





QUANTITATIVE SEPARATION OF SMALL AMOUNTS OF RARE EARTHS FROM THORIUM, URANIUM, AND ZIRCONIUM BY ION EXCHANGE

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VI.

QUANTITATIVE SEPARATION OF SMALL AMOUNTS OF RARE EARTHS

FROM THORIUM, URANIUM, AND ZIRCONIUM BY ION EXCHANCE

by

Henry J. Hettel and V. A. Fassel

ABSTRACT

A successful method has been developed for the determination of certain rare earths in thorium in the fractional ppm range. The procedure is based on the ion-exchange chromatographic separation of the rare earths plus added yttrium carrier from the thorium, followed by emission spectrometric determination of the rare-earth impurities in the yttrium carrier. A simultaneous separation from the rare earths of the common element impurities present in the thorium has been accomplished. A high degree of compensation for procedural errors is achieved by the use of a pure rare earth as both the carrier in the separation and purification procedure and the matrix material in the spectrographic determination.

The method fulfills the requirements of accuracy, sensitivity, and speed necessary for use in the routine analysis of reactor-grade thorium metal. It can find application, in its present form, also for the simultaneous determination of part-per-billion amounts of common element impurities in thorium.

*This report is based on an M.S. thesis by Henry J. Hettel submitted December, 1956, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

I. INTRODUCTION

The interest in thorium has greatly increased in recent years because of its growing importance as a fuel material for nuclear reactors. The most stringent specification on such thorium is that it be free from elements having high neutron cross-sections. Chief amongst these elements are gadolinium, samarium, europium, cadmium, dysprosium, and boron, which have in decreasing order the highest thermal neutron cross-sections of all elements.

Methods possessing the required sensitivity for the analysis of cadmium and boron in thorium are readily available. However, accurate procedures possessing the required sensitivity for the analysis of rare earths in thorium have not yet been developed. Methods which determine the total rare-earth content of thorium are insufficient for the problem, since the abundance ratio of the rare earths varies with the thorium ore which is used. The individual rare-earth content must be determined. The best available methods for the quantitative determination of individual rare earths are spectrophotometric and emission spectrometric procedures. However, the sensitivities of detection of the most sensitive spectrophotometric and emission spectrometric procedures for the determination of rare earths in thorium are in the 50-100 ppm range. Since it is essential that the cited rare earths, especially gadolinium, not be present in thorium in amounts greater than 0.1 ppm, prior concentration of the rare earths from the thorium is necessary to obtain the desired sensitivity.

The report describes a rapid and accurate procedure for the separation, concentration, and determination of fractional ppm quantities of rare earths in thorium.

II. SUMMARY OF EXISTING METHODS

A number of different methods have been proposed for the separation of trace amounts of rare earths from all or part of the thorium matrix. These separations have been comprehensively reviewed in a recent work (1). A brief summary of these procedures will be given here, citing in particular their limitations.

A. Precipitation Methods

The primary requirement for a precipitation separation in the trace range is that the impurities be precipitated away from the matrix element. Precipitation of the matrix yields an incomplete separation since part of the trace impurities are occluded by the large volume of matrix precipitate. Because of its lower basicity, thorium is precipitated by all reagents preferentially to the rare earths. It is for this reason that so few precipitation procedures are available for the separation of trace rare earths from thorium. Gordon and Shaver have, however, overcome this difficulty by complexing the major portion of the thorium with nitrilotriacetic acid (2) and ethylenediaminetetraacetic acid (3). Upon subsequent precipitation with oxalic acid, the uncomplexed thorium acts as a carrier for the trace rare earths. Data obtained using lanthanum as a test rare earth indicated 98% to 100% recovery on various test separations. However, when yttrium was used as the test rare earth, no greater than 15% recovery could be obtained. Consequently, the method is limited to the lighter rare earths only, thereby precluding its use as a concentration procedure for the rare earths of interest in reactor grade thorium analysis.

B. Extraction Methods

Several solvent extraction procedures have been developed for separation of trace amounts of rare earths from thorium.

