	78	88	127	176	244	322	674	3620
Ca(II)	156	195	273	468	712	1093	2888	10343
Sr(II)	214	322	390	674	995	1493	4128	17076
Ba(II)	488	625	732	1317	1903	3201	7611	
V(IV)	39	49	58	78	137	195	439	2527
Fe(II)	78	88	127	186	254	410	937	4440
Hg(II)	78	88	146	205	332	478	1444	5649
Mn(II)	78	88	127	205	263	458	976	5864
Zn(II)	58	88	146	225	342	468	1230	6118
Ni(II)	78	107	137	186	283	430	976	6157
Cu(II)	78	107	156	234	293	468	1541	6196
U(VI)	78	107	137	195	322	478	1698	6196
Zr(IV)	68	98	117	186	312	458	966	6430
Co(II)	98	107	137	186	234	507	976	6548
Cd(II)	107	137	156	283	371	674	1718	12197
Pb(II)	586	790	917	1444	2293	3561	13758	48300
Al(III)	332	488	771	1425	2547	4781	20783	
V(III)	546	966	1395	2254	4879	9699		
In(III)	556	1025	1474	2822	5113	9582	30834	
Fe(III)	517	810	1395	2673	4820	8899	38640	
Bi(III)	4225	6332	10246	15417	25955	65278		

Table X. Concentration distribution coefficients for rare earth cations using perchloric acid eluents. Chromatographic conditions are described in the text

	Perchloric Acid Concentration (molar)					
	1.00	0.850	0.750	0.600	0.500	0.400
Lu(III)	1288	1684	3171	6313	13075	24394
Yb(III)	1415	2488	3464	6830	13856	25369
Tm(III)	1434	2537	3640	7123	13953	27516
Y(III)	1513	2869	3952	7913	14538	28784
Er(III)	1532	2566	3825	7592	14734	28882
Ho(III)	1620	2713	4147	8070	15904	30639
Dy(III)	1825	2947	4469	8987	17271	34249
Tb(III)	2049	3059	5093	10050	19613	38249
Gd(III)	2361	4176	6030	11904	23028	44104
Eu(III)	2634	4469	6684	13270	25565	50739
Sm(III)	2917	5493	7455	14636	28687	56008
Nd(III)	3445	6586	8577	17076	33468	66546
Pr(III)	3610	6869	8967	18149	34444	68693
Ce(III)	4196	6976	10246	20881	39030	80987
La(III)	4674	7553	11514	23126	45275	90647

Table XI. Linear regression data for logarithm D_c versus logarithm {$HClO_4$} data. Chromatographic conditions are described in the text

	Slope			
Cation	This Work	Reference[a]	Intercept	r
Be(II)	-1.64	-1.02	1.637	-0.990
Mg(II)	-1.66	-1.25	1.698	-0.998
Ca(II)	-1.87	-1.54	2.037	-0.996
Sr(II)	-1.91	-1.66	2.186	-0.998
Ba(II)	-1.97	-1.92	2.470	-0.997
Al(III)	-2.88	-1.80	2.225	-0.999
Bi(III)	-2.67	-2.24	3.366	-0.992
Fe(III)	-2.99	-1.81	2.438	-1.000
In(III)	-2.78	-1.87	2.532	-0.999
Mn(II)	-1.89	-1.36	1.670	-0.998
Zn(II)	-1.98	-1.32	1.660	-0.998
Ni(II)	-1.87	-1.35	1.692	-0.998
U(VI)	-1.96	-1.32	1.841	-0.996
Cu(II)	-1.92	-1.33	1.723	-0.997
Fe(II)	-1.79	-1.36	1.687	-0.999
Co(II)	-1.86	-1.34	1.712	-0.992
Cd(II)	-2.08	-1.40	1.768	-0.997
V(IV)	-1.83	-1.11	1.365	-0.997
Pb(II)	-2.00	-1.88	2.551	-0.994
V(III)	-2.87		2.481	-0.996
Hg(II)	-1.92	-1.76	1.700	-0.997
Zr(IV)	-1.95		1.649	-0.999

[a]Calculated from data of Strelow and Sondorp (49).

Table XII. Linear regression data for logarithm D_c versus logarithm $\{HClO_4\}$ plots of the rare earths. Chromatographic conditions are described in the text

Cation	Slope This Work	Slope Reference[a]	Intercept	r
Lu(III)	-3.00		2.780	-0.998
Yb(III)	-2.95		2.887	-0.998
Tm(III)	-2.99		2.890	-0.999
Y(III)	-2.95	-2.20	2.934	-0.999
Er(III)	-3.00		2.909	-0.999
Ho(III)	-3.01		2.935	-0.999
Dy(III)	-3.01	-2.23	2.976	-0.999
Tb(III)	-3.04		3.013	-0.998
Gd(III)	-2.97		3.112	-0.999
Eu(III)	-3.01		3.146	-0.999
Sm(III)	-2.97		3.211	-0.999
Nd(III)	-2.97		3.282	-0.998
Pr(III)	-2.95		3.304	-0.998
Ce(III)	-3.01	-2.48	3.340	-0.999
La(III)	-3.04	-2.49	3.380	-0.999

[a]Calculated from data of Strelow and Sondorp (49).

Figure 2.   Linear regression plots of log (concentration
            distribution coefficient) versus log (perchloric
            acid activity) for the alkaline earths,
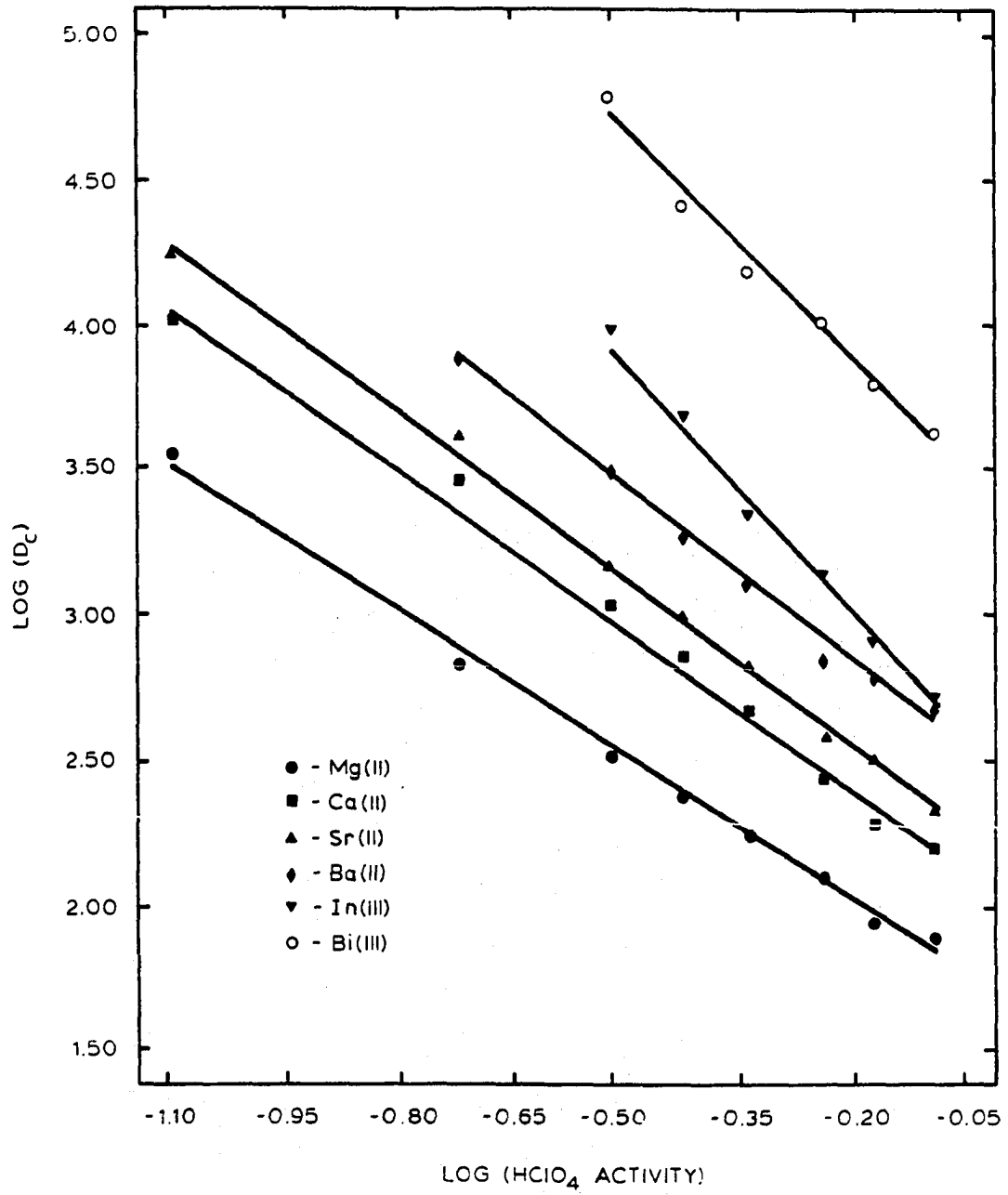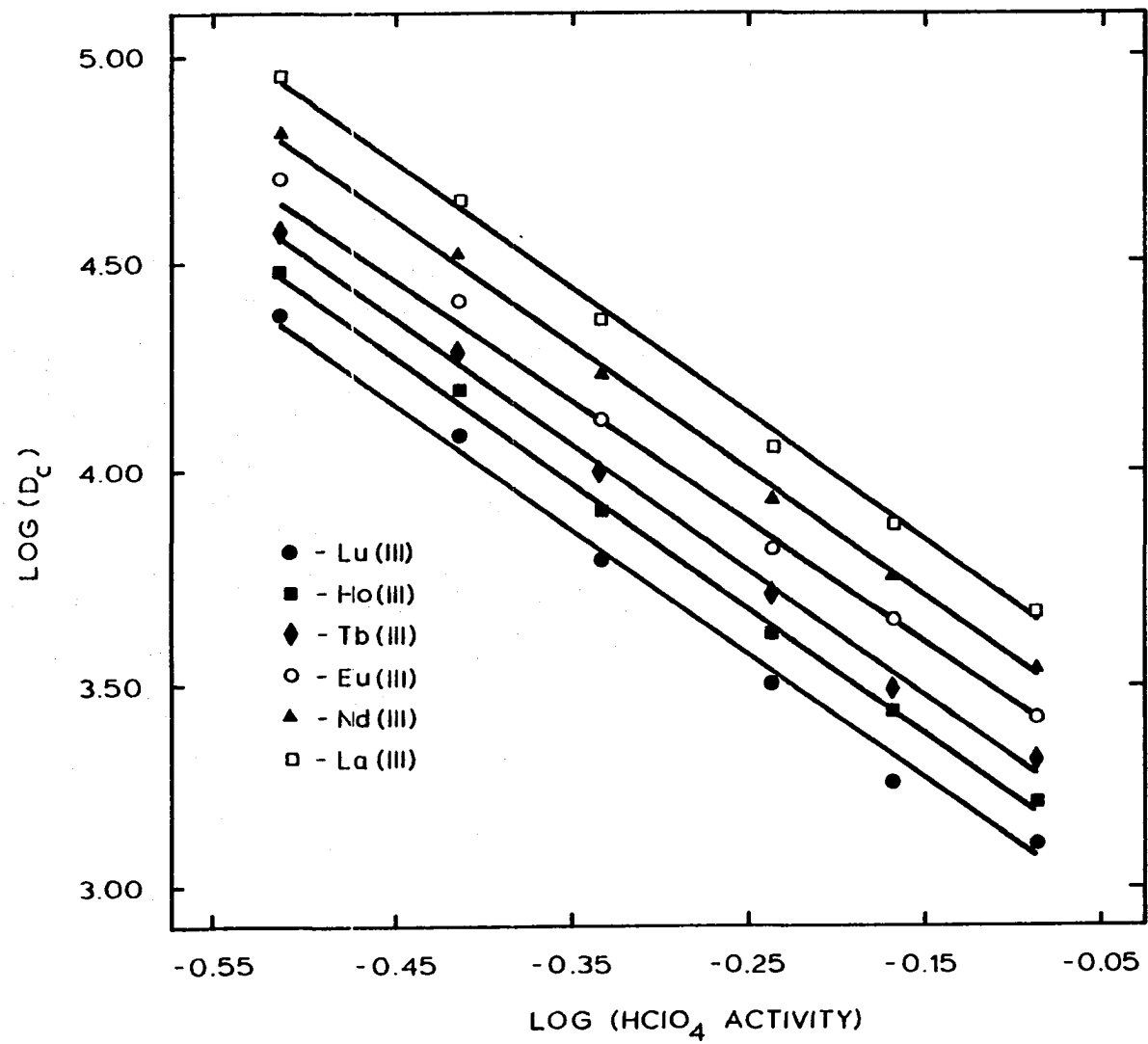   indium(III), and bismuth(III)

Figure 3. Linear regression plots of log (concentration distribution coefficient) versus log (perchloric acid activity) for several rare earth cations

about 20% hydrolyzed (51). Hydrolysis, of course, reduces the net cationic charge of the cation and consequently gives an overall decrease in the slope of the line.

Of particular interest is the occurrence of vanadium(III). This peak was discovered as a minor component in vanadyl solutions which increased in height as the dilute solution sat open to the atmosphere. As mentioned by Samuelson (52), this is a very useful method in determining the unknown charge of a cation.

The general elution order for the perchloric acid eluent was determined using the linear regression data. Sequences were arranged on the basis of intercept values as indicators of the selectivity coefficients (equation 10).

Bivalent: $V(IV) < Be < Zr(IV) < Zn < Mn \cong Fe \cong$ $Ni \cong Mg \cong Hg < Cu \cong Co < Cd < U(VI) < Ca < Sr$ $< Ba < Pb$

Tervalent: $Al < Fe < V < In < Yb < Dy < Ce < Bi < La$

Rare Earths: $Lu < Yb < Tm < Er < Y < Ho < Dy < Tb < Gd <$ $Eu < Sm < Nd < Pr < Ce < La$

Generally, the whole elution sequence does follow orders of increasing crystal ionic radii or decreasing hydrated radius as predicted by the models previously discussed. Alkaline earth and rare earth cations all behave as generally predicted, showing increased retention with decreased hydrated cation size. Transition metals exhibit very similar elution in cation exchange systems and as a

result are bunched closely together. Overall, these data are somewhat difficult to fit into an absolute scheme. Relative selectivity orders are notably different from a number of fully sulfonated resins of lower and higher crosslinking (2). As previously mentioned, some of these variations are known to exist merely because of differing exchange environments (32).

Studies of batch distribution coefficients of metal ions in perchloric acid solution have been performed by Strelow and Sondorp (49). They studied the distribution of metals on AG50W-X8 in perchloric acid in concentrations from 4.0 M down to 0.10 M. To develop a selectivity sequence, they only used data from 1.0 to 0.10 M perchloric acid. This selectivity sequence was:

Bivalent: Be $\cong$ V(IV) < U(VI) < Mg < Zn < Ca < Co
            < Ni < Mn < Fe < Cd < Ca < Sr < Hg < Pb <
            Ba < Zr(IV)

Tervalent: Al < Fe < In < Yb < Bi < Y < Dy < Ce < La

The selectivity sequence of Strelow and Sondorp (49) was very similar to the sequence determined in this work. This further supports the basic assumption that the system used here behaves in a "near-equilibrium" manner and simulates batch equilibria. Some differences do exist and can generally be accounted for, such as the order of beryllium and vanadyl ions.

The ion-exchange behavior of beryllium is quite peculiar and has been known to undergo selectivity reversals under the certain circumstances. The existence of aquo-species (e.g., $Be(H_2O)_4^{2+}$) formed from the beryllium cation in aqueous solution (53). These aquo-species are acidic in character and may lose a hydrogen to give a species of reduced charge (i.e., $Be(H_2O)_3(OH)^+$). The exact composition of the beryllium ion in the eluent is not sure. As with bismuth, the species will readily account for the reduced slope.

Mercury(II) is known to exist in aqueous solution as a binary cation linked by "oxo-type" bridges (54). The lower distribution coefficient might well be the result of the now relatively large "poly-cation" unable to penetrate the resin matrix and access the inner exchange sites of the resin. In effect, this "cation" does not see the full capacity available in the resin.

Other differences in the distribution sequence from the data of Strelow and Sondorp (49) appear due to the use of a higher crosslinked resin. In addition, the nature of the surface-sulfonated versus the fully sulfonated resin beads and effects on the selectivity are not exactly clear. From the published data, the slopes for logarithmic plots of distribution coefficients versus eluting cation activity were calculated. In all fairness, the same concentration

range was used as covered in this work with corrections made
for activities. The resulting slopes are listed in Tables
XI and XII for reference and do not correlate very well to
the theoretical values. The authors claimed good
correlation to theory were made for distribution coefficient
values from 1.0 to 2.0 M perchloric acid. This claim is
quite interesting since only two data points were given for
each cation.

Under the assumption that the chromatographic system
approaches true ion-exchange, one can determine the
thermodynamic equilibrium constants, $K^{\circ M}_E$, for each metal ion
versus hydrogen ion. This calculation is done through use
of equation 10 after rearranging to give the equation below.

$$\log K^{*M}_E = \text{Intercept} - \frac{y}{x} \log(\text{Capacity}/|x|) \qquad (13)$$

Values of $\log K^{*M}_E$ resemble available literature values
(55) for systems which are similar to the one here.
Disparity is easily encountered with slight variations
between ion-exchange systems as is the case here.

The true equilibrium constants are actually obtained by
integration of the isotherm over the whole composition range
of the exchanger.

$$K_E^{*M} = \int_0^1 \log k_E^{\circ M} \, d\bar{X}_M \tag{14}$$

In this study, $\bar{X}_M$ was very small and does not represent the whole exchange isotherm. The main point is the values are at least in the same general order of magnitude which makes the system useful for rough estimations of $K_E^{\circ M}$. The belief that a "near-equilibrium" state was achieved also seems supported.

The sodium perchlorate eluent system produced distribution coefficients which are about 2 to 3 times lower than those of the perchloric acid eluent system (Tables XIII and XIV). Smaller values for distribution coefficient compared to those of perchloric acid are expected because of the greater affinity of the sodium ion for the resin over the hydrogen ion.

Plots of the logarithm of D_c versus logarithm of the sodium perchlorate activity (Figures 4 and 5) produced straight lines for the rare earths with slopes close to the theoretical value of -3 (Table XV). The divalent cations gave reasonably good linearity but in most cases deviated from the predicted slopes of -2 (Table XVI).

The exact reason for the deviation from theory by the divalent cations is not readily predicted. Sodium perchlorate is known to have a limited solubility in water compared to most other metal perchlorates with exception of

Table XIII. Concentration Distribution Coefficients of various cations using sodium perchlorate eluents

Cation	Sodium Perchlorate Concentration (molar)				
	1.00	0.750	0.500	0.250	0.200
Be(II)	30	30	58		507
Mg(II)	30	49	88	351	595
Ca(II)	88	146	234	995	2108
Sr(II)	137	244	468	1746	2859
Ba(II)	361	586	1093		
V(IV)	68	78	458	665	1161
Zn(II)	49	58	146	498	1064
Ni(II)	30	68	127	527	1171
Zr(IV)	58		146	625	1308
Co(II)	39	78	98	605	1346
Cu(II)	98	146	225	634	1346
Hg(II)	49	88	176	537	1425
Cd(II)	78	107	322	722	1561
Mn(II)	78	98	127	586	1669
Fe(II)	39	68	156	556	1727
U(VI)	293	420	615	1708	3503
Al(III)		361	1122		
Pb(II)	556	732	1464		13368
Fe(III)				21369	
In(III)	1610	2420		21369	

Table XIV. Concentration Distribution Coefficients of rare earth cations using sodium perchlorate eluents

	Sodium Perchlorate Concentration (molar)			
Cation	1.00	0.750	0.500	0.250
Lu(III)	634	1269	3337	21369
Yb(III)	663	1385	3522	30248
Tm(III)	751	1464	3825	31322
Y(III)	742	1425	4001	31419
Er(III)	781	1464	4030	32395
Ho(III)	795	1600	4323	32785
Dy(III)	937	1922	5240	41567
Tb(III)	1031	1990	5474	42933
Gd(III)	1210	2361	6372	50251
Eu(III)	1346	2654	7104	56106
Sm(III)	1513	2898	7991	59716
Nd(III)	1551	3015	8138	63619
Pr(III)	1590	3093	8655	66937
Ce(III)	1649	3298	9855	71327
La(III)	1834	3796	10343	83817

Figure 4. Linear regression plots of log (concentration distribution coefficient) versus log (sodium perchlorate activity) for magnesium, calcium, strontium, and barium
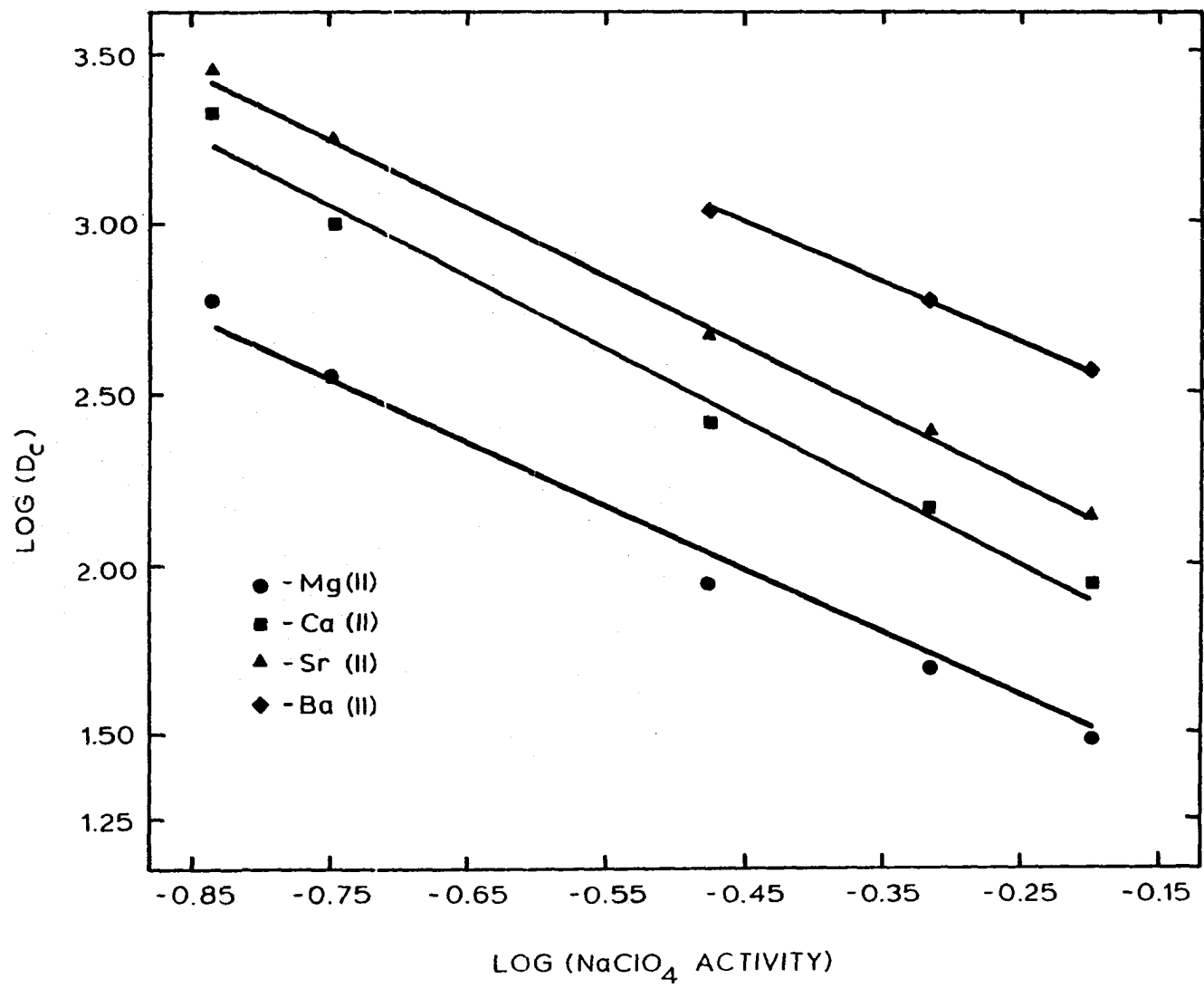
Figure 5. Linear regression plots of log (concentration
           distribution coefficient) versus log (sodium
           perchlorate activity) for several rare earth
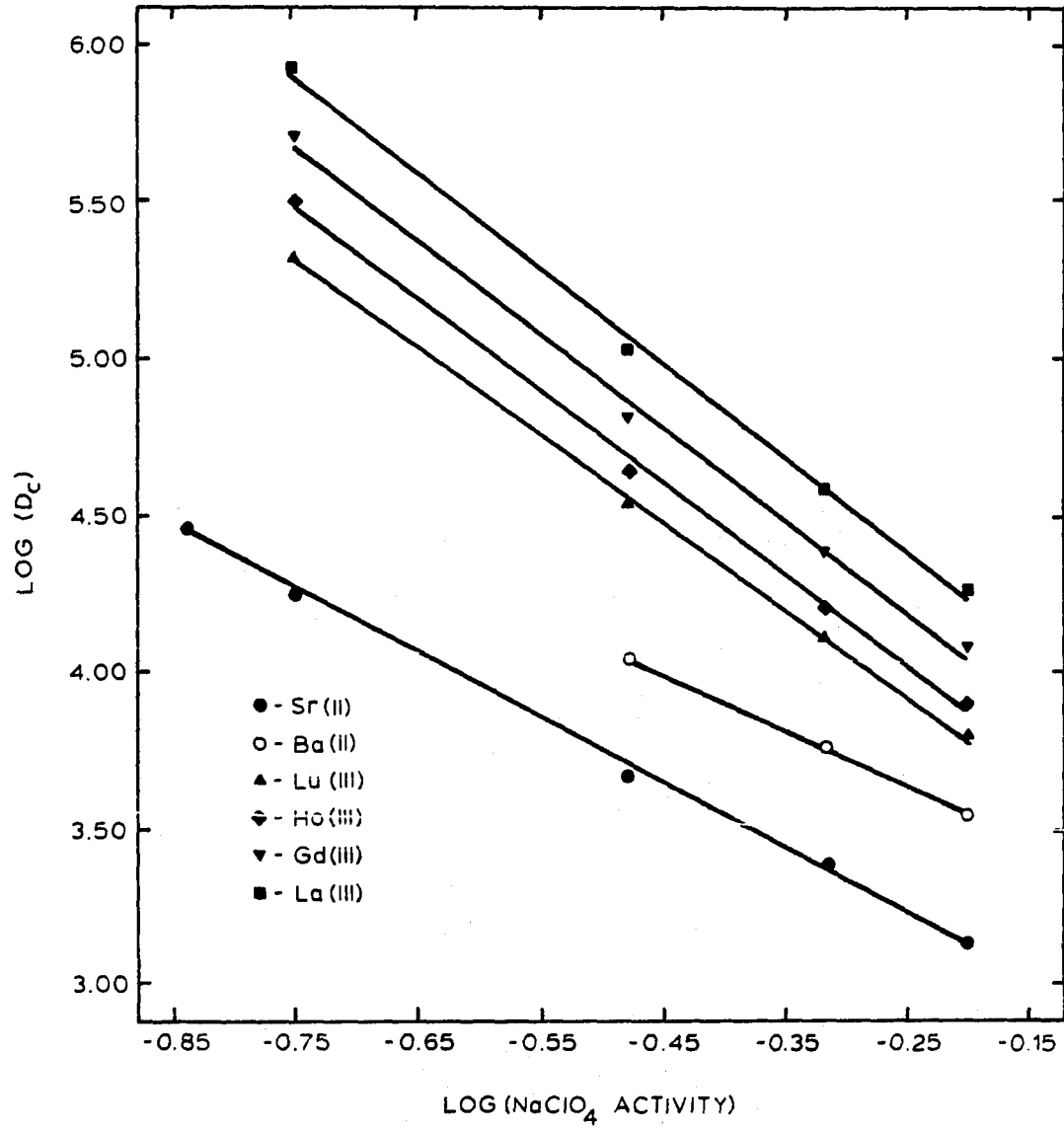   cations with strontium and barium as reference

Table XV. Linear regression data for logarithm D_c versus logarithm $\{NaClO_4\}$ data for rare earth cations. Chromatographic conditions are described in the text

Cation	Slope	Intercept	Correlation Coefficient
Lu(III)	-2.80	2.221	-0.999
Yb(III)	-3.03	2.178	-0.997
Tm(III)	-2.98	2.235	-0.997
Y(III)	-3.00	2.226	-0.998
Er(III)	-2.99	2.244	-0.997
Ho(III)	-2.96	2.274	-0.999
Dy(III)	-3.02	2.334	-0.998
Tb(III)	-2.98	2.374	-0.998
Gd(III)	-2.98	2.445	-0.998
Eu(III)	-2.98	2.494	-0.998
Sm(III)	-2.94	2.550	-0.998
Nd(III)	-2.97	2.554	-0.998
Pr(III)	-3.00	2.556	-0.998
Ce(III)	-3.02	2.584	-0.999
La(III)	-3.04	2.622	-0.998

Table XVI. Linear regression data for logarithm D_c versus logarithm $\{NaClO_4\}$ data for various cations. Chromatographic conditions are described in the text

Cation	Slope	Intercept	Correlation Coefficient
Be(II)	-2.06	0.909	-0.975
Mg(II)	-2.04	1.033	-0.998
Ca(II)	-2.11	1.472	-0.991
Sr(II)	-2.05	1.721	-0.999
Ba(II)	-1.75	2.210	-1.000
Ni(II)	-2.38	1.014	-0.995
Fe(II)	-2.44	1.063	-0.989
Co(II)	-2.34	1.070	-0.983
Zn(II)	-2.12	1.176	-0.991
V(IV)	-1.95	1.448	-0.952
Hg(II)	-2.15	1.243	-0.990
Zr(IV)	-2.10	1.276	-0.998
Mn(II)	-2.03	1.349	-0.960
Cd(II)	-1.99	1.471	-0.989
Cu(II)	-1.70	1.611	-0.987
U(VI)	-1.62	2.098	-0.986
Pb(II)	-2.24	2.201	-0.990
In(III)	-2.09	2.758	-0.998

the heavier alkali metals. In terms of the selectivity theory of Diamond and Whitney (35), sodium would find the mobile phase a less desirable solvating medium at high perchlorate concentration and prefer the exchange sites in the stationary phase. The result would be a decreased take-up of metals by the resin in favor of sodium. The effect of the change of selectivity should increase the slope of the lines. No data have been found covering the selectivity order of polyvalent metals versus sodium ion. Most selectivity studies are concerned with relative selectivities of alkali metals. An elution sequence for sodium perchlorate eluent has been compiled as follows.

