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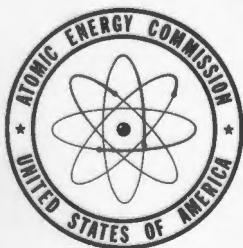
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METHODS OF PREPARING SPECTROGRAPHICALLY PURE PRASEODYMIUM SALTS

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METHODS OF PREPARING SPECTROGRAPHICALLY

PURE PRASEODYMIUM SALTS [1]

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I. ABSTRACT

An ion-exchange process was developed for the separation of spectrographically pure praseodymium salts in kilogram amounts from commercially available concentrates. The application of either 0.5% or 0.1% citrate solutions as eluting agents was shown to result in excellent separations of praseodymium from samarium, neodymium, and lanthanum when the mixed rare earths were eluted from Amberlite IR-100 or Nalcite HCR cation-exchange resins.

A number of variables were investigated which were shown to be important in the ion-exchange method for preparing pure praseodymium salts. It is desirable to approach equilibrium conditions as closely as possible during the elution process in order that the small differences between the equilibrium constants of the individual elements may be fully utilized. Sufficient time must be allowed for the cations to diffuse into and out of the resin so that an equilibrium may be established between the rare earths in the resin phase and those complexed by the citrate ions in the surrounding solution phase. Experimental evidence is given to show that a reduction in the flow-rate of the eluting solution and a decrease in resin particle size, which decreases the length of the diffusion path in the resin, resulted in a closer approach to equilibrium conditions and increased the separation of adjacent rare earths.

Small differences in the pH of the citrate solutions, used to elute the rare-earth band from the resin bed, resulted in both a qualitative and quantitative change in the shape of the elution curves. The variation in the shape of the curves was interpreted as being related to a change in the relative importance of different rare-earth citrate complexes in the eluting solution. The existence of at least five such

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[1] This paper is based on a PhD thesis by Thomas Butler, submitted in June, 1951.

complexes have been reported by Spedding and co-workers (4). In general, lower pH values of the citrate solutions, in the applicable pH range, resulted in better separations. However, in large-scale production, a compromise must be made between the increased time necessary to complete the elution, with somewhat better separation, at lower pH values, and labor cost.

There is little choice between the use of 0.5% or 0.1% citrate solutions for separating small amounts of pure praseodymium. However, 0.1% citrate is to be preferred for large-scale production since the cost of the operation is reduced.

Nalcite HCR resin was shown to be superior to Amberlite IR-100 for large-scale praseodymium separations. Nalcite HCR not only has a higher capacity but the spherical form of the particles permits better packing in a column, thus reducing the tendency of the rare-earth band to form streamers or to channel during the elution. Direct observation showed that irregularity of the band-fronts of the individual rare earths may account for a large percentage of the overlapping of adjacent rare earths. In other words, the region of mixed rare earths in an elution may be attributed in part to the mechanical difficulties of maintaining a horizontal rare-earth band-front during the elution.

Preliminary experiments showed that a greater percentage yield of the available praseodymium resulted from increasing the sample weight of the praseodymium concentrate with a proportionate increase in the column length. This increase in yield occurs because the region of overlapping rare-earth bands remains essentially constant if a minimum resin bed-length is provided for allowing full development of the component rare earths into bands. Further increase in resin bed height above the minimum length for a given column load does not result in further separation between adjacent rare earths.

A complete investigation of the relation between column load and column length was prevented by the formation of a slightly soluble rare-earth citrate compound which precipitated in the resin bed as the sample weight was increased. The rare-earth citrate precipitation in the resin bed was prevented by adding excess hydrochloric acid or ammonium chloride to the mixed rare-earth chlorides before the sample was adsorbed on the resin bed.

The conditions of elution were successfully scaled up from small column experiments to a pilot-plant which was demonstrated to have a capacity for producing 15 kilograms of spectrographically pure praseodymium oxide per year. In the spectrographically pure material, the emission lines of any possible rare-earth impurity were absent which showed that less than 0.1% of such contaminates were present.

During the course of these investigations, seven kilograms of spectrographically pure praseodymium oxide were prepared and made available to a number of investigators conducting theoretical researches on the properties of the rare earths.

II. INTRODUCTION

The series of elements with atomic numbers 58 through 71 are commonly known as the rare earths; recently, following Goldschmidt's suggestion, they are also designated as the lanthanide series. These elements are so remarkably similar in their chemical and physical properties that they have been the object of extensive investigations to determine means of obtaining adequate amounts of their pure compounds for detailed studies of their properties. Although rare-earth compounds have been studied for a long time, many of the reported physical-chemical data need revision because the results, in most instances, were obtained with relatively impure samples.

The synthetic production of plutonium by nuclear fission lent emphasis to the need for the general availability of pure rare-earth compounds. Isotopes of the rare earths are prominent among the fission products, and it became vitally important to determine their nuclear cross-sections for capture of neutrons as well as their chemical properties.

The transuranic elements constitute a closely related group known as the actinide series or rare earths Type 5f in analogy to the lanthanide series or rare earths Type 4f. It is evident that the lanthanide and actinide series of elements have analogous properties and, since the members of the actinide series are even less available for experimental work than are the members of the lanthanide series, it follows that the latter find important use for stand-ins and carriers in research on the transuranic elements.

The research described in this thesis was undertaken in order to develop a more rapid and economical separation procedure for the individual light rare earths, the cerium group, with particular emphasis on the preparation of praseodymium salts. Ion-exchange methods were chosen for study; it will be shown that this procedure has many advantages over those previously reported. The goal of this research was the development of a rapid, economical process for obtaining high yields of very pure praseodymium which could be scaled up to a plant having a production capacity of several kilograms of pure salt per year.

For some time, research has been conducted in these laboratories on the application of ion-exchange to the separation of the rare-earth elements. The results of these investigations have been reported in a

series of papers by F. H. Spedding and co-workers (1,2,3,4,5,6,7).
This thesis presents further applications of this technique as related
to the purification of praseodymium.

III. LITERATURE REVIEW

A. Chemical and Physical Properties

of the Rare Earths

The chemical properties of the elements in Group III-A of the
periodic system are so similar that ordinary chemical methods of separa-
tion are in most cases of relatively little value. Lanthanum and
yttrium are always present with the rare earths in nature and follow
them closely during separation schemes. The chemistry of the rare
earths has been reviewed rather extensively in a number of publications
(8,9,10,11,12,13,14). These references include a large body of quali-
tative chemical knowledge which has been obtained about rare-earth
compounds, which proved valuable in the development of better methods
for the separation and purification of these elements.

The normal tripositive valency state is common to all the rare
earths. Other valence states are known for some of the rare earths;
for example, tetrapositive cerium and bivalent ytterbium, europium and
samarium are well established. Some controversy exists regarding other
valence states of praseodymium and terbium. A search of the literature
failed to reveal a serious claim for the existence of any valence state
other than the tripositive in aqueous solutions for the above two ele-
ments. However, higher valence states have been shown to exist in the
oxides of these elements. The generally accepted oxides of praseodymium
are Pr_2O_3, Pr_6O_{11} and PrO_2. Marsh (15,16) has presented some evidence
of a divalent praseodymium in the form of PrO. Prandtl (17) has claimed
that praseodymium can exhibit a higher valency of 5; this claim has not
been verified and most workers now agree that the positive four oxidation
state is the maximum.

It is accepted that the black oxide obtained as a result of heating
Pr_2O_3, or salts such as the oxalate, in air at $700-1000°$ has an atomic
composition represented by the formula Pr_6O_{11}. The exact form of the
chemical binding in this oxide is questionable. Marsh (15) prefers to
represent Pr_6O_{11} as $PrO_{1.833}$. On the basis of tensionmetric measurements
and X-ray diffraction patterns, he would represent $PrO_{1.833}$ as being
effectively PrO_2 deficient in oxygen, and not $PrO_{1.5}$ with excess oxygen.
McCullough (18), on the other hand, presents evidence in support of the
existence of Pr_6O_{11} as a separate and distinct phase in the praseodymium-
oxygen system. He prepared the higher oxide, PrO_2, by heating Pr_6O_{11}
to $300°$ under a pressure of 50 atmospheres of oxygen.

Many of the physical and chemical properties of the rare earths may be adequately explained on the basis of the electronic configurations of the atoms. The rare earth ions have the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^n 5s^2 5p^6 \lbrack 5d^1 6s^2 \rbrack$; the value of n increases from 0 to 14 from lanthanum through lutetium. The $5d^1 6s^2$ electrons enclosed in brackets are involved in ordinary chemical reactions in aqueous solutions and account for the tripositive valence of all these elements. The addition of electrons at the 4f level has little effect on the chemical properties of the ion, since the normal valency is unaltered by their presence and they take no part in the formation of compounds. It becomes apparent that these elements should be similar chemically since they differ from each other only by the charge on the nucleus and the number of electrons in the 4f shell.

The absorption spectra of rare-earth ions in aqueous solution and in crystals furnish the basis of a good physical method for the analysis of several of these elements. The absorption spectra have been shown to result from "forbidden" transitions of the electrons between states within the 4f shell. These transitions give rise to sharp-line absorptions (19) which are of sufficient intensity to allow semi-quantitative determinations to be made of several of the rare-earth ions. Good evidence in support of the forbidden transition hypothesis has been given by Bethe and Spedding (20) and by Spedding (21).

The rare earths provide a unique series of elements for the application of modern concepts regarding the paramagnetism of ions. An outstanding property of the rare earths is the strong paramagnetism displayed by the metals and their compounds. This property has been utilized as a method of analysis. The paramagnetism arises from the 4f electrons which are shielded to a large extent from the fields produced by the adjacent chemically bonded groups. Thus the paramagnetism characteristic of a particular ion is not greatly perturbed by the presence of surrounding ions and may be used for semi-quantitative analyses.

One of the most important factors influencing the chemistry of the rare earths is the contraction of the rare earth ion as the atomic number increases. The admission of successive electrons into the 4f orbitals increases the nuclear charge which pulls all of the electrons toward the nucleus and results in a contraction of the atomic radius. This effect increases the strengths with which the electrons are held to the atom and results in a decrease in basicity going from lanthanum through lutetium. Yttrium has properties of atomic volume and basicity which places it roughly between dysprosium and holmium, and it is usually found between these elements in separation schemes. A review of the basicity characteristics of scandium, yttrium and the rare earth elements, as related to separation methods, has been published by Moeller and Kremers (22).

B. Methods for Separation

The rare earths occur so closely associated in nature that it is extremely difficult to separate them. They have been obtained, however, in varying degrees of purity by elaborate and laborious fractionations of two mixtures, "yttria" and "ceria". These mixtures were originally believed by their discoverers to be pure oxides. The persistent re-searches of Mosander, Delafontaine, Cleve, von Welsbach, Brauner, James, Hopkins, McCoy, and many others resulted in the separation of "yttria" into the oxides of Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu; and "ceria" into the oxides of La, Ce, Pr, Nd, Sm, Gd, and Eu.

Mosander discovered that "ceria" was not a pure material but was composed of at least three substances which he called ceria, lanthana and didymia. This last oxide was afterwards split by von Welsbach into praseodymia and neodymia. Biosbaudran found samaria and gadolinia to be present in didymia. Later, Demarcay made an elaborate series of frac-tionations of samarium magnesium nitrate which resulted in the discovery of a new rare earth oxide, europia.

In discussing the rare earths it is convenient to retain their classification into two groups: (1) the cerium group or light rare earths and (2) the yttrium group or heavy rare earths. The division is by no means as sharp as indicated above, but in general these are the major constituents. The elements of the cerium group are compara-tively easily separated from those of the yttrium group by the double sulfate method (23,24). By far the most abundant element of the first group is cerium. Since it is also the most easily purified due to its tetravalent state, most of the cerium-group concentrates obtained from industrial sources are nearly free from cerium.

The principal methods of separating praseodymium may be classified as follows:

1. Fractional recrystallization
2. Fractional precipitation
3. Chemical separations
4. Ion-exchange

Fractional recrystallization has received by far the most attention. The most successful fractional recrystallization methods have employed the double ammonium, magnesium or manganese nitrate. A typical example of a double nitrate is $2(R.E.)(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$. To be suitable for fractionation, the salts must have a marked temperature coefficient of solubility and must remain stable over long periods of time during which they are repeatedly heated and cooled. Baxter and Stewart (25) used the double ammonium nitrate method in the atomic weight determination

of praseodymium. The use of these salts and many others is adequately
reviewed in a number of publications (8,9,10,11,23,26). A fractional
recrystallization step is desirable in the concentration of praseodymium
from the ore. No other process offers a comparable concentration in an
equal number of operations in a given time. This process is especially
useful for concentrating praseodymium up to 50% in a mixture but becomes
less efficient after this concentration is reached. On the other hand,
ion-exchange methods become more efficient as the element is enriched in
the crude mixture. Therefore, a rapid, inexpensive concentration method
is desirable and further investigations of the older methods of frac-
tional recrystallization are important.

Chemical separations of praseodymium have involved the use of the
tetravalent state of the element, particularly in the form of the oxide.
The formation of PrO_2 has been used to separate praseodymium from
lanthanum by the nitrate fusion process (27). The presence of cerium
is desirable in this separation since the CeO_2 formed acts as a carrier
for PrO_2 and cleaner separations are thus obtained from lanthanum.

Fractional precipitation is mainly useful in separating lanthanum
and praseodymium mixtures, since lanthanum is considerably more basic.
The essential feature of this method is the controlled introduction of
a reagent such as ammonia, or a source of carbonate ion which preferen-
tially precipitates the praseodymium. A repetition of this process on
the increasingly enriched fractions results in an eventual purification.
The air-borne ammonia technique described by Vickery (28) is representa-
tive of this method. In this method, the slow, controlled addition of
NH_4OH to a solution of mixed rare earths is accomplished by bubbling
air through an ammonium hydroxide solution and leading the vapor to the
solution of rare earths where the hydroxides are fractionally precipi-
tated.

A separation method which may become increasingly important in the
future is that of solvent extraction. Only a few preliminary results
have been reported to date, and such work will be necessary before the
method can be fully evaluated. Appleton and Selwood (29) have reported
the use of n-butyl alcohol as a solvent for the extraction of aqueous
solutions of mixed rare-earth thiocyanates. The distribution of nitrates
between water and n-hexyl alcohol showed promise as reported by Templeton
and Peterson (30), and Templeton (31). The extraction of R.E.-5,7,-
dichloro-8-quinolinol chelates with chloroform is described by Moeller
and Jackson (32). These experiments have been performed in batch-wise
fashion; results with columns which can utilize multiple stages have not
been reported. No pure rare earths have been reported by solvent extrac-
tion methods to date.

In summarizing the separation methods indicated above, it must be
emphasized that, at best, they are laborious and require several hundred

separate fractionations, extending over a period of perhaps eight to 12 months, to obtain very pure praseodymium salts.

During the past 10 years, a tremendous advance in rare-earth separation chemistry has been developed. The ion-exchange technique has largely superseded all other methods for the final purification steps for individual rare earths.

The use of siliceous ion-exchange material, Crystallite No. 20, for the separation of the rare earths was reported by Russell and Pearce (33). They employed a column of the sodium-form exchanger through which a solution of mixed rare-earth nitrates was passed. The amount of exchangeable ions in the solution was greater than could be accommodated by the weight of exchanger used. Fractions from this adsorption operation indicated that lanthanum was adsorbed less strongly followed by the other rare earths in the order of increasing atomic number. It was demonstrated that the rare earths could be eluted from the exchanger with 10% sodium chloride. The lanthanum ion was the most loosely-held and was enriched in the first effluent followed by the other rare-earth ions in the order of increasing atomic number. The use of a complexing solution, such as ammonium citrate, for eluting the rare earths from cation-exchange resins results in a reversal in this order of elution and gives much better separations.