Lerner and Petretic (4) used an 8 molar nitric acid-dibutoxytetraethyleneglycol (pentaether) system for the extraction of the bulk of the thorium, followed by an 8-quinolinol (oxine)-chloroform extraction to remove the residual thorium. To eliminate interferences with the subsequent spectrographic determination, the calcium, magnesium, beryllium, and aluminum contents of the concentrate were reduced by standard precipitation separation. Following the addition of one milligram of lanthanum as a carrier and 50 micrograms of titanium as an internal standard, the rare earths were precipitated as hydroxides, ignited, and analyzed spectrographically. Mean recoveries for each of the five central rare earths tested varied between 90% and 96%, but individual spectrographic determinations varied by at least 20% from the mean.

In a modification of this general procedure, Atwell, Pepper, and Stukenbroeker (5) added thulium as a carrier for the rare earths before separation. Although the average rare-earth recovery was only 83.9%, the variable rare-earth losses were compensated to a large degree by the use of thulium lines as internal standards in the spectrographic analysis. However, as the authors state, much of the success of this analysis depends on technique.

The systems described above depend upon salting out the thorium from the high ionic strength aqueous phase into the low ionic strength organic phase. Some disadvantages of such systems for trace concentration are that the distribution coefficients for both thorium and the rare earths are pH and concentration dependent, and that the rare earths have small distribution coefficients in these systems. Consequently, small and variable losses of rare earths are always encountered, and mutual complete separation of thorium and rare earths can never be directly attained. Although adequate for production control checks, these methods cannot be considered to be strictly quantitative.

C. Ion-Exchange Methods

Two types of ion-exchange methods have been developed for the separation of rare earths from thorium: (1) those employing activated cellulose as the exchange medium, and (2) those employing sulfonated polystyrene resin polymers.

1. Separations using activated cellulose exchangers

Kember (6) employed a 12.5% HNO₃-ether-cellulose column technique for the determination of thorium in monazite and uranothorianite ores with good results. A modification of Kember's method was developed by Williams (7), who used a compound column of activated alumina over activated cellulose for the same determination, thereby eliminating the need for prior removal of phosphate ion from the sample. Recognizing the possibility of applying Kember's method to the determination of rare earths in thorium, Center, Henry, and Householder (8) modified Kember's method and employed a double cellulose column separation. The rare-earth residues were analyzed spectrographically using palladium as an internal standard. Average recovery of individual rare earths was 96%. Since various experimenters have encountered difficulty with this method, its success or failure for a given separation evidently depends to a large extent on the use of proper technique. This fact, together with the length of the procedure and the incomplete and variable recovery, precludes the use of this method for strictly quantitative work.

An additional modification of Kember's method was designed by Feldman and Ellenburg (9), who used the batch method of extracting the rare earths on activated cellulose rather than the column method. Recovery of Eu (152,154) tracer is stated to be greater than 98%. However, the method is listed at the present time as being tentative only.

2. Separations using sulfonated polystyrene exchangers

Sulfonated polystyrene ion-exchange resins have also been used for the analytical separation of rare earths from thorium. Radhakrishna (10) separated

lanthanum from thorium on a cation exchange resin bed using 10% citric acid (pH = 3) to elute the lanthanum, followed by 6N sulfuric acid to elute the thorium. No studies were made on the separation of other rare earths by this method. Gordon, Firsching, and Shaver (3) proposed the use of ethylenediamine-tetraacetic acid (EDTA) to chromatographically separate the rare earths from thorium. However, they state that their method is limited to the light rare earths only, since the stability constants for the heavy rare-earth-EDTA complexes approach that of thorium-EDTA complex.

All of the concentration methods so far listed have the additional disadvantage that no separation of the common element impurities present in the thorium is automatically made from the rare-earth impurities. Since the concentration of common elements is generally from 100 to 1000 times as much as the concentration of rare earths, supplementary time-consuming separations must be made to purify the rare earths.

D. Requirements for a Satisfactory Method

From the discussion of the existing methods described above, it is seen that no satisfactory quantitative procedure has yet been devised for the rapid and complete separation of trace amounts of all rare earths from thorium. The following requirements are proposed as being essential for a satisfactory procedure for the separation of trace amounts of rare earths from thorium:

1. Complete recovery of the desired impurities

Incomplete recovery indicates that some step in the method is critical, so that failure to exactly reproduce conditions at this step may lead to erratic and erroneous results. This is especially important where the separation of a group of elements, such as the rare earths, is desired. Not only may the total percentage loss be variable, but even more important, the percentage loss of individual elements may vary from one to another fractionation, so that the relative percentages of the elements in the residue after treatment may not be the same as their relative percentages in the original sample.