Divalents: Be < Mg < Ni < Fe < Co < Zn < Hg < Zr(IV) < Mn < V(IV) < Cd < Ca < Cu < Sr < U(VI) < Ba < Pb

Tervalents: (Yb < Lu <) Y < Tm < Er < Ho < Dy < Tb < Gd < Eu < Sm < Nd < Pr < Ce < La

In the rare earth sequence, lutetium and ytterbium have reversed orders from those in perchloric acid. This theoretically predicted reversal appears to be more of an artifact of experimental error in the studies. In fact, lutetium(III) always preceded ytterbium(III) in elution order. Consideration of how closely ytterbium(III) and lutetium(III) elute to each other and examination of their respective slopes shows the prediction as improper.

A limited number of cations were studied for the

Table XVII. Concentration distribution coefficients of
various cations for magnesium perchlorate
eluent at pH 2.5. Chromatographic conditions
in text

| | Magnesium Concentration (millimolar) | | | |
	10.0	5.00	1.00	0.500
V(IV)	322	771	3561	6460
Zn(II)	664	1346	6313	12002
Co(II)	751	1493	6850	12294
Fe(II)	693	1464	6567	12587
Ni(II)	702	1493	6762	12880
Cu(II)	927	1766	7640	12880
Zr(IV)	761	1502	6938	13173
Hg(II)	722	1522	7035	13368
Mn(II)	800	1639	7445	14344
Cd(II)	498	1220	7620	16100
U(VI)	1346	2849	10636	18442
Pb(II)	6313	15417	-	

magnesium perchlorate eluent. Distribution coefficient data
are listed in Table XVII for the cations examined. Analysis
of the equilibrium behavior is summarized in Table XVIII
with plots of the data in Figure 6. Good linear correlation
of the data was obtained overall.

A general selectivity sequence may also be proposed for
the data as follows:

Divalents: Cd < V(IV) < Zn <   Ni ≅ Hg ≅ Fe < Zr(IV) < Mn
   < Co < Cu < (Pb) < U(VI)

This sequence resembles the perchloric acid sequence
fairly well with the exception of cadmium. At higher
concentrations, cadmium seems to elute early (Table VI). A
reversal between cadmium and almost all other metals studied
occurs between 1.00 and 5.00 mM magnesium perchlorate. This
was also observed by Hsi (56) at lower eluent concentrations
and stands without exact explanation.

Magnesium perchlorate cation was used as an eluting
cation by Hsi (56) for cation separation with polarographic
detection. The eluent choice was based on the relative
strength of magnesium cation and its lack of
electroselectivity under the detection conditions. Hsi's
data followed general trends of decreasing retention with
increasing eluting ion. The linear correlation data
produced slopes from one-third to one-half those predicted
with good correlation coefficients. No explanation for the

Table XVIII. Linear regression data for logarithm D_c versus logarithm [Mg(ClO$_4$)$_2$] data for various cations. Chromatographic conditions are described in the text

Cation	Slope	Intercept	Correlation Coefficient
V(IV)	-0.990	0.5649	-0.998
Zn(II)	-0.934	0.8998	-0.999
Co(II)	-0.936	1.0128	-1.000
Fe(II)	-0.960	0.9360	-1.000
Ni(II)	-0.964	0.9358	-1.000
Cu(II)	-0.886	1.2046	-1.000
Zr(IV)	-0.951	0.9831	-1.000
Hg(II)	-0.969	0.9348	-1.000
Cd(II)	-1.156	0.4055	-1.000
Mn(II)	-0.958	0.9967	-1.000
U(VI)	-0.861	1.4363	-0.998
Pb(II)	-1.288	(1.2240)	(1)

Figure 6. Linear regression plots of log (concentration distribution
           coefficient) versus log (magnesium perchlorate concentration) for
           several cations
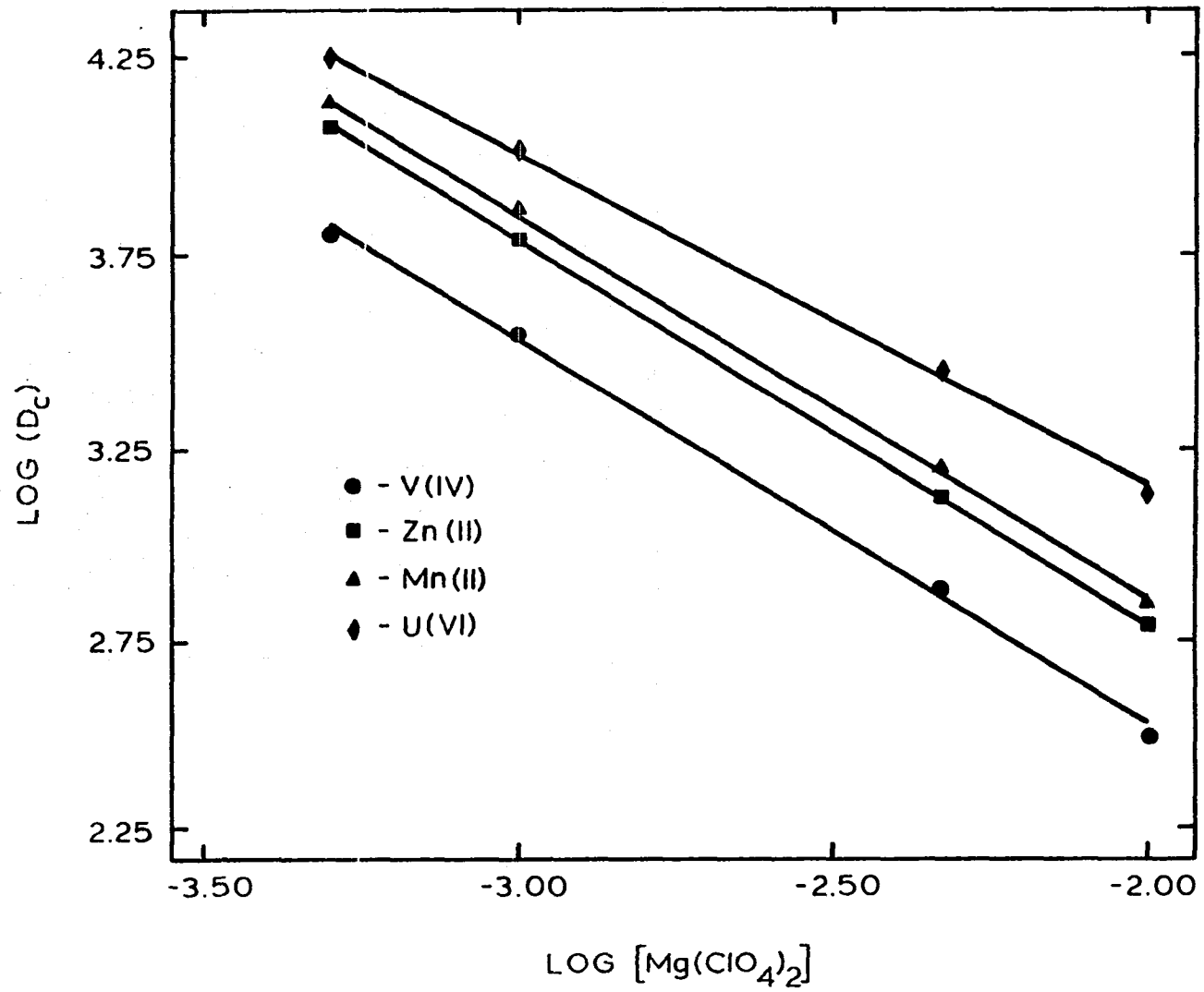
decreased slopes was given. A fully-sulfonated resin was used and it appears that the system was operated under "non-equilibrium" conditions.

Examination of the relative selectivity orders for each of the three eluents studied shows quite a few selectivity crossovers for sodium compared to magnesium and hydrogen ion. These crossovers may well be attributed to the effect of the eluent on the water structure. Hydrogen and magnesium cations actually enhance the water structure (57). The elution orders are then affected more strongly by the ability of the mobile phase to accept the eluent cations. Proof of this mechanism is a notable problem in itself since perchlorate is known to disorder the water structure even though it is of a tetrahedral configuration and supposedly should fit well into the proposed matrix of the water structure.

Modern ion chromatography of cations employs the use of diamines for elution of polyvalent cations for separation on low-capacity cation exchange columns. In light of their use, it seemed appropriate to briefly examine the relative elution behavior of such cations. Both the ethylenediammonium and p-phenylenediammonium cations were examined. Concentration distribution coefficient data are listed in Table XIX of equivalent concentrations of the two amines and magnesium. Included in the tables are values

Table XIX. Adjusted retention times (in minutes) of various cations with cationic eluents. Chromatographic conditions are described in the text

	Eluent				
Cation	$HClO_4$[a]	$NaClO_4$[b]	EnH_2^{2+}[c]	$PhenH_2^{2+}$[c]	$Mg(ClO_4)_2$[c]
Ba(II)	7611		6763	8587	
Be(II)	898	507	761		
Ca(II)	2888	2108	2322	2518	
Cd(II)	1717	1561	1776	1796	7621
Co(II)	976	1347	1434	1434	6850
Cu(II)	1542	1347	1191	1747	7641
Fe(II)	937	1727	1386	1376	6567
Hg(II)	966	1425	1337	1522	7036
Mg(II)	673	595	956	1161	
Mn(II)	976	1171	1425	1454	6763
Ni(II)	976	1171	1425	1454	7446
Pb(II)	13758	13369	9553	11710	
Sr(II)	4128	2859	3103	3513	
U(VI)	1698	3503	3015	2908	10637
V(IV)	439	459	1015	1073	3562
Zn(II)	1230	1064	1327	1405	6314
Zr(IV)	966	1308	1376	1493	6938

[a]Concentration of 0.250 M.

[b]Concentration of 0.100 M.

[c]Concentration of 1.00 mM, pH 2.5.

from comparable strengths of perchloric acid and sodium perchlorate eluents. Very similar behavior is seen for the ethylenediammonium and the p-phenylenediammonium eluents. The crossovers that do occur between the eluents are of little practical value because the peaks are situated so closely together. Of some interest is the early elution of copper with ethylenediammonium perchlorate compared to the p-phenylenediammonium perchlorate eluent. It appears that even at the low pH of the eluent (pH 2.5) some complexation of the copper may be occurring. Calculations show the amount of complexed copper to be very small so this effect was not expected and with all probability is the result of selectivity differences between eluents. Further work with other amines is being expanded by Fortier (58).

Capacity Effects

The effects of varied capacity on retention behavior were examined. Obvious trends of increased retention with increased total capacity are demonstrated by the data in Table VIII. As predicted by equation 10, the logarithm of D_c should vary in a linear fashion with the logarithm of the capacity. Linear plots with good correlation coefficients are obtained when the bulk capacity data are used. The slopes, on the other hand are two to three times lower than

the theoretical values.

Recalling the previous assumption of the density of the ionogenic groups in the resin being the same in the sulfonated layers discounts the use of measured resin capacities in terms of the bulk of the resin. In fact, the resin is sulfonated on a "layer-by-layer" basis as the reaction proceeds (50) and the capacity of the "active" volume of the resin should be the same in all cases. Of course, this assumes structural homogeneity throughout the resin bead.

Calculation of corrected distribution coefficients gave similar values of D_c for some metals with each of the resins tested in some cases. Most divalent cations demonstrated higher distribution coefficients for the resin of lowest total sulfonation followed by a sharp decrease in the distribution coefficient then a steep rise. All rare earths showed a continuous rise.

Again, the main basis of the above calculations assumed homogeneity throughout the whole of the resin bead. In the actual polymerization of m-divinylbenzene with styrene, beads are produced which have more densely crosslinked cores than outer layers. This crosslinking gradient is due to the faster polymerization of divinylbenzene over styrene (59). As described in Section I, the styrene moieties are preferentially sulfonated over the divinylbenzene groups and

because most of these sites are closer to the surface, a capacity gradient radiating outward from the core of the bead exists.

Another complication to the system is the increase of selectivity with increasing crosslinking of resins of the same total capacity (32). As the sulfonic acid groups are located further into the core of the resin bead (greater sulfonation depths), the distribution coefficients increase. Comparison of corrected distribution coefficients with superficially-sulfonated resins would show increases with increasing sulfonation depth. Variation of distribution coefficients may well account for excessive tailing of cations, especially on higher capacity surface-sulfonated resins.

Proof of this hypothesis may prove quite difficult because of the size and nature of ion-exchange resins. More exacting measures of the surface structure and bead composition are necessary to assess the impact of structural inhomogeneity of the resin beads on selectivity.

RAPID SEPARATION OF MAGNESIUM AND CALCIUM

System Optimization

The same basic system was used as previously described in the experimental part of this section. The only changes involved optimization of basic parameters for detection of magnesium and calcium.

Perchloric acid was chosen as an eluent because of the greater resolution it delivered over sodium perchlorate. A concentration of 0.85 M was chosen mostly on the merit of its resolution delivered per total separation time (expressed as resolution per unit time) as illustrated by Table XX. Even though greater resolution can be obtained with more dilute acid, it is compromised by the time taken for analysis. Lack of total resolution between magnesium and calcium is easily overcome with use of modern electronic integrators which compensate quite well for fused peaks.

A separation of magnesium and calcium using 0.75 M perchloric acid generates nearly the same resolution per unit time and the separation is only nine seconds longer. This translates to a 17 percent higher sample through-put. A distinct advantage of this system is its inherent lack of hazards allowing it to be run unattended with no real danger compared to atomic absorption analysis of magnesium(II) and

Table XX. Comparison of retention times, separation factor,
and resolution data of magnesium and calcium
peaks using perchloric acid eluent.
Chromatographic conditions are described in the
text

	Eluent Concentration (molar)					
	1.00	0.850	0.750	0.600	0.500	0.250
$t_r'(Mg)^a$	0.08	0.09	0.13	0.18	0.25	0.69
$t_r'(Ca)^a$	0.16	0.20	0.28	0.48	0.73	2.96
α_{Mg}^{Ca}	2.00	2.00	2.15	2.67	2.92	4.29
R_s	0.53	0.92	1.11	1.36	1.60	1.90
Run Time^b	0.82	0.90	1.05	1.15	1.40	3.90
R_s/minute	0.65	1.02	1.06	1.18	1.14	0.49

[a] Units of minutes.

[b] Time for elution of all peaks, in minutes.

calcium(II).

Arsenazo I was chosen as the post-column reagent because it its selectively for magnesium and calcium as demonstrated by Arguello (45). A dye concentration of 0.1% was in sufficient excess concentration to permit good color formation over a reasonable concentration range. Concentrations of magnesium and calcium in excess of the amount of color-forming reagent would exceed the limits of overloading the chromatographic column capacity and cause the system to deviate from linear elution behavior.

The post-column reagent was prepared in 3.0 M ammonium hydroxide which acts as an overpowering buffer. Over the concentrations studied (0.100 to 1.00 M perchloric acid), the effluent pH stayed within a narrow range (ca. pH 10.1 to 9.8). A strong advantage of this buffer is the precipitating or strong complexing capability it demonstrates for most metals. As a result, increased selectivity is demonstrated for magnesium and calcium which are hardly complexed at all. Figure 7 shows comparative injections of 0.200 mM magnesium and 0.200 mM calcium with responses under identical conditions for injections of aluminum(III) (20.0 mM), iron(III) (20.0 mM), and copper(II) (10.0 mM). Most metals are tolerated at moderate concentrations (up to 20 mM) (Table XXI). At higher concentrations, the metals formed precipitates after mixing

Figure 7. Comparative responses of (a) magnesium and (b) calcium (each 0.200
mM) versus (c) aluminum (20.0 mM), (d) iron(III) (20.0 mM), and (e)
copper(II) (10.0 mM) demonstrating the selectivity of post-column
detection using Arsenazo I in 3.0 M ammonium hydroxide. Eluent is
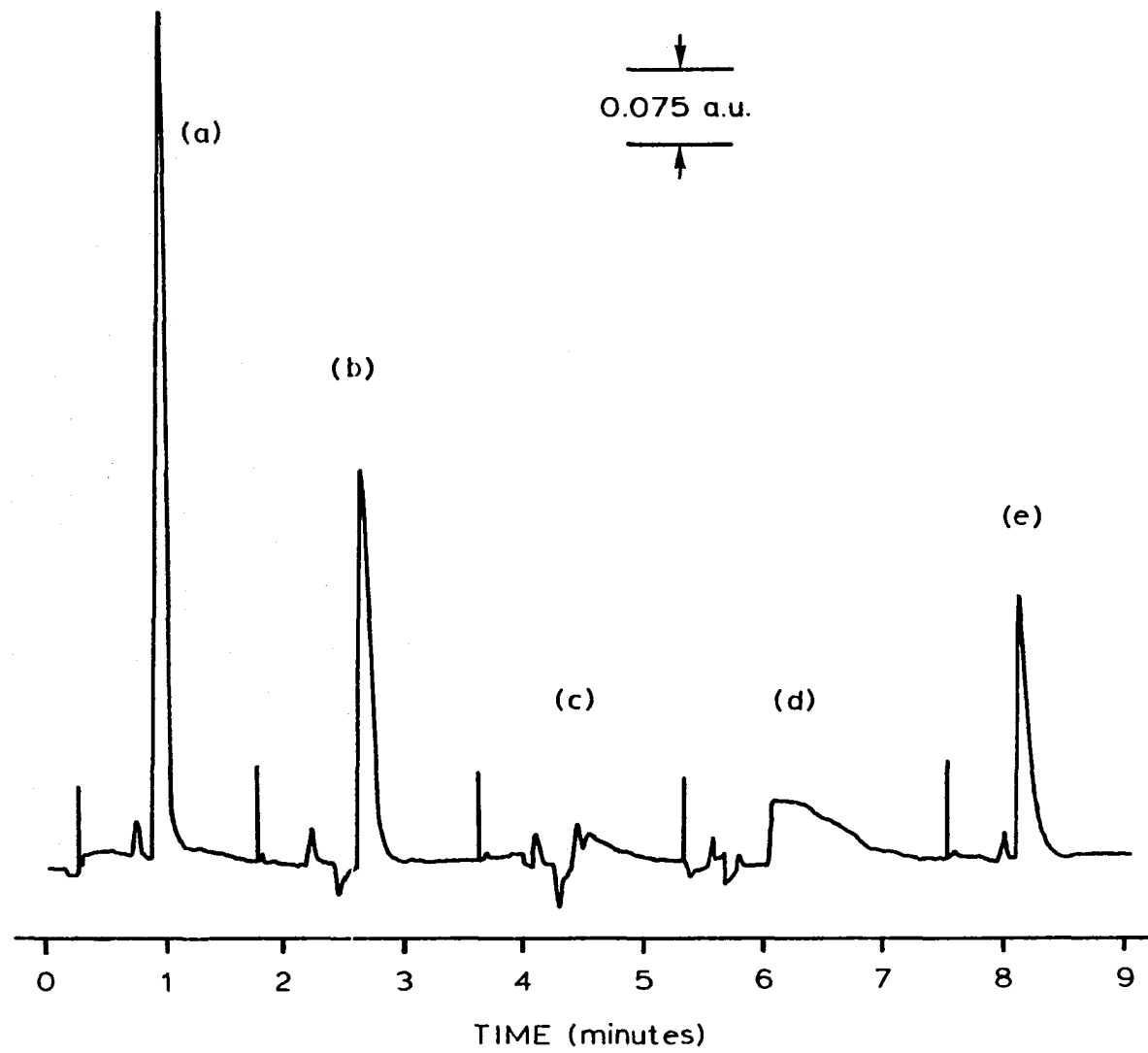0.85 M perchloric acid

Table XXI.   Maximum concentration of interfering metals
              tolerated for chromatographic analysis of
              magnesium and calcium.   Arsenazo I in 3.0 M
              ammonium hydroxide is the color-forming reagent.
              All other conditions are described in the text

Interfering Cation	Concentration (millimolar)
Cd(II)	0.20
Co(II)	0.20
Cu(II)	0.20
Mn(II)	0.20
Ni(II)	0.20
Hg(II)	2.0
V(IV)	2.0
Fe(III)	10
U(VI)	10
Al(III)	20
In(III)	20
Lu(III)	20
Mo(VI)	20
Pb(II)	20
Sb(III)	20
Sn(IV)	20
Th(IV)	20
Ti(IV)	20
Zn(II)	20
Zr(IV)	20

with the post-column reagent. This has resulted in severe perturbations in the chromatograms, the result of scattering the light in the detection cell. The flow rates were sufficiently fast enough and the detection system streamlined enough to prevent blockage of the tubing.

No real continuity seems to exist in the literature for choice of wavelength for detection of magnesium and calcium using Arsenazo I. It was therefore deemed necessary to study signal response with respect to wavelength. Replicate injections were made of magnesium and calcium for each selected wavelength. Even though maxima were obtained near 570 nm, the standard deviation of these measurements was also higher. The higher noise is due to the absorbance of free Arsenazo I. The highest signal to noise ratio was obtained at 590 nm. At 590 nm, the free Arsenazo I does not absorb and a reduction in background noise is realized.

Flow rate of the eluent was limited by the constraints of the chromatographic system, as does the flow for the post-column reagent system. Obvious trends of increased response with increased color-forming reagent were found. Pressure and wear limits of the reagent delivery system forced a compromise of 1 mL per min for the post-column reagent flow.

Results

Rapid, reproducible separations of magnesium and calcium are readily accomplished with this system. Figure 8 shows fourteen repeated injections of tap water. Reproducibility of peak areas is quite good for both magnesium ($\mp$ 1.10% RSD) and calcium ($\mp$ 2.14% RSD). The injections were made every 30 seconds so the peaks of the previous injection would be developing during the dead time of the following injection. This maneuver doubles the sample through-put with a slight increase in variability of peak area.

Good linearity of calibration curves is obtained for concentrations below 5.0 mM. Above this concentration, the peak shape and elution behavior degrade as a result of column overloading. Successive injections of 20.0, 40.0, 60.0, 80.0, and 100.0 µM in each of magnesium and calcium are illustrated in Figure 9. Correlation coefficients for calibration curves of magnesium and calcium peak heights were 0.9996 and 0.9994, respectively. Peak areas gave correlation coefficients of 0.9968 for magnesium and 0.9927 for calcium.

Analysis of an NBS standard iron ore sample was performed in duplicate and gave very good recoveries. The existence of the additional peak (Figure 10), identified as iron(III), did prolong the analysis time without causing a

notable interference in the determination. Recovery of magnesium as MgO was 3.50 $\mp$ 0.02% compared to an accepted value of 3.44%. While better results were obtained with calcium recovery (as CaO) of 2.63_5 $\mp$ 0.001% compared to the accepted value of 2.64%.

Figure 8.   Repeated injections of tap water showing reproducibility of analysis.
            Detection is by post-column reaction with Arsenazo I in 3.0 M
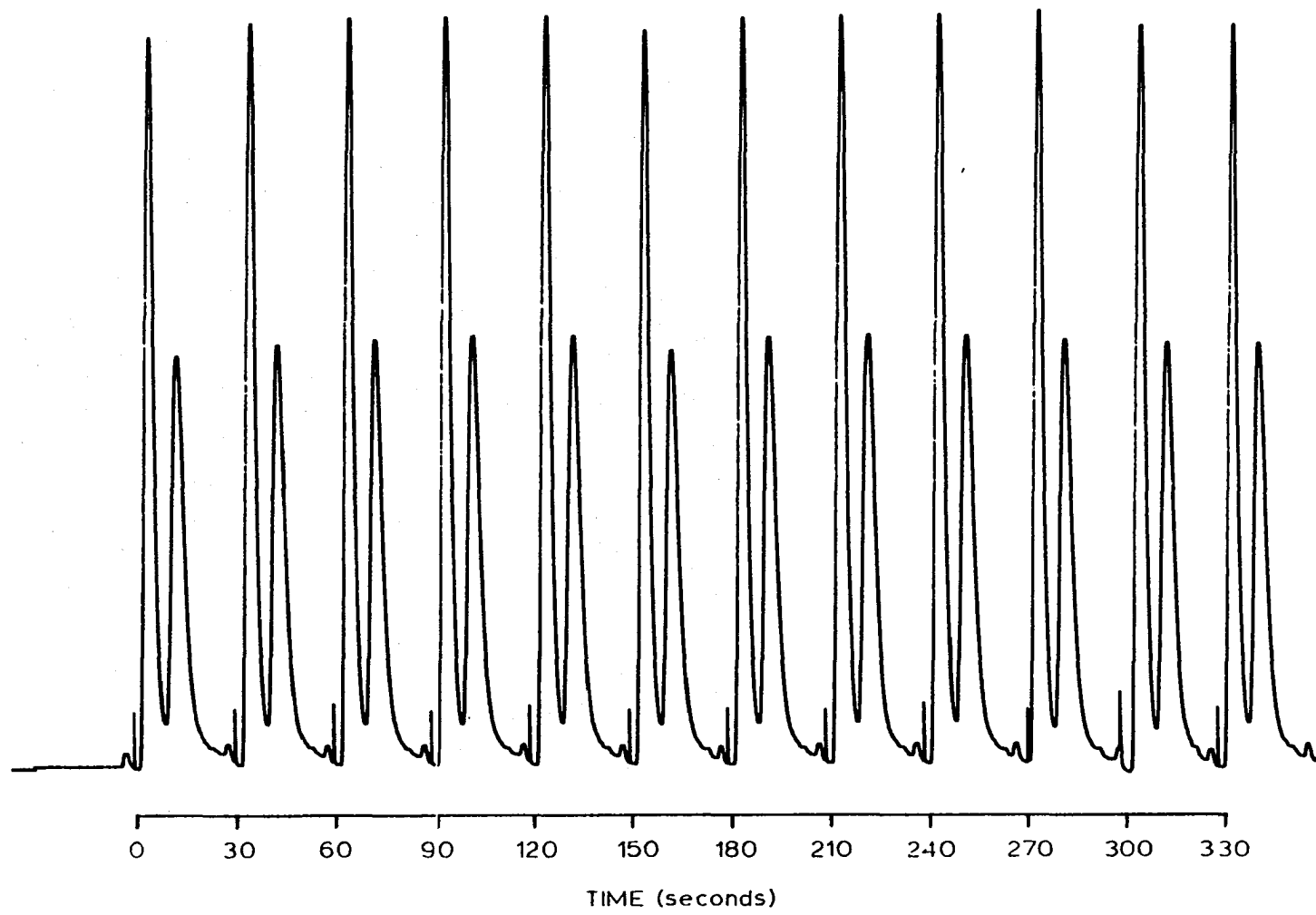   ammonium hydroxide.   Eluent is 0.85 molar perchloric acid

TIME (seconds)