The development of suitable synthetic ion-exchange resins, just prior to and during the late war years, enabled a rapid advance to take place in the application of this technique to rare-earth separation. As mentioned previously, the production of plutonium stimulated the further development of this method. The process as developed on the Manhattan Project was not released for publication until 1947. A history of its development was published by Johnson, Quill and Daniels (34).

Spedding, et al., (2) have reported the separation of the adjacent rare earths, praseodymium and neodymium, in gram amounts and of spectrographic purity. This was accomplished by eluting the rare earths from a bed of Amberlite IR-1 cation-exchange resin with 5% citrate solutions having pH values in the range of 2.50 to 2.80.

Harris and Tompkins (35) used a similar technique for separating the rare earths of the cerium group. They employed columns of Dowex-50 resin which also were eluted with 5% citrate solutions. It was claimed that excellent separations were obtained for the radioelements and for milligram quantities of the elements.

Ketelle and Boyd (36) reported the separation of radio-praseodymium, free of other rare-earth activities, using columns of 270-325 mesh size Dowex-50 resin which were eluted with 5% citrate at a pH value of 3.40 and at a temperature of 100°.

More recently, Spedding, et al., (3,4,5,6) have shown that the
elution of mixed rare earths from cation-exchange resins with citrate
solutions having concentrations of 0.5 and 0.1% citric acid and adjusted
to appropriate pH values with ammonium hydroxide, resulted in excellent
separations of the adjacent elements. These concentrations of citrate
are particularly advantageous for the preparation of large amounts of
the pure elements and result in lowering the over-all cost of the process.

C. Basic Principles of Ion-Exchange as Applied

to Rare-Earth Separations

The cation-exchange resins may be depicted as high molecular weight
polymers containing an acidic group, such as the sulfonic group, as an
integral part of the resin and an equivalent number of cations to assure
electrical neutrality. The following practical aspects must be considered
in the synthesis of these resins.

1. The resin must be rendered negligibly soluble by sufficient
    cross-linkage.

2. The resin must be sufficiently hydrophilic to permit diffusion
    of ions throughout the particle at a useable rate.

3. The resin must contain sufficient exchange groups to have a
    practical operating capacity.

4. The resin must be chemically stable under the conditions of
    application so as not to undergo degradation during use.

There are several excellent resins on the market which adequately
fulfill these requirements. These exchangers constitute a class of
electrolytes having properties that are in many ways similar to true
solutions of electrolytes. Cation exchangers are ionic solids in which
the anion is nondiffusible but has free access to diffusible cations
which may compete for positions on the active groups.

In many respects the action of the resin follows the law of mass
action. Chemical equations for the adsorption reaction on the hydrogen-
form cation exchanger may be written as follows, arbitrarily assuming
the behavior of trivalent praseodymium to be typical for any trivalent
rare earths.

$$Pr^{+++} + 3 \; HR \; \rightleftarrows \; PrR + 3H^{+}$$

In this equation, $\underline{R}$ represents a resin having nuclear sulfonic acid

groups. This equation represents the initial adsorption step and is
generally referred to as "leading the column". In a deep-bed resin
column the mixed rare-earth chloride solution is allowed to flow through
the bed, and the reaction is driven to completion since the hydrogen
ion is removed from the vicinity of the exchange and flows on down the
column as hydrochloric acid. The adsorption step results in a band of
rare earths at the top of the column, and the acid produced in the ex-
change is washed out of the bed with distilled water.

The column is now in condition to begin the elution. Since the
effective concentration of a cation in solution may be reduced by com-
plex formation, any cation can be replaced on the resin by a dilute
solution of a second cation and an anion which will form a complex with
the bound cation. The complexing agent most widely used for rare-earth
separations is a citric acid solution adjusted to a given pH with ammonium
hydroxide. When such a citrate solution is passed through a column of
exchanger in the hydrogen-form, exchange occurs between the ammonium
and hydrogen ions and the first effluent is citric acid. The ammonium
ion remains on the exchanger along with a small equilibrium concentration
of hydrogen ions which depends on the initial pH of the citrate solution.
The resin eventually becomes saturated with ammonium ions at the equili-
brium concentration, and the effluent reaches the composition of the
original solution.

If a mixture of rare-earth ions had been previously adsorbed at the
top of the column, as mentioned above, the release of the hydrogen ions
from the resin into the solution would prevent the formation of a rare
earth-citrate complex; the metal ions would remain adsorbed on the ex-
changer until the pH had increased to the point where the complex is
stable. As a result, no rare earth-complex ions can precede the pH
region which will permit their existence. This fact has been observed
in all the researches described in this thesis. In the separation of
the rare earths using 0.5 and 0.1% citrate solutions, the appearance of
the ammonium ion and rare-earth ion at the bottom of the column (generally
called breakthrough) occurs essentially simultaneously. This shows that
the rare earth-citrate complex is destroyed and the rare-earth ions re-
deposited upon coming in contact with the hydrogen-form exchanger.

During the elution, a complex series of equilibria occur within the
body of the resin which result in the separation of the individual rare-
earth ions into bands which are subsequently recovered in the effluent
from the column. The exact mechanism of this process is not known.

As stated previously, a single chemical operation gives only a small
enrichment of one adjacent rare earth over another; therefore, it becomes
obvious that a process which automatically repeats the operation many
times is desirable. The ion-exchange column provides such a method. The
exchange of rare earths between the resin and solution phases occurs

thousands of times as the rare earths move down the column, and the slight differences in the equilibrium values for the different rare earths are thus made effective in separating the elements.

It is generally recognized that the sharpness of separation depends upon several factors, such as

1. Nature of the eluting agent
2. Concentration of the eluting agent in the solution
3. The pH of the eluting solution
4. Temperature of the eluting solution
5. Size of resin particles
6. Size of column as related to the column load
7. Rate of flow of the eluting solution
8. Type of ion-exchange resin
9. The cation to be separated

The investigation of these variables requires that one variable be selected for study while holding the remaining variables constant. It is evident that a large number of experiments would be necessary to complete a thorough study of the process. Fortunately, it has been possible to extrapolate some data to fit other conditions without making a complete study of each individual variable. However, the extrapolation of data obtained from tracer scale (10^{-9} to 10^{-16} gm) experiments to multi-gram quantities has proved unreliable in several instances and should be avoided if possible.

No attempt has been made to review the extensive literature concerning the theories proposed to explain the ion-exchange process or the many applications of the process. Several excellent reviews (37,38, 39,40,41) are available which deal adequately with this material.

IV. EXPERIMENTAL PROCEDURE

A. Apparatus

The bulk of the data on the separation of praseodymium by ion-exchange was obtained from the operation of small columns designed to handle up to the equivalent of 10 grams of rare earth oxide per elution. These columns, shown in Figure 1, were 22 mm inside diameter Pyrex glass tubes with a porous glass disc sealed into one end. The end containing the glass disc was drawn down to accommodate a one-quarter inch inside diameter rubber or Tygon tube fitted with a glass nipple. A screw clamp on the flexible tubing allowed the flow-rate of the eluting solution to be adjusted. The column assembly was mounted in a vertical position so that the porous glass disc acted as a support for the resin bed.
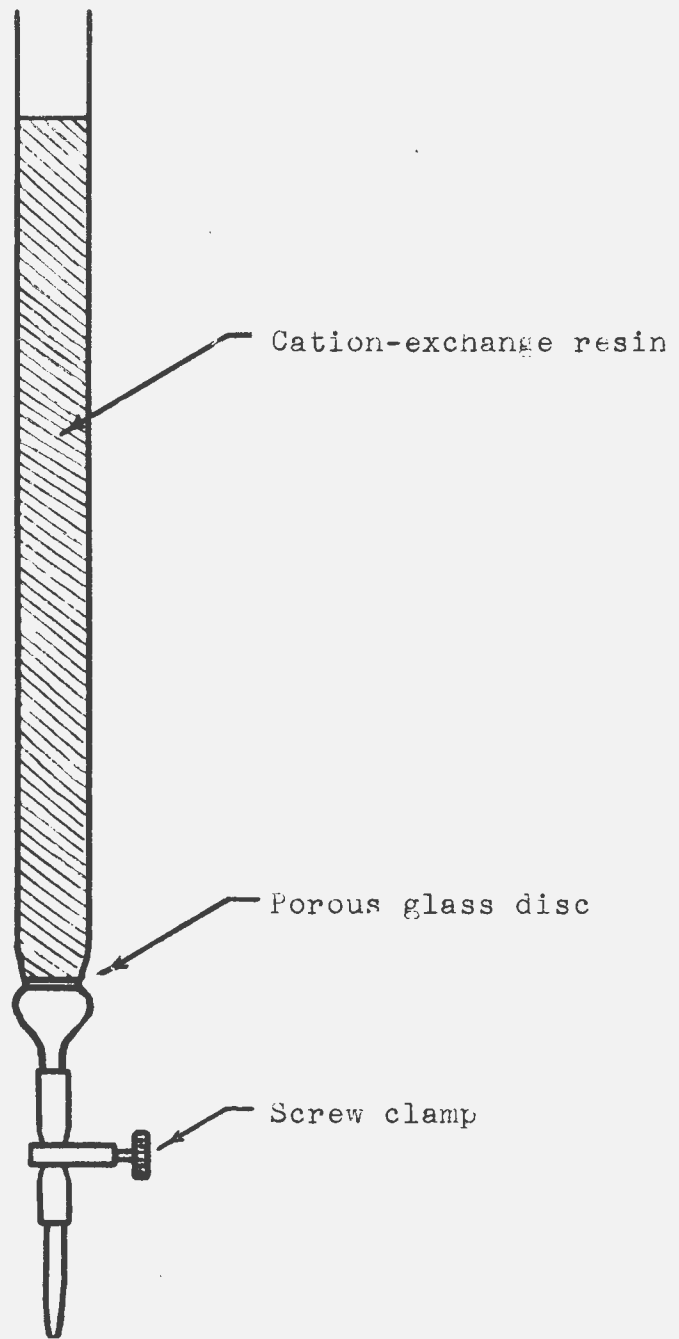
Figure 1 - Ion-exchange column assembly

The column was partially filled with water and the dry ion-exchange resin added slowly until a few centimeters over the desired bed height was obtained. The resin bed was then backwashed with water to remove any entrapped air bubbles. The detailed operation of such a column is described in a later section.

In addition to the small columns mentioned above, two pilot-plants were set up during the course of this investigation. The operational design was essentially the same as that for the smaller columns; it involved a reservoir for preparing the eluting solution, a means of supplying the columns with the solution and a means of collecting the effluent. The first pilot-plant consisted of 24 columns erected in a vertical position on 4-inch by 4-inch wood supports arranged in a manner convenient for the collection of 45-liter volumes of effluent. The columns were Pyrex pipes 10 feet long with 4-inch inside diameters. The tops of the columns were closed with standard flanges and stainless steel plates one-half inch thick. Neoprene gasket material was used between the glass and stainless steel plates to make an air and water-tight seal. The bottoms were closed in a similar manner, except that a 40-mesh stainless steel screen was sealed between two gaskets with rubber cement and inserted between the glass pipe and bottom plate to retain the resin. The top and bottom plates were fitted with one-half inch stainless steel pipes to serve as inlet and outlet. The eluting solutions were allowed to flow, by gravity, from a constant-head tank supplied from a main storage tank by means of a centrifugal pump. All tanks used to contain the solution were of stainless steel in order to reduce contamination of the solution due to corrosion.

The second pilot-plant which was constructed differed only in detail, but not in principle from that previously described. This unit consisted of 20 Pyrex pipe columns five feet long and six inches in diameter. These columns were mounted on an angle-iron framework in banks of 10 columns. The ends were closed with monel metal plates in a similar manner to that described for the 4-inch diameter columns. The make-up and storage tanks were of stainless steel as was the constant head tank. The columns were mounted about three feet from the floor in order that 45-liter carboys could be placed on carts and run under the columns for collection of the effluent solutions. Two views of this pilot-plant are shown in Figures 2 and 3.

Special note should be made of the efforts to obtain a uniform flow of the eluting solution through the columns. The rare-earth mixture forms into bands of individual rare earths on the resin during the elution process and it is important to the separation that these bands be maintained distinct and horizontal throughout the elution. A serious channeling in the bed would result if the solution were withdrawn from a limited area at the bottom of the column. In the case of the 22 mm diameter columns, a bulb of about 20 ml capacity was left between the

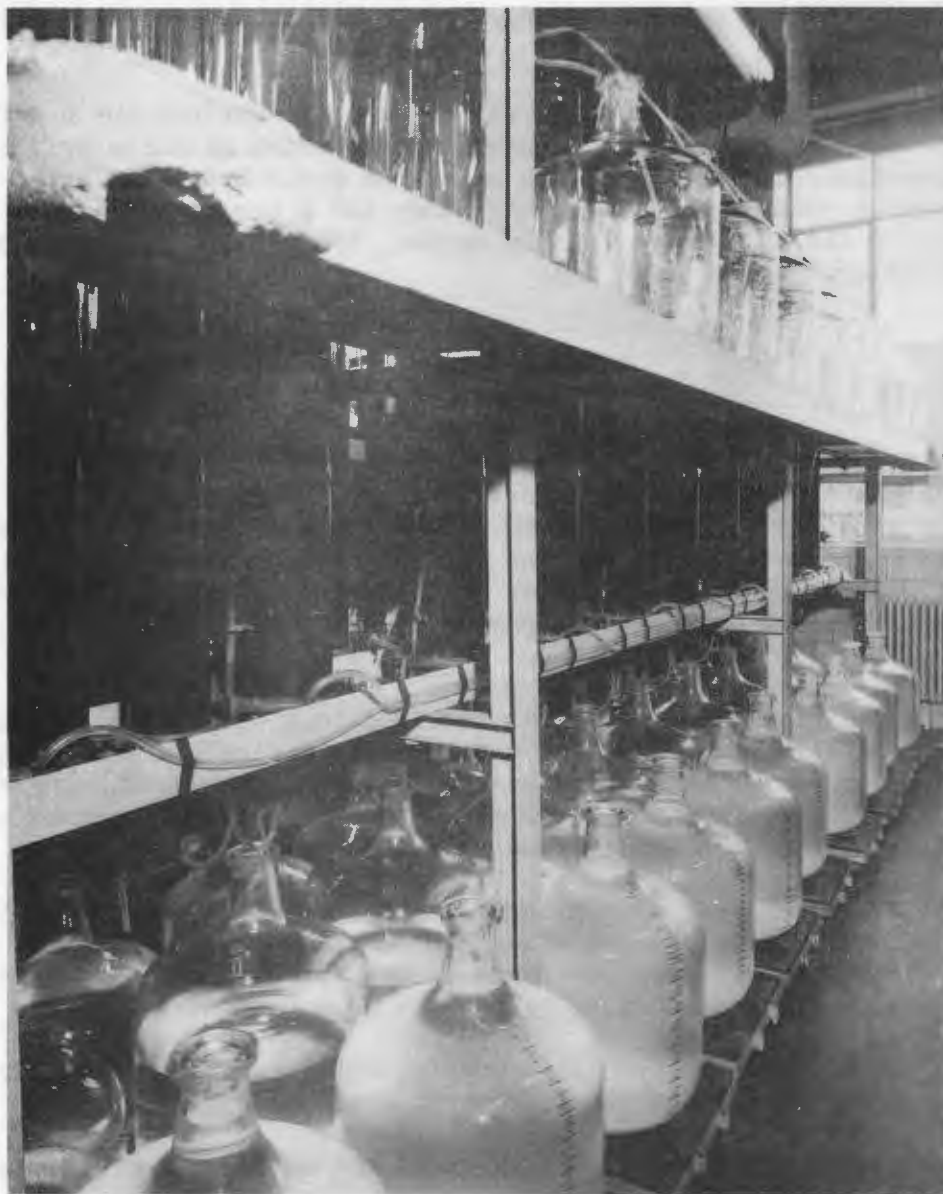Figure 2 - Pilot-plant for separating rare earths.