2. Simultaneous complete separation of the matrix

In those cases where the matrix will interfere with the subsequent determination of the impurities, the matrix should be simultaneously and completely separated from the impurities. Such is the case for the separation of rare earths from thorium, where lines of the thorium spectrum interfere with the subsequent spectrographic determination of the rare earths.

3. Removal of any interfering elements

In spectrographic determinations, interfering elements may be of three types: (a) those having spectral lines which coincide with the spectral lines of the impurities or internal standard, (b) those which disturb the excitation conditions in the spectroscopic discharge (extraneous element effect) and

(c) those which are present in such large amounts as to cause dilution of the impurities in the residue. All types should be automatically removed by the original matrix-impurity separation procedure, so that time-consuming sub-sequent chemical separations will not be necessary.

4. All reagents added must be easily removable

The use of reagents which are salts of metals must be avoided whenever a supplementary separation would be needed to remove the metal salts from the rare-earth residue. In particular, alkali metal salts should be avoided since even small amounts of the alkali metals affect the excitation conditions in spectroscopic discharges (11). The exclusive use of acids, ammonia, or ammonium salts satisfies this requirement, since these may be completely and automatically removed by evaporation or ignition.

5. The procedure must be rapid and easy

Since the concentration procedure may be used as a routine determination, it should require as little operator attention as possible so that one operator may run a large number of analyses simultaneously. In this respect, it should also be simple and foolproof, so that technicians may be used to perform the analyses.

A procedure for the separation of rare earths from thorium which fully satisfies all of these requirements has been devised. This procedure is the subject of this report.

III. ION EXCHANGE

During the past two decades, the scope of ion exchange as a chemical tool has expanded tremendously. The literature abounds with papers discussing its theory and applications. A complete discussion of just the physical and chemical properties of ion-exchange resins would require many more pages than are occupied by this report. Of necessity, therefore, the following discussion concerning the properties of ion-exchange resins has been severely restricted. Consideration is given only to the sulfonated polystyrene cation exchange resin used in this work. For more extensive information concerning ion exchange, reference may be made to the excellent book (12) and many fine reviews (13-22) available in the literature.

A. Introduction

The application of ion exchangers for analytical separations is based upon two different principles: (1) separation of exchangeable ions from nonexchangeable ions--the ion exchange method, and (2) separation of exchangeable ions from one another by means of differences in their exchangeability--ionexchange chromatography. The separation methods described in this report utilize ion exchange resins in both of these capacities.

1. Structure of organic ion-exchange resins

In principle, an organic cation exchanger consists of an insoluble substance to which acid groups--e.g., sulfonic acid groups or carboxyl groups--are firmly attached. The most important cation exchangers contain sulfonic acid groups, which are dissociated even in strongly acid media. The exchangeable ions of the exchanger--the hydrogen ions in the above mentioned types--are called counter ions. The cation exchangers can be regarded as polyvalent anions with attached positively-charged counter ions. A cation exchanger in the hydrogen form consists, therefore, of a high-molecular-weight insoluble organic acid.

Two very important requirements of an exchanger are insolubility and chemical stability. These can be realized only if the ion-active groups are attached to a cross-linked skeleton, such as exist within the group of network polymers. Dowex-50, the resin used in this work, is an exchanger formed by the sulfonation of a co-polymer of styrene and divinyl benzene. The divinylbenzene forms crosslinkages between the chains of polymerized styrene. Variation of the divinylbenzene content (% DVB) of the resin causes a proportional variation in the density of the network structure, which affects both the swelling properties and the exchange capacity of the resin.

2. Swelling properties of the resin

Changes in the composition of the external solution are accompanied by changes in the degree of swelling. As the ionic strength of the solution increases, the resin contracts. The greater the number of cross-linkages in the network

polymer, the lower is its flexibility. Hence, the degree of volume change (swelling) of the resin with change in solution composition is lower with highly cross-linked resins. Since swelling causes movement of the resin bed, stoppages or the formation of channels may result. For general purposes, therefore, an exchanger with a dense network structure is preferable.