Figure 9. Sucessive injections of magnesium and calcium for
a calibration curve. The injections contain
progressively 0.0, 20.0, 40.0, 60.0, 80.0, and
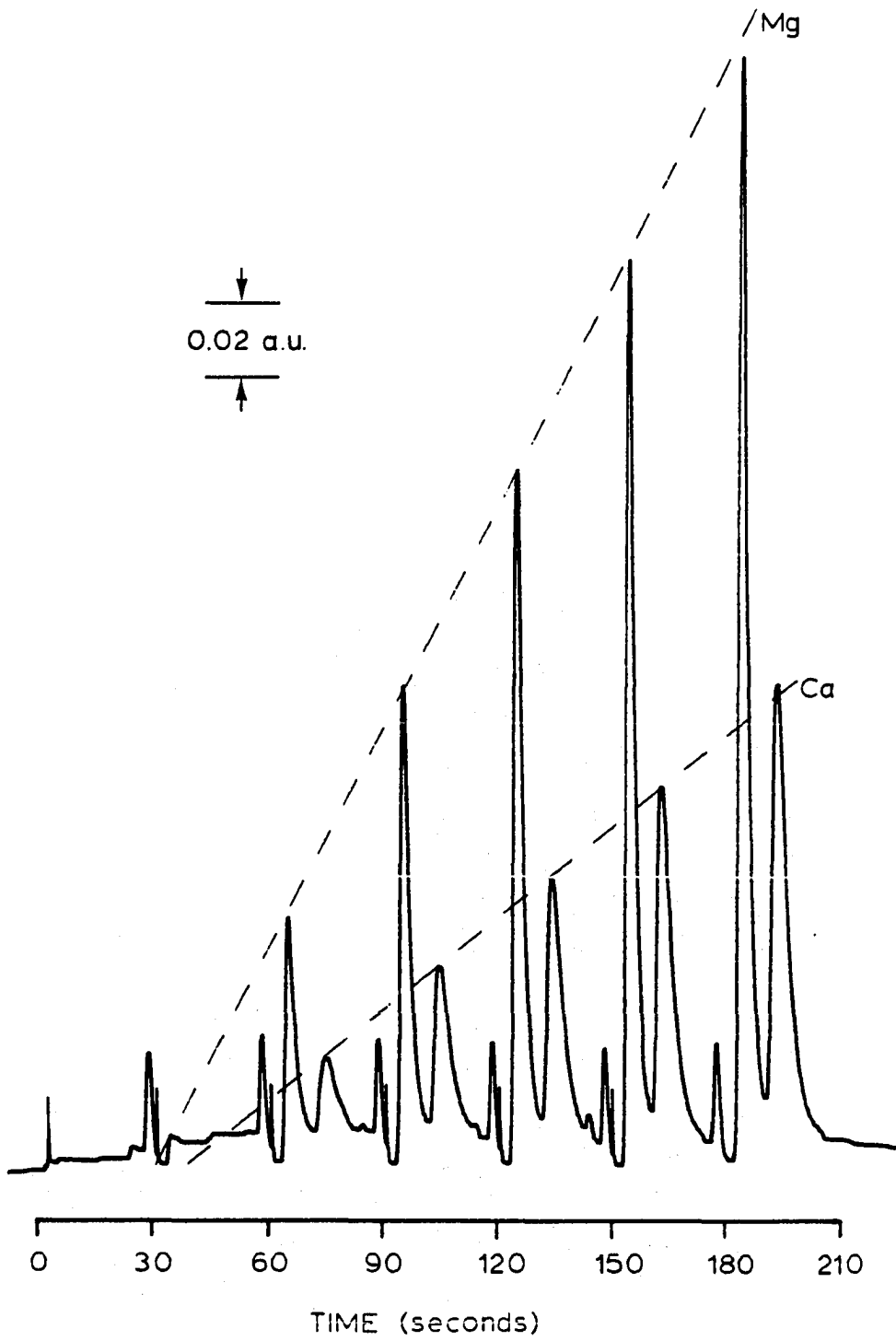100.0 μM each of magnesium(II) and calcium(II)

Figure 10. Chromatogram of NBS iron ore sample (NBS-26)
containing magnesium and calcium. Eluent is
0.85 M perchloric acid and detection by post-
column reaction with Arsenazo I in 3.0 M
ammonium hydroxide at 590 nm. Flow rate of
both separation and detection systems is 1.0
mL per minute and the bulk resin capacity is
6.1 µeq per dry gram
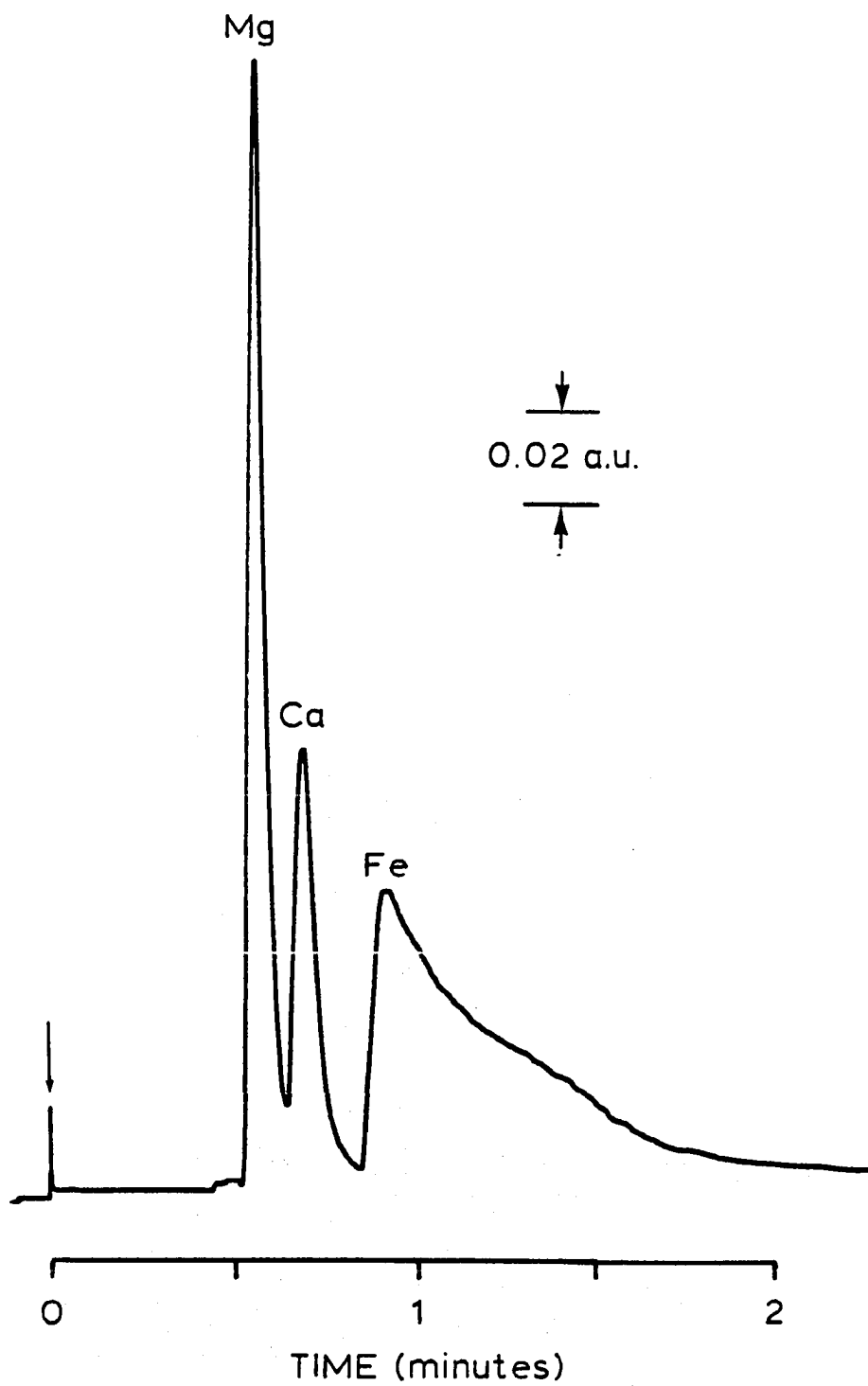
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SECTION III. COMPLEXING AGENT EFFECTS ON METAL ION
SELECTIVITY ON LOW-CAPACITY SURFACE-SULFONATED GEL RESINS

INTRODUCTION

Classical methods for the separation and determination of inorganic cations have tended to be rather time-consuming with extensive sample work-up. Determination of each metal required a specific technique or procedure which added to the amount of sample and the number of steps necessary for a complete analysis.

In 1975, Small, Stevens, and Bauman (1) devised a clever method for separation and detection of the alkali metals, alkaline earths, and a number of simple amines. The cations were separated on a lightly-sulfonated cation-exchange "separator" column by using dilute solutions of an appropriate cation for the eluent (either hydrochloric acid or m-phenylenediammonium hydrochloride). Conductivity was chosen as the mode of detection because of its universal response to all ions. The problem of an excessively high background from the eluent was greatly reduced by placing a column containing a high-capacity anion-exchange resin in-line between the separator column and the detector. As the effluent passes out the separator column and enters the suppressor column, the anions in the eluent exchange for hydroxide on the suppressor column and neutralize the acidic eluent. The analyte cations are generally not affected by the resin and pass through the suppressor column and are

detected. One severe drawback to the system is the inability to analyze many metal cations which hydrolyze and precipitate in the suppressor column.

One way to circumvent the hydrolysis problem is to select another eluent cation and design the suppressor column to selectively remove only the background eluent ions. Nordmeyer et al. (2) used lead(II) and barium(II) salt solutions as eluents and an anion-exchange suppressor column in the sulfate form. The eluent cations were precipitated in the suppressor column while the cations not precipitated as sulfates passed through the column and were detected. Even though several transition metal cations were detectable with the suppressed system, almost no mixtures could be analyzed because of poor resolution. Another problem with this system was the limited lifetime of the suppressor column (ca. 40 Hrs). Once exhausted, the column was usually discarded because it could not be economically regenerated. A similar type of cation separation system was developed using an iodate-loaded suppressor column and lead(II) as the eluent cation (3). No real advantage was obtained with the iodate-suppressed system over the sulfate suppressed system.

Another seemingly simple solution to the problem of metal cations precipitating in the hydroxide-form suppressor column is to eliminate the suppressor column completely. A

"state-of-the-art" review of ion chromatography by Pohl and Johnson (4) condemned such action and claimed detection of cations would be impossible.

In 1980, Fritz, Gjerde, and Becker (5) introduced a non-suppressed ion chromatographic system for cations. High-conducting, acidic eluents (dilute nitric acid or ethylenediammonium perchlorate at an acidic pH) were used for the separations. The analyte cations were detected by a subtractive signal of the background conductivity. Preliminary studies showed the system gave well-shaped peaks for several transition metal cations normally precipitated by a suppressor column. Work with ethylenediammonium cation eluents did not give adequate resolution between most divalent cations for mixtures of more than a few cations at a time (6).

Most transition metal cations exhibit similar selectivity behavior for cation exchange resins (7) and are normally difficult to separate. Several workers have incorporated complexing agents in forced flow cation-exchange systems to vary the effective selectivity of the cations. Takata and Muto (8) used a sodium tartrate/sodium chloride eluent for separation of transition metal cations on a cation-exchange column with coulometric detection. A very similar method was published by Girard some years later (9). Both methods are made applicable to a variety of

different cations by post-column addition of a copper(II) or mercury(II) complex of diethylenetriaminepentaacetic acid. Most metals studied displaced the copper or mercury from the complex and the freed metal was detected coulometrically.

Elchuk and Cassidy (10) used post-column color-forming reagents to detect various metal cations. Separation of the lanthanides were accomplished using α-hydroxyisobutyric acid.

The merit of conductivity detection over other forms of detection is its universality without having to adjust the detector for different cations. Incorporation of complexing agents for ion-chromatographic separation of polyvalent cations provide extended capability to the non-suppressed system. The parameters necessary to effect a useful separation and the scope of the cation chromatography system are examined in this work.

In many cases, performance of analytical techniques and instrumentation are demonstrated under ideal operating conditions using ideal samples. The real world, on the other hand, is not so generous and often presents samples laden with large amounts of interfering species. In systems where the detection system is also sensitive to the interferences, the whole chromatogram may be severely obscured and of no use.

Sample preparation by traditional methods to eliminate

these interferences prior to injection can be very time
consuming, tedious, and prone to errors due to excessive
sample handling. As a result, there is a growing need for
simple masking techniques or sample "clean-up" amenable to
automated systems.

"Clean-up" of samples containing various cations is done
quite simply on cation-exchange columns by a single-pass
method. The cations in the sample are separated into two or
more groups after passing the sample through the cation-
exchange column. The sample and eluting buffer are prepared
so some of the cations are complexed and not retained by the
ion-exchange column. The other cations are not complexed
and are taken-up by the column. The retained metal cations
may be removed by changing the eluting buffer.

Umbreit (11) separated several binary mixtures using
ethylenediaminetetraacetic acid and maintaining strict
control of pH. Fritz and Palmer (12) accomplished
separations for a notable number of binary mixtures using 5-
sulfosalicylic acid. Strelow (13) has compiled an extensive
list of data useful for separations of most metal cations
with a wide variety of systems. Other methods also exist
but are too numerous to mention here.

Preparation of a sample under the proper complexing
conditions and injection into an ion chromatograph allows
determination of various cations while masking other

interfering cations. The intent of part of this study is to describe the parameters and scope involved for single-pass separations on an ion chromatograph followed by immediate chromatographing of the retained cations.

THEORETICAL AND SYSTEM CONSIDERATIONS

Complexing Eluents

The process of ion-exchange is considered a reversible chemical reaction of sorts. The process is given by equation 1 for exchange of an eluent cation E and a metal cation M of charges x and y, respectively.

$$y\bar{E} + xM \rightleftharpoons yE + x\bar{M} \tag{1}$$

The exchange can be represented by activities in terms of a selectivity coefficient, K^{*M}_{E}.

$$K^{*M}_{E} = \frac{\{E\}^y\{\bar{M}\}^x}{\{\bar{E}\}^y\{M\}^x} \tag{2}$$

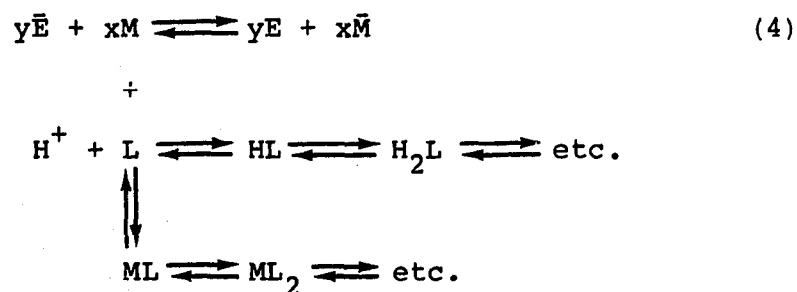The terms in braces represent the activities of the cations the barred terms represent the resin phase.

The exchange behavior can be represented in quantitative terms by equation 3.

$$\log D_c = \log K^{*M}_{E} - \frac{y}{x}\log\{E\} + \frac{y}{x}\log(Capacity/|x|) \tag{3}$$

The predictability of ion-exchange systems based on equation 1 was derived in Section II along with the basic

factors influencing ion-exchange selectivity. To avoid
redundancy they will not be discussed here. On the other
hand, altering the effective selectivity of a cation-
exchange system through the use of complexing agents will be
covered. Further derivations are made using concentrations
since the assumption that activity coefficients of ions in
solution approach unity is a good one for the conditions and
dilute solutions in this section.

The addition of a complexing ligand (L) to an ion-
exchange system shifts the exchange equilibria and in effect
alters the selectivity of the metal ion for the resin. The
ligand complexes the free metal in solution and shifts the
equilibrium away from metal take-up by the resin. This is
illustrated by equation 4.

$$y\bar{E} + xM \rightleftharpoons yE + x\bar{M} \qquad (4)$$

$$+$$

$$H^+ + L \rightleftharpoons HL \rightleftharpoons H_2L \rightleftharpoons etc.$$

$$ML \rightleftharpoons ML_2 \rightleftharpoons etc.$$

Derivations for such situations of competing equilibria
between complexing agents and ion-exchange resins are given
by Ringbom (14) and outlined here.

The total concentration of metal M in solution in all

forms (both complexed and non-complexed) is represented by [M']. The fraction of metal not complexed by ligand L is given by $\alpha_{M(L)}$. The value of $\alpha_{M(L)}$ may readily be calculated from stepwise-formation constants for the metal complex and is defined by equation 5.

$$\frac{1}{\alpha_{M(L)}} = 1 + \beta_1 [L] + \beta_2 [L]^2 + \ldots + \beta_n [L]^n \qquad (5)$$

where β_1, β_2, and β_n represent the step-wise formation constants for the metal complexes of metal M with ligand L $(\beta_n = K_{M(L)1} \times K_{M(L)2} \times \ldots \times K_{M(L)n})$. In many cases, the complexing ligand is a carboxylic acid which only acts as a ligand when when the acidic groups are deprotonated. The complexing capability of the ligand is therefore highly dependent on the pH of the solution. As with the metal cation, the amount of the free ligand capable of complexing (illustrated for a diprotic acid, H_2L) is given by

$$[L] = \alpha_{(H)L} [L'] \qquad (6)$$

where [L] is the concentration of free ligand, [L'] is the total ligand concentration in solution in all forms, and $\alpha_{(H)L}$ represents the fraction of the total ligand concentration that is present in the complexing form. For a diprotic ligand, $\alpha_{(H)L}$ can be calculated by equation 7.

$$\frac{1}{\alpha_{(H)L}} = 1 + [H^+]\frac{1}{k_2} + [H^+]^2\frac{1}{k_1 k_2} \tag{7}$$

k_n represents the nth dissociation constant of the acid.

The product of the total concentration of all forms of metal in solution [M'] and the fraction of total metal complexed $\alpha_{M(L)}$ gives the concentration of free metal present in solution ([M]).

$$[M] = [M']\ \alpha_{M(L)} \tag{8}$$

The concentration distribution coefficient for metal B may now be written as

$$D_c' = \frac{[\bar{B}]}{[B']\ \alpha_{M(L)}} \tag{9}$$

and the selectivity coefficient is given by equation (10).

$$K'^M_E = \frac{[E]^Y[\bar{M}]^X}{[\bar{E}]^Y[M']^X\alpha^X_{M(L)}} \tag{10}$$

Proceeding with the derivation gives the retention of metal ions in terms of the chromatographic parameters of the system, including the addition of a complexing agent (equation 11).

$$\log D_c' = \frac{1}{x}\log K'_E^M + \frac{y}{x}\log(\text{Capacity}/|x|)$$

$$- \frac{y}{x}\log[E] + \log\alpha_{M(L)} \qquad (11)$$

In the case of the resin used in this work, the size distribution is not well-defined and, as a consequence, the actual depth of the active layer of functionalized resin varies with bead size. This variation of functionality with bead size was shown to be important by Schmuckler and Goldstein (15). Even though much smaller beads were used in this work there is still variation in the depth of functionality from bead to bead. The complication of inhomogeneity of crosslinking was expounded upon earlier. Lack of a precise measure of the active layer of the beads or even a good estimate makes calculation of an accurate value of D_c futile.

As described in Section I, the retention time of a metal cation in an ion-exchange system can be related to the concentration distribution coefficient through equation 11. Each of the retention parameters are related by constants which correct for variations in the amount of resin present in the chromatographic column and normalize the results for ready comparison to other similar systems.

The retention of ions for a particular system can be represented by equation 12.

$$\log t_r{}' = \frac{1}{x}\log K'{}_E^M + \frac{y}{x}\log(\text{Capacity}/|x|)$$

$$- \frac{y}{x}\log[E] + \log \alpha_{M(L)} + C \qquad (12)$$

The constant (C) contains the dimensional parameters of the particular chromatographic system (flow rate, amount of resin, column dimensions, etc.). It is important to notice that the only change that occurs in equation 11 to give equation 12 is the addition of the terma constant term. If $t_r{}'$ or D_c are plotted against the log of the capacity, eluent concentration, or $\alpha_{M(L)}$ the same slope will be obtained in all cases with a change in the intercept. As discussed previously, a plot of the log of the resin capacity is not well defined for surface-sulfonated resins.

A logarithmic plot of the cation retention versus the eluent concentration is predicted to give a slope equal to the negative of the charge ratio of the metal cation and the eluent cation (equation 12). A plot of the log of the cation retention versus the log of $\alpha_{M(L)}$ should give a slope of -1.

This derivation assumes all complexes of the metal cations are either anionic or neutral and not bound by the cation exchange sites of the resin. The presence of metal complexes having a partial positive charge are known for higher valence cations. It is also assumed that no polynuclear complexes are formed.

Obviously, the strength with which a ligand binds to a metal and the conditions (ligand concentration and pH) regulate the degree of exchange the metal has with the resin. Weak metal complexation will have little effect on the exchange process. Moderate complexation will allow both the complexing and ion-exchange equilibria to work in unison affecting the overall exchange selectivity. These conditions are usually employed for forced-flow chromatographic separations where metals are continuously adsorbed and desorbed in competition with the eluent cation for the exchange sites. As the metal is released from an exchange site and enters the mobile phase, it can then form complexes with the free ligand, reducing the ability of the metal to be adsorbed to the resin. The strength of the complex will dictate how far the newly formed complex will travel down the column before the complex dissociates. Selecting the eluent for its eluting and complexing ability may promote separations that are otherwise quite difficult.

If the complex formed with the metal is very strong, then exchange of the metal by the resin may not take place at all or to such a limited extent that the metal complex would be swept through the column in the void volume. Such strong complexation by the eluent may be useful in masking certain interferences.

Sample Masking

Single-pass ion-exchange methods are designed primarily for class or group separations of certain species. The method involves placing a sample at the top of an ion-exchange column and following it with a continuous flow of a complexing buffer. The buffer is chosen to selectively elute certain metals in the void volume as unretained complexes. The other metals in the sample solution are retained by the exchange sites of the column and are not eluted. These cations are removed by using a different eluting solution. Equation 4 illustrates the effect a complexing agent has on the elution of cations in a complexing eluent. According to LeChatlier's principle, if a metal cation is complexed very strongly it may be present only as the metal complex. With no free metal present to be exchanged at the resin sites the effective distribution coefficient for that metal approaches "zero" and it is eluted in the void volume of the system. Very weakly or non-complexed metals behave almost as if there were no complexing ligand present.

Once the cations are removed from the column they are either analyzed by some other method or further separated. Much of the tedium of the separation process may be eliminated if the two methods of single-pass ion-exchange

and ion chromatography could be combined into a system which allows removal or masking of certain cations and immediate analysis of the balance of the sample with minimal sample handling. The obvious advantage would be a highly versatile system capable of analysis of a number of different sample types with limited sample preparation. Time consuming system change-overs would be eliminated.

Incorporating single-pass separation methods into an ion chromatograph is very similar to the classical methods and yet imposes some unique demands on the system, a result of the conductivity detector. The main restriction imposed on masking samples in cation chromatography is the universal response of the conductivity detector. Because the detector is so sensitive to the background conductance of the eluent, gradients and changes of eluent are not readily accomplished without some necessary equilibration time (about 30 minutes or more). The basic system must be set-up for optimum isocratic elution of the retained metal ions. The conditions of masking are designed to permit complete removal of the interferent and must allow for rapid recovery of the baseline after injection.

When the sample is injected into the chromatograph, it is introduced as a "plug" of solution into the eluent stream with some mixing at either end. As the sample plug enters the separator column, non-complexed sample cations are

taken-up as a tight band at the top of the column. It is important to note that the sample plug is followed immediately by the eluent solution. So, the masking capability of the cations is lost outside the volume of injected sample solution.

Several requirements of the complexing agent are essential to make the single-pass method of masking work successfully in the ion chromatographic system. In general, complexing agents should form strong complexes of known composition with metals of interest over a reasonable pH range near that of the eluent pH. Samples with a pH significantly different or of a much higher ionic content than the eluent can cause disturbances in the equilibrium of the system more severe than the interfering cation.

The complex or complexing agent should not adsorb onto the resin matrix because this only prevents rapid elution of the masked cations and prolongs the time needed to reequilibrate the system. The kinetics of complex formation would be ideal if formation of the complexes was very rapid. This allows sample injection soon after sample preparation. Also, slow dissociation of the complex is preferred. This greatly reduces the chance of the complex breaking up and the interfering cation being taken up by the resin as the sample "plug" is eluted through the column.

Prediction of which metals might be masked and the

conditions of masking is relatively simple and involves only enough assumptions to permit a general picture of the system. Exacting calculations prove more tedious than useful. Approximate calculations are made by determining the conditions under which the metal to be masked is essentially all complexed (> 99%). These simple calculations along with a more rigorous treatment of the system are outlined by Ringbom (14).

EXPERIMENTAL

Apparatus

The instrument used in this work was constructed in a modular fashion from individual components. The pump was a model 396 Milton Roy Singlex pump (Riviera Beach, FL). The flow rate for all work was 0.85 mL per minute unless otherwise specified. The injector was a Rheodyne model 7010 injector (Rainin Instrument Co., Woburn, MA) with interchangeable sample loops (100-, 50-, and 20-μL). A pressure gauge (0-5000 psig) and coil-type pulse dampener (LiChroma Damp, Norristown, PA) were placed off-line in a parallel configuration between the pump and injector. The detector was a model 213 conductivity detector from Wescan Instrument Co. (Santa Clara, CA) with a 2-μL flow through detector cell. All fittings in contact with the eluent were either glass, Teflon, Kel-F, or 316 stainless steel.

Chromatographic columns were constructed of thick-walled glass and measured 35 cm long with a 2 mm i.d. (Rainin Instrument Co.). The ion-exchange resin was a surface-sulfonated gel-type resin having a bulk cation exchange capacity of 0.059 meq per dry gram. The average bead size of the resin was 20 μm, with a range of particle sizes from about 5 to 30 μm. The cation-exchange material was obtained

by special order from the Benson Co. (Reno, NE).

The separator columns were packed by a stirred slurry, upward packing method as described by Barron (16). The resin was packed in an aqueous solution of ethylene glycol (45% v/v) at about 2000 psig. After packing, the column was rinsed by pumping distilled-deionized water through the column. Additional resin was added to the top of the column as necessary. At least one hour of equilibration time with the eluent was allowed before use. The chromatographic column, detector electronics, flow cell, and eluent were all located in styrofoam lined enclosures to minimize temperature effects. All chromatograms were obtained at room temperature (ca. 23°C).

Reagents

Reagent grade ethylenediamine (stored under a nitrogen atmosphere) was used after redistillation. Tartaric acid, oxalic acid, citric acid, 5-sulfosalicylic acid, atrolactic acid, ethylenediaminetetraacetic acid, nitrilotriacetic acid, and α-hydroxyisobutyric acid were reagent grade (at least 99% pure) and used as received.

Metal Ion Solutions

All metal solutions were prepared from highest purity reagent grade salts or metals available. An appropriate amount of perchloric acid was added to the solutions to prevent hydrolysis. Distilled-deionized water was used for dissolving and dilution of all solutions.

Rare Earths solutions were prepared from the oxides obtained in purity of at least 99.99% (Dr. J. E. Powell, Ames Laboratory, Ames, IA). Dissolution of each oxide was with the appropriate acid.

The metal stock solutions, typically 0.200 to 0.020 M, were kept at appropriately low pH values with perchloric acid to prevent hydrolysis. Retention times were measured from injections of 1.0 mM metal solutions. Enough perchloric acid was added to each solution to prevent hydrolysis.

Eluent Preparation

Eluents were prepared by dissolution of the appropriate reagents in distilled-deionized water and adjusting the pH to near the final desired value. The solution was then diluted to volume, mixed thoroughly, and the pH adjusted to the final desired value. Relatively concentrated solutions

of perchloric acid or sodium hydroxide were used for pH
adjustment of the eluents to minimize dilution of the
eluent. Each eluent was filtered through a 0.45 μm membrane
filter and degassed under suction prior to use.

Preparation of Masked Samples

Samples were prepared by mixing appropriate amounts of
metal ions to be determined and interfering metal ion
solutions. Enough excess complexing agent was added to the
sample to completely mask the interfering metal ions. The
pH of the solution was monitored and adjusted to near the
final desired value. After dilution and mixing, the pH of
the sample solution was checked to make sure it was in the
desired range for optimum masking.

The use of buffers in the sample solutions to control pH
was examined briefly and deemed not necessary. In most
cases, the complexing agent provided sufficient buffering
capability. The use of buffers added to the total ionic
content of the sample and caused a slightly longer recovery
of the baseline after injection of the masked sample.

RESULTS AND DISCUSSION

Complexing Eluents

The system used in this work was similar to that
previously described for the separation of alkali metals and
alkaline earth cations on a low-capacity cation-exchange
resin (5). Better separations were obtained with a resin of
a somewhat higher capacity (0.059 meq per gram).

The use of conductivity as the detection method posed a
series of constraints on the separation system. Aqueous
solutions generally exhibit a 2% change in total
conductivity with each degree change (Celcius) in
temperature (17). The eluents used here are relatively high
conducting to begin with and are subject to significant
background noise unless adequate care is taken to thermally
insulate and stabilize the system. Despite the broad range
of "noise suppression" accessible by the detector, a lower
pH limit was set at about 3.0. At more acidic pH values,
much of the complexing strength of the eluent is lost and
the sensitivity of the system is significantly lower as a
result of the higher background and noise associated with
it. A practical upper pH limit of 5.0 was established
because the ethylenediammonium cation is incompletely
protonated and starts losing its strength as an eluent

cation (Table I). At the same time, the ethylenediamine gains complexing strength and the eluent behaves unpredictably.