Figure 3 - Pilot-plant for separating rare earths

porous glass disc and th point of outlet. This volume was sufficient
to allow the pressure to equalize over the entire surface of the glass
disc and resulted in fairly even flow through all parts of the resin
bed.

The bottom plate for each of the 6-inch diameter columns was fit-
ted with seven symmetrically-arranged outlets which withdrew solution
from a reservoir one inch in depth below the resin bed. The seven out-
lets joined a common glass bulb which then had a single outlet for
discharge of the solution. In this manner, the flow was rendered more
uniform throughout the resin bed.

B. Materials

Two types of resins were used in the experiments described in this
thesis, a low capacity resin, Amberlite IR-100*, and a high capacity
resin, Nalcite HCR**. Amberlite IR-100 is a phenol formaldehyde conden-
sation product containing methylene sulfonic acid groups and phenol
groups. Nalcite HCR is a copolymer prepared from a mixture of styrene
and divinyl benzene which is sulfonated with sulfuric acid yielding
nuclear sulfonic acid groups.

The commercial-grade resin was received in a damp state and was
allowed to air-dry for several days before classification according to
particle size. U. S. Standard sieves were used to screen the dry resin.
A resin which is designated -30+40 mesh size, for example, passed through
a No. 30 sieve, but was retained on a No. 40 sieve.

The citric acid was of ordinary commercial U.S.P. grade. A spec-
trographic analysis of the ash after igniting some of the material showed
only traces of impurities. Two forms of the solid citric acid were used,
the mono-hydrate and anhydrous.

The oxalic acid employed as a precipitating agent for the rare
earths was Mallinkrodt analytical reagent grade.

The hydrochloric acid, sulfuric acid, and ammonium hydroxide were
all of C. P. reagent grade.

The filter paper was S & S No. 589 White Ribbon having below 0.07 mg
of ash per 11 cm circle.

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*Manufactured by the Resinous Products and Chemical Company.
Philadelphia, Pennsylvania.

**Distributed by National Aluminate Corporation. Chicago, Illinois.

The rare-earth cruds used as starting materials were obtained from Lindsay Light and Chemical Company, West Chicago, Illinois. Lindsay code No. 630 "neodymium carbonate" is a readily available but poor source of praseodymium; a typical analysis of oxide obtained from this source showed 76% Nd_2O_3, 11% Sm_2O_3, 9% Pr_6O_{11}, and 4% other rare earth oxides. One of the best commercial sources of praseodymium is Lindsay "praseodymium ammonium nitrate", which has a 30% R_2O_3 content, analyzing 43.5% Pr_6O_{11}, 10.2% Nd_2O_3, 46% La_2O_3 and traces of Sm_2O_3 and CeO_2. In addition to these two source materials, several experiments utilized pure or mixed rare earths obtained as a result of column separations in this laboratory.

C. Typical Experiment

A detailed description of an elution experiment will serve to illustrate the general procedure. Any essential changes in procedure will be noted in connection with the particular experiment described.

The glass column was mounted in a vertical position and half-filled with water. The sieve-graded resin was poured into the column until the desired bed depth was exceeded by five or six centimeters. The resin in the column was then backwashed for not less than a half hour with water. The backwash period served to remove adhering air bubbles and fine resin dust from the bed. The backwash procedure also served to classify the resin in the column according to particle size which led to better flow characteristics with a resultant increase in the separation of the rare earths.

The resin was conditioned to receive the rare earth charge by removing all cations other than hydrogen. To accomplish this, a 5% citrate solution was adjusted to pH 5.5 with concentrated ammonium hydroxide and then passed through the column at a linear flow-rare of 0.5 cm per minute. After the resin had been converted to the ammonium-cycle, a 5% hydrochloric acid solution was passed through the bed to convert the resin to the hydrogen-cycle. If, after the above precedure, the resin was still contaminated with difficutly-removable cations, it was desirable to pass a 5% sodium chloride solution through the column which was followed with 5% hydrochloric acid. The sulfonic acid groups were thus converted to the hydrogen-ion cycle. The distilled water and reagents used for these regenerating solutions was free of undesirable cations. This was especially true of the hydrochloric acid solution used in the final step. The column was next flushed with distilled water to remove the excess acid and adjusted to the desired bed height, after which it was ready to receive the rare-earth sample.

The rare-earth sample was usually prepared from the oxide, and all sample weights in this thesis are given in terms of the oxide. A given weight of oxide was dissolved in a minimum of 6N hydrochloric acid and diluted with distilled water so that a liter of solution contained from 0.005 to 0.05 moles of rare-earth oxide. The dilute rare-earth chloride solution was passed through the column at a linear flow-rate of 1.0 cm per minute. The rare-earth ions replace the hydrogen ions on the sulfonic acid groups to form a saturated rare earth-resin band at the top of the resin bed. After rinsing the column with distilled water to remove the acid formed in the adsorption process, the column was considered ready for elution and was attached by means of a siphon to a reservoir of the eluting solution which is generally called the eluant.

The eluant used to effect the separation is designated as 0.5% or 0.1% citrate solution. It is to be understood that the solution was made up with the proper weight of citric acid monohydrate per liter of distilled water and then adjusted to the desired pH with concentrated ammonium hydroxide. Beckman pH meter, Laboratory Model G, was used in adjusting the pH of the solutions; the values thus obtained were probably accurate to $\pm$ 0.02 of a pH unit. In order to prevent the growth of mold, a gram of phenol was added for each liter of the solution (3).

The column was operated under the conditions prescribed for the particular experiment with regard to flow-rate, pH of the eluant and any other special conditions. It was necessary to maintain all conditions of elution fixed with the exception of the particular variable being investigated. The elution was continued at the chosen flow-rate until the leading edge of the rare earth band neared the bottom of the resin bed. The solution was collected in volumetric flasks and the breakthrough of the rare earth-citrate complexes was tested by the addition of oxalic acid. When the breakthrough had occurred, the measured volumes of eluate were transferred to beakers. The precipitation of the rare-earth oxalates was accomplished by adding oxalic acid crystals to the solution and heating to about 80° for one hour. The oxalate precipitate was allowed to settle, and the solution allowed to cool for not less than 12 hours. The filtered samples were then ignited at 700-800° for at least six hours to form the oxides and then weighed. The total elution curve was obtained by plotting the grams per liter of oxide against the volume of eluant passed through the column. The elution curve was further expanded by recording the analysis of the individual fractions on the curve.

When the elution had progressed long enough to furnish the information desired from the experiment, the remainder of the material, if any, on the column was removed by stripping with a 5% citrate solution adjusted to a pH value of 5.5 with concentrated ammonium hydroxide.

The stripped resin was again converted to the hydrogen-form by the method previously described for regeneration. The column was thus made ready for the next experiment.

In practice, several columns were operated simultaneously to reduce the time required for investigation of the variables under consideration. The operation of 10 columns required about two months to complete the elution and analysis of the fractions.

D. Methods of Analysis

A rapid and accurate analytical method is essential in evaluating any fractionation scheme employed for the separation of rare-earth mixtures into their individual elements. Because of the chemical similarity of these elements, the usual methods of quantitative analysis are not applicable to the rare earths with the exception of cerium, samarium, europium and ytterbium which have valence states other than tripositive.

The average atomic-weight method proposed by Gibbs in 1893 has been found very useful in following fractionations where the atomic weight differences are large. However, the atomic weight of adjacent elements are close together, and the method has not been found sufficiently sensitive for following the fractionation to limits of high purity.

The magnetic susceptibility of the rare earths was used by Urbain (42) to analyze rare-earth mixtures. This method is quite sensitive due to the paramagnetism exhibited by the individual members. Podashevskii and Kondoguri (43) reported an experimental error of 1.0 to 1.5% for the analysis of binary mixtures of neodymium oxide and praseodymium oxide. This method requires a highly-developed technique and does not lend itself to rapid determinations. The accuracy, while good, is not adequate for following the final purification steps.

Other methods such as the X-ray emission spectra and fluorescent spectra, while showing promise of high sensitivity, are subject to rather large experimental errors and are difficult to adapt to routine procedures necessitated by the hundreds of analyses required in the course of the investigation described in this thesis.

It soon became apparent that the analytical procedures best suited to this investigation were (1) the absorption spectra method and (2) the emission spectra method.

The absorption spectra method employed was similar to that described by Rodden (44). The sepctrophotometer was a Beckman, Model DU, manufactured by the National Technical Laboratories, South Pasadena, California.

A complete description of this instrument and its operation is given elsewhere (45). The absorption cells used gave a light path of 1.000 ± 0.003 centimeter. The elements associated with praseodymium which have useable absorption bands are neodymium and samarium.

In order to put the spectrophotometric analyses on a quantitative basis. The molar extinction coefficients for chlorides of praseodymium, neodymium and samarium were determined for those absorption peaks which were free from interference by other ions. The complete spectrum from 340 m μ to 1000 m μ was investigated for each of these salts and absorption bands chosen which were sufficiently intense to be detectable in low concentrations. The absorption bands meeting these requirements had peaks occurring at 444 m μ for praseodymium, 740 m μ for neodymium and 401 m μ for samarium.

Table 1

Data for Spectrophotometric Analysis

Element	Absorption band, (m μ)	Band width, (m $\cdot$)	Molar absorbancy index, a_M (l x moles^{-1} x cm^{-1})
Pr	444	5	10.07
Nd	740	10	6.53
Sm	401	5	3.09

The influence of excess hydrochloric acid in the solution was investigated and found to be without effect on the molar absorbancy indexes up to concentrations 2N with respect to the acid. Beer's law was obeyed up to concentrations of 200 milligrams of oxide dissolved in hydrochloric acid and diluted to a volume of 10 milliliters. The data used in the spectrophotometric analyses are summarized in Table 1. Using this method for analysis, it was found that samarium could be detected in amounts down to 0.5% and the lower limit for detecting neodymium and praseodymium was about 0.3%.

The steps involved in analyzing the samples of eluate consisted in precipitating the rare earths from the citrate solution as oxalates by adding 10 grams of oxalic acid per liter of solution. The precipitates were allowed to settle, then filtered and ignited to the oxides. A weighed amount, 50 to 200 mg, was dissolved in 0.6N HCl and diluted to

10 ml with the same acid. The log (I_o/I) (absorbancy) value was determined for the absorption peak of each rare earth present in the solution. The amount of a particular rare earth may be calculated from the relation

$$\log \frac{I_o}{I} = a_M cb$$

in which a_M is the molar absorbancy index, c is the concentration in moles per liter and b is the length of the light path through the solution in centimeters.

In practice it was found convenient to modify the calculation somewhat. Since the rare-earth solutions obey Beer's law, and the light path was essentially constant at 1.000 centimeter, the percentage of each rare-earth oxide in an oxide sample was calculated by determining the ratio of the absorbancy value to the predetermined value for the pure rare earth measured under the same conditions.

The absorption spectra method was found to be reliable for determining any individual rare earths listed above within the limits of 0.5 to 99.0%. None of the frequently small and rare samples were lost during the analyses which was a very desirable feature of this method. For the detection of the smaller quantities of the elements, recourse was made to quantitative spectrographic analyses.

The quantitative spectrographic analytical method for the rare earths as developed by Fassel and Wilhelm (46,47) was used to extend the limits of detection for neodymium in praseodymium to less than 0.1%. The presence of lanthanum and cerium, for which the spectrophotometric method is not applicable, were also measurable in amounts less than 0.1%. The spectrograph used was the Jaco-Wadsworth, 21-foot grating instrument, manufactured by the Jarrell-Ash Company of Boston, Massachusetts. The author wishes to thank Dr. V. A. Fassel and members of his group for performing the many spectrographic determinations so necessary to these researches.

V. RESEARCH

A. Investigations Using Five-Tenths Per

Cent Citrate Solutions

The application of 5%, 0.5% and 0.1% citrate solutions to the separation of the rare-earth elements by means of ion-exchange has been mentioned previously. The separations achieved with 0.5% and 0.1% citrate solutions were excellent and were particularly suitable for

large-scale operations since the cost of the operation was considerably reduced. Therefore, it was decided to make a detailed study of the variables affecting the purification of praseodymium using the 0.5% and 0.1% citrate solutions for eluting the mixed rare-earth samples from ion-exchange resin beds.

1. Preparation and loading of resin beds

The cation-exchange resin selected for use in the following experiments was Amberlite IR-100 having a capacity of 1.75 milliequivalents per dry gram (40). The commercial ion-exchange resins are not prepared for research purposes. It was therefore necessary to prepare a homogeneous batch of the resin for use throughout the investigation in order that the conclusions drawn from the data obtained from the operation of several different columns would be free of variables introduced by non-homogenity of the exchanger. The homogeneous batch was prepared by drying and thoroughly mixing the resin after which it was sieved to obtain the desired mesh sizes.

Another variable which may be introduced into the experiments involves the preparation of the resin bed in the columns. Amberlite IR-100 resin particles are irregularly shaped and may pack in the bed in such a manner that channels would result. Therefore, the same procedure for preparing the resin beds was followed as nearly as possible in each experiment. It would be desirable to have the same number of exchange groups, or a proportional number, in each column in order to make comparisons of the data. Since this was not practical to achieve, it was decided to prepare similar bed heights using the standardized packing procedure.

Praseodymium concentrates were not available in the beginning of the investigations using 0.5% citrate solutions. Therefore, several of the early experiments were performed with neodymium to determine the nature of the elution curves.

2. Effect of pH on the elution of pure neodymium at two flow rates

Five columns having beds of -30+40 mesh size Amberlite IR-100 resin, 120 cm long and 22 mm in diameter, were loaded with 1.683 grams (0.005 mole) of pure Nd_2O_3 per column. The samples were eluted at a linear flow-rate of 0.5 cm per minute (1.9 ml per minute) at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80.