3. Exchange capacity of the resin

The more ion exchanging groups introduced into the network skeleton, the higher is the exchange capacity calculated on unit weight basis of the exchanger. Simultaneously, however, an increase in the tendency of the exchanger to swell ensues within certain limits. This increased swelling counteracts to a certain extent the increase in exchange capacity since, for practical analytical purposes, this is based on a certain filter volume and not on unit weight of exchanger. A large number of ion exchanging groups is not enough, therefore, to ensure an exchanger with high capacity. It is also necessary to have a relatively large number of cross-linkages in the molecular network in order that the swelling remain moderate.

4. Donnan equilibria within resin particles

Although not quantitatively accurate except in dilute solutions, the Donnan theory of ion exchange equilibria is quite useful for predicting qualitatively the changes in ion exchange equilibria caused by changes in the composition of the external solution. Distinction should be made here between the equilibria occurring within the solution external to the resin particles--the solution phase--which are governed by the well-known laws for normal solutions, and the equilibria existing in the solution within the resin particles--the resin phase-where the high charge concentration of the sulfonic acid groups exerts a serious perturbing effect.

Discussing the latter first, consider the simple case in which a sulfonic acid resin in the hydrogen form is immersed in a solution containing sodium chloride. An ion exchange will result; i.e., sodium ions together with a certain amount of chloride ions will diffuse into the resin phase, while the amount of hydrogen ions necessary to maintain electrical neutrality will leave the ion exchanger. Regarding the ion exchange as a Donnan equilibrium, the following relationship holds between the ion activities (a) in the resin phase (r) and those in the solution phase (s):

a	+ H r	а •	Cl r	888 611	a	+ H s	a ,	- Cl s		(1)
a	+ Na r	a .,	- C1	=	a	+ Na	•	- C1	0	(2)

Division of Equation 1 by Equation 2 yields:

$$a + a + Na H$$

$$r = r$$

$$a + a + Na H$$

$$Na H$$

$$s s$$

$$(3)$$

The acid concentration in the resin phase is essentially constant because of the high concentration of fixed sulfonic acid groups (3-7 N in Dowex-50).

Three important conclusions may be deduced from these relations. First, Equation 3 indicates that the sodium concentration will be high in the solution phase and small in the resin phase when the acid concentration of the solution phase is high. This explains why cations displace hydronium ions from resins in dilute acid solutions (the sorption step) and are in turn displaced by hydronium ions in strong acid solutions (the elution step).

Secondly, Equation 3 also shows that the relative concentrations of two or more cations in the resin phase at a given time will be a function of the activities of the cations. This explains the different exchange-abilities (relative affinities) observed for ions on a resin bed.

The third conclusion concerns the effect of the resin phase on complex ion formation. Remembering that the acid concentration in the resin phase is large and relatively invariant because of the presence of fixed sulfonic acid groups, Equation 1 indicates that the concentration of the mobile anions in the resin phase will be lower than in the solution phase, especially in dilute acid solutions. Consequently, cations complexed by anions--e.g., CuCl₃--may be quantitatively taken up by a cation exchanger since the resin phase equilibrium will be displaced toward decomposition of the complexes by both the lower anion concentration and the removal of cations by exchange when formed. As will be discussed further in sections IV B 2 and IV C 2, this does not preclude the possibility of achieving separations by anionic complex formation, since this effect is minimal with strong and inert complexes, but it does reduce the efficiency of the column for separations of this type.

5. Relative affinity of the resin for cations

Cation exchangers have an affinity for all positively charged species existing in solution. In addition to simple hydrated ions, cation exchangers retain hydrolyzed ions such as $Fe(OH)_2^+$, basic ions such as BiO^+ , and cations in complex form such as $Cu(NH_3)_{1}^{+2}$. However, the degree of affinity of the resin for a given cation is dependent on the charge of the cation, its activity, and the total ion concentration in the resin phase (the degree of crosslinkage). Relative affinity decreases with cationic charge in the order:

Tetravalents, trivalents, divalents, monovalents; major differences being observed between successive classes.