The behavior of a number of cations were studied with this system. Well-shaped peaks were obtained for the following metal cations: barium(II), beryllium(II), calcium(II), cadmium(II), cobalt(II), iron(II), magnesium(II), manganese(II), nickel(II), lead(II), strontium(II), and the trivalent rare earth cations with the exception of promethium which was not tested (for obvious reasons). Other metal cations did not give peaks because of hydrolysis (tin(IV) and antimony(III)), very early elution in the void volume (aluminum(III), copper(II), mercury(II), zirconium(IV), uranium(VI), vanadium(IV), and silver(I)) or very late elution (thorium(IV)).

The eluent composition was varied to examine the effect of each on the elution of the above cations. The parameters varied included: a) eluent cation concentration, b) complexing agent concentration, and c) eluent pH. It is intuitively obvious that increasing each parameter will shift the equilibrium shown in equation 4 to favor less free metal cation in solution to be taken up by the exchange sites of the resin. This results in faster elution of the metal.

Tables II and III clearly depict the trend of increasing

Table I. Relative percentage of all ethylenediamine species as a function of pH

pH	% enH_2^{2+}	% enH^{1+}	% en
3.00	99.99	0.01	(8×10^{-10})
3.50	99.97	0.03	(8×10^{-9})
4.00	99.91	0.09	(8×10^{-8})
4.50	99.73	0.27	(8×10^{-7})
5.00	99.12	0.88	(8×10^{-6})
5.50	97.38	2.27	(8×10^{-5})
6.00	95.24	4.76	(8×10^{-4})

Table II. Adjusted retention times (in minutes) of various cations with varied ethylenediammonium cation concentration. All eluents are 2.00 mM in tartaric acid at pH 4.50. Chromatographic conditions as described in the text

| Cation | Ethylenediammonium Concentration (millimolar) | | | | |
	1.00	2.00	3.00	4.00	5.00
Mg(II)	5.28	2.86	2.02	1.43	1.27
Ca(II)	11.6	6.10	4.33	3.20	2.82
Sr(II)	19.9	10.3	7.21	5.36	4.56
Ba(II)	55.7	29.6	19.9	15.5	12.7
Zn(II)	3.56	2.00	1.46	1.14	1.06
Ni(II)	4.22	2.37	1.72	1.40	1.21
Co(II)	5.22	2.86	2.03	1.59	1.40
Fe(II)	6.32	3.32	2.37	1.76	1.55
Mn(II)	7.32	3.83	2.73	1.99	1.77
Cd(II)	8.39	4.47	3.21	2.41	2.11
Pb(II)	12.4	7.78	5.69	5.05	4.15

Table III.   Adjusted retention times (in minutes) of various
             cations with varied ethylenediammonium cation
             concentration. All eluents are 2.00 mM in
             tartaric acid at pH 4.50. Chromatographic
             conditions as described in the text

Cation	Ethylenediammonium Concentration (millimolar)				
	1.00	2.00	3.00	4.00	5.00
Lu(III)	5.37	2.65	1.51	1.33	1.30
Yb(III)	6.10	2.96	1.62	1.42	1.37
Tm(III)	7.86	3.74	2.24	1.73	1.65
Er(III)	10.2	4.66	2.75	2.43	2.02
Ho(III)	12.0	5.62	3.27	2.73	2.38
Dy(III)	13.3	6.14	3.67	3.12	2.61
Tb(III)	14.2	6.64	4.26	3.70	2.93
Gd(III)	14.5	6.75	4.02	3.26	2.87
Eu(III)	13.8	6.29	3.70	3.15	2.69
Sm(III)	13.84	6.54	3.90	3.30	2.78
Nd(III)	20.4	9.34	5.47	4.41	3.86
Pr(III)	26.6	12.4	7.11	5.66	5.00
Ce(III)	42.3	18.6	10.6	7.57	7.41
La(III)	74.9	33.7	18.7	15.0	12.7

retention of the metal cations for increasing

ethylenediammonium cation concentration. The tartrate

concentration (2.0 mM) and pH (4.50) were held constant.

The ethylenediammonum concentration was varied from 1.0 mM

to 5.0 mM. A proportionate decrease in retention time with

increasing concentration of the eluent cation is seen for

the divalent cations and the same basic trend for the rare

earth cations.

Equation 11 predicts the slope for plots of the log of

the retention time versus the log of the eluent

concentration should be -1 for the divalents, while that for

the trivalents should be -1.5. The data are plotted in

Figures 1 and 2. Experimentally obtained slopes for

divalent cations are around 10% less than those predicted.

For the rare earth cations, the slopes are between about

-1.0 to -1.1. These data suggest the metals are acting as

cations of reduced charge.

It had been assumed in the derivation of equation 11

describing the retention behavior of cations in the presence

of complexing eluents that only free cations would bind with

the ion-exchange sites of the resins. In fact, the

adsorption of complexes on chromatographic supports is known

and has been used for separation of metal complexes (18).

The actual interactions which are instumental in adsorption

of complexes by the ion-exchange resin are described quite

Figure 1. Linear regression analysis plots of log adjusted
            retention time versus log eluent cation
            concentration for several divalent cations. Each
            eluent contains 2.00 mM tartaric acid and is at
            pH 4.50. Ethylenediammonium cation is varied
            from 1.00 to 5.00 mM. Specific chromatographic
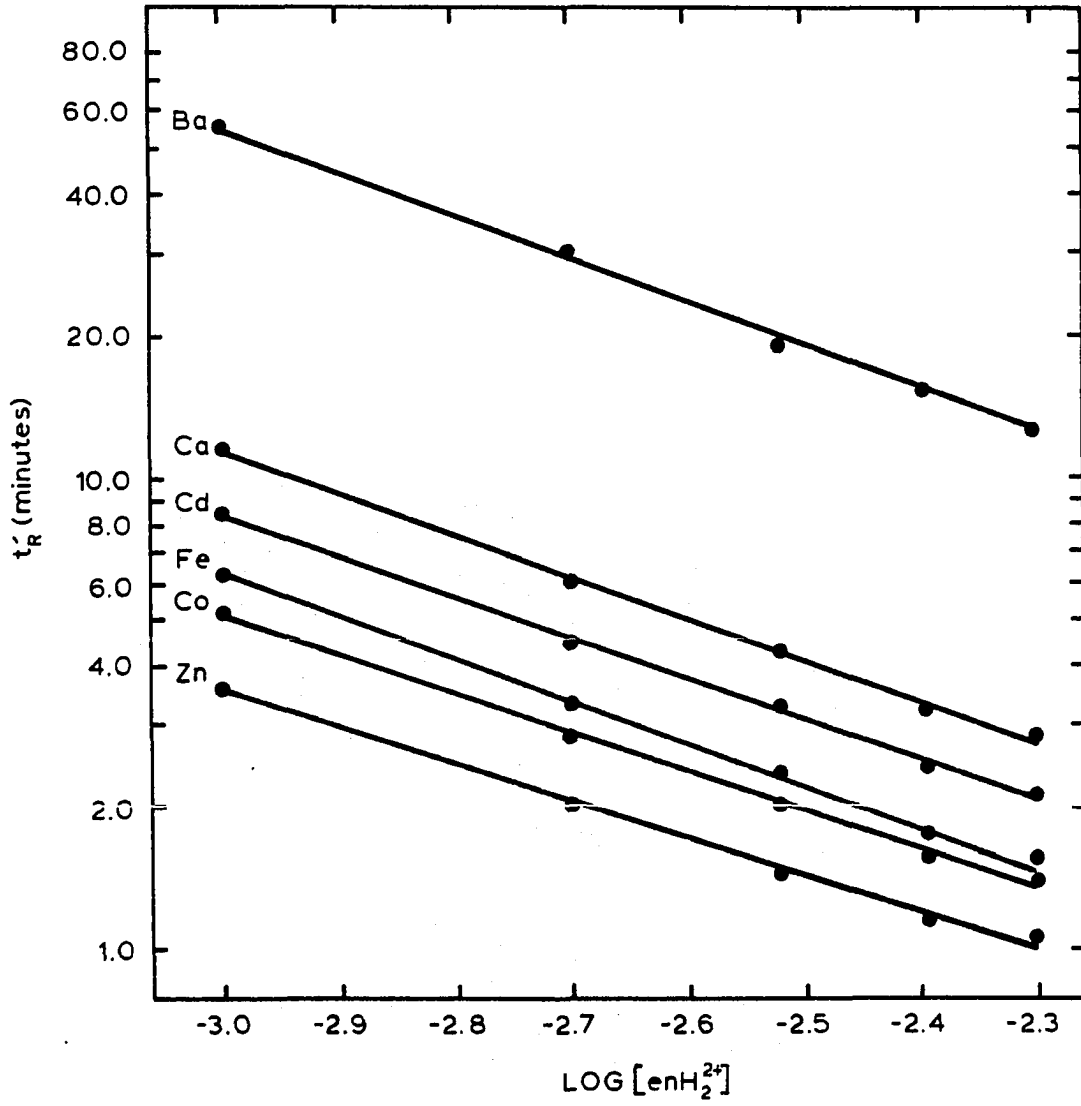   conditions are in the text

Figure 2. Linear regression analysis plots of log adjusted
          retention time versus log eluent cation
          concentration for several rare earth cations.
          The dashed lines represent a "dot-to-dot"
          estimate of the actual trend of the data points.
          Each eluent contains 2.00 mM tartaric acid and is
          at pH 4.50. Ethylenediammonium cation is varied
          from 1.00 to 5.00 mM. Specific chromatographic
          conditions are in the text
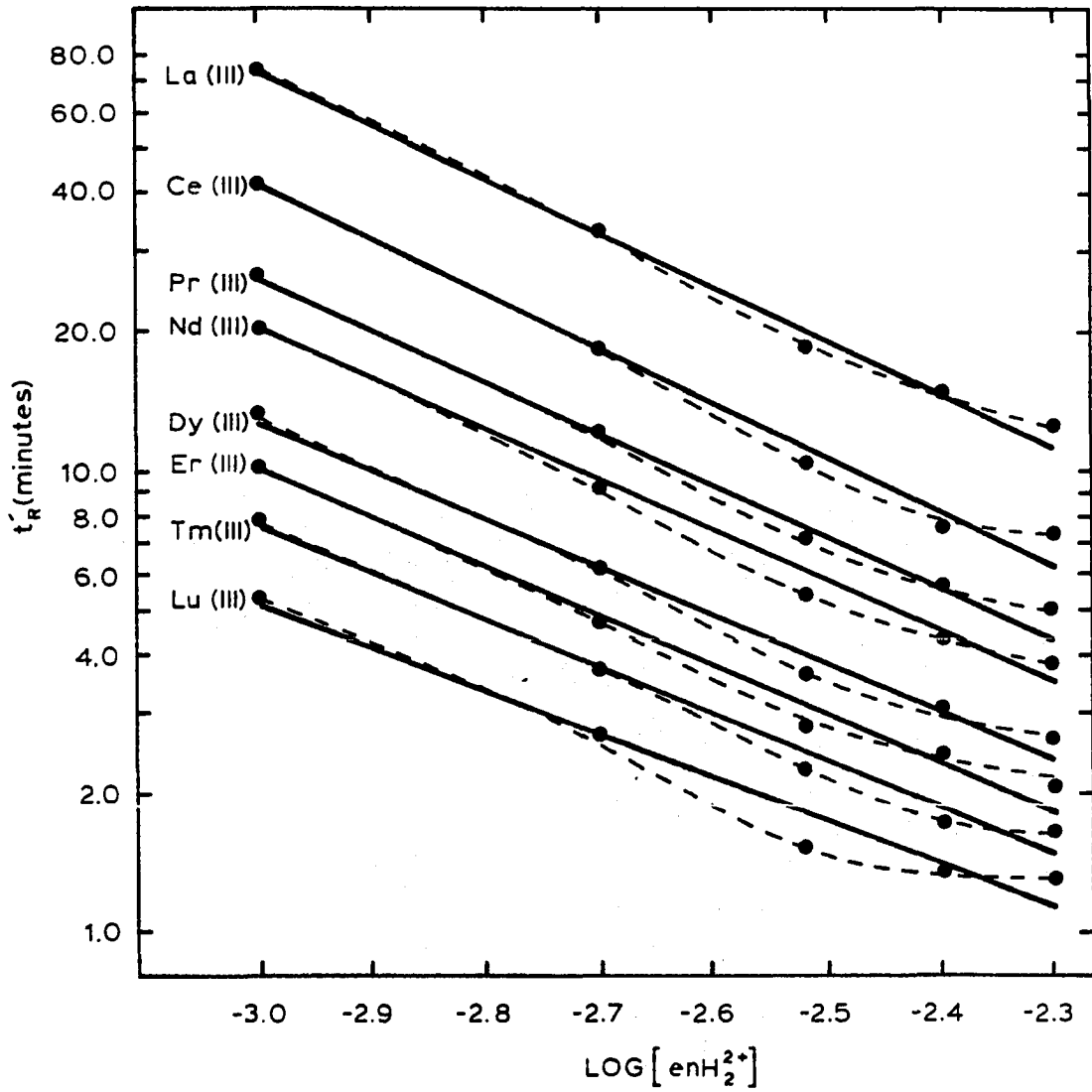
well by Diamond and Whitney (19). The effect this phenomenon has on the system is an increased retention of the metal as an ion-pair. Adsorption onto the hydrophobic part of the resin matrix or penetration into the inert core of the resin bead is suspected. An effective decrease in eluent strength from what is expected is observed with increased eluent cation concentration. This effect appears as a slight leveling of the line. If the neutral complex is retained strongly enough, there will be a minimum retention of the cation, even when the eluent concentration is high enough to supposedly prevent any interaction at all between the resin and the free metal cation.

Additional complications arise because the partly protonated ligand (i.e., HL^-) has been shown to form stable complexes with divalent cations (e.g., Cu, Mg, Ca, Sr, Ba, Ni, and Pb) of the type MHL^+. Lanthanum and bismuth also form complexes with the partly protonated tartrate ligand (MHL^{2+}) (20,21,22). Derivations by Helfferich (23) show the resin phase prefers metal complexes of lower ligand number. Ligands may therefore be stripped from the metal to give a complex having fewer ligands and a reduced positive charge. Thus, more metal may be present in the resin phase than first assumed from calculations from existing data.

The existence of metal complexes of reduced positive charge and their ability to penetrate the resin matrix helps

to account for the reduced slope seen for several cations in Table IV.

These additional modes of metal ion adsorption complicate the ion-exchange expression significantly. The distribution ratio of the neutral and the reduced charge complexes is not known nor is it readily measured because of competing equilibria with each other and the presence of free metal cations in the resin. The values of retention time do show somewhat reasonable correlation to theory for the limited range of eluent composition studied.

Effects of the complexing ligand on the retention of the cations were studied in a similar manner. The concentration of the complexing tartrate was varied over a range of 0.0 to 5.0 mM. The ethylenediammonium cation concentration was held constant at 2.0 mM and the pH was adjusted to 4.50 for each eluent. Retention times are listed in Tables V and VI. Significant changes are seen in the retention times of metals strongly complexed by tartrate between eluents 0.0 and 1.0 mM in tartrate. The rare earth cations are prime examples, where the retention times of each cation are cut by more than half. Iron (III) was found to elute quite late with this system when no tartrate was present in the eluent. Addition of tartrate, on the other hand, draws the iron(III) right through the system in the dead volume. Very little change is seen in the retention of alkaline earths

Table IV. Linear regression data from plots of log adjusted retention time versus log ethylenediammonium cation concentration. Eluent is 2.00 mM in tartaric acid with the pH at 4.50. Ethylenediammonium cation concentration is varied from 1.00 to 5.00 mM. Chromatographic conditions are in the text

Cation	Slope	r	Cation	Slope	r
Lu(III)	-0.938	-0.980	Mg(II)	-0.905	-0.998
Yb(III)	-0.987	-0.981	Ca(II)	-0.893	-0.999
Tm(III)	-1.02	-0.992	Sr(II)	-0.924	-1.000
Er(III)	-1.02	-0.992	Ba(II)	-0.925	-1.000
Ho(III)	-1.04	-0.993			
Dy(III)	-1.03	-0.994	Cd(II)	-0.869	-0.999
Tb(III)	-0.974	-0.995	Co(II)	-0.831	-0.999
Gd(III)	-1.04	-0.994	Fe(II)	-0.887	-0.999
Eu(III)	-1.04	-0.993	Mn(II)	-0.899	-0.999
Sm(III)	-1.02	-0.994	Ni(II)	-0.781	-0.999
Nd(III)	-1.07	-0.994	Pb(II)	-0.670	-0.998
Pr(III)	-1.08	-0.994	Zn(II)	-0.775	-0.997
Ce(III)	-1.15	-0.991			
La(III)	-1.13	-0.995			

Table V. Adjusted retention times (in minutes) of various cations for eluents of varied tartaric acid concentration. All eluents are at pH 4.50 and 2.00 mM in ethylenediammonium cation. Chromatographic conditions are described in the text

Cation	Tartaric Acid Concentration (millimolar)					
	0.00	1.00	2.00	3.00	4.00	5.00
Mg(II)	2.84	2.88	2.85	2.80	2.90	2.82
Ca(II)	7.17	6.75	6.10	5.56	5.50	5.13
Sr(II)	11.3	11.0	10.3	9.65	9.59	9.12
Ba(II)	31.1	31.6	29.6	26.9	26.5	25.3
Zn(II)	3.05	2.61	2.00	1.64	1.51	1.43
Co(II)	3.57	3.34	2.86	2.49	2.34	2.17
Fe(II)	3.71	3.56	3.32	3.01	2.91	2.76
Ni(II)	3.37	2.97	2.37	1.97	1.78	1.63
Mn(II)	4.07	3.99	3.83	3.69	3.65	3.51
Cd(II)	5.05	4.93	4.47	4.04	3.95	3.67
Pb(II)	19.0	12.7	7.78	5.66	4.90	4.14

Table VI. Adjusted retention times (in minutes) of rare earth cations for eluents of varied tartaric acid concentration. All eluents are at pH 4.50 and 2.00 mM in ethylenediammonium cation. Chromatographic conditions are described in the text

	Tartaric Acid Concentration (millimolar)					
Cation	0.00	1.00	2.00	3.00	4.00	5.00
Lu(III)	15.9	5.98	2.65	1.66	1.31	1.08
Yb(III)	17.3	6.52	2.96	1.84	1.42	1.14
Tm(III)	21.2	8.15	3.74	2.27	1.79	1.40
Er(III)	25.5	9.93	4.66	2.86	2.19	1.73
Ho(III)	33.3	12.1	5.62	3.38	2.55	2.02
Dy(III)	37.0	13.5	6.14	3.63	2.82	2.18
Tb(III)	-	15.7	6.64	4.07	2.97	2.33
Gd(III)	38.4	15.1	6.75	3.96	2.98	2.29
Eu(III)	36.1	14.1	6.29	3.67	2.75	2.14
Sm(III)	36.4	14.0	6.54	3.81	2.84	2.23
Nd(III)	50.4	20.6	9.34	5.51	4.29	3.30
Pr(III)	-	25.73	12.4	7.43	5.85	4.45
Ce(III)	-	38.1	18.6	11.5	8.78	6.85
La(III)	-	67.6	33.7	21.1	16.4	12.8

especially in the case of magnesium(II) which shows no real

variation in retention time except of experimental error.

As predicted by equation 11, the log of t_r' plotted

against the log of $\alpha_{M(L)}$ should give a slope of -1. The

linear regression data for the cations studied is listed in

Table VII. Regression analysis data could not be obtained

for cerium(III) and cadmium(II) because formation constants

of these metals with tartrate could not be found. The

retention of magnesium(II) was essentially independent of

the tartrate concentration at pH 4.50. Magnesium(II) is

very weakly complexed by tartrate and is expected to show

almost no variation with ligand concentration.

The plots of log t_r' versus $\alpha_{M(L)}$ for several rare earth

cations are illustrated in Figure 3. The data for the rest

of the rare earth cations is quite similar. Interpretation

of the divalent cation data are quite difficult as a result

of discontinuity between formation constants in the

literature. One compilation of formation constants lists

two values of K_1 for nickel(II) that differ by almost two

orders of magnitude (22). Conditions under which the

constants were determined were nearly identical.

Because of the variations of the formation constants,

only speculation may account for some of the trends. Of

more use is the adjusted retention time of the cations

plotted as a function of tartrate concentration at constant

Table VII. Linear regression data from plots of log adjusted retention time versus log $\alpha_{(M)L}$ for metal cations. Eluent is 2.00 mM in ethylenediammonium cation with pH at 4.50. Tartaric acid concentration is varied from 1.00 to 5.00 mM. Chromatographic conditions are in the text

Cation	Slope	r	Cation	Slope	r
Lu(III)	1.12	0.997	Ca(II)	1.97	0.974
Yb(III)	1.14	0.999	Sr(II)	1.88	0.973
Tm(III)	1.16	0.998	Ba(II)	2.53	0.974
Er(III)	1.16	0.999			
Ho(III)	1.19	0.999	Co(II)	1.52	0.988
Dy(III)	1.21	0.998	Fe(II)	0.897	0.992
Tb(III)	1.28	0.999	Mn(II)	0.252	0.973
Gd(III)	1.25	0.999	Ni(II)	2.73	0.985
Eu(III)	1.23	0.999	Pb(II)	1.12	0.993
Sm(III)	1.21	0.999	Zn(II)	0.986	0.978
Nd(III)	1.20	0.999			
Pr(III)	1.17	0.999			
La(III)	1.19	0.999			

Figure 3.   Linear regression analysis plots of log adjusted
            retention time versus log of fraction of
            uncomplexed rare earth cation.   Eluent contains
            2.00 mM ethylenediammonium cation with pH
            adjusted to 4.50.   The tartaric acid
            concentration is varied from 1.00 to 5.00 mM.
            Specific chromatographic conditions are described
            in the text
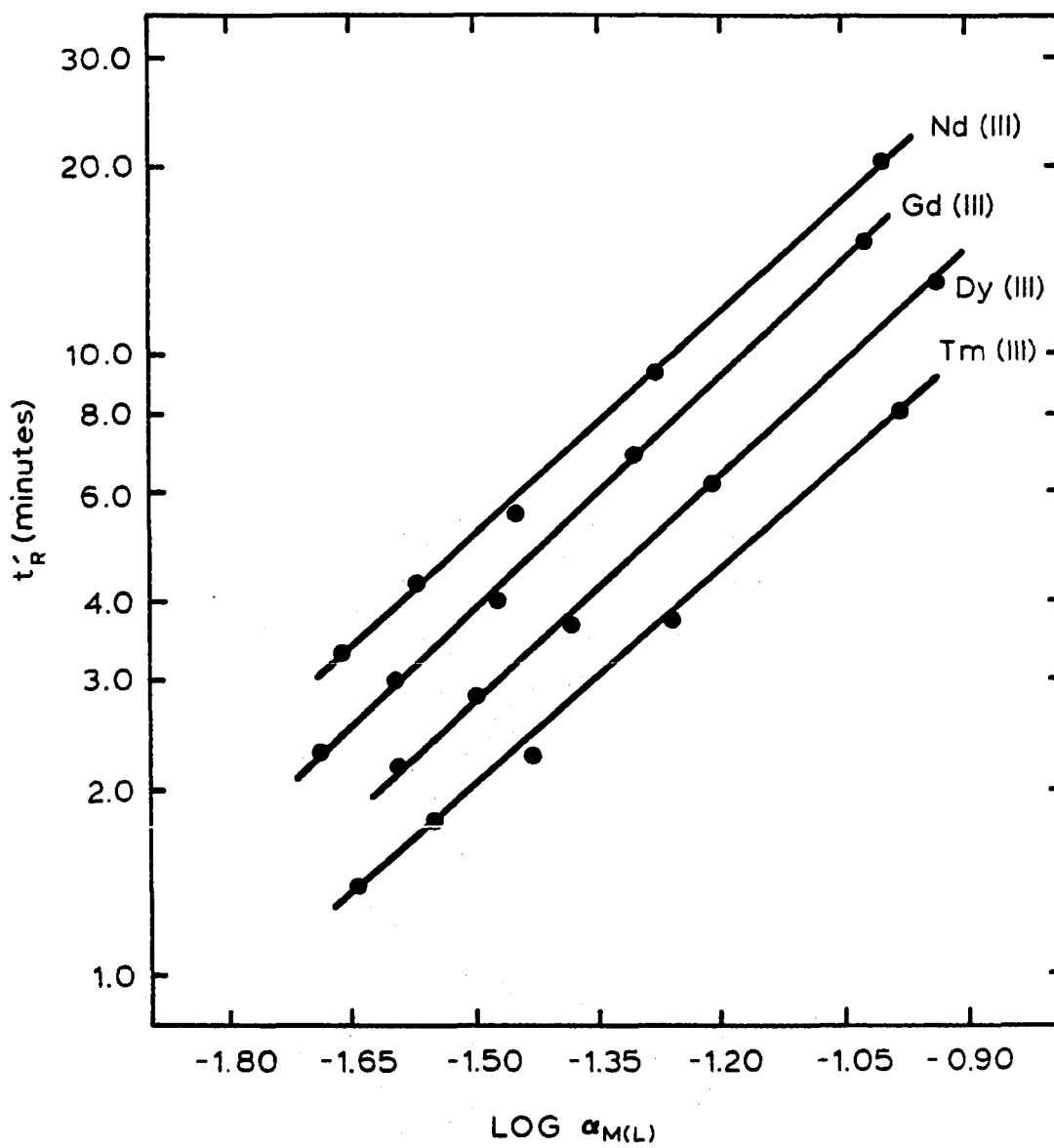
pH (Figure 4). The changes in effective selectivity are quite pronounced for the lanthanides as represented by lutetium(III) and cerium(III). The weak complexation of the alkaline earths by tartrate is well illustrated, as is the stronger complexation of lead. The effect of complexation on the transition metals is not as drastic as with lead. These metals are grouped around magnesium(II) and calcium(II).

The eluent pH is one of the more sensitive parameters of complexing eluents that can be adjusted. The eluent pH was varied from 3.0 to 6.0 for eluent solutions 2.0 mM in ethylenediammonium cation and 2.0 mM in tartrate. Adjusted retention times decreased with increasing pH up to about 5.0. This trend is expected because more tartrate is available to complex at the higher eluent pHs. The adjusted retention times increased for most cations above pH 5.0. The reversal of retention times is due to incomplete protonation of the ethylenediamine at more basic pH values (Tables VIII and IX).