At the completion of the elutions, the columns were reconditioned and the experiment repeated at a linear flow-rate of 2.0 cm per minute; all other conditions being the same as before. The elution curves for these runs are given in Figure 4. The pH of the eluting solution
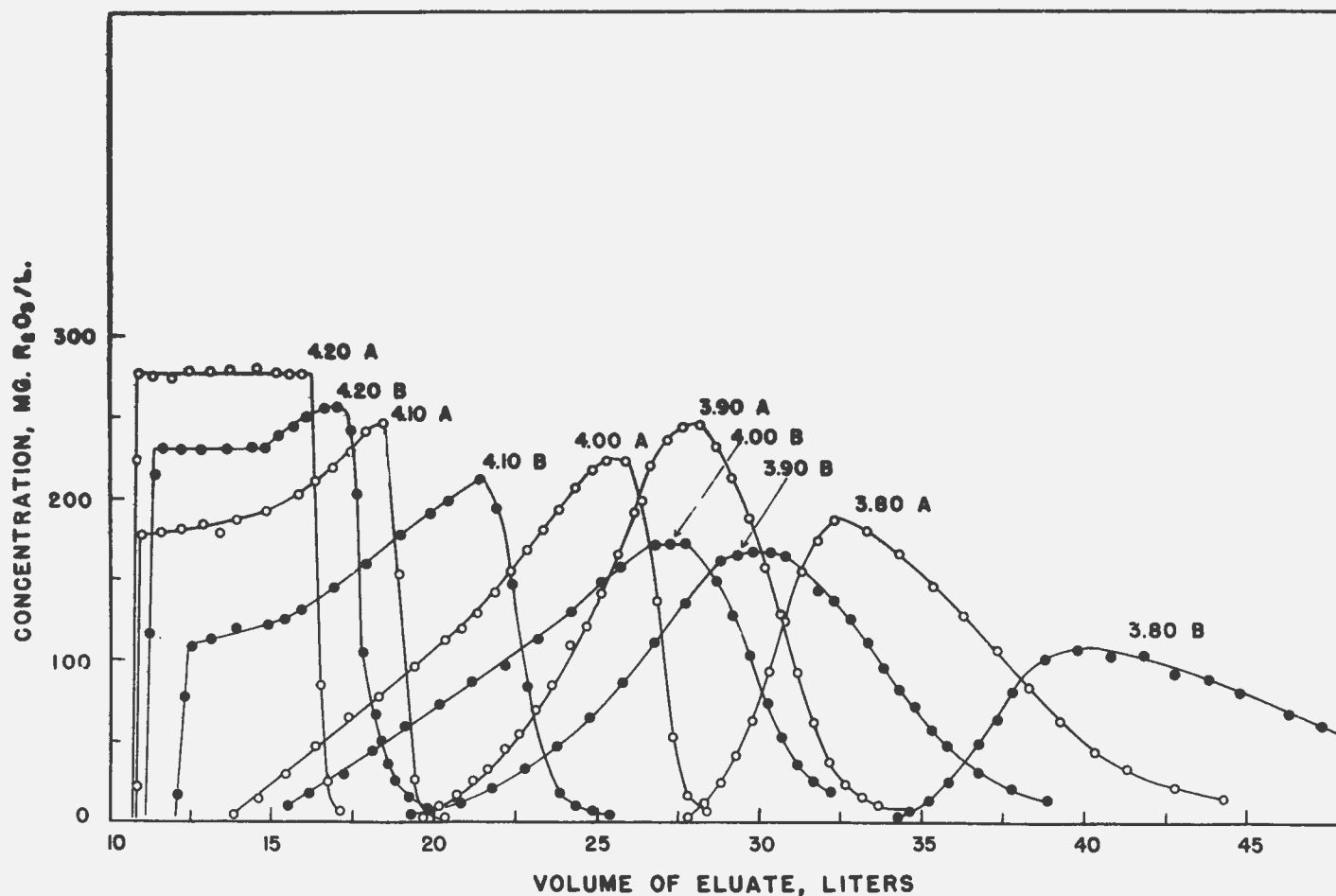
Figure 4 - The effect of pH on the elution of 1.683 gram samples of Nd_2O_3
from 2.2 x 120 cm beds of -30+40 Amberlite IR-100 resin using
0.5% citrate solutions at two flow-rates: O, 0.5 cm/min;
●, 2.0 cm/min. [From Spedding, Fulmer, Butler and Powell (5)]

(eluant) is indicated beside the curve to which it corresponds; "A" refers to the slower flow rate and "B" to the faster flow rate. It is evident that a sufficient number of fractions of the effluent from the columns (eluate) were taken to trace accurately the characteristics of the elutions.

From this experiment, the nature of the elution curves at different pH values was determined and the effect of flow-rate ascertained. The significant effect of using the faster flow-rate was to reduce the rare-earth concentration in the eluate, thus causing the volume of eluate for total elution of the sample to increase. It is also evident that decreasing the pH of the eluant increased the volume required for break-through of the rare earths. At pH values of 4.00 and above the effect is small, but it becomes more pronounced at lower pH values.

Attention should be given to the elution curves for the pH values 4.00, 3.90 and 3.80. The curve for 3.90 shows a nearly symmetrical form while those for 4.00 and 3.80 are roughly mirror images. From the shape of the curves, it is possible that as the pH of the eluant is changed the relative importance of various citrate complexes active in the elution changes rapidly in this pH range. Evidence has been given by Spedding, et al., (4) for the existence of several rare-earth citrate complexes.

3. Effect of resin particle size on the elution at two flow rates

Two columns with beds of -30+40 and -60+80 mesh sizes of Amberlite IR-100 resin, respectively, each 120 cm long and 22 mm in diameter were loaded with 1.683 grams of pure Nd_2O_3. These two columns were eluted at a pH value of 3.80 using a linear flow-rate of 0.5 cm per minute. The experiment was repeated at a linear flow-rate of 2.0 cm per minute.

The data are shown in Figure 5. The mesh size of the resin parti-cles is indicated beside the corresponding curve. The letter "A" refers to the linear flow-rate of 0.5 cm per minute; "B" refers to the 2.0 cm per minute flow-rate.

The elution curves show that the breakthrough volume was reduced and the peak concentration of neodymium in the eluate was increased when the finer resin was used. It was also observed that the maximum concen-tration of rare earth was reached more rapidly in the case of the finer resin. This more vertical front of the elution curve for the finer resin was interpreted to mean that equilibrium conditions were more nearly approached. Again the faster flow-rate spread out the elution curve and lowered the concentration maxima. A comparison of curves -30+40 A and -60+80 B indicates that decreasing the particle size of the resin tends to counteract the effect of increased flow-rate.
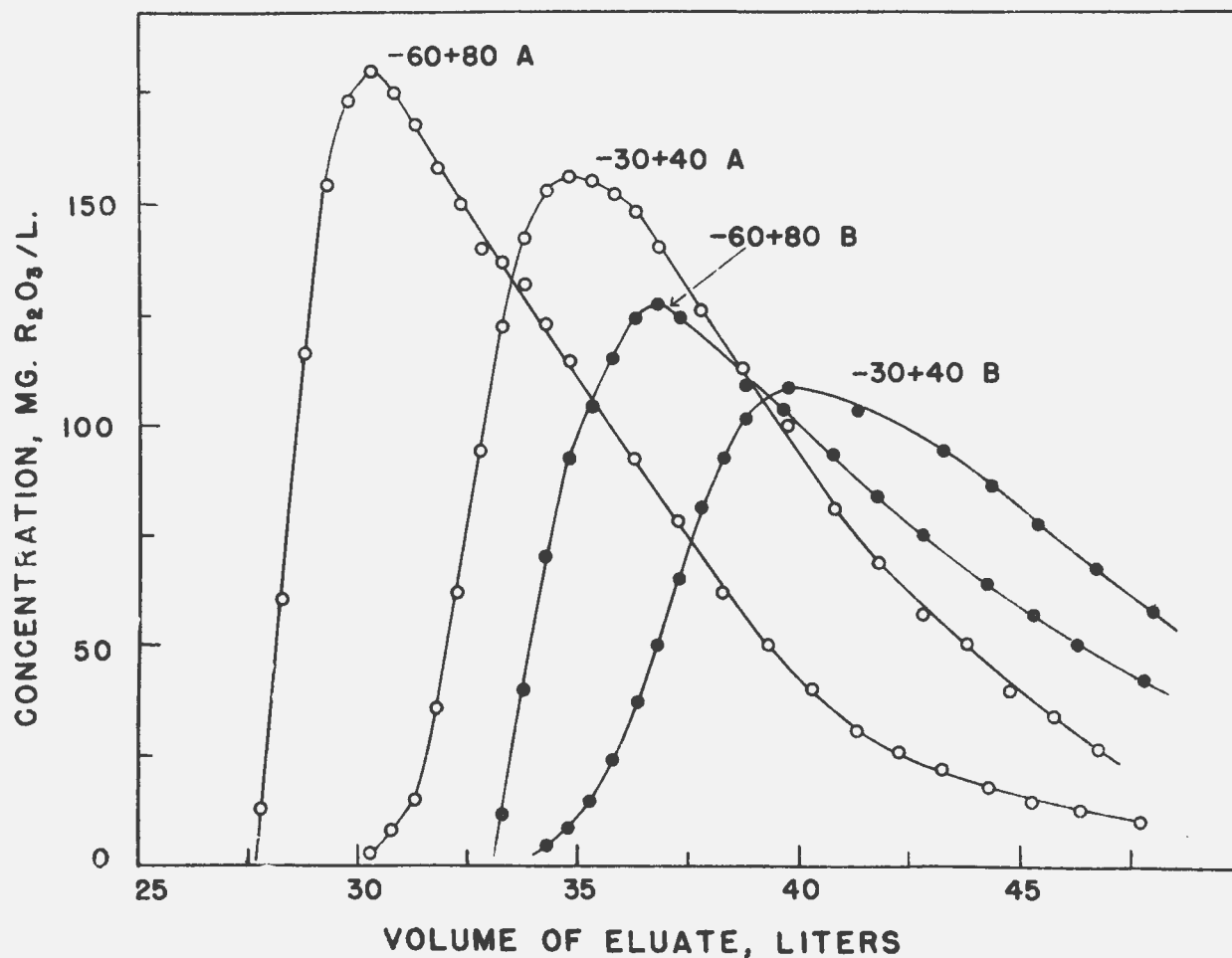
Figure 5 - The effect of particle size of resin on the elution of 1.683 gram
samples of pure Nd_2O_3 from 2.2 x 120 cm beds of Amberlite IR-100
resin using 0.5% citrate solutions at a pH value of 3.30 and
two flow-rates: 0, 0.5 cm/min; ●, 2.0 cm/min. [From Spedding,
Fulmer, Butler and Powell (5)]

It may be concluded from the data presented above in Sections 2 and 3, that the separation of mixed rare earths would be improved by operating at a flow-rate not greater than 0.5 cm per minute. It also appears that a -60+80 mesh size resin would give a closer approach to equilibrium conditions which should result in better separations.

Although it was concluded that finer mesh sizes of resin would be desirable, such resins are difficult to obtain in large quantities. One of the primary objects of these investigations was to determine conditions for separations which could be scaled up to pilot-plant size. Therefore, it was decided to use -30+40 mesh size resins, for the most part, in the following studies since they are available in larger quantities.

4. Effect of pH on the elution of neodymium-praseodymium mixtures

Seven columns containing -30+40 mesh size Amberlite IR-100 beds, 120 cm long and 22 mm in diameter, were each loaded with samples made up from 1.695 grams of a mixture containing equal weights of Nd_2O_3 and Pr_6O_{11}. The mixture closely approximates equimolar amounts of the two rare earths and is equivalent to the number of moles used in the previous experiments. The mixtures were eluted with 0.5% citrate solutions having pH values of 4.40, 4.20, 4.10, 4.00, 3.90, 3.80 and 3.70. The flow-rate was 0.5 cm per minute. The data are given in Figure 6.

This experiment was repeated at pH values of 4.20, 4.10, 4.00, 3.90 and 3.80, holding all other conditions the same except that the flow-rate was increased to 2.0 cm per minute. The data are shown in Figure 7. The pH values used for the elution are recorded beside the corresponding curve in both figures.

All of the analyses were made using the spectrophotometric method which easily detected amounts of one rare earth in the other down to 0.5%. The data are summarized in Table 2 which shows the per cent of the individual rare earth, originally available in the mixture, which was obtained greater than 99.5% pure. The results of elution at pH 3.70 were not included since the elution rate was too slow for practical purposes and also showed a rather poor separation.

A number of conclusions may be drawn from this experiment. Referring to Table 2, the separations using a 2.0 cm per minute flow-rate were in every case inferior to those obtained with a 0.5% cm per minute flow-rate. This was expected in view of the results obtained from the elution of pure neodymium described in Sections 2 and 3 since the columns were operating far from equilibrium conditions.

Figure 6 - The effect of pH on the elution of 1.695
          gram samples of a mixture containing equal
          amounts of Nd_2O_3 and Pr_6O_{11} by weight from
          2.2 x 120 cm beds of -30+40 mesh size
          Amberlite IR-100 resin using 0.5% citrate
          solutions at a flow-rate of 0.5 cm/min: O,
          Nd_2O_3; O, mixed fractions; O, Pr_6O_{11}. From
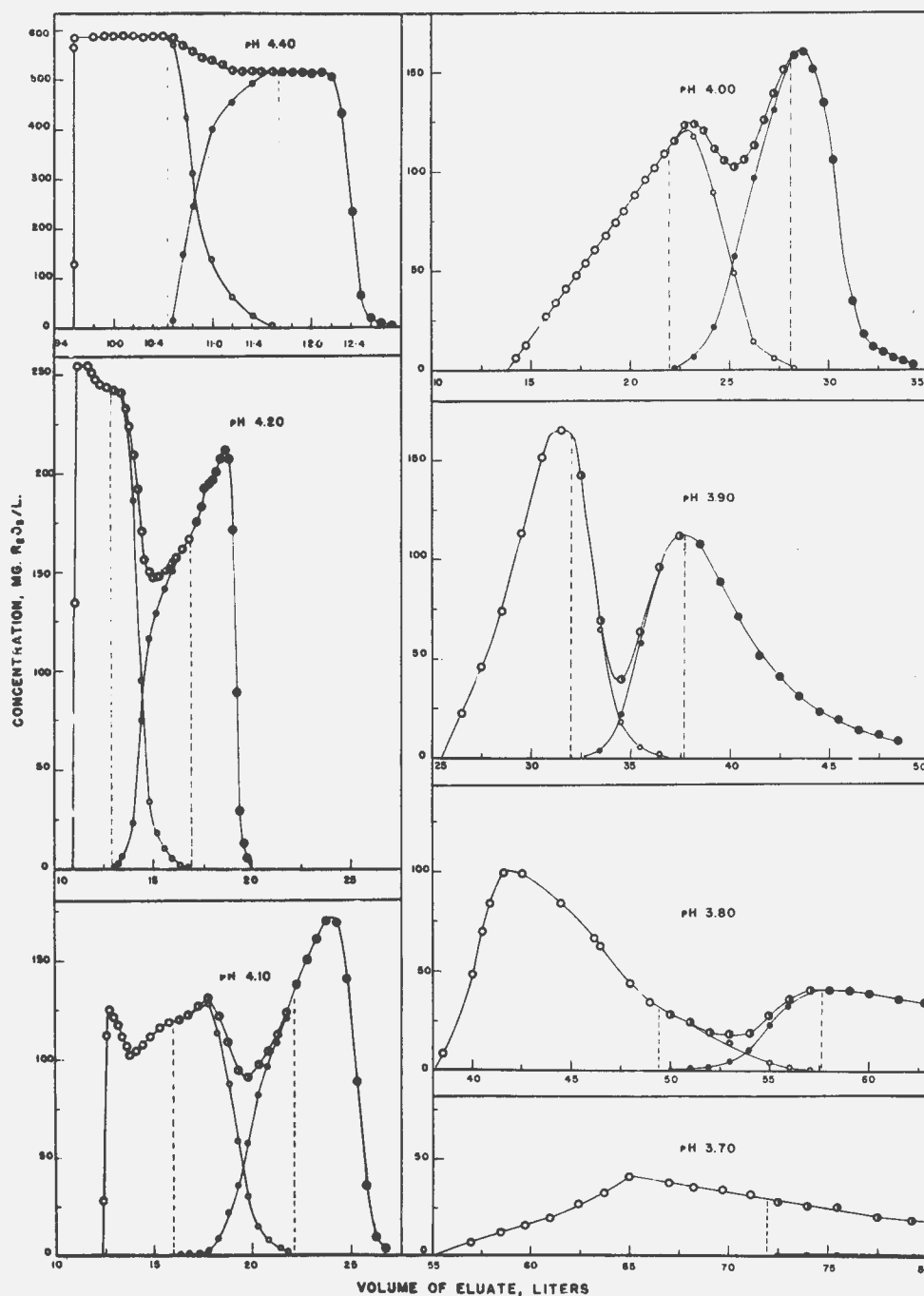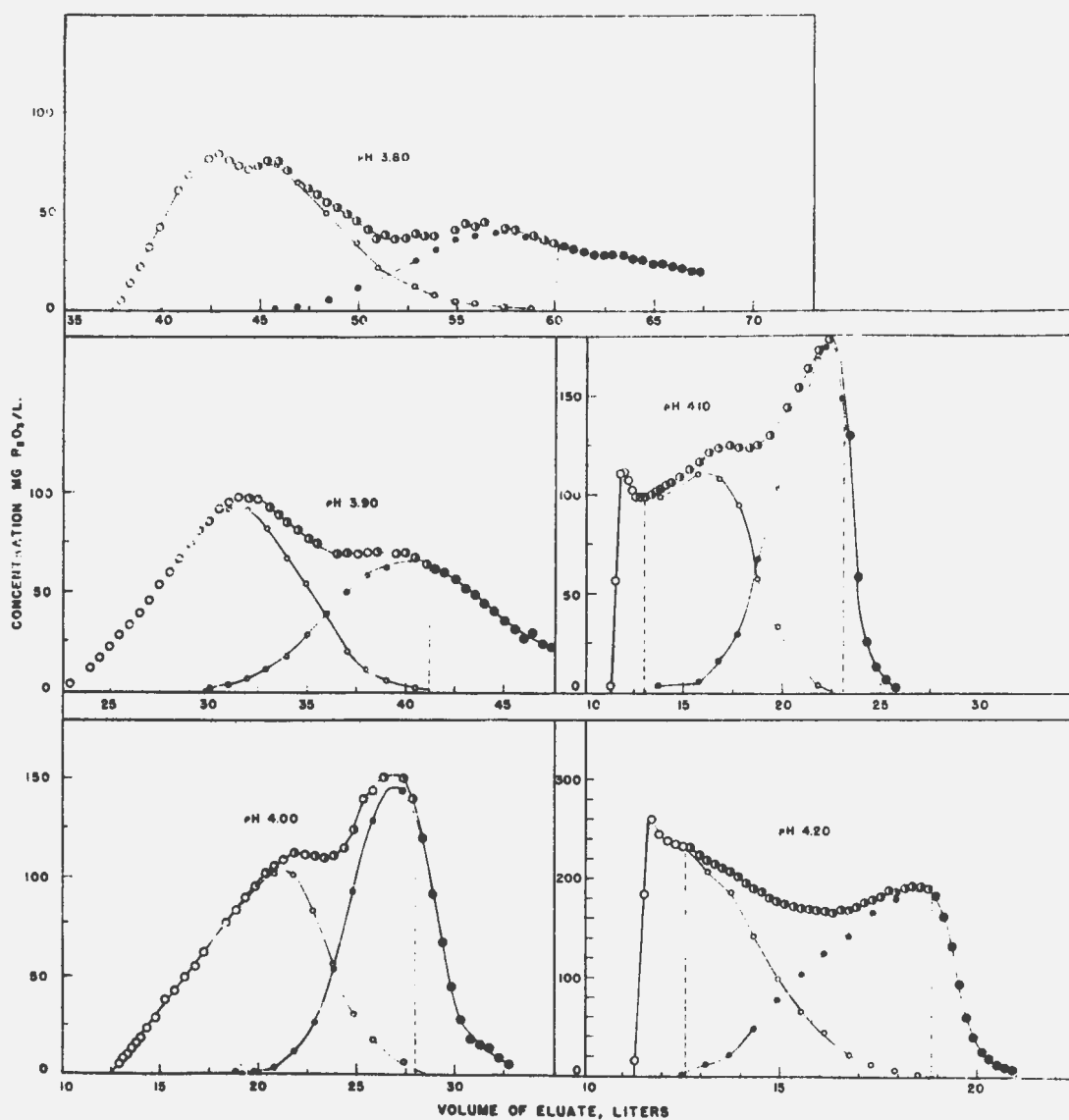   Spedding, Fulmer, Butler and Powell (5)