Within each class, smaller differences are observed in the sequence of affinities. The differences in the relative affinities can, in the main, be attributed to differences in the activity coefficients in the resin phase. It should be noted that the replacing ability is related to the radii of the ions. Ions with larger radii (non-hydrated) are held more strongly by the ion exchanger than are ions with smaller radii. This relationship supports the view that differences in affinity can be associated with activity coefficients in the resin phase, since a relationship between ionic radii and activity coefficients also holds in common electrolyte solutions. Some examples of the sequence within each valence class are presented below in order of decreasing affinity.

Tetravalents:	Th, U(IV), Zr, Ti
Trivalents:	Y, Fe, Cr, Sc, Al
Divalents:	Ba, Sr, Ca, Mg
Monovalents:	Ag, Tl, Cs, Rb, K, NH, Na, H ₃ O, Li

The sequence of affinities given above is largely independent of the degree of cross-linkage of the resin used. However, the absolute difference in affinity between adjacent members of a sequence increases with increasing degree of cross-linkage of the resin. Consequently, highly cross-linked resins are used when maximum ion selectivity is desired.

6. Ion-exchange kinetics

Resin beds in column operation under flow never completely reach equilibrium. However, to achieve the maximum separation efficiency of the column, the approach to equilibrium should be as close as possible. As is generally true in nature, however, speed and equilibrium are diametrically opposed in ion exchangers. Although speed is of lesser importance in analytical than in industrial applications, a knowledge of the kinetics operative in resin beds and the effect of various factors on them may often allow the optimum combination of speed and separation efficiency to be obtained.

The rate at which an ion exchange system approaches equilibrium is a function of four processes:

- (1) The rate of diffusion in the solution phase.
- (2) The rate of diffusion through the Nernst liquid film surrounding the resin particles.

- (3) The rate of diffusion through the resin phase.
- (4) The exchange reaction rate.

The rate of diffusion in the solution phase is influenced by temperature and flowrate. For convenience, most analytical separations are conducted at room temperature. Consequently, the diffusion rate in the solution phase is, for practical purposes, a constant. The flowrate affects the separation efficiency by affecting the ratio of the ion velocity down the column to the lateral ion velocity (diffusion). As the flowrate is increased ions move down past more resin particles before they can diffuse laterally into one. From the viewpoint of Process 1, therefore, separation efficiency increases as flowrate decreases.

Concerning Process 2, a stagnant layer of solution surrounds each resin particle. The rate of diffusion through this layer decreases with increasing thickness of the layer. Increased flowrates decrease the thickness of the stagnant layer by their increased stirring action. Consequently, from the viewpoint of Process 2, separation efficiency increases with increasing flowrate.

Process 3-- the rate of diffusion through the resin--is controlled by cross-linkage and particle size. Resin particles having the ion-active groups accessible through very small pores (high cross-linkage) inhibit diffusion through the resin. Particles of small diameter facilitate resin diffusion since, effectively, more of the ion-active groups are near the surface than in large diameter particles. Process 3, therefore, suggests the use of high-mesh resin with low cross-linkage.

The exchange reaction rate--Process 4--is essentially instantaneous, and need not be considered further.

Studies of ion-exchange kinetics indicate that under normal conditions Processes 1 and 3 are the rate-determining factors (23-25). Consequently, from the viewpoint of ion-exchange kinetics, low flowrates plus low crosslinkage, high-mesh resin should increase the separation efficiency of an ion exchanger. As will be seen in the following section, however, other factors must also be taken into consideration in choosing the optimum conditions for a given problem.

B. Technique of Ion Exchange

1. Nomenclature

Ordinarily the column is operated downflow by running the solution through the exchanger from top to bottom. The solution which enters the column is called the influent, and the filtrate from the column is called the effluent. The first operation in an exchange cycle is the addition of the sample to the exchanger--the sorption step. At the beginning of this step the exchanger normally contains only one kind of exchangeable ion. The influent, which may contain one or several exchangeable ions, is passed through the column. After the column is rinsed with water, the exchanger contains the exchangeable ions from the solution as well as a certain amount of the ions originally present in the exchanger. The next step is the regeneration or elution. The latter term is used especially in chromatographic procedures. The retained ions are removed by passing an excess of electrolyte solution (elutriant) through the column.