In varying the pH while holding all other parameters constant, the only term in equation 11 that should be affected is $\alpha_{M(L)}$. Lines obtained for varied pH should all be about +1. Linear regression analysis for available points from pH 3.0 to 5.0 are listed in Table X. Calculations of $\alpha_{M(L)}$ show most divalent cations are about

Figure 4. Plot of adjusted retention time versus tartaric
acid concentration (varied from 1.00 to 5.00 mM).
Ethylenediammonium cation concentration is
constant at 2.00 mM and pH is 4.50. Specific
chromatographic conditions are described in the
text
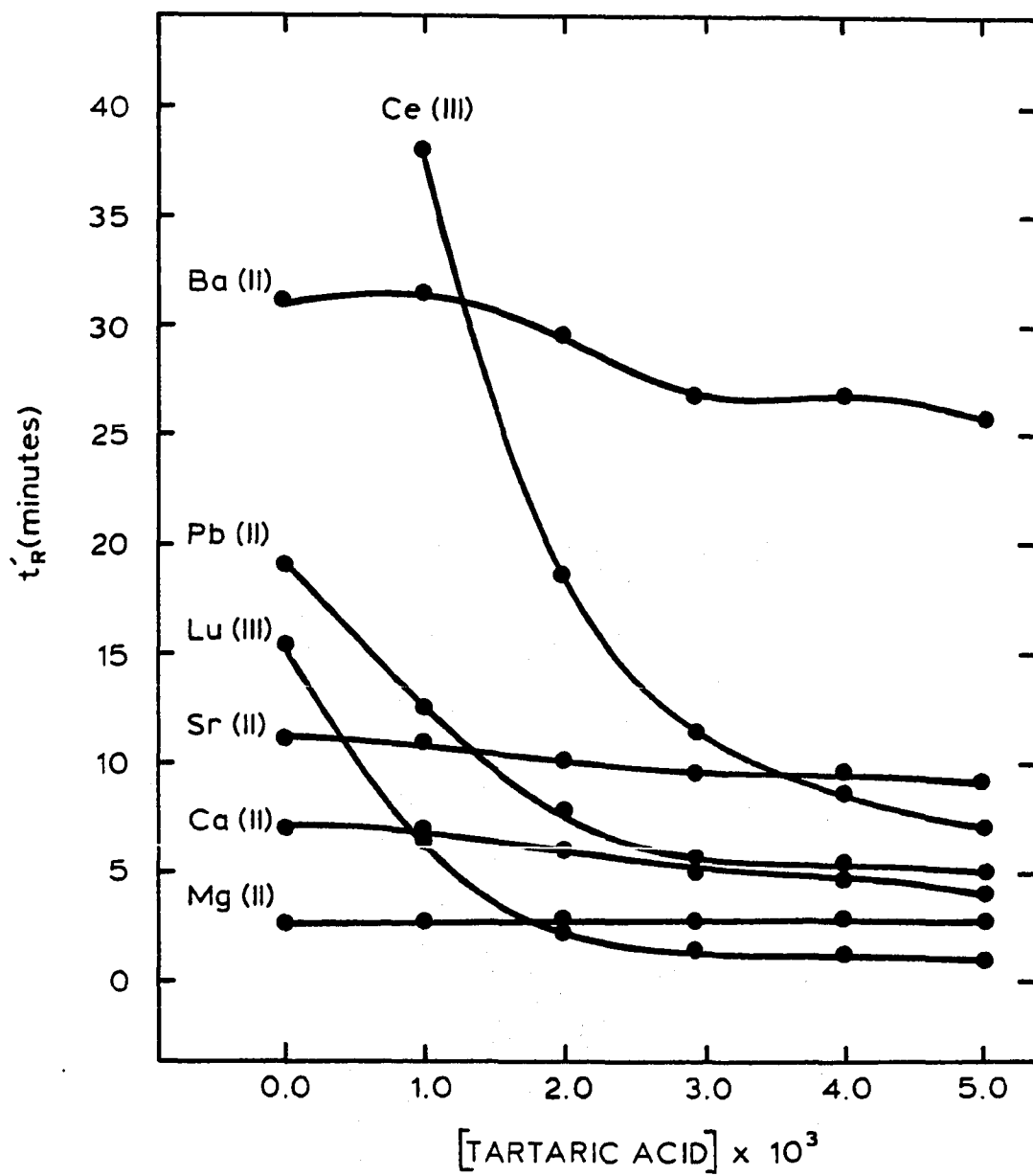
Table VIII. Adjusted retention times (in minutes) of various cations for eluents of varied pH. All eluents are 2.00 mM in tartaric acid and 2.00 mM in ethylenediammonium cation. Chromatographic conditions are described in the text

Cation	Eluent pH						
	3.00	3.50	4.00	4.50	5.00	5.50	6.00
Mg(II)	2.84	2.84	2.84	2.85	2.78	2.97	3.17
Ca(II)	7.48	7.17	6.42	6.10	5.71	6.06	6.46
Sr(II)	11.7	11.3	10.7	10.3	9.67	10.3	11.0
Ba(II)	33.5	31.1	29.4	29.6	27.3	28.0	30.8
Zn(II)	3.49	3.05	2.46	2.00	1.91	2.01	2.91
Co(II)	3.72	3.57	3.25	2.86	2.78	3.31	4.21
Fe(II)	3.76	3.71	3.50	3.32	3.13	3.56	3.56
Ni(II)	3.80	3.37	2.81	2.37	1.51	2.70	8.80
Mn(II)	4.02	4.07	3.96	3.83	3.62	4.08	4.41
Cd(II)	5.30	5.05	4.80	4.47	4.31	5.39	7.30
Pb(II)	-	19.0	12.5	7.78	7.34	7.76	12.2

Table IX. Adjusted retention times (in minutes) of various cations with varied pH. All eluents are 2.00 mM in tartaric acid and 2.00 mM in ethylenediammonium cation. Chromatographic conditions are described in the text

Cation	Eluent pH						
	3.00	3.50	4.00	4.50	5.00	5.50	6.00
Lu(III)	–	15.43	5.00	2.65	2.25	3.23	5.14
Yb(III)	–	17.3	5.73	2.96	2.44	2.64	–
Tm(III)	–	21.2	6.89	3.74	2.76	2.58	–
Er(III)	–	25.5	8.58	4.66	3.74	3.88	3.56
Ho(III)	–	33.3	10.2	5.62	4.37	4.78	–
Dy(III)	–	37.0	13.2	6.14	4.67	5.12	–
Tb(III)	–	–	15.5	6.64	6.12	8.03	–
Gd(III)	–	38.4	11.6	6.75	5.36	6.16	–
Eu(III)	–	36.1	11.5	6.29	4.90	5.85	–
Sm(III)	–	36.4	12.5	6.54	4.90	6.18	6.95
Nd(III)	–	50.4	17.2	9.34	7.17	8.33	–
Pr(III)	–	–	20.1	12.4	9.21	10.7	–
Ce(III)	–	–	34.0	18.6	14.2	16.0	20.3
La(III)	–	–	52.3	33.7	24.8	26.9	–

Table X. Linear regression data from plots of log adjusted retention time versus log $\alpha_{(M)L}$ for metal cations with eluent pH varied from 3.00 to 5.00. Eluent is 2.00 mM in ethylenediammonium cation and 2.00 mM in tartaric acid. Chromatographic conditions are in the text

Cation	Slope	r	Cation	Slope	r
Lu(III)	0.998	0.993	Mg(II)	0.747	0.590
Yb(III)	1.03	0.978	Ca(II)	2.75	0.976
Tm(III)	1.07	0.997	Sr(II)	2.58	0.988
Er(III)	1.03	0.995			
Ho(III)	1.08	0.994	Co(II)	0.568	0.984
Dy(III)	1.12	0.999	Fe(II)	0.849	0.968
Tb(III)	1.01	0.965	Mn(II)	0.271	0.954
Gd(III)	1.05	0.991	Ni(II)	3.04	0.963
Eu(III)	1.02	0.996	Pb(II)	1.08	0.984
Sm(III)	1.03	0.999	Zn(II)	1.10	0.978
Nd(III)	1.02	0.997			
Pr(III)	0.797	0.999			
La(III)	0.832	0.998			

50% complexed while the rare earth cations are about 90%

complexed. Most rare earth cations gave slopes that were

slightly high. The rest of the data deviate in an

unpredictable fashion. Dissociation of the

ethylenediammonium cation was considered for higher pH

values and did not account for the trend of increased

retention times. It appears that the increase is the result

of multiple retention mechanisms and is not readily

accounted for by simple ion-exchange equilibria derivations

as presented here.

A practical illustration of the effect of pH on adjusted

retention time is given in Figure 5. The retention of the

alkaline earths is affected very little by pH while most

other metals show large changes in retention time,

especially lead.

Conditions for separation of various cations are

selected relatively easily merely by examination of the

plots of retention time versus the varied parameter. Figure

6 shows a separation of common divalent cations. Eluent

cation concentration was chosen for optimal separation of

the alkaline earths and the rest of the eluent composition

was adjusted to accommodate the other metals. The pH was

chosen to permit early elution of lead and maintain maximum

resolution with the other metals. A separation of seven

rare earth cations is shown in Figure 7 using slightly

Figure 5. Plot of adjusted retention time versus pH.
Ethylenediammonium cation concentration and
tartaric acid concentration are constant at 2.00
mM. Specific chromatographic conditions are
described in the text
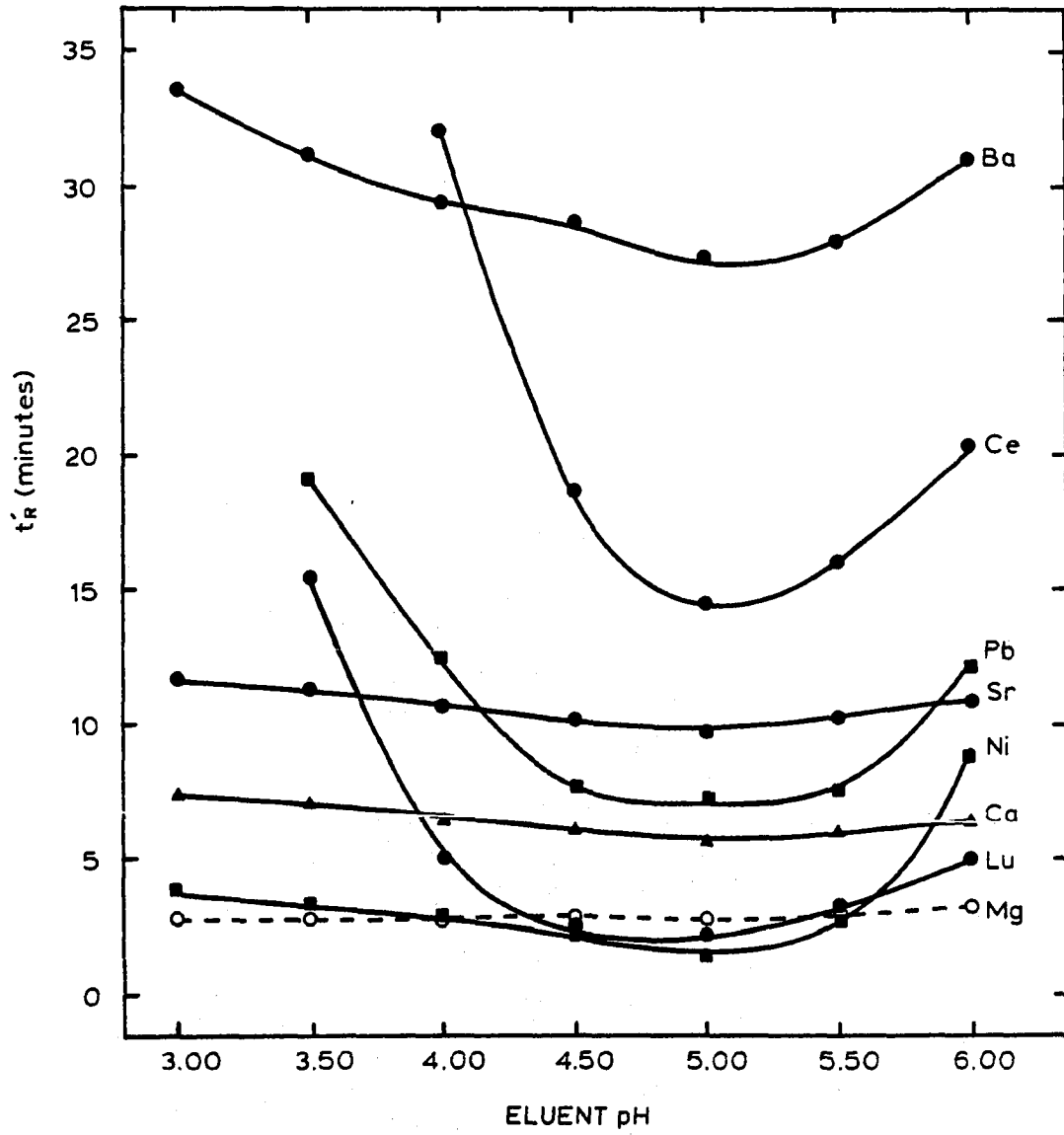
Figure 6.   Separation of zinc(II) (10.3 ppm), cobalt(II)
            (9.1 ppm), manganese(II) (16.0 ppm), cadmium(II)
            (16.1 ppm), calcium(II) (17.1 ppm), and
            strontium(II) (20.3 ppm).   Eluent is 1.5 mM
            ethylenediammonium cation and 2.00 mM tartaric
            acid at pH 4.00
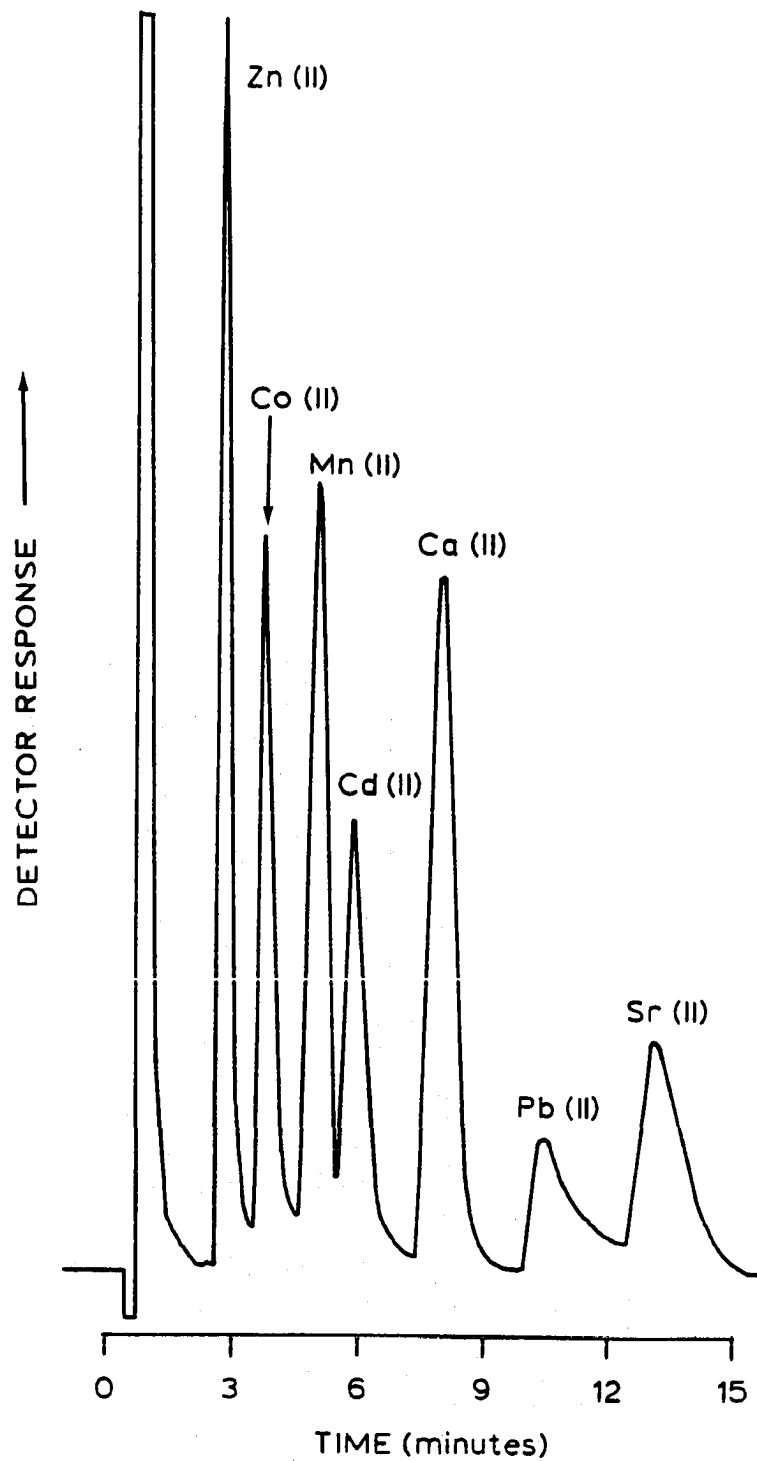
Figure 7.   Separation of lutetium(III), thulium(III),
gadolinium(III), neodynium(III),
praseodynium(III), cerium(III), and
lanthanum(III). Eluent is 2.00 mM in
ethylenediammonium cation and 2.00 mM tartaric
acid at pH 4.50
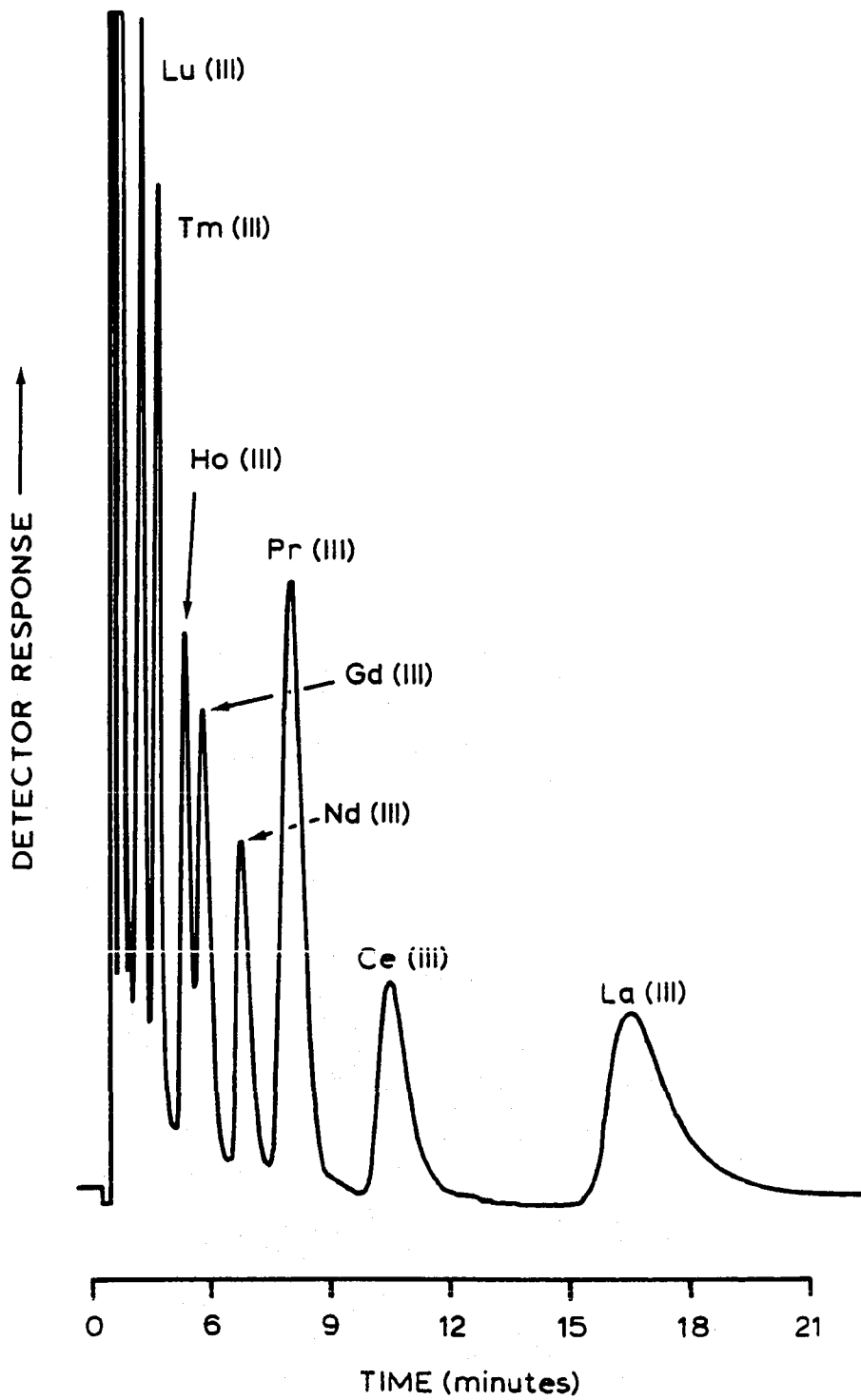
different conditions.

A useful ligand for rare earth separations is α-hydroxyisobutyrate (24,25). This ligand showed no particular advantage over tartrate for divalent cations. On the other hand, this ligand did aid in obtaining somewhat better elution characteristics of the seven heaviest rare earth cations (Figure 8).

It was thought that atrolactic acid ($C_6H_5CHOHCO_2H$) might improve resolution of early eluting rare earths, but was much too weak a ligand to be effective at the allowable operating concentrations.

Other ligands such as oxalate and citrate formed complexes that were much too strong and forced most metals to elute very early with no resolution between them.

Plots of peak height for ethylenediammonium tartrate eluents gave linear calibration curves for magnesium(II) over a concentration range of 1.0 to 15.0 ppm (r = 0.9991), for calcium(II) over a range of 2.0 to 30.0 ppm (r = 0.9995), and for zinc(II) over a range of 2.0 to 14.0 ppm (r = 0.9998). Other cations behave similarly with both tartrate and α-hydroxyisobutyrate eluents. Figure 9 shows excellent reproducibility obtained for a rapid separation of magnesium(II), calcium(II), and strontium(II). Retention times did not vary by more than a few seconds as recorded by an electronic integrator. Manually measuring the retention

Figure 8. Separation of the seven heaviest lanthanides using α-hydroxyisobutyrate eluent. All metal cation concentrations are 10.0 ppm. Eluent is 4.00 mM in ethylenediammonium cation and 3.00 mM in α-hydroxyisobutyric acid (eluent pH is 4.50)
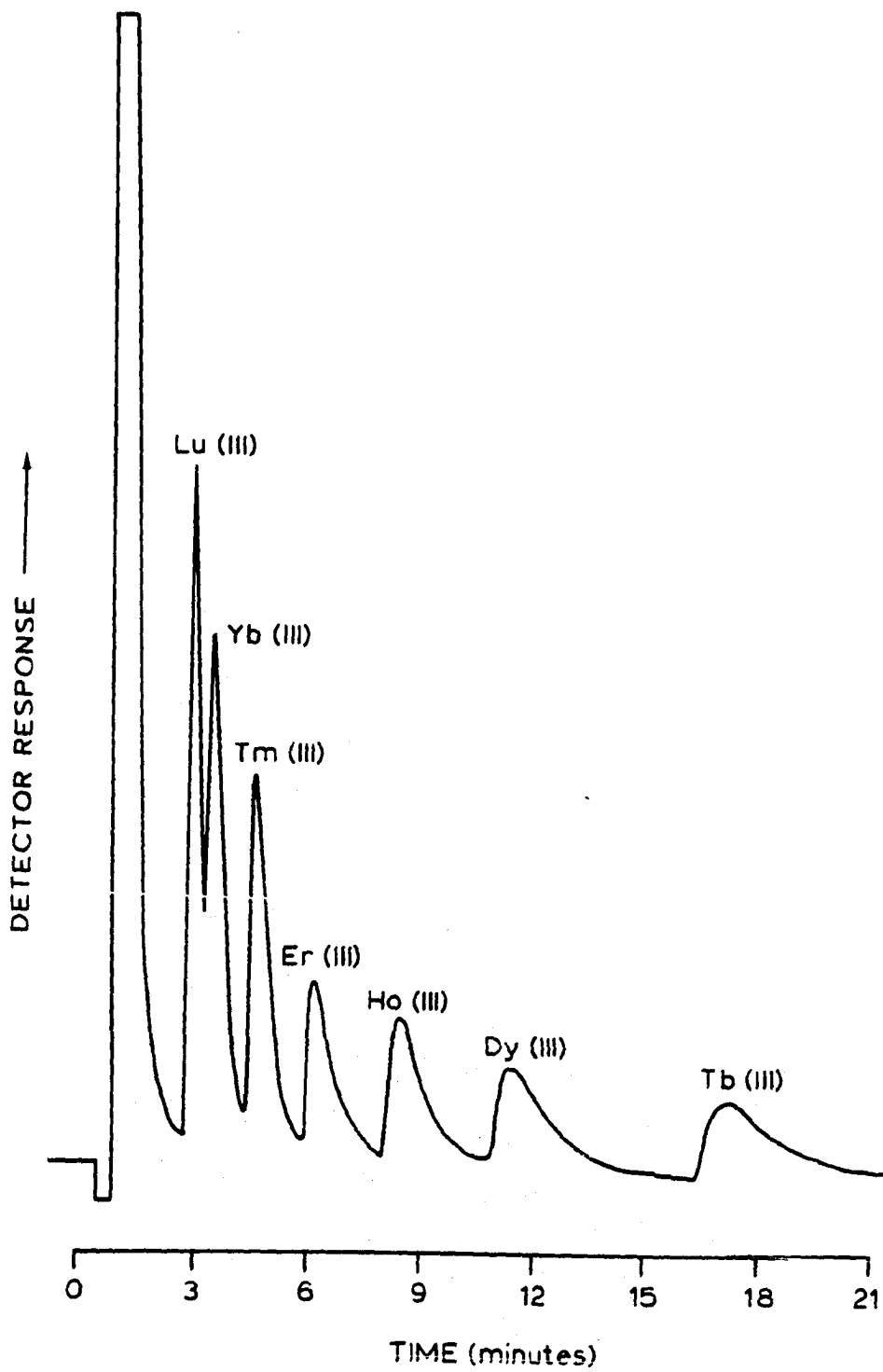
Figure 9.   Rapid separation of magnesium(II), calcium(II),
and strontium(II) for successive injections of
the same solution.   Each metal cation is 0.50 mM.
Eluent is 4.00 mM ethylenediammonium cation and
3.00 mM in tartaric acid (eluent pH is 4.50)

DETECTOR RESPONSE ⟶

TIME (minutes)
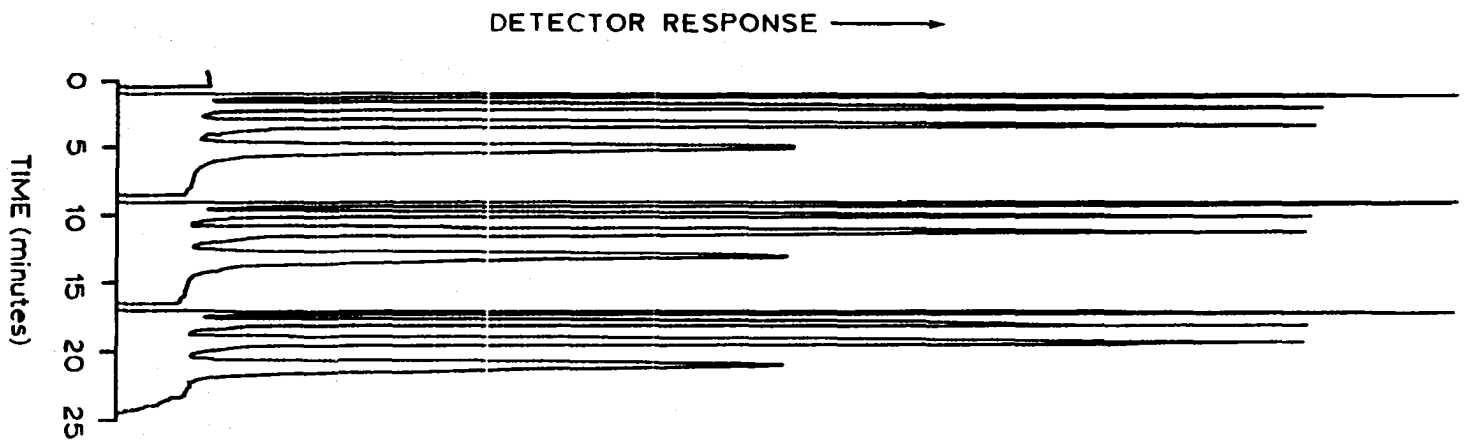
times showed no noticeable variation.

Quantitative measurements are not limited to the concentration ranges mentioned above. The detector sensitivity can be adjusted to work in different concentration ranges quite easily. The practical detection limit of this system is 49 ppb magnesium and 80 ppb calcium, which represents only 200 picomoles of each metal ion for a 100-μL injection. A surge of more sensitive detectors recently marketed may help exceed present limits of detection.

One unique advantage of this system is its ease of adapting to analysis and determination of monovalent cations (5) simply by switching to a dilute nitric acid eluent (Figure 10).

Sample Masking

Ethylenediaminetetraacetic acid (EDTA)

Ethylenediaminetetraacetic acid (EDTA) is one of the most commonly used chelating agents for masking metal cations. The formation constants of the metal complexes are all relatively large (26) with large differences between them. The large differences in complex formation constants and their magnitude makes EDTA an effective and selective masking agent. Of the metal cations complexed, the alkaline

Figure 10. Separation of alkali metals and ammonium cation.
Eluent is 1.0 mM HNO$_3$ at a flow rate of 1.0 mL
per minute. Column is 35 cm x 2 mm i.d. packed
with 4% crosslinked gel resin. Resin capacity
is 0.59 meq per gram

DETECTOR RESPONSE ⟶

TIME (minutes)

0
3
6
9
12

Li⁺
Na⁺
NH₄⁺
K⁺
Rb⁺
Cs⁺

218
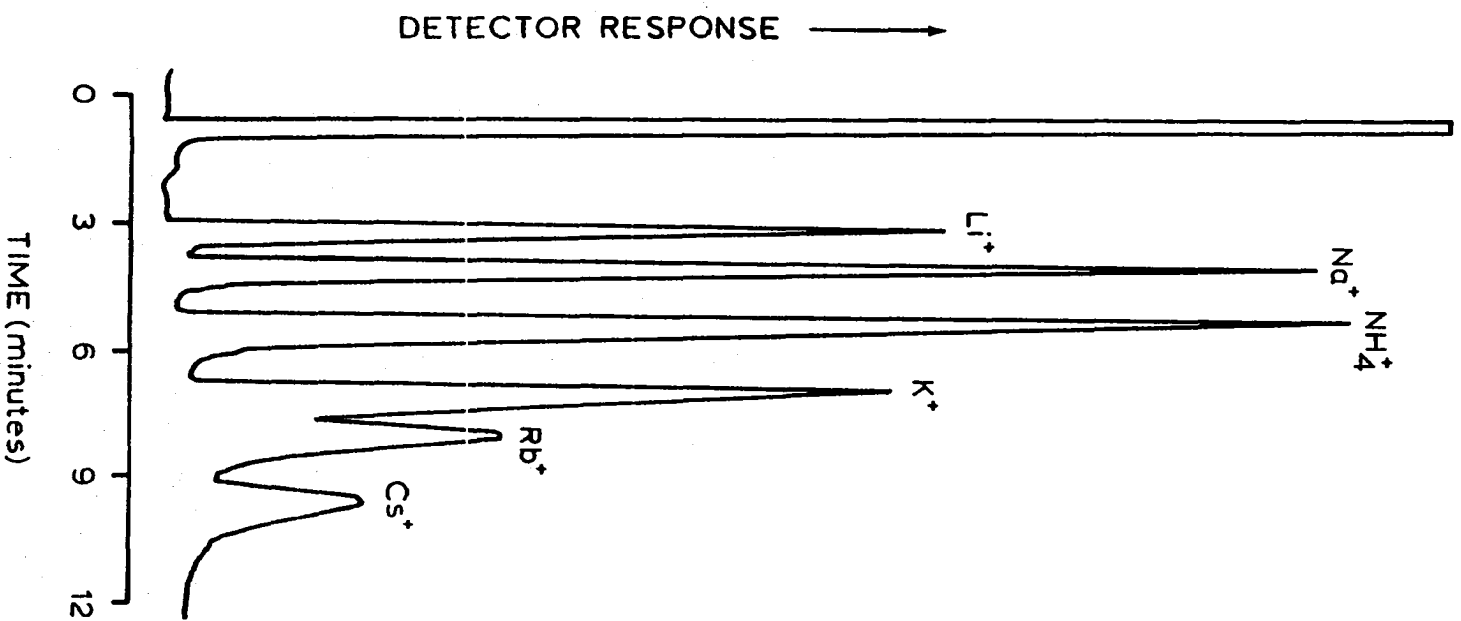
earth cations form the weakest complexes with EDTA. Calculations of $\alpha_{(M)L}$ for the alkaline earths show that minimum complexation (< 1% complexed) occurs at a sample pH of about 3.0. At this same pH, most other metal cations are very strongly complexed. It seemed possible to complex most metals with EDTA near pH 3.0 and leave the alkaline earths relatively uncomplexed. Injection of a masked sample would give peaks for the alkaline earths and none for the masked cations.