Figure 7 - The effect of pH on the elution of 1.695 gram
samples of a mixture containing equal amounts of
Nd_2O_3 and Pr_6O_{11} by weight from 2.2 x 120 cm beds
of -30+40 mesh size Amberlite IR-100 resin using
0.5% citrate solutions at a flow-rate of 2.0
cm/min: O, Nd_2O_3; ◐, mixed fractions; ●, Pr_6O_{11}.

The elution curves resulting from a flow-rate of 0.5 cm per minute
show the best separations at pH values of 4.40 and 3.80 with decreasing
separation at the intermediate values. This effect is clearer in the
case of neodymium but is apparent in the case of praseodymium, especially

Table 2

Separation of Neodymium-Praseodymium Mixtures

Eluant (pH)	Flow-rate (cm./min.)	Elution volume (liters)	R_2O_3 Obtainable $>99.5\%$ Pure	
			$\%Nd_2O_3$	$\%Pr_6O_{11}$
3.80	0.5	90	84	82
3.90	0.5	50	71	64
4.00	0.5	35	55	48
4.10	0.5	27	52	64
4.20	0.5	20	57	55
4.40	0.5	13	70	67
3.80	2.0	90	51	57
3.90	2.0	50	36	51
4.00	2.0	37	38	40
4.10	2.0	26	21	19
4.20	2.0	21	37	22

when the 2.0 cm per minute flow-rate experiments are also considered.
This may be taken as further evidence that the mechanism of the separation
changes with respect to the nature of the rare-earth citrate complex
formed.

Considering the above results from the standpoint of obtaining the
most pure praseodymium in a given length of time, the elution at a pH
value of 4.40 was preferable in some respects. The total liters of

eluate which must be caught in order to complete the elution were
directly proportional to the time necessary for elution since the flow-
rate was constant. The best separation was achieved with citrate of pH
value 3.80, and the next best with citrate of pH value 4.40, both at
0.5 cm per minute linear flow-rate. Assume a column load equivalent to
10.0 grams of 50-50 neodymium-praseodymium oxide for comparative pur-
poses. The 90 liters of eluate necessary for the elution at a pH value
of 3.80 is equivalent to 790 hours or about 33 days which would yield
4.1 grams of $>$99.5% Pr_6O_{11} in this time. On the other hand, the 13
liters of eluate from the elution at a pH value of 4.40 would require
140 hours or about 6 days to yield 3.35 grams of $>$99.5% Pr_6O_{11}. Thus
in a 33-day period about 5 elutions could be completed with citrate of
pH value 4.40 which would yield 16.75 grams of $>$ 99.5% Pr_6O_{11}. Since
the columns must be regenerated after each individual separation and re-
loaded with the rare-earth mixture, the advantage gained in using the
higher pH value would be lessened somewhat because more runs are required.
The comparison given above will serve to point out that the conditions
giving the best separation are not necessarily the best for practical
operation.

5. Pilot-plant operations

     A pilot-plant consisting of 24 4-inch inside diameter columns 10
feet tall was set up as a cooperative effort with other members of the
laboratory. A description of this plant was given in Part IV, Section A.
Each column was loaded with Amberlite IR-100 which was regenerated and
adjusted to a bed height of eight feet.

     The pH value of the eluant used for the operation of these columns
was 3.90. The results of the experiments described above in Section 4
would indicate that a different pH value should have been chosen. How-
ever, other factors of a practical nature indicated the use of this elut-
ing solution. Among the more important considerations was the number of
fractions of eluate which could be processed per day. Twenty-four
columns, each contributing two fractions in 24 hours, were more con-
veniently operated with the man power and equipment available. The rate
of elution with citrate of pH value 3.90 and flow-rate of 0.5 cm per min-
ute (40.5 ml per minute) was the best, consistent with good separations
and also allowed time for the processing and analysis of the fractions
while the run was in progress.

     The optimum weight of rare-earth mixture per column for the elution
conditions mentioned above was determined by a set of experiments in
which rare-earth samples equivalent to 50, 75, 100 and 125 grams of R_2O_3
were eluted from the columns. It was found that the separation of the
component rare earths was practically the same for sample weights up to
and including 100 grams, but was poor for the 125-gram sample. In

subsequent operations, the load was standardized at the equivalent of
100 grams of R_2O_3 per column.

A typical elution curve is shown in Figure 8 which was obtained from
the 4-inch diameter columns using Lindsay Light and Chemical Company
"neodymium carbonate" as the source of crude rare earths. This material
analyzed 76% Nd_2O_3, 11% Sm_2O_3, 9% Pr_6O_{11} and 4% other rare-earth oxides
on the basis of the oxide obtained from the carbonate. The elution curve
shown resulted from the elution of 50 grams of the crude oxide with citrate
of pH value 3.90. The amount of praseodymium concentrate obtained from
this source was necessarily small and no pure praseodymium fractions were
obtained from the initial elution since neodymium, cerium and lanthanum
overlapped slightly in the praseodymium-rich region.

The praseodymium concentrate was usually broken down into four degrees
of purity which were: 50% Nd_2O_3, 50% Pr_6O_{11}; 90% Pr_6O_{11}, 10% Nd_2O_3; 99%
Pr_6O_{11}, 1% Nd_2O_3 and 90% Pr_6O_{11} containing oxides of Ce and La. Similar
fractions were combined from each column and stored until a sufficient
amount had been collected to load a column for additional purification.
In each case, spectrographically pure praseodymium was obtained from these
fractions. The mixed fractions from the second separations were added to
the appropriate stock of concentrate and reprocessed.

B. Investigations Using One-Tenth Per

Cent Citrate Solutions

In the previous section of this thesis, data were presented showing
the successful use of 0.5% citrate solutions as the eluting agent in the
ion-exchange method for the separation of praseodymium in high purity and
at a lower cost than that involved in the use of 5% citrate solutions.
Preliminary investigations in this laboratory, using 0.1% citrate eluting
solutions, showed sufficient promise to warrant more detailed investiga-
tions of the variables involved in separations performed with this lower
citrate concentration.

1. Elution of equimolar mixtures of neodymium and praseodymium

Two columns with beds of -30+40 mesh size Amberlite IR-100 resin,
120 cm long and 22 mm in diameter, were prepared as previously described.
Two 1.695 gram samples of an equimolar mixture of neodymium and praseodymium
oxides were dissolved in hydrochloric acid and adsorbed on each column.
The samples were then eluted with 0.1% citrate solutions having pH values
of 5.50 and 5.00, respectively; the linear flow-rate was 0.5 cm per minute.
The elution curves are shown in Figure 9. The pH of the eluting solution
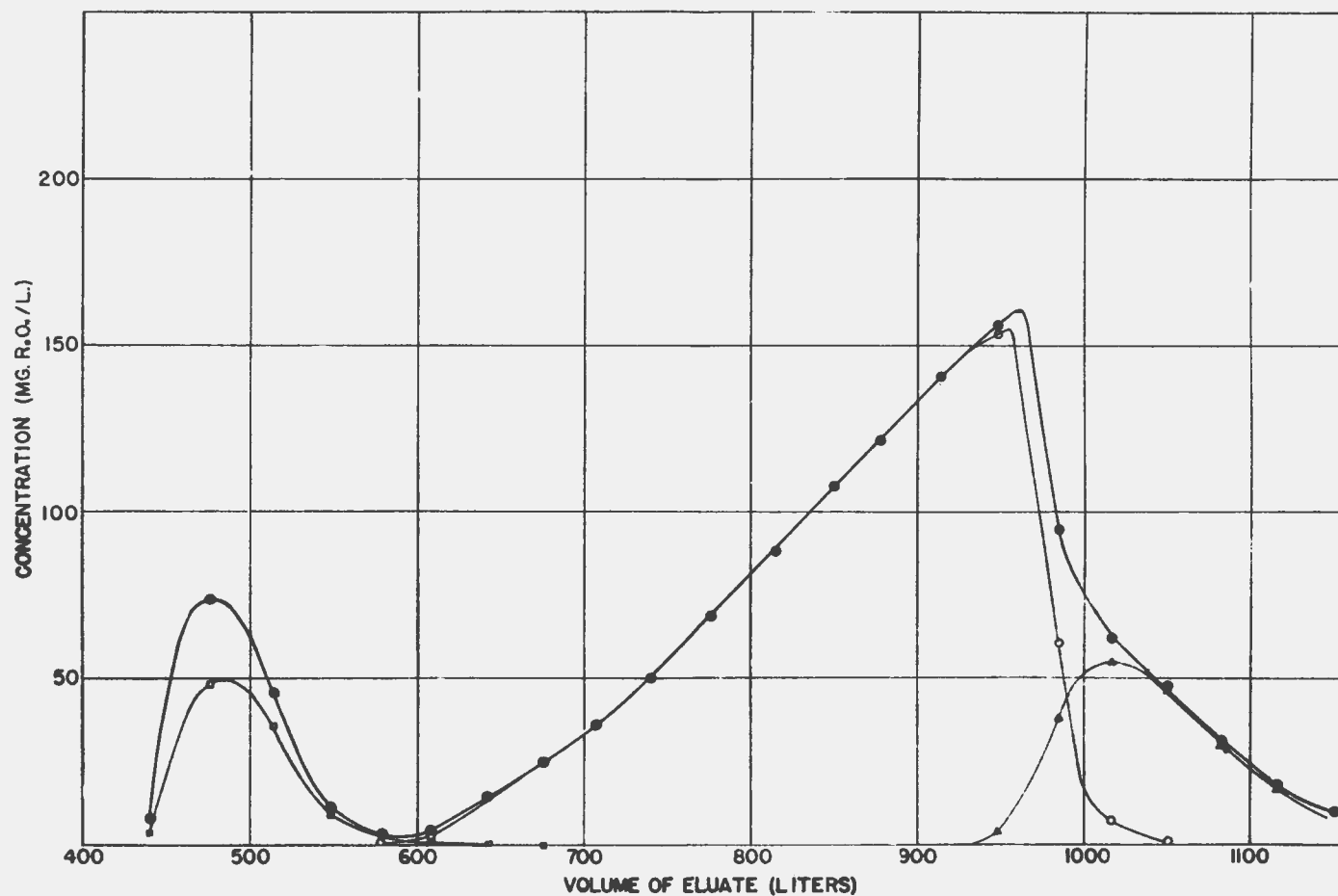is given beside the corresponding curve.