The total number of exchanging groups in the column, conveniently expressed as milliequivalents, is called the total capacity of the column.

2. The sorption step

Consider, as a simple example, the exchange between a solution of sodium chloride and a bed of a sulfonic acid type exchange resin in the hydronium cycle. The sodium chloride solution is introduced into the top of the column. When the first part of the influent comes into contact with the top layer of the resin bed, an exchange takes place so that sodium ions are absorbed by the exchanger and an equivalent quantity of hydronium ions is transferred to the external solution. In ideal cases this reaction can continue until equilibrium has been attained. As the solution moves downwards, the first part comes into contact with a new layer of hydronium-saturated ion exchanger. The absorption of sodium ions continues; the reaction attempts to attain a new state of equilibrium in which the amount of sodium ions in the solution is less than in the original. Simultaneously, a new part of the sodium chloride solution comes into contact with the top layer of the ion exchanger, which in this way takes up a further amount of sodium ions. When the first part of the solution comes into contact with the third layer of the ion exchanger, a third portion of the solution simultaneously comes into contact with the top layer of the ion exchanger, etc.

After a certain amount of solution has been introduced into the column, the upper part of the resin bed is saturated with sodium ions whereas the lower parts are still in the hydrogen form. The concentration of sodium ions (C) in the solution phase is, in the upper part of the column, the same as the influent (C_0) , whereas in the lower parts C is equal to zero. In an intermediate zone of the column both sodium and hydrogen ions are present in the solution as well as in the resin. In this boundary zone the concentration is different at different points, the composition of the solution being a function of the distance (d) from the top of the resin bed. The ratio C/C_0 as a function of (d) at a given time (exchange isochrone) is indicated schematically in Figure 1.

If equilibrium could have been attained continuously throughout the sorption step, the curve would everywhere satisfy the Donnan equilibrium







Figure 2 Typical Chromatographic Elution Curves

formula (Equation 3) and would have been as sharp as possible (Figure 1, dotted curve). In practice, differences between the theoretical and experimental isochrones are obtained for various reasons, the foremost being that equilibrium is not attained in the various parts of the layer and that deviations exist from the ideal condition concerning the liquid flow. These factors will cause the actual breakthrough curves to be less sharp than the theoretical curves. With a lower flowrate the curves are naturally sharper than with a higher flowrate. Only if the flowrate is extremely low must the diffusion in the void space between the resin particles be taken into account. This factor will cause a broadening of the curve. Any factor which contributes to an increased rate of reaction--e.g., a diminished particle size or an increased temperature--will involve a sharpening of the curves.

3. The elution step

In ordinary separations of exchangeable ions from non-exchangeable components in a solution--e.g., separations of cations from anions by means of cation exchange columns--the elution is usually made with a solution containing one exchangeable ion. For ordinary analytical purposes hydrochloric acid is generally chosen as elutriant when cation exchangers are used, since it is available in high purity at low cost. A systematic investigation concerning the elution of cation exchange columns (sulfonic acid type) with hydrochloric acid has been published (26).

The course of the elution is illustrated either by integral elution curves--plots of the percentage elution versus effluent volume or by differential elution curves in which the effluent concentration is plotted against effluent volume.

In the elution step a separation of different exchangeable ions from each other may be obtained because of differences in relative affinities. The most important applications of ion exchange chromatography are based on separations during the elution of retained ions. Common elutriants are acids, salts, and complexing agents. The principle of chromatographic separation by means of elution may be illustrated by the following example. Consider the separation of sodium and potassium. The solution to be analyzed is introduced into a column containing a considerable excess of resin in the hydronium form (cycle). Following sorption, the sodium and potassium ions are retained in a band at the top of the column. The ions are eluted by passing dilute hydrochloric acid (e.g., 0.1 N) through the column. When the first part of the acid enters the column, sodium and potassium ions are partially replaced and carried downwards. As a new portion of acid is brought into contact with the upper resin layer, the replacement proceeds. At the same time the first part of the solution comes into contact with a second portion of the resin, causing a new shift in the compositions of the solution and resin phases. As mentioned in Section III A 5, the activity of potassium ions is greater than the activity of sodium ions. The composition of the solution phase will, therefore, be successively shifted so that the sodium/ potassium ratio will increase as the solution moves downwards. Under proper