Samples containing magnesium (0.10 mM), calcium (0.10 mM), and 0.010 M EDTA were prepared at a different pHs. Samples (100-μL) were chromatographed with an eluent of 2.00 mM ethylenediammonium tartrate (pH 4.50). The resulting peak areas were plotted against pH to determine the optimum pH range for sample masking. As illustrated in Figure 11, determination of magnesium(II) and calcium(II) can be performed with a sample pH less than 4.0. Strontium(II) and barium(II) form weaker complexes with EDTA and may also be determined. Below pH 4.0 the calcium peak begins to show significant effects of complexation with the EDTA.

Figure 12 shows comparative chromatograms of identical samples of various divalent cations. The only difference between the two chromatograms is the addition of EDTA to the second sample. The advantages to this "clean-up" method are most obvious in determination of magnesium(II) in the

Figure 11. Plot of relative peak area of magnesium(II) and calcium(II) versus
sample pH. Each sample contains 1.00 mM each of magnesium and calcium
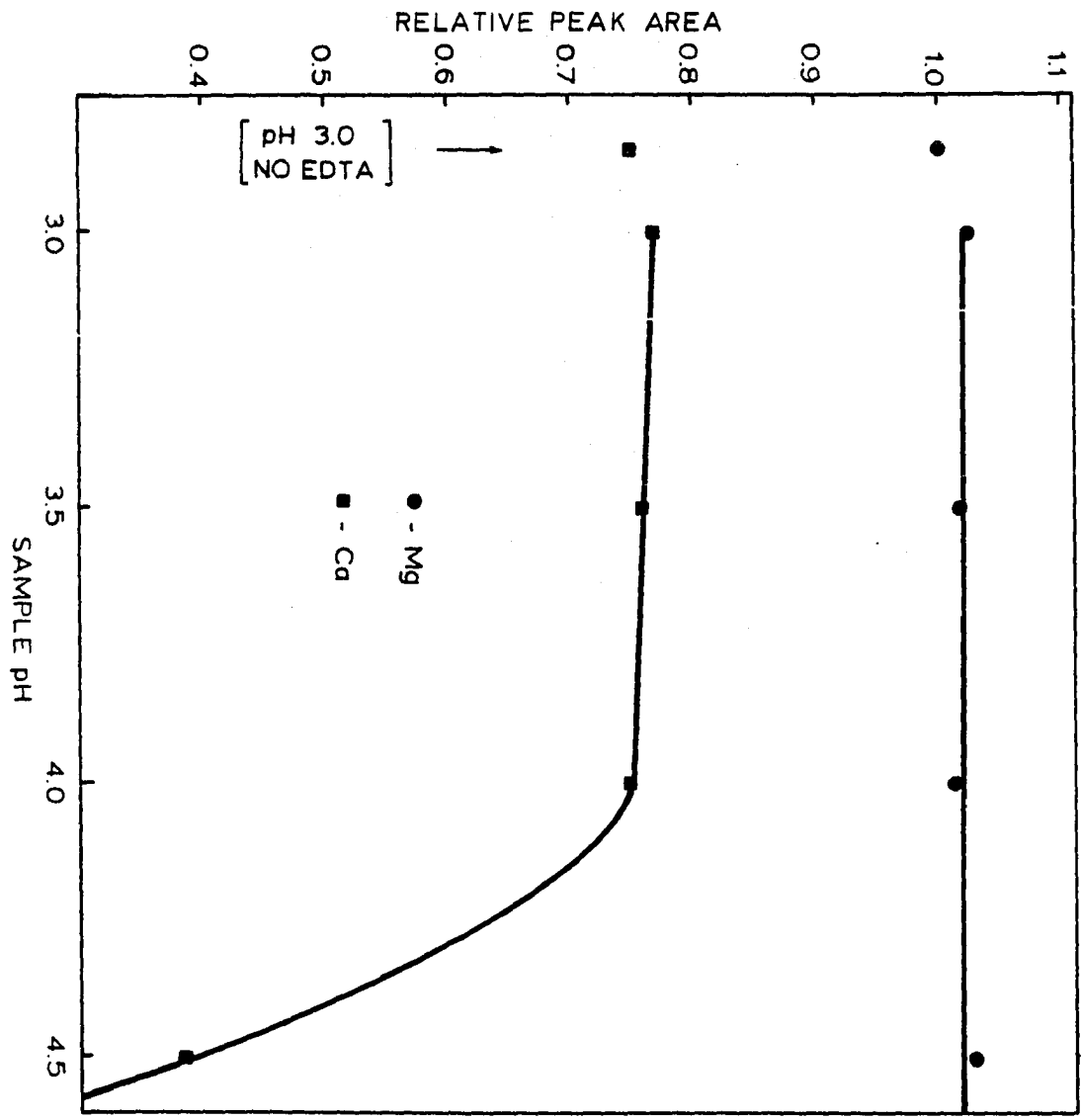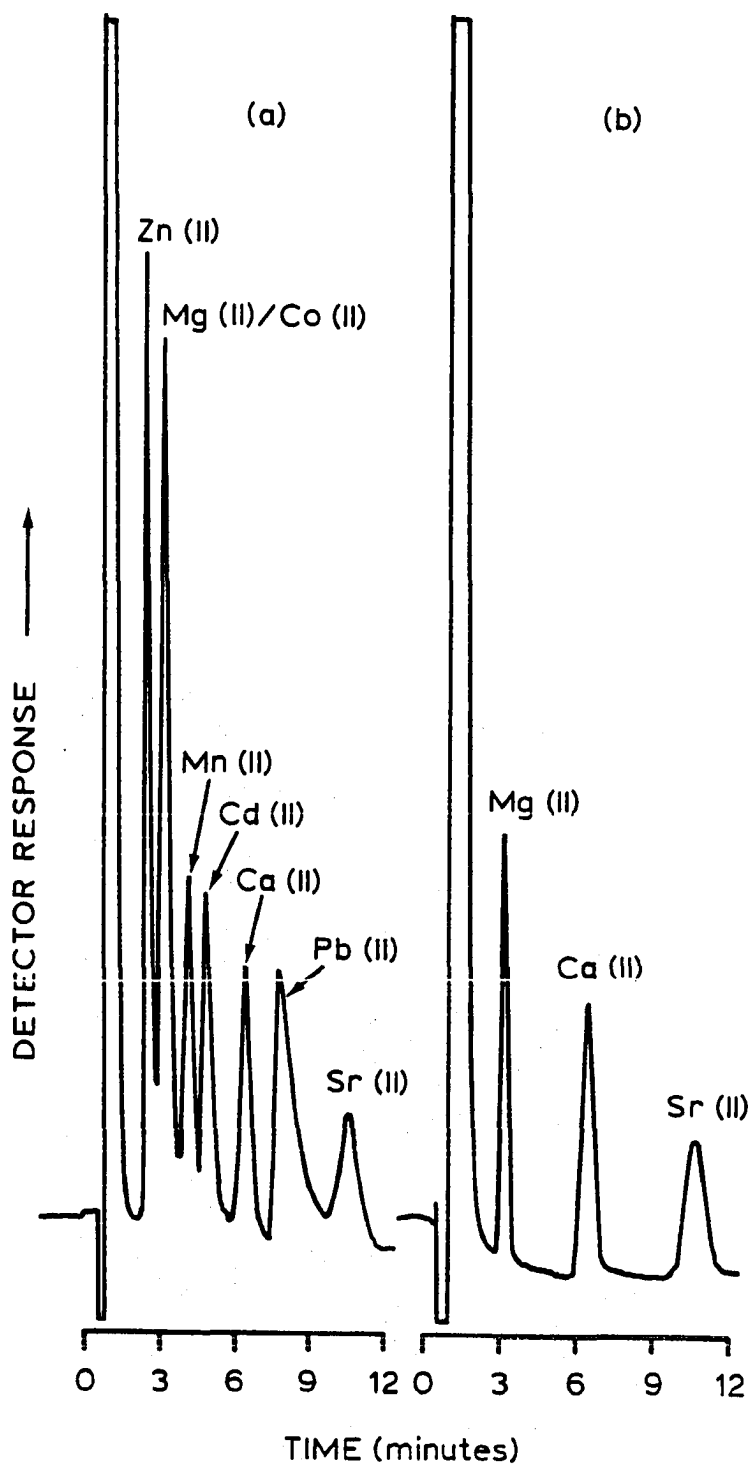and 0.010 M EDTA. Peak areas are measured relative to a sample at pH
3.00 containing no EDTA

Figure 12. Comparison of samples (100-µL injection)
containing 2.0 mM each of zinc(II), cobalt(II),
magnesium(II), manganese(II), cadmium(II),
calcium(II), lead(II), and strontium(II). Each
sample is at pH 3.99 with (a) containing no
EDTA, and (b) containing 0.010 M EDTA

presence of cobalt(II). Without the EDTA in the sample, the cobalt peak co-elutes with magnesium making it impossible to determine either cation without a preliminary separation. Addition of EDTA to the sample eliminates the cobalt interference and partial overlap of adjacent peaks with the alkaline earth cations. The sample matrix peak is somewhat wider with sample masking, but proper choice of eluent has helped to minimize its effect on the final chromatogram.

As demonstrated in Figure 12, samples with small concentrations of interfering metal cations can be handled with little trouble. Determination of small amounts of certain metals in solutions containing large excesses of other interfering metal cations poses a more demanding problem. Figure 13 shows masking of iron(III) present in large excess (100-fold) over magnesium(II), calcium(II), and strontium(II). The sample pH could only be adjusted as high as 1.7 because of hydrolysis problems with iron(III). Even at this low pH, iron(III) is masked quite well because of its large complex formation constant with EDTA (log $K_{Fe(III)}$ = 25.1). The appearance of the iron peak in Figure 13 is the result of photo-reduction of iron(III) to iron(II) (27). The appearance of this peak and its identification led to the work in section IV of this dissertation.

Recovery studies for magnesium(II), calcium(II), and strontium(II) were done in 10- and 100-fold excess of

Figure 13.   Comparison of samples containing 0.10 mM each of
             magnesium(II), calcium(II), and strontium(II) in
             100-fold excess of iron(III) with (a) no EDTA
             present in the sample (sample pH 1.7) and (b)
             0.010 M EDTA added to the sample (sample pH
             1.7). Eluent is 2.00 mM ethylenediammonium
             tartrate at pH 4.50
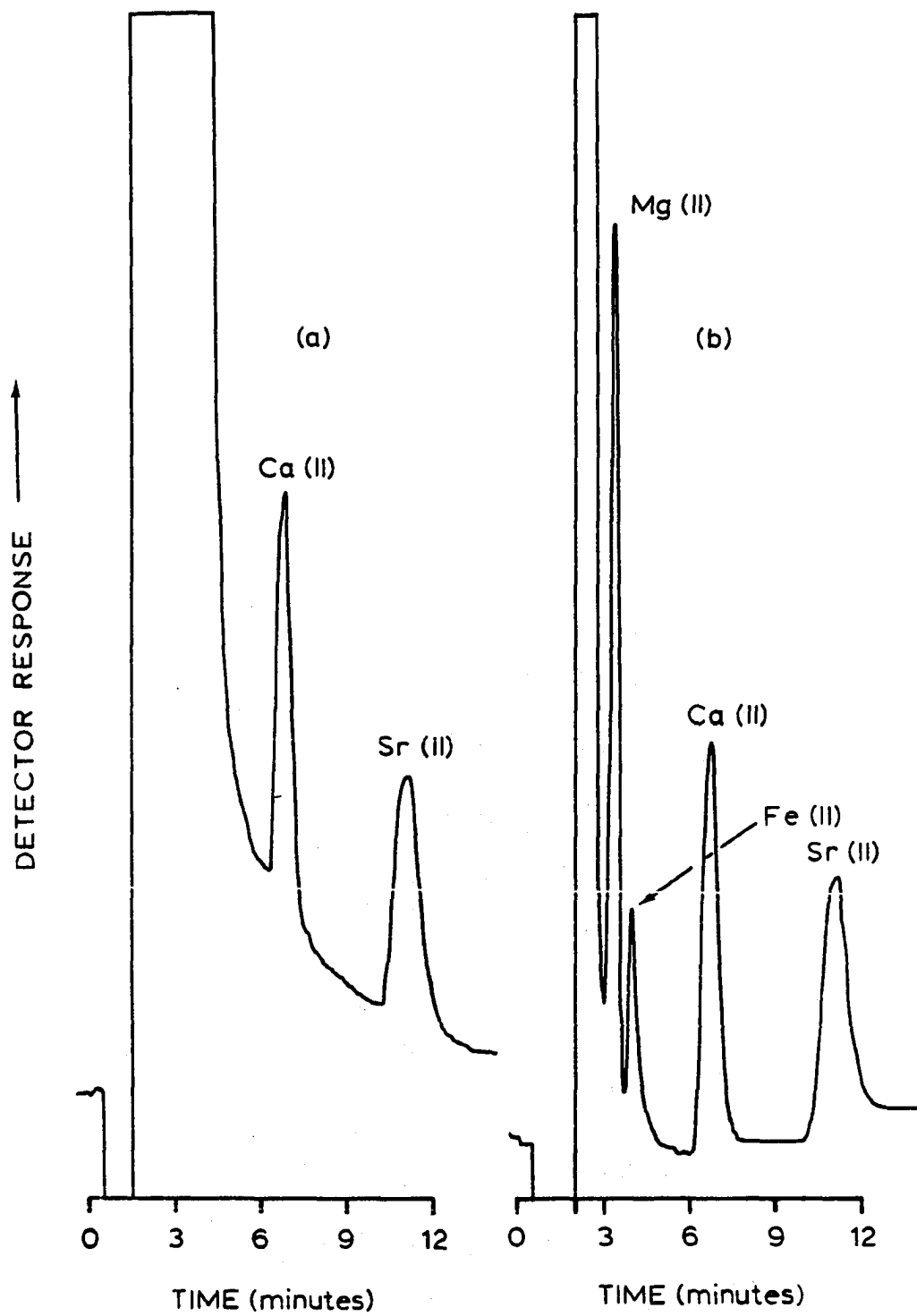
interfering metals (Table XI). All samples contained 0.10 mM each of magnesium(II), calcium(II), and strontium(II) and an excess of EDTA (0.010 M). The pH of each sample was adjusted to 3.7 before injection. Although a 100-fold excess causes slightly high results in some cases, the results are definitely good enough to show the usefulness and selectivity of the method.

Calibration curves for magnesium(II), calcium(II), and strontium(II) are linear with correlation coefficients of at least 0.999 in each case.

Baseline perturbations resulting from adsorption of the masking agent (EDTA) onto the resin or other possible sample matrix effects were minimal. Figure 14 shows consecutive injections of masked samples containing magnesium(II), calcium(II), and a 50-fold excess of interfering metal cation.

Nitrilotriacetic acid (NTA)

The choice of NTA as a masking agent is based upon its resemblance to and previous success with EDTA. NTA is effectively one-half of an EDTA molecule.

Calculations of $\alpha_{M(L)}$ (i.e., the ratio of free metal to all other forms of metal in solution) showed that manganese(II) and the alkaline earths were not significantly complexed (< 1% complexed) below a pH of about 3.0.

Calculations showed iron(II) could be included with a

Table XI. Recovery data for magnesium(II), calcium(II), and strontium(II) (each 0.10 mM) from a large excess of interfering metal cation. Excess metal cations were masked with 0.010 M EDTA at a sample pH of 3.75

Cation	Molar Excess	Percentage Recovered Mg(II)	Ca(II)	Sr(II)
Al(III)	10X	102.5	101.7	99.5
	100X	107.4	108.1	102.0
Co(II)	10X	100.1	99.0	97.7
	100X	107.3	97.9	95.8
Cu(II)	10X	99.4	98.2	96.4
	100X	104.0	103.1	92.3
Fe(III)	10X	99.8	96.7	96.0
	100X	107.0	96.5	96.6
Ni(II)	10X	102.5	102.8	102.1
	100X	150.2	104.2	98.8
Pb(II)	10X	99.5	98.3	97.3
	100X	107.8	104.9	97.5
Zn(II)	10X	100.9	98.1	96.4
	100X	106.0	104.9	102.3

Figure 14. Determination of magnesium(II) and calcium(II)
(2.00 mM each) in a 50-fold excess of iron(III),
copper(II), and aluminum(III), respectively.
Each sample contains 0.010 M EDTA added to mask
the interfering metal. Sample pH ws as follows:
iron(III), 1.7; copper(II), 3.7; and
aluminum(III), 3.7. The eluent is 2.00 mM
ethylenediammonium tartrate at pH 4.50
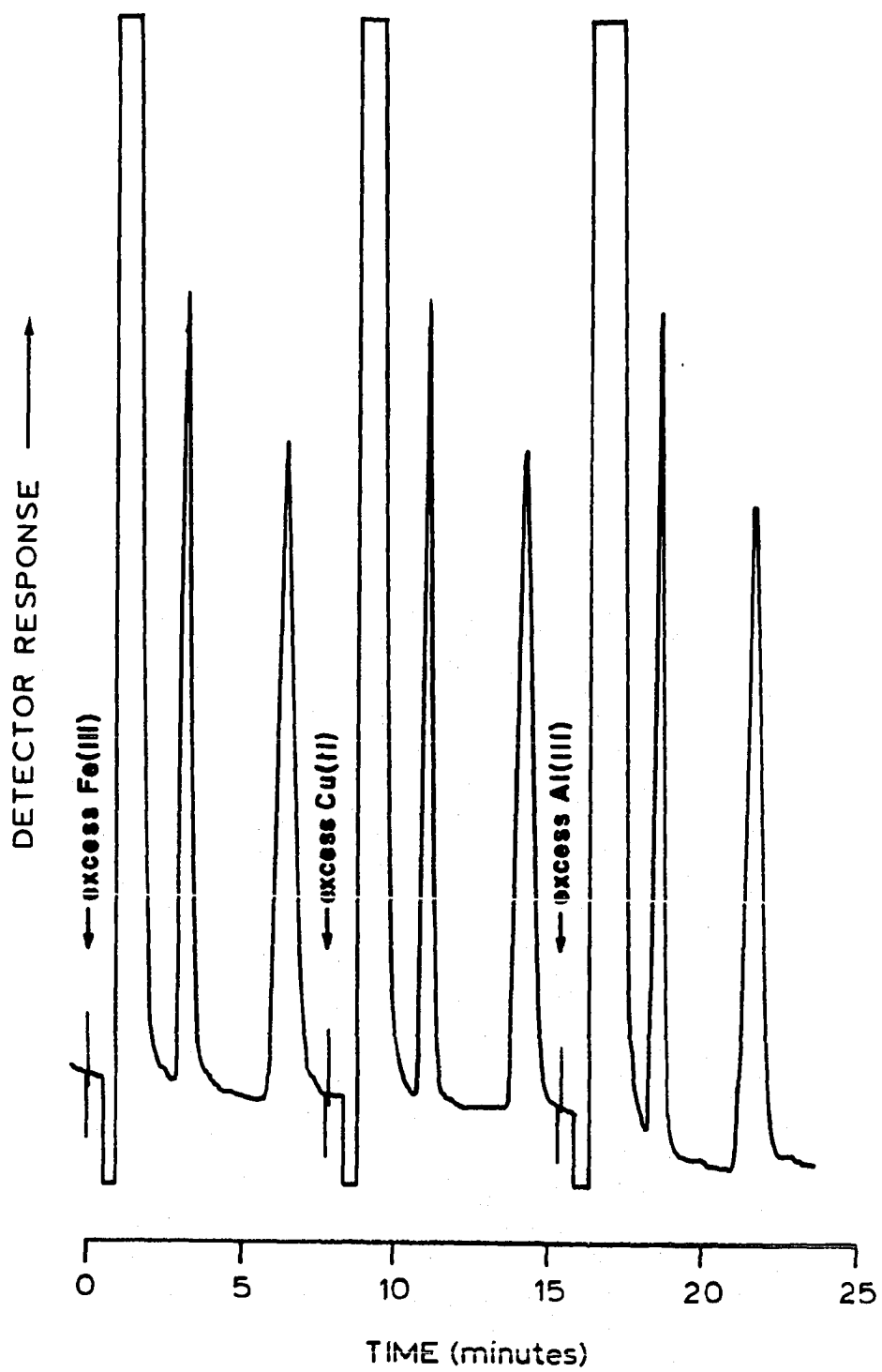
sample pH just below 2.0. Work with iron(II) was severely

hampered by oxidation of iron(II) to iron(III) and

subsequent complexation with NTA. Even with excesses of

reducing agent present in the sample to prevent the

oxidation, iron(II) could not be determined.

The actual usable sample pH range for quantification of

manganese(II) was determined by preparation of a number of

samples containing manganese, a large excess of NTA, and

each adjusted to a cover a pH range of 1.5 and higher.

Relative peak height versus pH showed significant

complexation of manganese(II) in the sample to occur above

pH 3.0 with complete complexation near pH 5.1 (Figure 15).

Masking with excess NTA near pH 3.0 allows for the

determination of a significant list of cations in the

presence of a number of interfering cations (Table XII).

Although the system has been studied for determination of

manganese(II), it readily includes metal cations that form

weaker complexes with NTA such as the alkaline earths.

Other metals forming stronger complexes are expected to be

completely masked if not for their higher selectivity

coefficients in the chromatographic system. The higher

affinity of these cations for the ion-exchange resin forces

the complexes to dissociate and the metal to be retained by

the resin. In the meantime, the NTA is swept through the

system void volume preventing reforming of the complex.

Figure 15. Plot of relative peak height for manganese(II) versus sample pH.
Each sample contains 1.00 mM manganese(II) and 0.010 M NTA. Peak
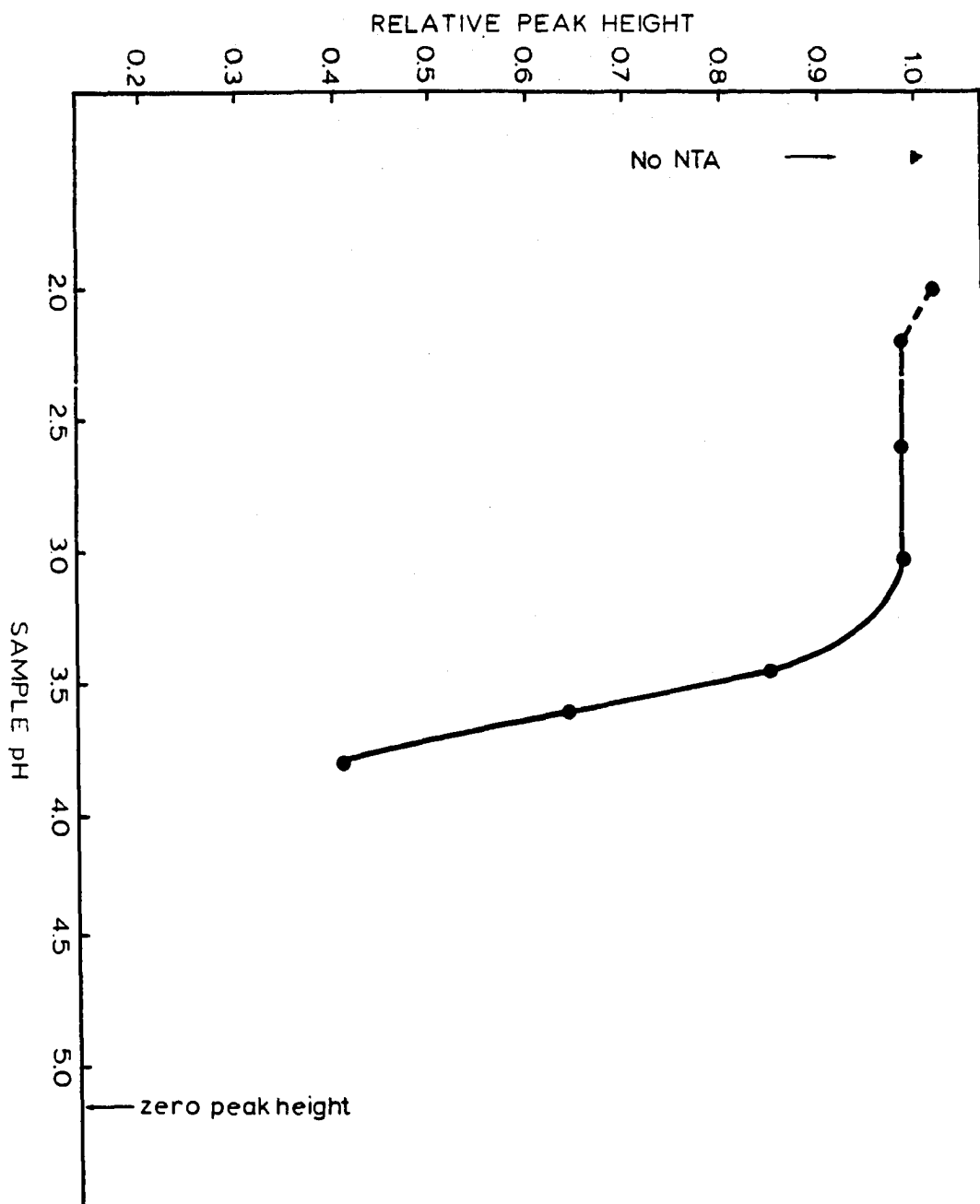heights are measured relative to sample containing no NTA (pH 2.0)

Table XII. Interfering metal cations tested for masking
with nitrilotriacetic acid at pH 3.0. The
samples contain 50 µM each of magnesium(II),
manganese(II), and calcium(II). 100 µL sample
injection volume

Cation	Molar Excess Tested	Percentage of Metal Complexed[a]	Metal Masked?
Fe(III)	10-,100X	100.0	Yes
Al(III)	10-,100X	100.0	Yes
Cu(II)	10-,100X	100.0	Yes
Th(IV)	10-,100X	-[b]	Yes
Ni(II)	10X	99.8	Yes
	100X		Partly
Y(III)	100X	99.7	Partly
Pb(II)	10-,100X	99.7	No
U(VI)	20-,50-,100X	-[b]	No
Zn(II)	10-,100X	98.5	No
Co(II)	10-,100X	97.1	Partly
Cd(II)	10-,100X	90.4	No

[a]Calculated for pH 3.0 and 0.010 M NTA.

[b]No values were available for calculations.

Several metal ions were examined for their interference
with the manganese(II) peak (manganese(II) concentration of
50 µM) with and without NTA being added to the sample.
These include iron(III), aluminum(III), copper(II),
thorium(IV), nickel(II), cobalt(II), yttrium(III), lead(II),
zinc(II), uranium(VI), cadmium(II), zirconium(IV), and
vanadium(IV).