Figure 8 - Elution curve for "neodymium carbonate" at pH value 3.90: O, total R_2O_3; □, Sm_2O_3; ○, Nd_2O_3; △, Pr_6O_{11}. [From Spedding and co-workers (3)]
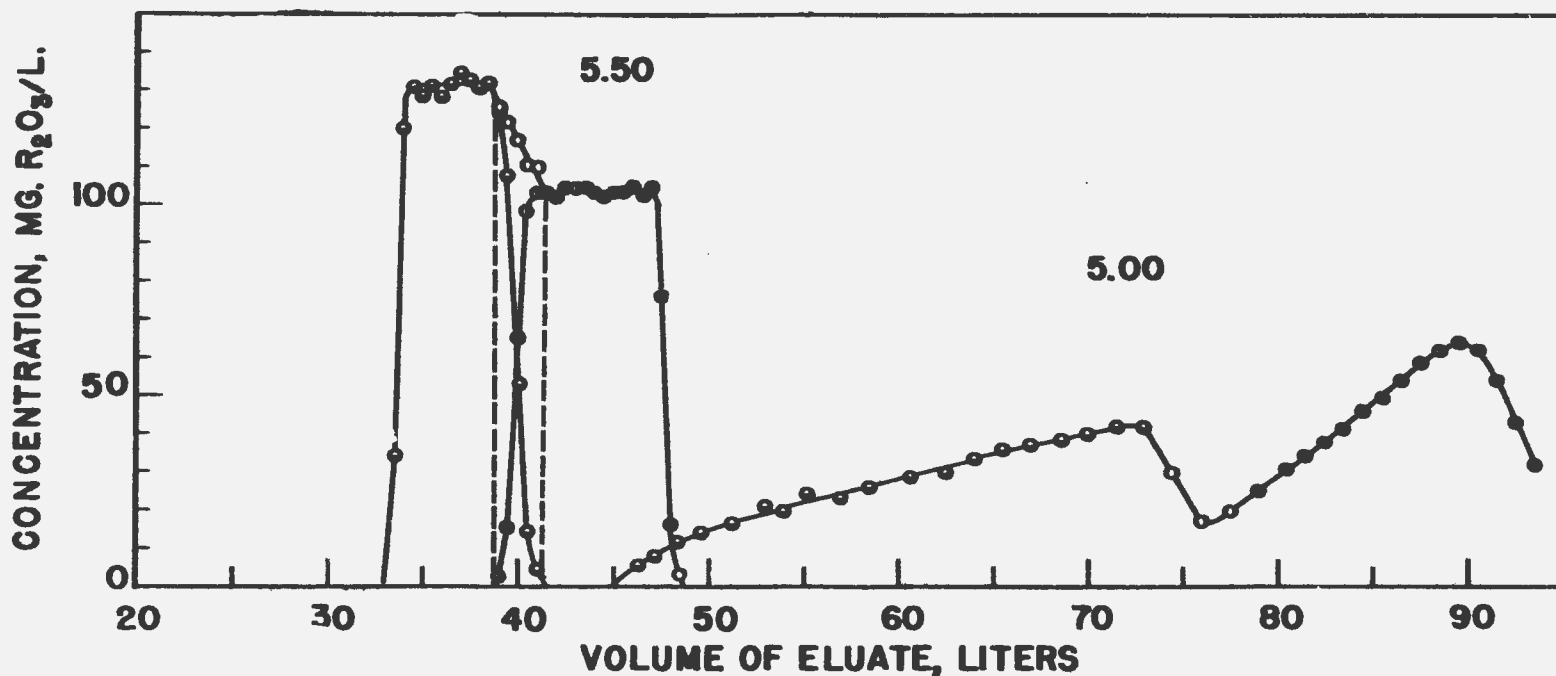
Figure 9 - The effect of pH on the elution of 1.695 gram samples of equimolar
mixtures of Nd_2O_3 and Pr_6O_{11} from -30+40 mesh size Amberlite IR-100
resin beds, 2.2 x 120 cm, using 0.1/ citrate solutions at pH values
of 5.50 and 5.00 and a flow-rate of 0.5 cm/min: O, mixed fractions;
●, Nd_2O_3; ◐, Pr_6O_{11}. [From Spedding, Fulmer, Powell and Butler (○)]

At the pH value of 5.50, 82% of the available Nd_2O_3 and 83% of the available Pr_6O_{11} were obtained with purities greater than 99.5% as determined spectrophotometrically. The elution at the lower pH value of 5.00 was not carried to completion and the fractions were not analyzed since the elution rate was so low that it would not be suitable for large scale fractionations. However, the elution was carried beyond the region of overlap between the neodymium and praseodymium and judging from the color of the oxides a very good separation was obtained.

It will be noted that the conditions for these elutions were identical with those described in part 4 of the previous section with the exception of the concentration and pH value of the citrate solutions. A comparison of Figures 6 and 9 shows the same change in shape of the elution curve with changes in pH values of the eluting solution as were found for the 0.5% citrate solutions. This is again suggestive of changes in the mechanism of the elution as a function of pH. The best separation of neodymium from praseodymium, with 0.1% citrate, was obtained at a pH value of 5.50 with yields of 84% of the available Nd_2O_3 and 82% of the available Pr_6O_{11}. It is noteworthy that these yields are practically identical with those previously obtained with 0.5% citrate at a pH value of 3.80. Since liters of eluate are equivalent to time, for a constant flow-rate, the superiority of 0.1% citrate at a pH value of 5.50 is clearly demonstrated.

The effect of flow-rate was determined for the 0.1% citrate solutions by duplicating the elution at a pH value of 5.50 in all respects except for increasing the flow-rate to 1.0 cm per minute in one case and 2.0 cm per minute in another experiment. The per cent yield of available Pr_6O_{11} was reduced to 55% and 35% respectively. This clearly establishes the superiority of the 0.5 cm per minute flow-rate for elutions with both 0.5% and 0.1% citrate solutions.

2. Effect of particle size of the resins

A column of -60+80 mesh size Amberlite IR-100, 120 cm long and 22 mm in diameter, was loaded with 1.695 grams of 50-50 Nd_2O_3-Pr_6O_{11} as described in the preceding experiment. The sample was eluted with 0.1% citrate at a pH value of 5.50 using a linear flow-rate of 0.5 cm per minute. The conditions thus duplicate the elution at pH value 5.50 shown in Figure 9 with the exception of resin particle size. Figure 10 compares the elution curves obtained for the two mesh sizes of resin. The two curves are drawn to the same scale which allows a direct comparison to be made of the width of the mixed rare earth region between the dashed verticle lines. The per cent of the available Nd_2O_3 and Pr_6O_{11} obtained greater than 99.5% pure is given in Table 3.
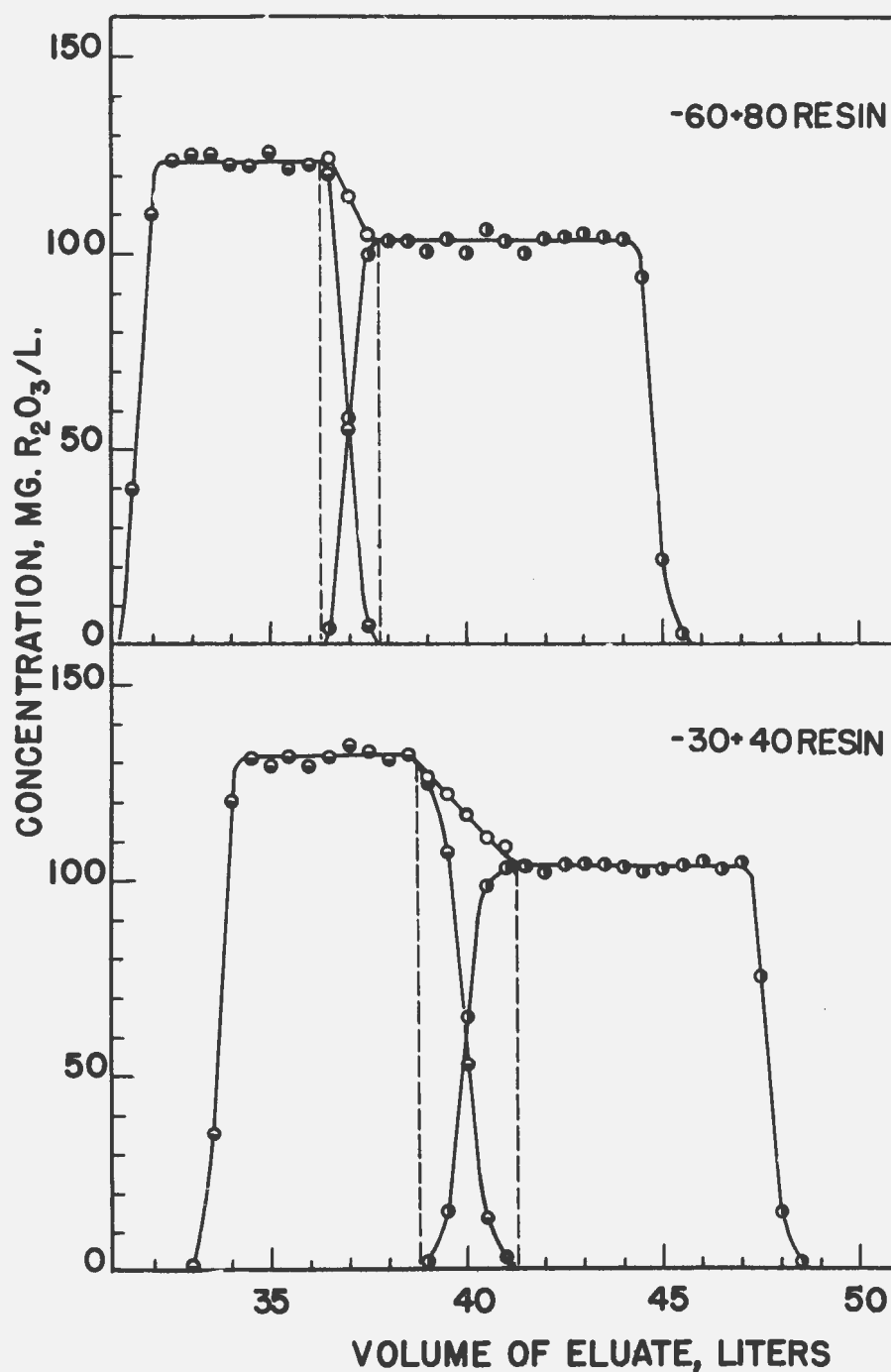
Figure 10 - The effect of particle size of the resin on the
           elution of 1.695 gram samples of equimolar
           mixtures of Nd_2O_3 and Pr_6O_{11} using 0.1% citrate
           solutions at a pH value of 5.50 and a flow-rate
           of 0.5 cm/min: O, mixed fractions, ●, Nd_2O_3,
           ◐, Pr_6O_{11}. ⌐From Spedding, Fulmer, Powell and
           Butler (6) ⌐

The superiority of small resin particles is thus demonstrated for both the 0.1% and 0.5% citrate solutions as eluting agents.

Table 3

Effect of Resin Particle Size on the Separation

of Neodymium and Praseodymium

Eluant (pH)	Volume of Eluant, (liters)	Resin Particle Size (mesh range)	Per Cent Rare Earth Available >99.5% Pure	
			%Nd_2O_3	%Pr_6O_{11}
5.50	45.5	-60+80	85.5	90.3
5.50	45.5	-30+40	82.0	83.0

3. Lower citrate concentrations

This experiment was designed to determine whether citrate concentrations of less than 0.1% would be useful for the ion-exchange separation of neodymium and praseodymium. It is generally true that the rate of elution of rare earths from a given ion-exchange resin varies directly with the citrate concentration and pH of the eluting solution at least for 5%, 0.5% and 0.1% citrate concentrations and in the pH range 2.5 to 6.5. Therefore, citrate solutions below 0.1% should have higher pH values in order to maintain a practical elution rate.

It was decided to use as a reference point the conditions which resulted in the elution curve at pH value 5.50 shown in Figure 9. In order to obtain a 0.1% citrate solution having a pH value of 5.50 it was found that about 10 millimoles of NH_4OH must be added to each liter of 0.1% citric acid monohydrate. Two eluting solutions were made up containing 10 millimoles of NH_4OH per liter, one being 0.05% with respect to citric acid and the other 0.025%. The resulting pH values were 8.63 and 9.15, respectively.

Two columns were prepared and loaded with 50-50 neodymium-praseodymium as described above. All conditions of the elution were the same as those used to obtain curve 5.50 in Figure 9, except for the eluting solutions mentioned above. The column eluted with the 0.05% citrate solution required 39 liters of eluant before a rare earth breakthrough was detected.

Within an eluate volume of six liters after breakthrough, the R_2O_3 concentration in the eluate had reached a maximum of 84.4 mg per liter and declined to about 26 mg per liter. During the next 20 liters this concentration had slowly declined to 15 mg per liter. Spectrophotometric analyses showed 5% Pr_6O_{11} in the first fraction after breakthrough and gradually increasing amounts up to 50% Pr_6O_{11} when the sample was half eluted from the column which required about 60 liters of eluate. The elution was discontinued at this point. The column eluted with the 0.025% citrate solution was abandoned after 53 liters of eluate were collected without having observed a rare earth breakthrough.

The above experiment indicated that citrate concentrations much below 0.1% were not useful for the separation of the neodymium-praseodymium pair. The subsequent experimental work was, therefore, exclusively concerned with the use of 0.1% citrate solutions as eluting agents.

4. Effect of column length on the separation of mixtures of samarium,

    neodymium and praseodymium

Three columns having beds of -30+40 mesh size Amberlite IR-100, 22 mm in diameter and 30, 60 and 120 cm in length, were each loaded with a chloride solution equivalent to 1.71 grams of R_2O_3. The composition of this sample was 33.6% Sm_2O_3, 28.8% Nd_2O_3 and 34.7% Pr_6O_{11} which approximated 0.005 mole of mixed oxides. The samples were eluted from the resin bed with 0.1% citrate solution, adjusted to a pH value of 5.30, at a flow-rate of 0.5 cm per minute. The elution curves are shown in Figure 11 and other pertinent data are recorded in Table 4.

This experiment served the double purpose of illustrating the effectiveness of the 0.1% citrate solution for the separation of a more complex mixture as well as the influence of column length on the separation. The height of the resin bed was the only variable introduced in this experiment and it is obvious that the 120 cm bed produced the best separation. It will be noted that the concentration of the rare earths in the eluate increases toward the latter part of the elution in the case of the 30 and 60 cm beds. The overlapping of the individual rare earth bands increased in the case of the shorter bed lengths. These results show that a certain length of free resin bed is required to allow full development of the individual rare earth bands.

More complete studies have been made by Spedding, et al., (6) on the length of free bed necessary to allow formation of the fully developed type of elution curve. They have made extensive studies of the factors influencing the separation of samarium from neodymium including the height of resin bed to use with various rare earth loads that was just sufficient to give maximum separation at various pH values of 0.1%
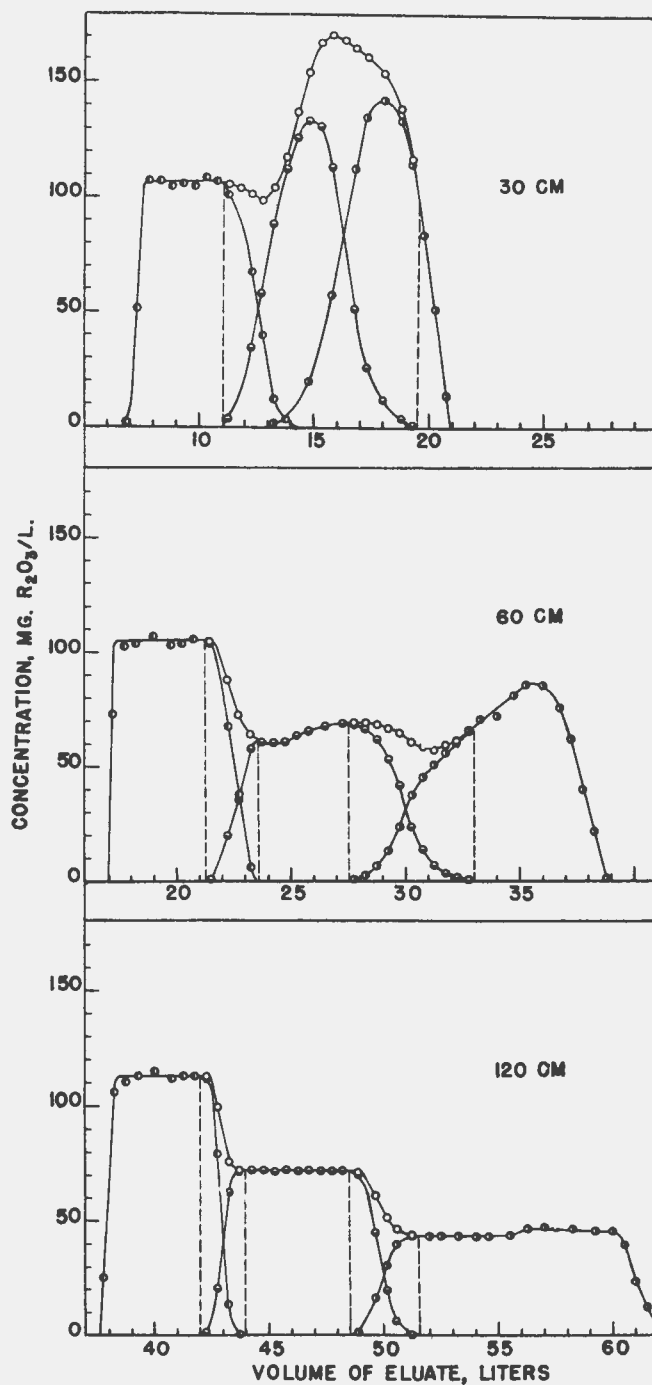
Figure 11 - The effect of resin bed length on the elution of
            mixtures of Sm, Nd and Pr from -30+40 mesh size
            Amberlite IR-100 resin beds, 2.2 cm in diameter
            and 30, 60 and 120 cm. long, with 0.1% citrate
            solutions at a pH value of 5.30 and a flow-rate
            of 0.5 cm/min: O, mixed fractions; ●, Sm_2O_3;
            ●, Nd_2O_3; ●, Pr_6O_{11}. From Spedding, Fulmer,
Powell and Butler (6)

citrate solutions. It was also clearly established that no further
separation of the rare-earth pair would result from using beds of resin
longer than necessary to give a fully developed elution curve. The re-
sults of their studies should be directly applicable to separations
involving praseodymium.