conditions this shift in composition will proceed so far that a complete separation of sodium ions and potassium ions into different bands will be obtained. These bands move downwards at different rates. In the effluent the sodium ions will appear in a certain interval and the potassium ions in a subsequent interval. It must be pointed out that in this case, where the exchangeable ion in the elutriant (H^+) has a lower affinity than the ions to be separated (Na⁺ and K⁺), the effluent contains during the whole course of the elution also the exchangeable ion present in the elutriant (H^+). The eluate is divided into small fractions which are analyzed. If the concentrations of the fractions are plotted against effluent volume, an elution curve is obtained. A typical elution curve is reproduced in Figure 2a. In the curve each exchangeable ion is represented by a peak.

A disadvantage sometimes encountered in chromatographic separations is that the peaks have a considerable width (tailing), which may render the separation difficult. The choice of elutriant has the greatest influence upon the shape of the peaks. The peaks representing the ions which are held most strongly by the resin show the most marked broadening of the trailing edge. In order to facilitate the separation, it is oft-times advisable to carry out a stepwise elution; i.e., first to elute one or several ions with one elutriant and then to complete the elution with a second elutriant which is more effective in displacing the ions still left on the column.

4. Factors affecting the shape of the elution curve

Particle size, flowrate, and elutriant concentration exert the predominant influences on the elution curve shape, and hence also on the separation efficiency of the column.

Decreasing the particle size narrows the elution bands, with consequent increase of separation efficiency. In addition, the volume of elutriant required for the elution of the column decreases greatly as the resin particle size is decreased, with consequent saving of elutriant and elution time.

A study of the effect of flowrate was made by Djurfeldt and Samuelson (26). Ion exchange columns partially transformed into the Cu^{2+} and Fe^{3+} forms were eluted with 3.3 N HCl at different flowrates. The experiments show that the integral elution curves (percent elution versus effluent volume) are sharpened considerably for decreased flowrates. If, instead, percent elution is plotted against time the curves will, within wide limits, be almost independent of the flowrate. It is the "contact time" of the elution process that determines the efficiency, not the flowrate or the volume of acid used. Since the rate of diffusion through the resin particle is constant at a given temperature, a point will be reached on increasing the flowrate at which the resin diffusion will be the rate determining factor. It is useless to attempt to hasten the elution by increasing the flowrate over that value. The efficiency of the elution will not be increased, nor will the elution be achieved in a shorter time. Further increase in flowrate will simply result in the use of a larger volume of elutriant.

The effect of elutriant concentration was also studied in the same experiment (26). Using hydrochloric acid as the elutriant on cation exchange columns containing K^+ , Cu^{+2} , Al^{+3} , and Fe⁺³, it was observed that for the cations studied the elution can be performed with a minimum volume of the elutriant if a certain optimum concentration of hydrochloric acid is chosen. This optimum concentration is about 3-4 N HCl and is approximately the same for all the ions examined.

Increased acid concentration increases the elution rate because of a displacement of the ion exchange equilibrium. On the other hand, the resin shrinks at higher acid concentrations, causing a diminished diffusion velocity of the ions in the network structure of the resin, and consequently a lowered rate of elution. The increasing viscosity of the more concentrated acid has an influence in the same direction. The interaction between these effects explains the occurrence of an optimum acid concentration for K⁺, Cu^{+2} , and Al^{+3} . For Fe⁺³, the optimum concentration is 5-6 N HCl, due probably to optimum chloride complexing at this concentration.

The amount of acid which is necessary to obtain complete elution is greatly dependent upon the nature of the cations, and increases generally for increasing valence of the cation.

5. Band length and minimum bed length

The degree of separation of two ions which can be attained is a function of the length of the resin bed and of the quantity of each element present in the sample. A description of the mechanics of the separation of sodium and potassium on a resin bed was presented in Section III B 3. Although not explicitly stated therein, the implication is present that if a greater difference existed between the relative affinities of the two ions, the concentration shift on passing through a given lamina of resin would have been more pronounced. Consequently, the trailing edge of the band of the faster moving ion would have passed the leading edge of the band of the slower moving ion--the condition for separation--in a shorter length of column. Excess column length over this amount would increase the distance between the bands, but would not increase the degree of separation since the two bands were already completely separated. It is seen, therefore, that the relative affinity differences of the ions to be separated affects the minimum length of column required for their separation.