The ethylenediammonium tartrate eluent does not give
peaks for iron(III), aluminum(III), and copper(II). These
cations are complexed relatively strongly by the tartrate
eluent and are eluted in the void volume of the system. At
high concentrations of these cations, the complexing
capacity of the eluent is exhausted and a significant amount
of the uncomplexed cation is bound at the ion-exchange sites
of the separator column. Despite a continuous flux of
tartrate and ethylenediammonium cation into the column,
elution of these cations is typically slow causing
interference with later eluting cations. Addition of NTA to
the sample and sample pH adjustment effectively prevented
the bleed associated with this system overloading. Large
excesses of iron(III) (10-fold, 100-fold), aluminum(III)
(10-fold, 100-fold), copper(II) (10-fold, 100-fold),
thorium(IV) (10-fold, 100-fold), and nickel(II) (10-fold)
were essentially eliminated. Chromatograms for iron(III)
and copper(II) present in large excess over magnesium,

Figure 16. Comparison of samples containing 5.0 mM
iron(III) and 0.050 mM each of magnesium(II),
manganese(II), and calcium(II). Samples contain
(a) no NTA and (b) 0.010 M NTA at pH 2.96
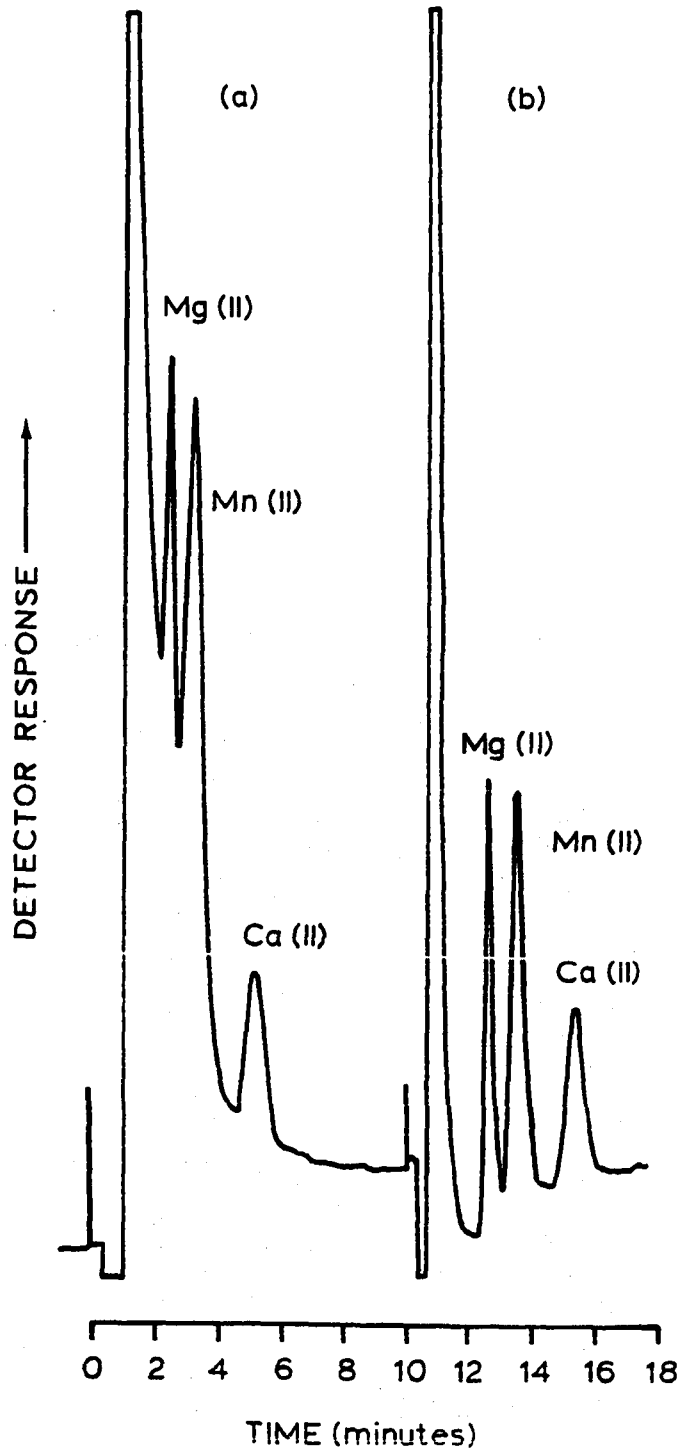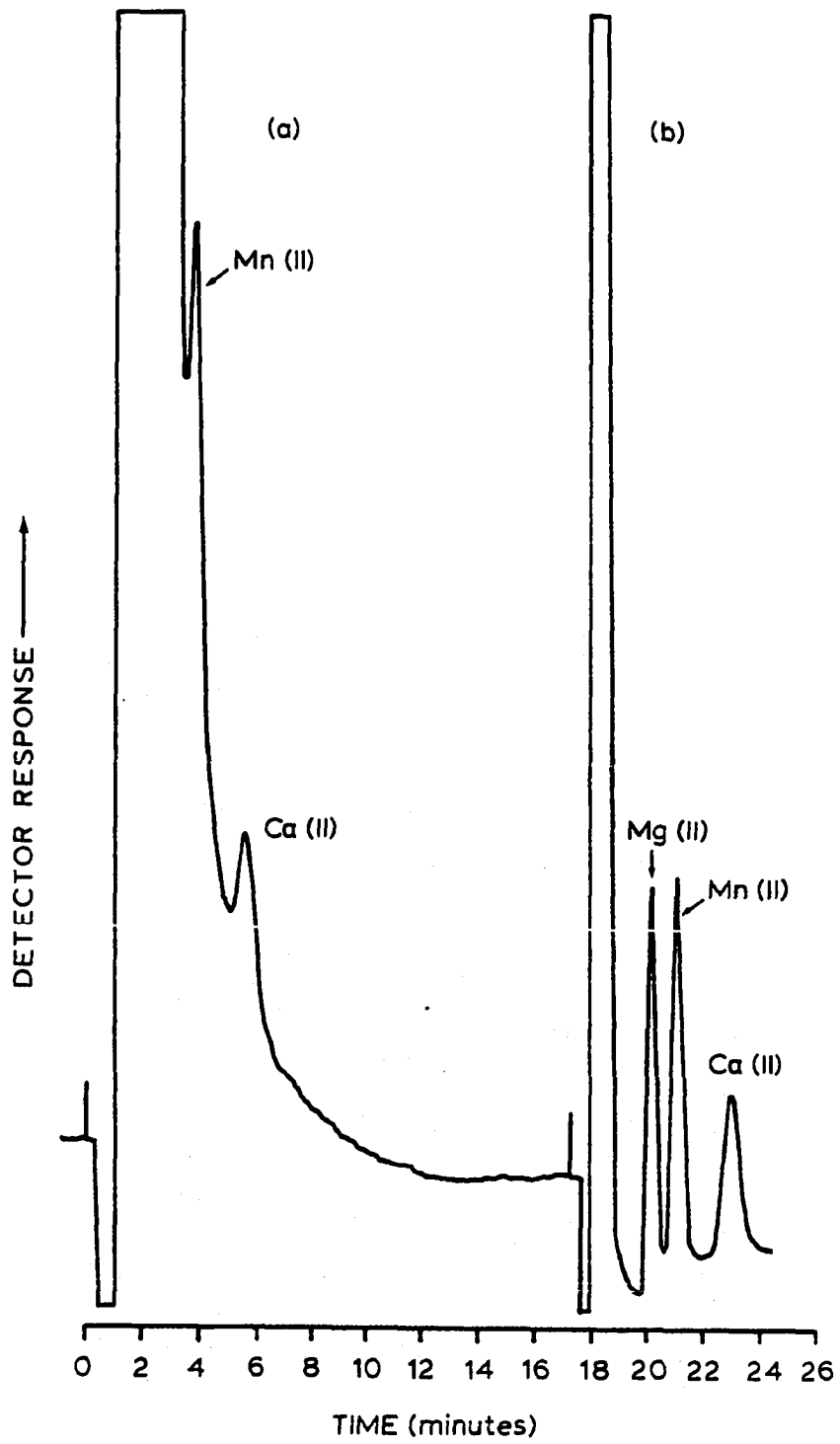
Figure 17.   Comparison of samples containing 0.050 mM each
             of magnesium(II), manganese(II), and calcium(II)
             and 5.0 mM copper(II). Samples contain (a) no
             NTA at pH 2.99, and (b) 0.010 M NTA at pH 2.99

manganese, and calcium are shown in Figures 16 and 17, respectively.

Partial masking (sample pH ca. 3) was demonstrated by several interfering metals studied. These included cobalt(II) (10-fold, 100-fold), nickel(II) (100-fold), vanadium(IV) (20-fold, 100-fold), and yttrium(III) (100-fold). Partial masking is defined here as some improvement in the sample chromatogram, such as reduction in peak size of the interferent cation without complete elimination of the peak or a notable shift to a lower retention time of the same peak. This behavior was demonstrated by nickel(II) (100-fold) and cobalt(II) (10-fold, 100-fold). As noted above, nickel(II) in a 10-fold excess was completely masked. In a 100-fold excess, a small amount of nickel(II) was not complexed by the NTA and appeared to overlap with the magnesium(II) and the manganese(II) peaks giving the appearance of poor resolution between the two. No distinct nickel(II) peak was present. The calcium(II) peak was not at all disturbed by this effect. A higher sample pH would eliminate the nickel(II) interference but only at the expense of the manganese(II) peak.

Yttrium(III) normally elutes relatively late with this system and did not interfere with the manganese(II) peak in molar excesses up to 390-fold. Addition of NTA to samples containing yttrium(III) only degraded the determination by

making the yttrium(III) elute much earlier and totally obscure the manganese(II) peak.

Vanadium(IV) was examined in 20- and 100-fold excess over manganese(II). Some improvement was noted in the recovery of the sample matrix peak; however, the recovery was slow and manganese(II) was not totally resolved from the tail of the matrix peak. Any cations eluting before manganese(II) could not effectively be analyzed because of the wide matrix peak.

Metal cations not effectively masked by NTA (sample pH 3.0) included lead(II) (10-fold, 100-fold), cadmium(II) (10-fold, 100-fold), zinc(II) (10-fold, 100-fold), uranium(VI) (20-fold, 50-fold, 100-fold), and zirconium(IV) (10-fold). Some of these metals (cadmium(II), zinc(II), and lead(II)) did show some changes in their elution times to suggest that each might be masked at a higher pH.

Obviously, excesses of some metal cations certainly do not preclude determination of all other metals. For example, lead(II) elutes relatively late in an excess of less than about 10-fold and determination of magnesium(II) and manganese(II) could still be performed with little or no problem. The case of manganese(II) determination in samples containing excess yttrium(III) is another example.

Both peak height and retention times are reproducible with excess NTA in the sample. Calibration curves of

manganese(II) with an excess of aluminum(III) present (5.0 mM) masked by NTA (10 mM) were linear over a range of 0.020 to 0.50 mM with a correlation coefficient of 0.999.

5-Sulfosalicylic acid (5-SSA)

The successful application of 5-sulfosalicylic acid in single-pass ion-exchange chromatography was demonstrated by Fritz and Palmer (28). Aluminum(III), iron(III), uranium(VI), and vanadium(IV) were effectively masked in solutions containing several other cations. Using the single-pass method in an ion chromatograph permits the determination of 12 metal cations and the rare earths in the presence of the above mentioned metals (Table XIII).

Zinc(II) (at a concentration of 50 µM) was chosen as a model compound because it elutes fairly early in the ethylenediammonium tartrate eluent system. This situation allowed for the examination of the effect 5-SSA has on the sample matrix peak. Notable loss of resolution between the sample matrix peak and the zinc(II) peaks indicate inadequate masking of the interfering cation.

Calculations of $\alpha_{M(L)}$ for zinc(II) showed less than 1% of the amount of zinc was complexed at a pH of 5.5 or less. Experimental determination of relative peak height versus sample pH demonstrated no significant complexation below pH 4.6. At sample pH values above 4.6, a baseline "dip" appeared immediately following the matrix peak and caused

Table XIII.   Interfering metal cations tested for masking
with 5-sulfosalicylic acid (0.010 M) at pH 4.5.
The samples contain 50 µM zinc(II). 100 µL
sample injection volume

Cation	Molar Excess Tested	Percentage of Metal Complexed[a]	Metal Masked?
Fe(III)	20-,50-,100X	100.0	Yes
Al(III)	20-,50X	99.9	Yes
Th(IV)	4-,20X	99.9	Yes
V(IV)	20X	99.8	Yes
U(VI)	4-,20X	99.1	Yes
Zr(IV)	4-,20X	-[b]	Yes
Be(II)	20X	99.8	Partly
Cu(II)	20X	71.4	No
Pb(II)	20X	-[b]	No
Lu(III)	-	1.6	No
Tm(III)	-	1.5	No
Co(II)	50X	0.1	No
Cd(II)	-	0.0	No
Y(III)	4X	0.0	No
Mn(II)	50X	0.0	No

[a]Calculated for pH 4.5 and 0.010 M 5-SSA.

[b]No values were available for calculations.

some difficulty in peak height measurement. This
disturbance is apparently due to adsorption of a finite
amount of 5-SSA onto the organic matrix of the resin (29).

As mentioned above, aluminum(III) (20-fold, 50-fold),
thorium(IV) (4-fold, 20-fold), vanadium(IV) (20-fold),
uranium(VI) (4-fold, 20-fold), and iron(III) 20-fold, 50-
fold, 100-fold) were effectively masked by 5-SSA at a sample
pH slightly below 4.5. All excess metal concentrations are
relative to 50 μM zinc(II). Determination of thulium(III)
in a 50-fold molar excess of aluminum(III) was possible at a
sample pH up to about 5.0. Thulium(III) is representative
of the behavior of other rare earths.

Metal cations partly complexed by 5-SSA include
zirconium(IV) (4-fold, 20-fold), and cobalt(II) (50-fold, pH
4.0). Beryllium(II) (20-fold, > pH 5.0) was not totally
masked by 5-SSA but can be reduced to a concentration of
minimal interference at a sample pH slightly greater than
5.0.

Metal cations that are not masked by 5-SSA and could be
analyzed include: the rare earths (thulium(III) was used as
a model because it has the smallest formation constant of
the rare earths), zinc(II), yttrium(III), nickel(II),
lead(II), cadmium(II), and cobalt(II). Copper(II) was not
masked sufficiently and gave a very wide matrix peak totally
obscuring the zinc(II) peak. Titanium(IV), bismuth(III),

antimony(III), and tin(IV) hydrolyzed at millimolar concentrations and did not lend themselves to analysis.

Molybdenum(VI) initially posed no interference and gave no change in behavior with 5-SSA masking. This is expected since molybdenum(VI) exists as an oxo-anion in aqueous solution and should not be held up by the ion-exchange resin. Other metals which exist as oxo-anions in solution are expected to pose little or no interference with this system.

Analysis of rare earth samples using 5-SSA to mask large excesses of aluminum(III) proved quite successful. Calibration curves are linear (correlation coefficient of 0.9991) over at least one order of magnitude (0.049 to 0.492 mM Lu(III) with 2.0 mM aluminum(III) and 10 mM 5-SSA; sample pH 4.5). Figure 18 shows the determination of 0.1% nickel in a simulated steel sample. The equivalent nickel(II) concentration is 53 ppb (0.90 μM). The iron(II) peak is an artifact of all samples containing an excess of iron(III) and has been reduced in size by addition of hydrogen peroxide and boiling. Complete elimination of this peak has never been practically accomplished.

The success of sample masking with conductivity detection systems only supports its application with other systems that are not so temperamental to background or changes in the system equilibrium. For example, post-column

Figure 18. Injection of simulated steel sample containing
0.1% nickel(II) (equivalent concentration of 53
ppb). Iron(III) is masked with 5-sulfosalicylic
acid (0.010 M) at pH 3.50. Eluent is 1.5 mM
ethylendiammonium cation and 2.00 mM tartaric
acid at pH 4.2 (natural pH)
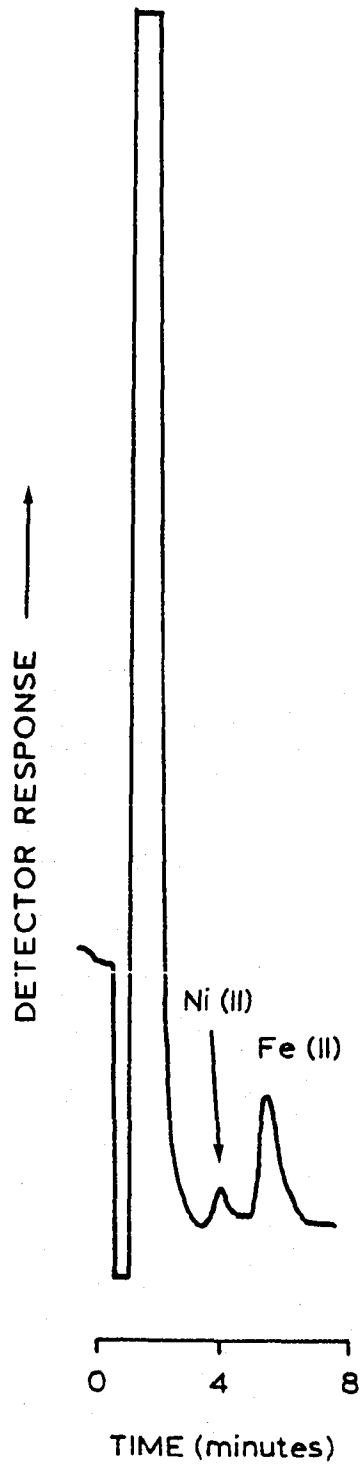
reaction using color-forming reagents detection or electrochemical detection. Other systems may well tolerate a much wider sample pH range and thus a greater variety of masking agents. Increased selectivity for specific metal cations may also be enhanced.

Preliminary studies have shown that sample masking can be used in a preconcentration mode where the unmasked cations are taken up on a concentrator column and the masked cations pass straight through the column. The concentrator column is a short cation exchange column put in place of the sample loop. An NTA masked sample solution containing 11 0.20 µM manganese(II) and 1.0 mM iron(III) was passed through a concentrator column that replaced the sample loop in the injector. Essentially all of the manganese(II) was taken up from the sample solution that was passed through the concentrator column while no iron(III) was present except that in the dead volume of the injector. Loading of the concentrator column corresponded directly to the amount of sample passed through and was independent of flow rate. Significant blanks were obtained with preconcentration. The lack of high quality water precluded further work.

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SECTION IV. SPECIATION OF IRON BY REDUCTION AND DETERMINATION BY CATION CHROMATOGRAPHY

INTRODUCTION

Iron is one of the cheapest and most abundant metals in the earth. It is not found as the pure metal and is usually combined with some other element before use. The applications and importance of iron are commonly seen in everyday life and can be traced as far back into the past as the time of Adam (1).

Analysis of iron encompasses a wide range of techniques. The most extensively used of which is a spectrophotometric method based on the color formation of iron(II) with 1,10-phenanthroline (2). This procedure involves oxidation of all metallic iron present in the sample to iron(III) then reduction of the ferric ion to iron(II) with hydroxylamine hydrochloride. Iron(II) forms a distinct red colored complex with 1,10-phenanthroline that has a maximum absorption at 510 nm. Iron(III) forms no distinct color. Care must be taken to ensure other interfering metals which form colored complexes with 1,10-phenanthroline are properly masked.

Iron(II) can be determined apart from Iron(III) merely by skipping the reduction step. The color of the complex without excess reducing agent present is not stable for very long and fades after a relatively short period of time.

Bathophenanthroline has been suggested as a more

accurate color-forming reagent for the direct determination of iron(II) in the presence of iron(III). The bathophenanthroline method apparently does not upset the iron(II)/iron(III) as much as 1,10-phenanthroline, pyridyls, of other spectrophotometric reagents (3,4). This procedure involves the extraction of the iron(II)-bathophenanthroline complex from the sample solution. This causes a slight but noticeable shift of the equilibrium and slightly high results for iron(II).

Iron(II) may be determined by direct titration with permanganate (5). The endpoint is reached when the an orange tint appears from excess permanganate and iron(III). No problems are encountered when the only acid present is sulfuric acid. Chloride ions give high results which may be avoided by addition of manganous salts and a mixture of phosphoric and sulfuric acids (i.e., addition of Reinhardt-Zimmerman solution). Chloride ions are typically present from addition of hydrochloric acid during sample dissolution.

Flaschka and Zavagyl (6) obtained good results by titrating iron(III) with ascorbic acid. The indicator was ammonium thiocyanate. Another titration of iron(III) with ascorbic acid involves the use of Variamine Blue (4-amino-4'-methoxy-diphenylamine) (7). The color of the solution showed dependence on the anions present.

Each of the above titration methods can be used for speciation of iron by first determining either iron(II) or iron(III). Then, the total iron is determined after conversion of the iron present to the proper oxidation state for analysis. The remaining form is obtained by difference.

Verdier (8) found that in tartrate media the ferric-tartrate complex produced a cathodic wave while the ferrous-tartrate complex produced an anodic wave. Both were well-behaved and the anodic wave was recommended for polarographic determination of iron in magniferrous materials.

Atomic absorption, flame emission, and atomic fluorescence can be used for determination of iron, but these methods only give total iron unless some separation is performed beforehand.

The list of methods for iron determination is seemingly endless. The multitude of techniques and procedures seems well to highlight the immense interest in iron determination and the diversity of difficult samples encountered. Surprisingly, very little is found in the literature on speciation of iron(II) and iron(III).

Iron can also be determined on liquid chromatographic systems based on ion-exchange separations (9,10,11). Complexing agents are usually added to the eluent which improves the overall selectivity of the system and makes the

metals elute more rapidly. However, iron(III) is usually
complexed relatively strongly and is eluted very close to
the dead volume of the system. Despite specificity of the
detection modes used, the iron(III) peak usually overlaps
with other early eluting peaks (e.g., copper(II)) or it can
be distorted by baseline fluctuations typically caused by
the sample matrix peak passing through the detector.
Iron(II) is not complexed as strongly and elutes somewhat
later.

Iron(II) can readily be determined by single-column ion
chromatography using conductivity detection and complexing
eluents as described in section III of this dissertation.
Iron(II) is complexed weakly enough to be held up by the
cation-exchange column and give a distinct peak. On the
other hand, iron(III) is strongly complexed as either a
neutral or anionic complex and swept through the system in
the dead volume after injection. The ability to readily
analyze iron(II) and not iron(III) suggests the possibility
of speciation of iron as iron(II) and iron(III) with proper
sample preparation.

A method of iron speciation is presented here which
incorporates the convenience, speed, and simplicity of a
single-column cation chromatography. The procedure requires
minimal sample preparation. Iron(II) is determined by
direct injection of the sample into the chromatograph

without any pretreatment. Total iron is determined after
all the iron(III) is reduced to iron(II) by addition of a
reducing agent to the sample. The iron(III) concentration
is determined by difference. Several reducing agents are
compared and recoveries are discussed. A number of possible
interferences of the reduction are also discussed.

This method of iron speciation is in no way intended to
replace other methods of iron analysis. Such claims are
ludicrous since each method has its own merit depending on
the sample type, accuracy required, and availability of
instrumentation. Instead, this work was performed to
enhance cation chromatography and expand its scope.

EXPERIMENTAL

Chromatograph

The ion chromatographic system used was as described in section II of this dissertation. The chromatographic column measured 25 cm long with a 2.1 mm i.d. and was packed with a lightly sulfonated gel resin of low capacity (0.059 meq per gram). The resin had a particle size of about 20 μm. All injections were made with a fixed 50-μL sample loop. The eluent flow rate was set at 1.0 mL per minute. Conductivity was used as the mode of detection.

Eluent Preparation

The eluent was 1.5 mM in ethylenediamine and 2.0 mM in tartaric acid, giving a pH of 4.2. The eluent was prepared from reagent grade ethylenediamine that was purified by distillation and stored under nitrogen. The tartaric acid was reagent grade and used as received. The eluent was prepared in distilled-deionized water. Removal of oxygen from the water used for eluents is necessary to prevent oxidation of iron(II) during analysis. This was done by boiling the water and maintaining an inert atmosphere over the eluent solutions whenever possible. Eluent solutions

were filtered through a 0.2 μm membrane filter under suction and degassed before use.

Solution Preparation

As with the eluent, the sample solutions were prepared in distilled-deionized and deoxygenated water. Iron(III) stock solutions were prepared from electrolytic iron (ignited in moist hydrogen) (G.F.Smith Chemical Co., Columbus, OH) dissolved in 1:1 nitric acid. Concentrated hydrochloric acid was added and the solution fumed until all traces of nitrate were removed. The solution was then diluted to the appropriate volume.

Iron(II) solutions were also prepared from electrolytic iron. The metal was dissolved in 1:1 hydrochloric acid under a nitrogen atmosphere and diluted to volume after dissolution was complete. The iron(II) solution was stable for several weeks when kept from light and under an inert atmosphere in a tightly stoppered bottle.

L-ascorbic acid, hydroxylamine hydrochloride, and sodium hydrosulfite solutions were prepared from reagent grade salts. The shelf-life of ascorbic acid solutions, of course, depends on exposure to light and oxidizing agents. Ascorbic acid stock solutions (10 mM) were kept from light in clear, tightly sealed bottles had a shelf-life of about

one week. Lack of success with hydroxylamine hydrochloride and sodium sulfate precluded any examination of their stability in solution.

Stability of most solutions exceeded several weeks as long as the containers were tightly sealed. Maintaining an atmosphere of inert gas (helium or nitrogen) over the solution helped prevent absorption of oxygen. Significant care of the sample must be taken to ensure oxidation of the iron(II) does not occur. Typically, solutions containing iron(II) are preserved merely by adjusting the pH to a low value with hydrochloric acid.

RESULTS AND DISCUSSION

Survey of Reducing Agents

Several reducing agents were examined for their usefulness in reducing iron(III) to iron(II). A "clean" reaction involving minimal sample preparation and essentially no interfering by-products was sought. Sample preparations that have a high ionic character can greatly disrupt the chromatogram by giving a "pseudo-" or sample matrix peak that is so large it totally obscures the analyte peaks. In the same vein, the presence of organic reactants or by-products of the reaction that can absorb onto the resin matrix should also be avoided. These compounds can "poison" the resin in the chromatographic column and destroy its efficiency. They may also elute relatively late from the column and interfere with other peaks.

Sodium hydrosulfite was tried as a reducing agent and gave immediate reduction of iron(III). After a short period of time, the solution developed a cloudy, white precipitate and a pungent "sulfur-like" odor.