Table 4

Effect of Column Length for a Three-Component Mixture

of Samarium, Neodymium and Praseodymium

Resin bed height (cm)	30	60	120
Free bed height (cm)[*]	20	50	110
Breakthrough volume (l)	6.7	17.5	37.6
Total volume of eluant (l)	20.5	38.9	62.5
% Sm_2O_3 obtainable $>$ 99.5% pure	70.5	71.2	81.5
% Nd_2O_3 obtainable $>$99.5% pure	none	44.5	67.3
% Pr_6O_{11} obtainable $>$99.5% pure	8.8	67.4	88.0

[*]Centimeters of hydrogen-form resin remaining in the resin bed after
adsorbing the mixed rare earths.

Such a study was hampered in the case of praseodymium-rich mixtures
by the formation of a rare-earth citrate precipitate in the resin bed
when the sample weight exceeded a certain value. This critical sample
weight for 50-50 neodymium-praseodymium mixtures eluted from 22 mm dia-
meter columns with 0.1% citrate at pH value 5.50 was determined to be
about 2.0 ± 0.1 grams based on the weight of the oxide from which the
sample was prepared. This value corresponds to a column loading of about
0.5 gram of R_2O_3 per square centimeter of resin bed cross-section for
Amberlite IR-100. This fact is given since it was determined that this
value for the critical sample size applied to resin beds up to four
inches in diameter under the same conditions of elution. In general, it
was found that the tendency toward precipitate formation in the resin bed
increased with increasing amounts of praseodymium and lanthanum in the
samples; increased with increasing weights of the rare earth mixture
adsorbed on the column; and increased with increasing pH of the citrate
solution.

The precipitate usually formed shortly after the beginning of an elution in the region near the bottom of the adsorbed band of rare earths. The precipitate could become so dense, depending on the conditions noted above, as to obstruct the flow of solution through the resin bed thus causing serious channeling to result.

More quantitative data concerning this precipitate and a method for preventing its formation will be given in a later section.

5. Nalcite HCR resin

A quantity of Nalcite HCR cation-exchange resin was procured from the National Aluminate Corporation, Chicago, Illinois. The resin is a nuclear sulfonic acid type having a cation capacity of 4.15 milliequivalents per dry-gram (40). According to a private communication from the Dow Chemical Company, the National Aluminate Corporation is licensed to distribute Dowex-50 resin under the trade name Nalcite HCR. Harris and Tompkins (35) reported that the high capacity resin types, such as Dowex-50, are superior to Amberlite IR-100 for rare-earth separations. Their conclusions were based on experiments performed with yttrium and cerium mixtures, using 5% citrate solutions in the pH range 2.75 to 3.30. It was decided to investigate the use of this resin for the separation of praseodymium employing 0.1% citrate solutions.

Nalcite HCR has characteristics which should be advantageous for use in column separations of the rare earths. It is produced in spherically shaped particles having a larger percentage of particles less than 30 mesh size than does Amberlite IR-100. The spherical shape of the particles makes it easier to prepare a uniformly packed resin bed with less chance for the formation of channels during the elution. The higher capacity of this exchanger allows a larger load of rare earth mixture to be adsorbed and separated per column.

Shortly before the initiation of the experiments with Nalcite HCR, a better source of praseodymium crude was made available by the Lindsay Light and Chemical Company which they called "praseodymium ammonium nitrate." This material was found to have an R_2O_3 content of 30% by weight. The oxide was analyzed spectrophotometrically and found to contain 43.5% Pr_6O_{11}, 10.2% Nd_2O_3, 46% La_2O_3 and traces of Sm_2O_3 and CeO_2. In subsequent discussions the oxide obtained from this material shall be referred to as the "praseodymium crude."

Full advantage was taken of the information gained from the elution of neodymium-praseodymium mixtures from Amberlite IR-100 with 0.1% citrate solution in this study using Nalcite HCR.

A few preliminary experiments indicated that the 0.1% citrate would have to be adjusted to a pH value in the neighborhood of 6.00 in order to obtain a practical elution rate from Nalcite HCR resin; this value is higher than that used for Amberlite IR-100.

Another useful property of this resin was discovered during the elution experiments. By shining a bright light on the column of resin, the front edge of the rare earth band was clearly defined as evidenced by a difference in the shade of brick red in the rare-earth form resin and the hydrogen-form resin; the band front could thus be followed in this manner until the breakthrough point was reached. The back edge of the band was more difficult to distinguish.

6. Increasing column length with a constant sample weight

Three column beds of -40+50 mesh size Nalcite HCR resin, 22 mm in diameter, and 20, 40, and 60 cm in length, were prepared. Each column was loaded with the equivalent of 3.5 grams of praseodymium crude and then eluted with 0.1% citrate solution having a pH value of 6.10; the flow-rate was 0.5 cm per minute. The citrate solution used in this experiment and the following experiments was made up from anhydrous citric acid. The elution curves are shown in Figure 12. The amount of pure praseodymium obtained from each column is given in Table 4. Special note should be made that the analyses were performed by a combination of spectrophotometric and spectrographic methods. The pure Pr_6O_{11} had less than 0.1% of impurities.

The per cent yield of the available praseodymium was in good agreement with the results obtained from Amberlite IR-100 resin. In addition, the actual amount of the pure material obtained was increased since the column would handle a larger initial load. The effect of column length was to increase the separation for lengths increasing to the point necessary for the attainment of the fully developed type of elution curve.

It will be noted that the sample load used in this experiment exceeded the load which caused a precipitate to form in the Amberlite IR-100 resin beds as mentioned previously. Only a slight trace of the precipitation was observed in this experiment and it dissolved completely before the rare earth band had progressed half way through the free resin bed length. This slight precipitation apparently had no adverse affect on the separation.

7. Increased sample weight on a fixed column length

Each of two columns with resin beds of -40+50 mesh size Nalcite HCR, 60 cm long and 22 mm in diameter, was loaded with the equivalent of 4.5
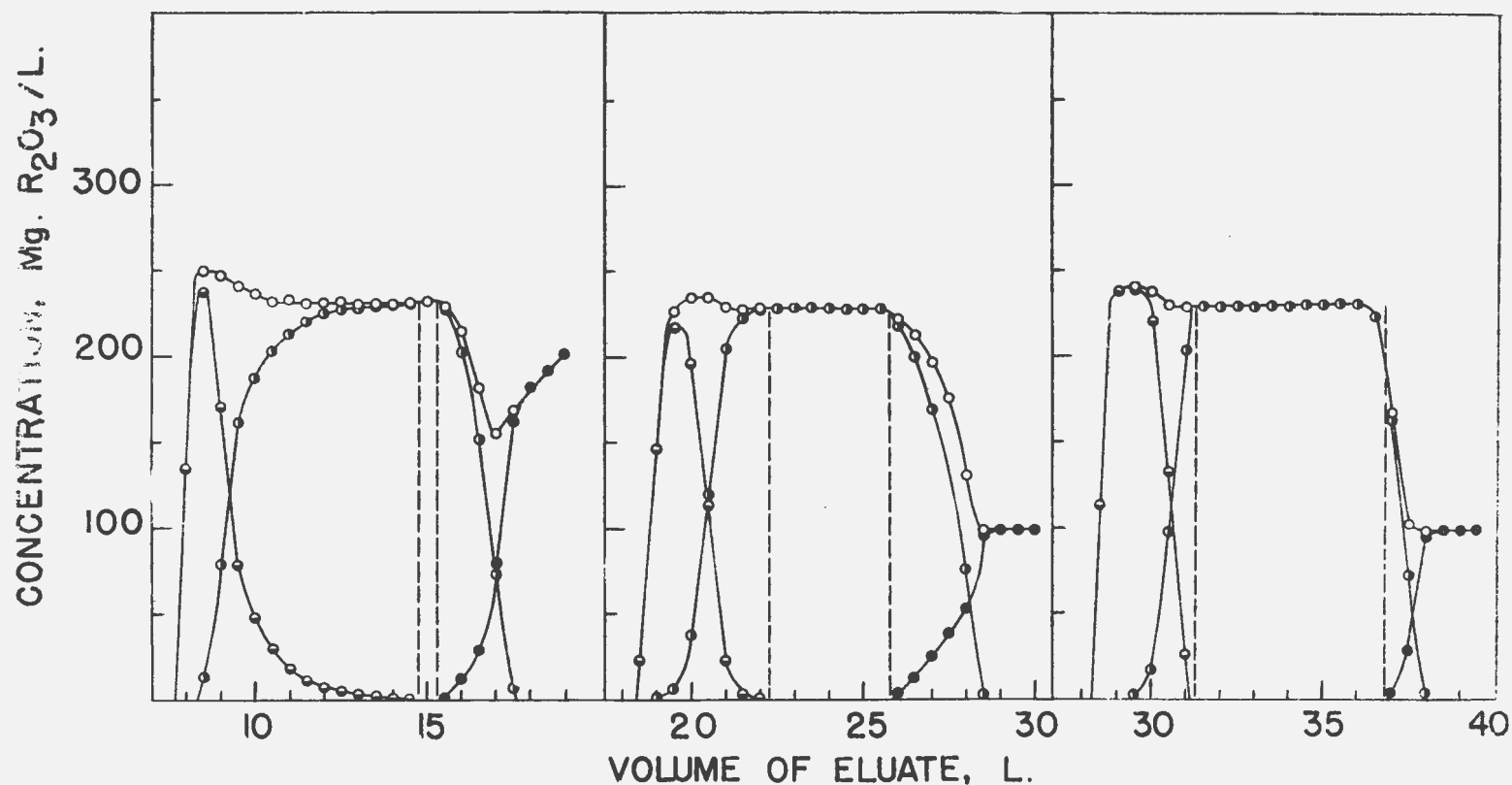
Figure 12 - The elution of 3.5 gram samples of praseodymium crude from -40+50 mesh size Nalcite HCR resin beds, 2.2 cm in diameter and 20, 40 and 60 cm long, with 0.1% citrate solutions at a pH value of 6.15 and a flow-rate of 0.5 cm/min: ◕, Nd_2O_3; ◑, Pr_6O_{11}; ●, La_2O_3; ○, mixed fractions.

and 5.0 grams of praseodymium crude, respectively. The elution was
performed with 0.1% citrate having a pH value of 6.10 and at a flow-
rate of 0.5 cm per minute.

Table 4

Praseodymium Separations on Columns of Varied Length

Sample Wt. (grams)	Column length (centimeters)	Amt. Pr_6O_{11} obt. >99.9 (grams)	Yield of available Pr_6O_{11} >99.9% (per cent)
3.5	20	0.116	7.6
3.5	40	0.800	52.6
3.5	60	1.260	82.9

The column with 4.5 grams of crude yielded 1.37 grams of >99.9%
Pr_6O_{11} representing 70% of the available praseodymium; the 5.0 grams
of crude yielded 1.49 grams of >99.9% Pr_6O_{11} representing 68% of the
available praseodymium.

A very heavy precipitate formed in both of these columns near the
beginning of the elution but it slowly dissolved before the breakthrough
occurred. The reduced percentage yield of the available praseodymium
was attributed to the formation of the precipitate. The number of grams
of >99.9% Pr_6O_{11} continued to increase slightly over the amount obtained
with the 3.5 gram load of crude described above in experiment 6.

8. Separation of praseodymium from lanthanum

Three columns having beds of -40+50 mesh size Nalcite HCR resin,
22 mm in diameter and 30 cm in length, were each loaded with the equiva-
lent of 2.0 grams of a mixture of praseodymium and lanthanum oxides.
The composition of the sample was 73.9% Pr_6O_{11} and 26.1% La_2O_3. The
samples were eluted with 0.1% citrate solution adjusted to pH values of
6.20, 6.00 and 5.80, respectively. The flow-rate was held constant at
0.5 cm per minute. The elution curves for this experiment are shown in
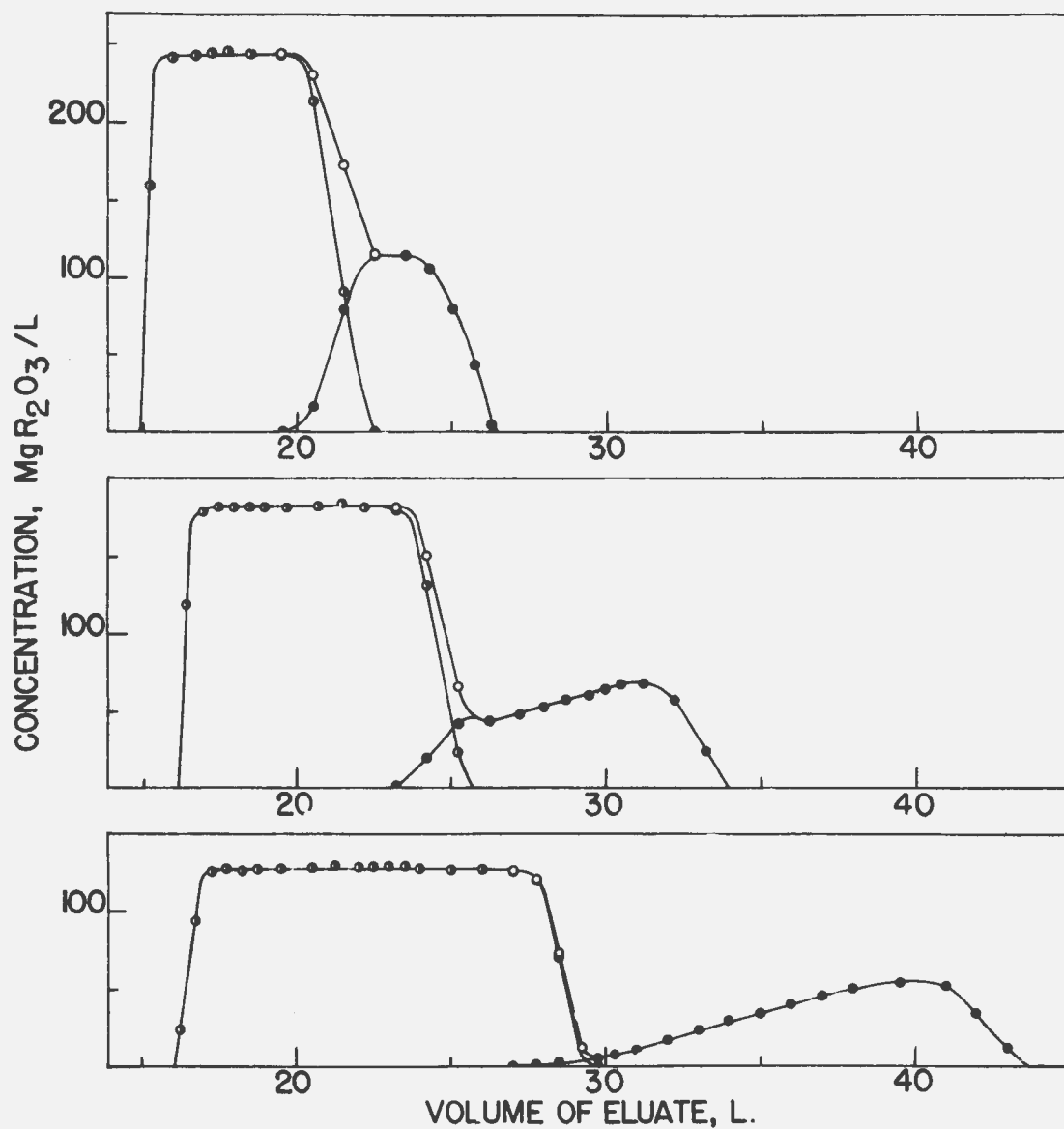Figure 13.

Figure 13 - The elution of 2 gram samples of a mixture of
          Pr and La oxides from -40+50 mesh size Nalcite
          HCR resin beds, 2.2 x 30 cm, with 0.1% citrate
          solutions at pH values of 6.20, 6.00 and 5.80
          and a flow-rate of 0.5 cm/min: $\mathbf{0}$, Pr_6O_{11};
          ●, La_2O_3; O, mixed fractions.

The percentage of the available Pr_6O_{11} which was obtained $> 99.9\%$ pure was: 79.7%, 77.7% and 93.5% in the order of decreasing pH of the citrate eluting solutions.

9. Nature of the column precipitate

A 4-inch inside diameter column was loaded with greater than 20 mesh size Nalcite HCR and the resin bed loaded with the equivalent of 150 grams of praseodymium crude. The column was eluted with 0.1% citrate of pH value 6.10 at 0.5 cm per minute flow-rate. These conditions were designed to produce a large amount of precipitate and they were successful.

The resin plus precipitate was removed from the top of the column and allowed to air dry. It was found to be relatively easy to remove the precipitate from the coarse resin particles by screening the mixture. The precipitate was converted to the oxide and analyzed for its rare earth content; the analysis showed 11.4% Nd_2O_3, 59.5% Pr_6O_{11}, and 29.1% La_2O_3. This showed that all the rare earths in the praseodymium crude were present in the column precipitate. Thus to operate under conditions which produce the precipitate, sufficient free resin bed length must be allowed to separate the rare earths in the precipitate after it has dissolved. This was a serious limiting factor in large-scale praseodymium separations since the advantage of increased sample weights with proportionately lengthened resin beds could not be utilized. A very positive deterent was the blocking of the resin bed with precipitate if larger samples were employed.

The chemical composition of the precipitate was not determined but it is believed to have an empirical formula of R(Citrate)·2H$_2$O where R represents a rare earth. Tevebaugh (48) has found that such a compound forms from lanthanum-citrate solutions.

10. Prevention of the column precipitate

The property of Nalcite HCR resin which allowed observation of the front and back boundaries of the rare earth band was helpful in devising a method for preventing rare earth precipitation in the resin bed. It was observed that the length of the original band of rare-earth mixture adsorbed on the column increased to at least twice its original length and reached a steady state during the elution. Coupled with the fact that the precipitate in the bed dissolved during the elution and did not reform gave rise to the idea of spreading out the band of rare earths during the column-loading operation. Two methods for accomplishing this were considered: (1) adding excess hydrochloric acid to the rare earth chloride solution to be adsorbed on the resin bed or (2) adding ammonium

chloride to this solution. In either case, the added cation would com-
pete with the rare earth ions for positions on the resin and result in
a lower concentration of rare earths per unit volume of resin.

The praseodymium crude, used in testing these methods, was assumed
to be composed of a rare earth of atomic weight 140. Solutions of rare
earth chlorides were prepared from 5.25 grams of praseodymium-crude
oxide. To one of the samples, 15 ml of 12 N hydrochloric acid was added
and 30 ml of the acid was added to the other. One solution was left
free of excess acid to be used for comparative purposes. The amounts of
acid added corresponded to a ratio of 2 equivalents of HCl per equivalent
of RCl_3 and 4 equivalents of HCl per equivalent of RCl_3, respectively.
The three solutions were diluted to one liter and adsorbed on -40+50
mesh size Nalcite HCR resin beds which were 60 cm in length and 22 cm
in diameter. Each column was eluted with 0.1% citrate at a pH value of
6.10 and a flow-rate of 0.5 cm per minute.

A large quantity of precipitate formed in the column having no acid
added to the solution. A few scattered particles of precipitate formed
in the column having acid added in the 2/1 ratio; no precipitate was
observed in the other column.

In a subsequent experiment, the effect of adding NH_4Cl to the rare
earth chloride solution in the ratios given above gave analogous results
to those obtained with the acid.

An experiment was designed to test the use of hydrochloric acid
for a larger sample load. A column of -40+50 mesh size Nalcite HCR,
22 mm in diameter and 100 cm in length, was loaded with the equivalent
of 9.5 grams of praseodymium crude. Six equivalents of hydrochloric
acid were added per equivalent of RCl_3. The column was eluted with 0.1%
citrate of pH value 6.10 and at a flow-rate of 0.5 cm per minute. The
elution curve for this experiment is shown in Figure 14. The weight
of Pr_6O_{11}, obtained > 99.9% pure, was 3.12 grams which represented a
75.6% yield of the available praseodymium. An excellent separation of
praseodymium from lanthanum was achieved. The rather broad overlapping
of the neodymium and praseodymium curves may be explained by a very
crooked rare earth band front which was observed during the elution.

The results reported in this section are of a preliminary nature
and further experiments will be necessary to determine the maximum size
sample for various column lengths which will give a fully developed
type elution curve.

11. Pilot-plant operation

The results of the investigations using 0.1% citrate solutions for
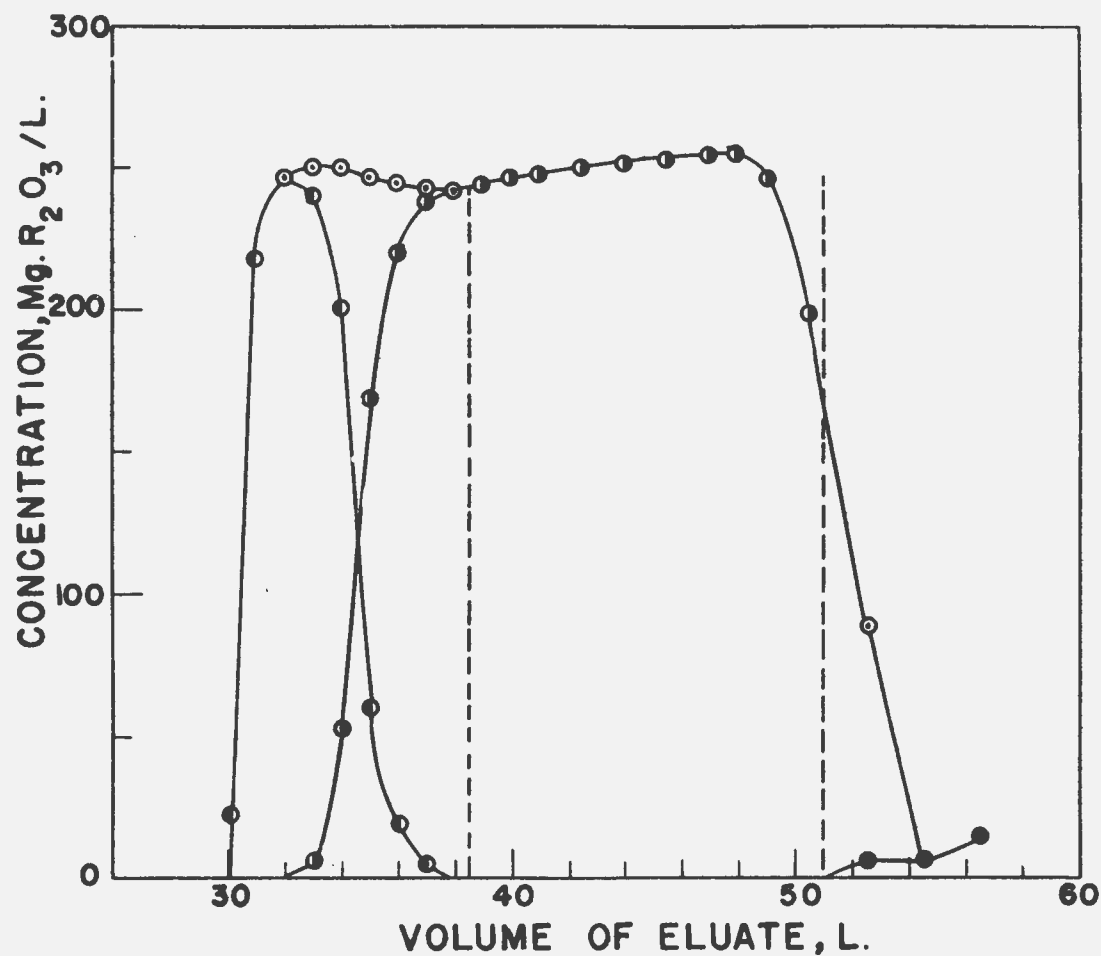the separation of praseodymium, especially those obtained with Nalcite

Figure 14 - The elution of a 9.5 gram sample of praseodymium crude from a -40+50 mesh size Nalcite HCR resin bed, 2.2 x 100 cm, with 0.1% citrate solution at a pH value of 6.10 and at a flow-rate of 0.5 cm/min: O, Nd_2O_3; ◑, Pr_6O_{11}; ◎, mixed fractions.

HCR resin, were employed in large-scale production of spectrographically
pure praseodymium. The pilot plant shown in Figures 2 and 3 was set
up in cooperation with other members of Dr. Spedding's group. Each of
the twenty 6-inch diameter columns was loaded to a depth of 76 cm with
-30+40 mesh size Nalcite HCR resin. All of the separations were per-
formed with 0.1% citrate at a pH value of 6.10 using a flow-rate of
0.5 cm per minute. The sample load of praseodymium crude which should
be used on these columns was roughly determined by extrapolation from
the 22 mm diameter columns with 60 cm bed lengths. The ratio of the
area of the 6-inch diameter column to the area of the 22 mm diameter
column is 48.5. Based on a 5-gram load for the 22 mm diameter column,
this would indicate a sample load near 250 grams for the 6-inch diameter
column. The first separations made on this column were done without
the addition of excess hydrochloric acid to the rare-earth solution
being adsorbed. As a result, it was found that 250 grams was the
maximum load which could be eluted without excessive precipitate forma-
tion in the columns. The columns were eluted to the point where all
the praseodymium had been recovered and then the remaining lanthanum
was stripped from the column.

The results obtained from the operation of a number of columns
are given in Table 5. The per cent yield of available Pr_6O_{11}, obtained
> 99.9% pure, was lower than would be expected from the results obtained
on the 22 mm diameter columns. It was found more difficult to maintain
horizontal band fronts on the 6-inch diameter columns which could
easily account for the reduced percentage yields. The increase of sample
weight with proportionate increases in column length should lead to
higher production rates of pure praseodymium. In addition to the
spectrographically pure praseodymium obtained from these operations,
other fractions rich in praseodymium, having a single rare-earth im-
purity, were obtained which constituted excellent sources of the element
for further purification.

It is recognized that the conditions given above are not optimum
for the operation of a pilot-plant scale unit and further investigations
need to be pursued along the lines indicated. It was, however, demon-
strated that 90 grams of spectrographically pure praseodymium oxide
was obtainable per column operated using the praseodymium crude men-
tioned. An elution of this material plus the necessary operations
attendent to the run required a period of six weeks to complete. Thus
if 20 columns were operated with 325 gram smaple loads, based on weight
as oxide, it would be possible to produce spectrographically pure
Pr_6O_{11} at a rate of approximately 15 kilograms per year.

Table 5

Pilot-Plant Scale Separation of Praseodymium

Column Load as Oxide (grams)	No. of Columns operated	Av. wt. of >99.9% Pr$_6$O$_{11}$ obtained per column (grams)	Percentage of available Pr$_6$O$_{11}$ obtained >99.9% pure (per cent)
225	10	67.6	69.1
250	10	76.5	70.2
300	1	74.6	61.0
325*	8	90.0	63.6

*Hydrochloric acid was added in the ratio of six equivalents of HCl per equivalent of RCl$_3$ to the solution used to load the column.

VI. SUMMARY AND CONCLUSIONS

An ion-exchange process was developed for the separation of spectrographically pure praseodymium salts in kilogram amounts from commercially available concentrates. The application of either 0.5% or 0.1% citrate solutions as eluting agents was shown to result in excellent separations of praseodymium from samarium, neodymium, and lanthanum when the mixed rare earths were eluted from Amberlite IR-100 or Nalcite HCR cation-exchange resins.

A number of variables were investigated which were shown to be important in the ion-exchange method for preparing pure praseodymium salts. It is desirable to approach equilibrium conditions as closely as possible during the elution process in order that the small differences between the equilibrium constants of the individual elements may be fully utilized. Sufficient time must be allowed for the cations to diffuse into and out of the resin so that an equilibrium may be established between the rare earths in the resin phase and those complexed by the citrate ions in the surrounding solution phase. Experimental evidence is given to show that a reduction in the flow-rate of the eluting solution and a decrease in resin particle size, which decreases the length

of the diffusion path in the resin, resulted in a closer approach to equilibrium conditions and increased the separation of adjacent rare earths.

Small differences in the pH of the citrate solutions, used to elute the rare-earth band from the resin bed, resulted in both a qualitative and quantitative change in the shape of the elution curves. The variation in the shape of the curves was interpreted as being related to a change in the relative importance of different rare-earth citrate complexes in the eluting solution. The existence of at least five such complexes have been reported by Spedding and co-workers (4). In general, lower pH values of the citrate solutions, in the applicable pH range, resulted in better separations. However, in large-scale production, a compromise must be made between the increased time necessary to complete the elution, with somewhat better separation, at lower pH values, and labor cost.

There is little choice between the use of 0.5% or 0.1% citrate solutions for separating small amounts of pure praseodymium. However, 0.1% citrate is to be preferred for large-scale production since the cost of the operation is reduced.

Nalcite HCR resin was shown to be superior to Amberlite IR-100 for large-scale praseodymium separations. Nalcite HCR not only has a higher capacity but the spherical form of the particles permits better packing in a column, thus reducing the tendency of the rare-earth band to form streamers or to channel during the elution. Direct observation showed that irregularity of the band-fronts of the individual rare earths may account for a large percentage of the overlapping of adjacent rare earths. In other words, the region of mixed rare earths in an elution may be attributed in part to the mechanical difficulties of maintaining a horizontal rare-earth band-front during the elution.

Preliminary experiments showed that a greater percentage yield of the available praseodymium resulted from increasing the sample weight of the praseodymium concentrate with a proportionate increase in the column length. This increase in yield occurs because the region of overlapping rare-earth bands remains essentially constant if a minimum resin bed-length is provided for allowing full development of the component rare earths into bands. Further increase in resin bed height above the minimum length for a given column load does not result in further separation between adjacent rare earths.

A complete investigation of the relation between column load and column length was prevented by the formation of a slightly soluble rare-earth citrate compound which precipitated in the resin bed as the sample weight was increased. The rare-earth citrate precipitation in the resin

bed was prevented by adding excess hydrochloric acid or ammonium
chloride to the mixed rare-earth chlorides before the sample was
adsorbed on the resin bed.

The conditions of elution were successfully scaled up from small
column experiments to a pilot-plant which was demonstrated to have a
capacity for producing 15 kilograms of spectrographically pure praseodym-
ium oxide per year. In the spectrographically pure material, the emission
lines of any possible rare-earth impurity were absent which showed that
less than 0.1% of such contaminates were present.

During the course of these investigations, seven kilograms of spec-
trographically pure praseodymium oxide were prepared and made available
to a number of investigators conducting theoretical researches on the
properties of the rare earths.

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VIII. ACKNOWLEDGMENTS

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