Hydroxylamine hydrochloride is one of the most commonly used reducing agents for converting iron(III) to iron(II). Reduction of iron(III) with hydroxylamine hydrochloride proceeds by the following reaction (12).

$$2NH_2OH + 4Fe^{3+} \rightleftharpoons N_2O(\uparrow) + 4Fe^{2+} + 4H^+ + H_2O \quad (1)$$
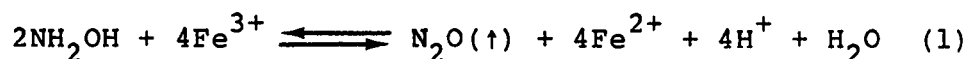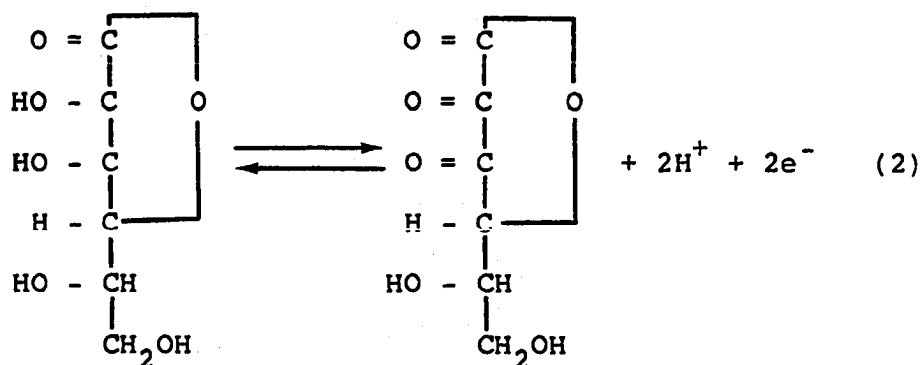
Experimental results showed complete reduction of iron(III) required a minimum of about a 2-fold molar excess of hydroxylamine hydrochloride despite the predicted 1:2 ratio of hydroxylamine to iron(III) (equation 1). The kinetics of iron(III) reduction appear relatively slow under these conditions, even in excess hydroxylamine. Studies of iron(III) reduction versus time for a 14-fold excess of hydroxylamine showed that complete reduction of iron(III) required a minimum of about 50 minutes at room temperature (ca. 21°C) (Figure 1). Slow reactivity is, in part, a result of the acidity of the samples which acts to shift the equilibrium away from iron(III) reduction. Adjustment of sample pH to higher values only served to precipitate the iron(III) as the oxide. Boiling the samples greatly decreased the reaction time but in turn required additional time for cooling of the solutions before they could be properly diluted and injected. The evolution of N_2O gas as a by-product of the reduction caused some minor problems with outgassing in the chromatographic system. Molar excesses up to 30-fold in hydroxylamine hydrochloride gave reasonably good chromatographic behavior with a

Figure 1.   Plot of relative peak height for iron(II) versus reduction reaction
time showing the relative reduction rate of iron(III) with
hydroxylamine hydrochloride at room temperature (23°C)
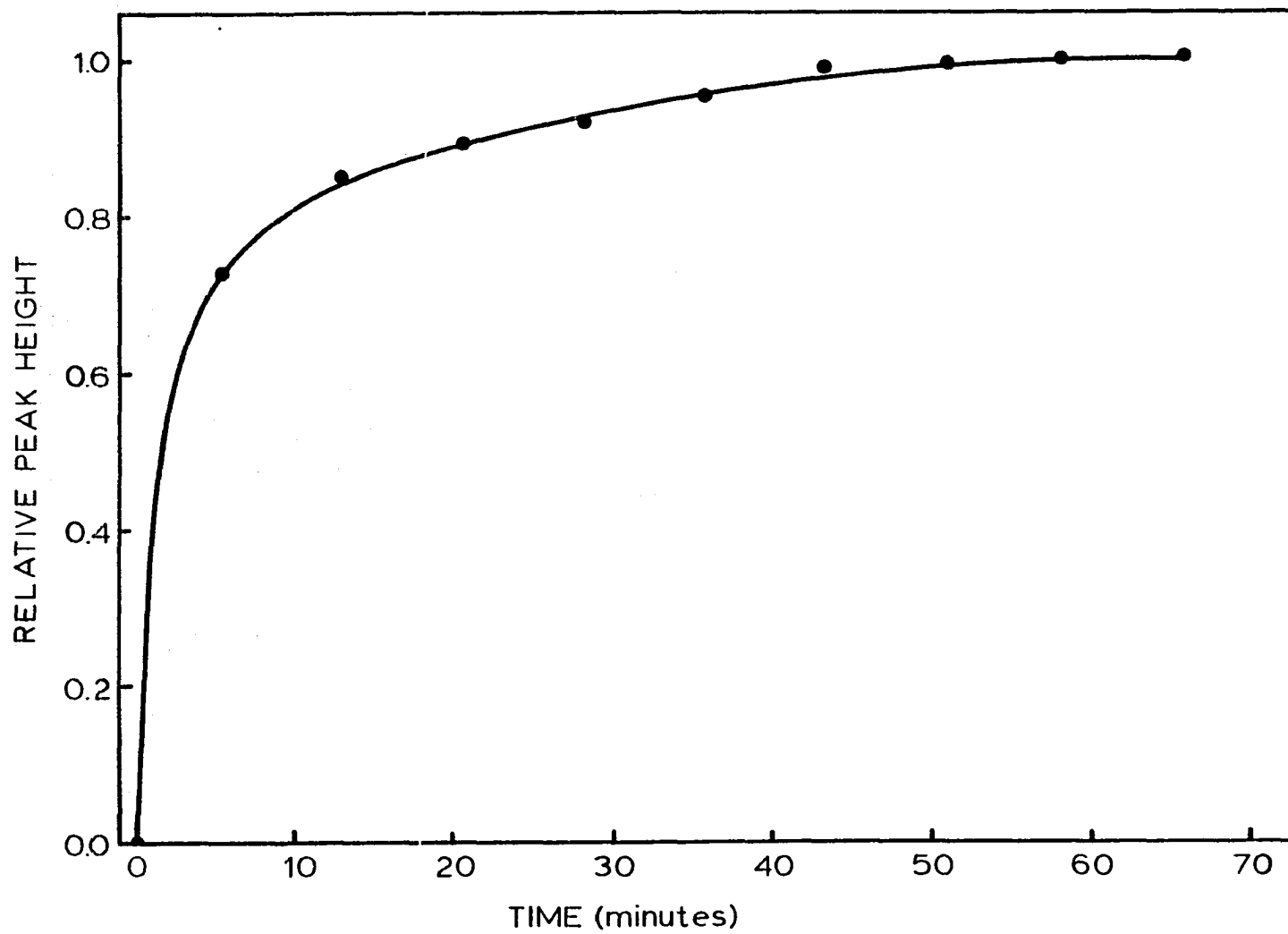
progressively increasing baseline distortion. This
distortion presented itself as a "baseline dip" between the
sample matrix peak and the iron(II) peak. Peak height
measurement became more difficult as the molar excess was
increased. At a 93-fold molar excess of hydroxylamine, the
iron(II) peak was no longer discernible and completely lost
in the "baseline dip".

Addition of L-ascorbic acid to solutions to reduce
iron(III) to iron(II) was examined and gave good results
with minimal sample preparation. The reduction of iron(III)
involves the following half-reaction in the oxidation of L-
ascorbic acid (13).

$$
\begin{array}{ccc}
O = C & & O = C \\
| & & | \\
HO - C \quad O & & O = C \quad O \\
| & \longleftrightarrow & | \\
HO - C & & O = C \\
| & & | \\
H - C & & H - C \\
| & & | \\
HO - CH & & HO - CH \\
| & & | \\
CH_2OH & & CH_2OH
\end{array}
\quad + \; 2H^+ + 2e^- \quad (2)
$$

The oxidized product in L-dehydroascorbic acid ($E' = -0.012$
V (pH 8.7) to +0.326 V (pH 1.05)) (14).

As with the hydroxylamine hydrochloride, the relative
amount of iron(III) reduced versus molar excess of ascorbic
acid was examined. Complete reduction of iron(III) was
obtained with a reaction ratio of 2 moles of iron(III)

reduced per mole of ascorbic acid added (Figure 2). This was demonstrated by a maximum iron(II) peak height for a 2:1 mole ratio of iron(III) to ascorbic acid. Samples with less ascorbic acid present gave a generally linear relation between the amount of iron(III) reduced and ascorbic acid added to the sample. This relation also gave a slope corresponding to reaction ratio of two moles of iron(III) for each mole of ascorbic acid. The curve leveled off and maintained a constant value for amounts of ascorbic acid added above this ratio. The reaction is spontaneous and appears to be complete with mixing. Highly acidic samples may require slightly longer before reduction is complete (15); however, no obvious pH dependency was noticed here. This suggests that the oxidation of ascorbic acid is a very efficient process. No perturbations in the baseline were noticed for samples reduced with ascorbic acid, even with the 95-fold molar excess. The iron(III) was completely reduced on addition of excess ascorbic acid and confirmed by using a post-column reactor system with pyridylazoresorcinol as the color-forming reagent.

Good linearity (correlation coefficient of 0.999) was obtained from 0.100 mM iron(III) to 4.00 mM iron(III) after reduction with a 7-fold excess of ascorbic acid. Significant blanks were obtained at lower concentrations (down to 5.0 µM iron(III)) and blamed on impurities in the

Figure 2.   Relative amount of iron(II) reduced (relative peak height) versus
ratio of ascorbic acid to iron(III) present in the sample
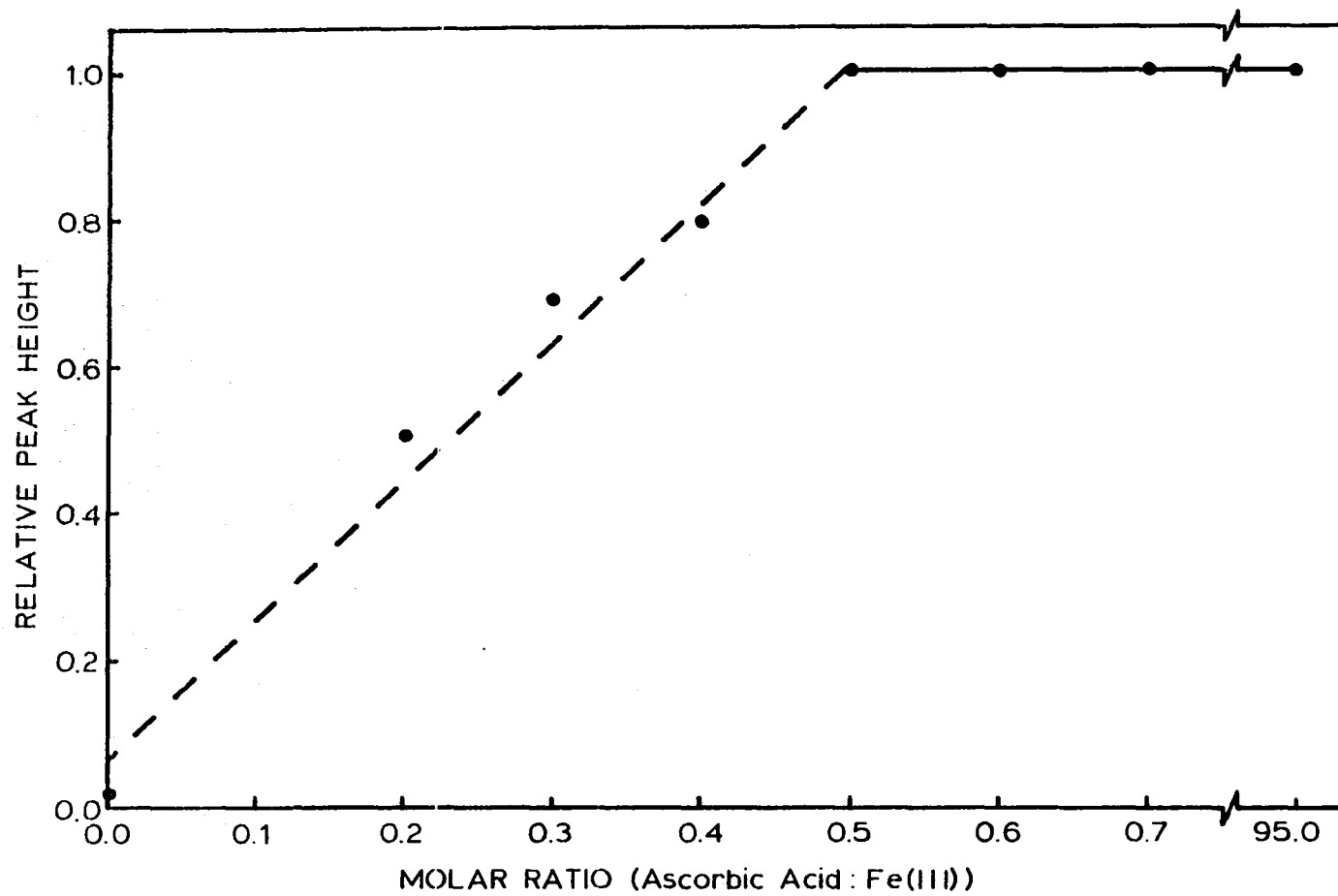
water supply. These blanks were not of any consequence at
lower sensitivities and were lost in the baseline. Figure 3
shows calibration curves for iron(II) and iron(III) (both
with and without ascorbic acid added to the samples)
superimposed on each other. Sensitivity (slope) for the
three calibration curves is similar with good agreement in
blanks (intercepts) and good linearity (Table I). An upper
limit on concentration by direct injection appears to be a
function of column-loading of the ion chromatograph as shown
by a slight curvature in the plot. The small iron(II) peaks
for injections of "week old" iron(III) without ascorbic acid
added to the sample are the result of photochemical
reduction of iron(III) to iron(II) (16) (Figure 3). Freshly
prepared iron(III) solutions did not exhibit noticeable
iron(II) peaks.

Recoveries

Recoveries of iron(II) and iron(III) from solutions
containing both species were examined. Each sample solution
was made up in duplicate and contained different quantities
of iron(II) and iron(III). One solution was diluted and
injected directly into the ion chromatograph, while the
other had an excess of L-ascorbic acid added to it before
dilution and injection. Total iron(II) present was

Figure 3. Calibration curves for solutions from differing
          stock solutions of iron(II) and iron(III)
          solutions showing correlation of peak heights
          with concentration

Fe(II) (freshly prepared)
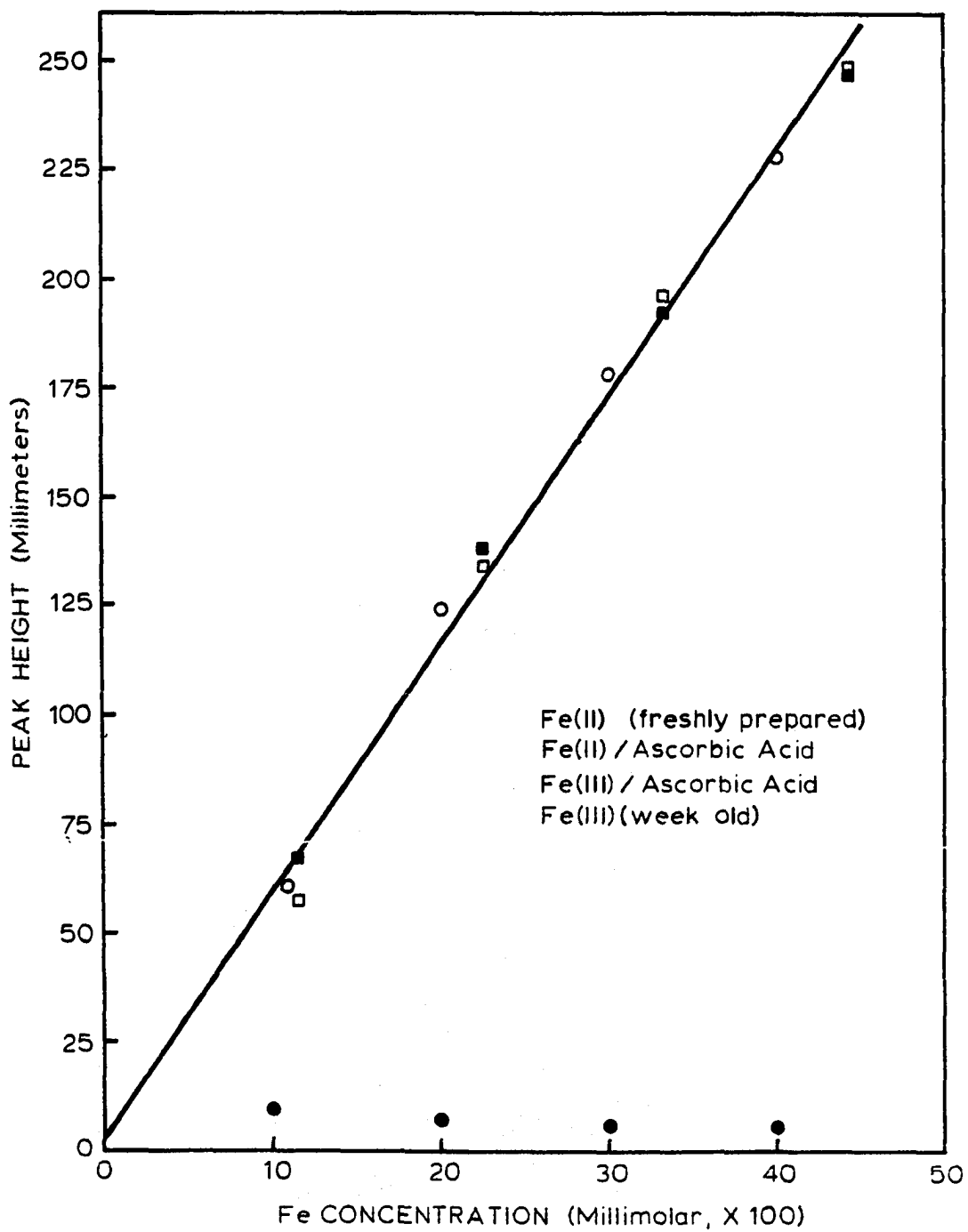Fe(II) / Ascorbic Acid
Fe(III) / Ascorbic Acid
Fe(III) (week old)

Table I. Comparison of calibration curves for iron(II) using iron(III) with ascorbic acid added to the samples (Fe(III)-VC), iron(II) with ascorbic acid to the samples (Fe(II)-VC), and iron(II) without ascorbic acid added to the samples (Fe(II)), and all three curves combined

Curve	Sensitivity[a]	Intercept[b]	r
Fe(III)-VC	5.79	0.039	0.999
Fe(II)-VC	5.74	0.003	0.998
Fe(II)	5.89	0.052	0.998
Combined	5.78	0.038	0.998

[a]Units of μmhos per mM.

[b]Units of μmhos.

determined from the first sample, while iron(III) was
determined by the difference in iron(II) peak height between
the two samples (Figure 4). Excellent agreement was
obtained with the 1,10-phenanthroline method (Table II).
All samples were run immediately to minimize equilibrium
changes. With appropriate care taken in preparation, the
samples showed no significant change in composition over a
period of about one day. The presence of excess ascorbic
acid should provide sample stability for a significantly
longer period of time; however, this was not examined. The
convenient form ad stability of solid ascorbic acid makes it
ideal to ad directly to the solution as the solid.

Interferences

A number of possible interfering species were examined
for their effect on the reduction of iron(III) with ascorbic
acid. Obvious interference would be found with species that
co-elute with the iron(II), such as manganese(II) (17).
Cadmium(II), cobalt(II), ytterbium(III), and thulium(III)
elute close to iron(II) and would give peaks that overlap
the iron(II) peak with this system if their concentrations
are high enough (about 10 times that of iron(II)). Strong
complexing agents of iron(III) or iron(II) would carry the
iron through the chromatographic column in the void volume

Figure 4. Sample containing 0.360 mM iron(II) and 0.286 mM iron(III) with: (a) no ascorbic acid added, (b) 10 mM in ascorbic acid
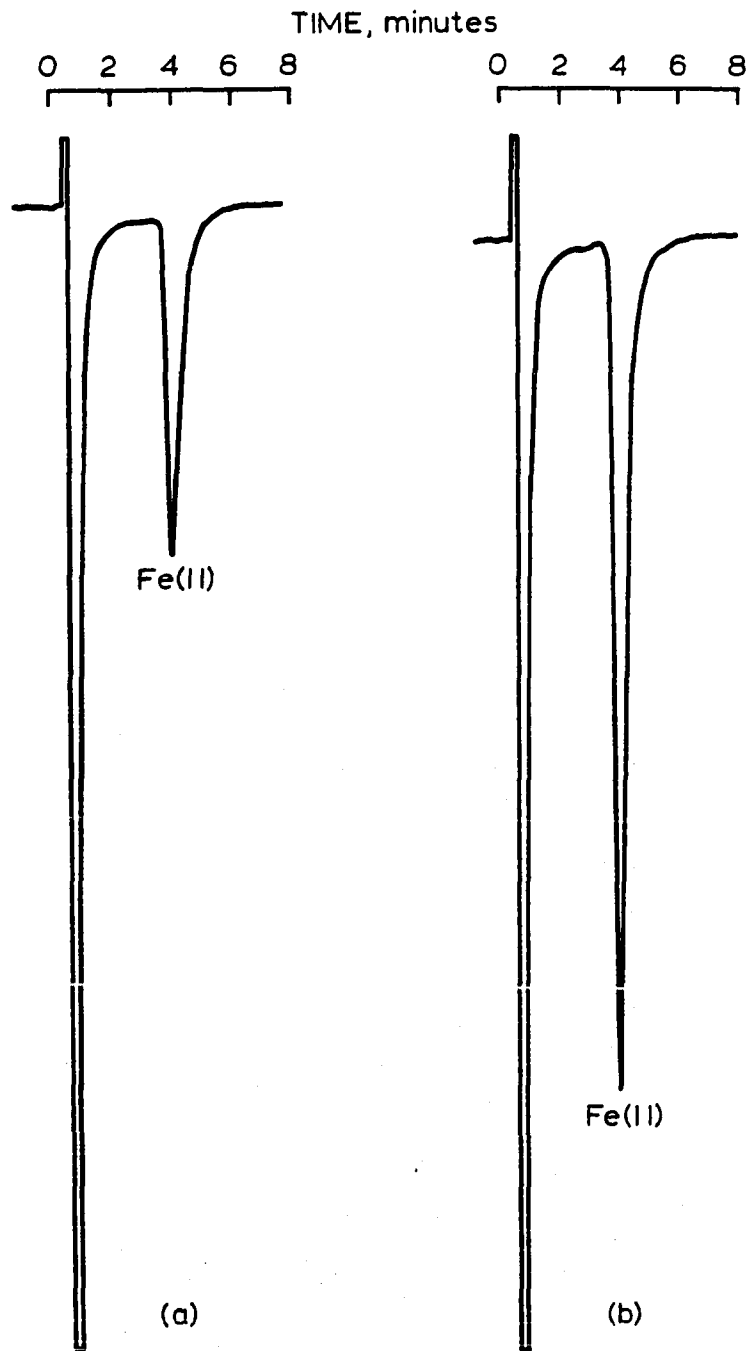
TIME, minutes

Fe(II)

(a)

Fe(II)

(b)

Table II. Recoveries of iron(II), iron(III), and total iron from prepared solutions using cation chromatography and reduction with ascorbic acid. Values in parentheses are for identical samples using 1,10-phenanthroline

Micromoles taken			Micromoles found			Difference		
Fe(II)	Fe(III)	total	Fe(II)	Fe(III)	total	Fe(II)	Fe(III)	total
12.7	30.1	42.8	12.4	30.2	42.6	- 0.3	+ 0.1	- 0.1
			(12.4)	(30.2)	(42.6)	(- 0.3)	(+ 0.1)	(- 0.1)
22.3	20.1	42.4	22.5	20.3	42.8	+ 0.2	+ 0.2	+ 0.4
			(22.6)	(20.2)	(42.8)	(+ 0.3)	(+ 0.1)	(+ 0.4)
33.5	10.0	43.5	33.4	10.3	43.7	- 0.4	+ 0.3	+ 0.2
			(33.1)	(10.6)	(43.7)	(- 0.4)	(+ 0.6)	(+ 0.2)
5.5	15.0	20.5	5.0	15.1	20.1	- 0.5	+ 0.1	- 0.4

of the system. As a result, no iron(II) peak appears.

Other compounds tested are listed in Table III along with the maximum concentration allowed for quantitation of iron(II). Above an interferent concentration of about 50 mM, recovery of the "pseudo-peak" to baseline was slow enough to obscure the iron(II) peak and prevent accurate measurements. Other compounds studied (such as $NaNO_2$ and $Na_4P_2O_7$) directly affected the reduction of iron(III) by either reoxidation of iron(II) or oxidation of the ascorbic acid. Thiocyanate complexed the iron(III) and prevented it from being reduced. Cerium(IV), permanganate, and dichromate each gave additional peaks identified as cerium(III), manganese(II), and chromium(III), respectively. Of these extra peaks only manganese(II) interfered directly with the iron(II) peak. The chromium(III) and cerium(III) peaks eluted fairly late and did not interfere directly with the iron(II) peak. The late elution of these extra peaks significantly prolonged the analysis time. The presence of excess cerium(IV) gave a very large "pseudo-peak" resulting in very slow recovery of the baseline after injection. This slow recovery directly interfered with quantification of iron(II). The chromium(III) peak was more noticeable when hydroxylamine was used as a reducing agent instead of ascorbic acid. Evolution of nitrous anhydride (N_2O_3) (18) was evident in solutions containing $NaNO_2$ when ascorbic acid

Table III. Interference study of iron(III) reduction using ascorbic acid as the reducing agent. Each sample contains: iron(II) (0.25 mM), Ca(II) (0.75 mM, as an internal standard), ascorbic acid (25 mM, unless listed otherwise), and an interferent

Interference Tested	Maximum Allowable Concentration (millimolar)	Molar Ratio
V(IV)	50	200:1
Ce(IV)	0	--
Formic acid	50	200:1
$Na_4P_2O_7$	0^a	--
Na_2SO_3	5	20:1
NaSCN	25^a	100:1
$K_2Cr_2O_7$	2	8:1
$NaClO_4$	50	200:1
$NaClO_3$	50	200:1
$NaBrO_3$	25	100:1
Na_2MoO_4	10^b	40:1
$KMnO_4$	0	--
$NaNO_2$	30^{ab_2}	120:1
$NaNO_3$	50	200:1
H_2O_2	200^c	800:1

[a] Iron(II) peak height decreases at higher concentrations of interferent.

[b] 20 mM ascorbic acid.

[c] 30 mM ascorbic acid.

was added. After agitation and/or sonication to remove the
gas, the solution became a lighter brown in color. No
significant degassing from this reaction was noticed in the
chromatographic system.

This method of iron determination has only been applied
to ion chromatography with conductivity detection, which is
significantly more sensitive to eluent changes than most
other types of detectors. Systems that are not so sensitive
to the ionic nature of the sample or eluent could tolerate
higher concentrations of interferents and reducing agents
are readily adapted to this procedure with little or no
modification. Also, problems with baseline recovery after
injection of complex samples should not be a significant
factor. Such systems might also be more amenable to
variations in eluent composition in terms of gradient
programming. Gradient capability readily allows for the
optimization of the system to prevent co-elution of
interferences such as manganese(II).

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GENERAL CONCLUSIONS

As was mentioned in the General Introduction, each section of this dissertation is interrelated yet is self-contained. Specific observations or conclusions about the system under study in that section were already defined.

Surface-sulfonation of gel resins appears to be functionalized through a "layer-by-layer" mechanism. Retention data suggest that resin homogeneity is still prevalent, even in the most carefully synthesized resins. Preliminary data from scanning transmission electron micrographs taken of thin slices (~ 1000 Å) of resin beads in the uranyl form suggest that the depth of sulfonation into the bead is very shallow. The sulfonation depth appears to be much shallower than predicted by calculation. The high density of exchange sites might well support the hypothesis of a gradient of crosslinking within the bead leading to a capacity gradient. Severe surface heterogeneity is also seen in the micrographs.

The behavior of the low-capacity surface-sulfonated resins is similar to that of high capacity resins in the same environment ($HClO_4$). The selectivity behavior and exchange equilibria correlate well to theoretical predictions because the retention of the cations has been predominantly limited to ion-exchange. Having the exchange

groups located on the outermost resin surface also exhibits relatively good kinetics.

The addition of complexing agents to eluents in cation chromatography causes significant deviation from theory. Much of the deviation is believed to be the result of interactions other than exchange (e.g., ion-pair and surface adsorption of the metal complexes) taking place within the resin. Complexing eluents are still useful and work well to improve and sharpen existing separations. Addition of complexing agents to samples for masking also enhances the capability of the system and greatly expands its scope.

A method for indirect speciation of iron is presented at "face value" and shows some of the versatility gained by incorporating simple pre-column derivatization methods. Indirect speciation of other cations by oxidation or reduction is quite possible. For example, reduction of cerium(IV) to cerium(III) and manganese(VII) to manganese(II) have shown limited success.

It is quite obvious that this work is in no way a complete description of low-capacity surface-sulfonated gel resins and their application to ion chromatography. This dissertation merely serves as a meager guide in the overall quest for better cation separations.

FUTURE WORK

Working to solve research problems always creates more research. The work in this dissertation, as with any other, has many loose ends which may be pursued. Many of the problems were not investigated simply because of a lack of time. It is sincerely hoped that the work here is not forgotten for too long.

· Sulfonation

The process of resin sulfonation is relatively complex. Control of the degree of sulfonation and the products is often difficult. Hot aqueous sulfuric acid has been used effectively and the reaction can be controlled with proper precautions. Dehydrating conditions with acetic anhydride, which also acts as a diluent for sulfuric acid, should allow the reaction to be run easily at room temperature. Both reaction control and safe operating conditions would be achieved.

Scanning Transmission Electron Microscopy was used to examine thin slices of surface-sulfonated resin beads. The resins were placed in the uranyl form which is opaque to the electron flux. The sulfonation depths varied over a range of about tens of angstroms for a sulfonation depth estimated

at best to be between 15 and 30 A. Inhomogeneity of neutral resin beads is a problem that needs to be examined and solved. Work in progress at the time of this writing showed significant heterogeneity of the resin surface. This appears as a very coarse texture on the surface of the resin bead.

The kinetics of sulfonation may be examined easily by Scanning Transmission Electron Microscopy. Several reaction mixtures of progressive sulfonated resins could be examined. The degree of sulfonation for each reaction could be used to define the kinetics of the reaction.

Cation Selectivity

Only one resin was studied specifically for its selectivity for various cations. Work with monovalent cations was not done but is strongly recommended. As seen in Figure 10 of Section III, the separation of alkali metals is quite good but lacks resolution between Potassium(I), Rubidium(I), and Cesium(I). Use of a resin with higher degree of crosslinking may improve the later part of the separation because smaller, more highly hydrated cations are more readily affected by increased resin crosslinking. The result should be more rapid elution of earlier cations and little change seen with the later cations.

Post-column detection was found to quite useful in this work. The buffering agent (ammonium hydroxide) for the color-forming reaction conveniently masked other metal cations that might interfere. Selective masking by use of other complexing agents in the post-column reaction system would enhance the detection system. If ethylenediamine is used in the eluent it would serve as an effective masking agent after neutralization in the post-column reaction chamber.

Rapid separation of magnesium and calcium has been demonstrated but not applied. The system used in Section II would easily be applied to dedicated work and more complex samples. A vast stock of selective color-forming reagents is available to tailor detection to the metal of interest.

Eluent cations have usually been limited to those giving immediate success. Further studies to find other eluting cations is needed to include higher valence metal cations (such as thorium(IV), tin(IV), and antimony(III)). Also of interest are the changes in selectivity imposed by such eluent cations.

Complexing Eluents

Complexing eluents have given good results where both moderate a complexing agent and a relatively strong eluent

cation are used. Limited work has shown that a strong eluent cation is not necessary for low-capacity resins if the complexing agent is strong enough. Several divalent cations were obtained in the same chromatogram as several monovalent cations using oxalate or citrate as the complexing agents and hydrogen or lithium as the eluting cations. Proper choice of eluent conditions (EDTA as the free acid or the lithium salt) may produce a chromatogram having both alkali metals and alkaline earths in it.

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