The quantity of each element present affects the minimum length also. The elution curve for sodium and potassium from the minimum length of a hypothetical column is presented in Figure 2a, page 12. The area under each curve is a measure of the quantity of that element present. If the quantities had been greater, the areas would have been greater (Figure 2b). However, since the shapes of the larger curves would remain symmetrical with those of the smaller, the base widths would be increased so that overlap of the two curves would now occur (Figure 2b, shaded portion). Consequently, the quantity of the elements present also affects the minimum column length needed for separation.

For a given separation under given conditions, the effect of both of the above-mentioned factors may be simultaneously studied by determining the ratio between the minimum length of column required for elution and the column length occupied by the sample before elution. Denoting the column length occupied by the sample after sorption as the "band length", the separation is said to require, for example, three band lengths, signifying that the additional column length over that required for sorption which must be provided for elution is three times the sample sorption length. This value will be constant as either, or both, column diameter and sample size are varied, so long as factors affecting the separation efficiency are reproduced. Listed here for convenience, these factors are resin type, degree of cross-linkage, resin particle size, elutriant concentration, elutriant flowrate, volume of sample solution, and elutriant concentration in the sample solution.

Although a minimum bed length is required to effect a given separation, excess length over this amount is, in fact, undesirable. The use of too long a resin bed increases the elutriant volume required to remove the elements from the column, and the flowrate is reduced by the increased impedance of the excess resin, with the result that the required analysis time is increased.

IV. EXPERIMENTAL

A. Approach to the Problem

As indicated in the Introduction, it is desired to quantitatively determine certain rare earths in thorium in the fractional part per million range. The insufficient sensitivity of the methods available for the determination of individual rare earths necessitates their concentration prior to analysis. Since it possesses the greatest sensitivity for the rare earths of interest, the use of the emission spectrometric method for the analysis of the concentrate seemed most promising. However, because of its complex emission spectrum, thorium is a serious interference for the emission spectrometric determination of the rare earths. Consequently, the chemical concentration procedure must provide for the complete mutual separation of rare earths and thorium.

In order that the rare-earth analysis be quantitative, a mode of separation must be chosen which is efficient in the fractional part per million range. Ion exchange was selected since its separation efficiency is not concentration dependent, consequently it exhibits the same high efficiency in the fractional part per million range as in the fractional per cent range.

Since an emission spectrometric method had already been devised for the determination of samarium, gadolinium, terbium, dysprosium, holmium, and erbium--the rare earths of interest--in yttrium (27), the concentration procedure was adapted for the use of this method by the additon of pure yttrium to the thorium sample before rare-earth separation. After separation, the rare-earth residue contains the rare-earth impurities originally present in the thorium sample plus a known excess amount of added yttrium. This residue may be directly analyzed spectrographically for its individual rare-earth content, each of which may then be back-calculated to determine its concentration in the original thorium sample.

The added yttrium, therefore, serves as both a carrier for the rare earths in the chemical separation procedure and the matrix material for their spectrographic analysis. This procedure contributes the feature that it automatically corrects for accidental rare-earth losses in the separation procedure due to poor analytical technique. Upon dissolution of the thorium sample and yttrium carrier to form a homogenous solution, the ratio between each rare earth and yttrium is established, so that subsequent loss of sample yields a proportional loss of both rare earth and yttrium. Since the spectrographic analysis determines the rare-earth-yttrium ratio, and this ratio is not altered by the proportional loss of some of each, accidental losses of sample do not affect the analytical results.

B. Separation of Rare Earths from Thorium

1. Separation mechanism in the resin bed

The rare-earth-thorium-common element separation is achieved by chromatographic elution of the sample with four molar hydrochloric acid. As discussed in section III A 5, chromatographic separation by acid elution utilizes the differences in the relative affinity of the resin for the ions of different elements. The rare-earth-thorium separation is based on the much greater affinity of the resin for tetravalent thorium than for the trivalent rare earths (chargedifference mechanism). The simultaneous rare-earth-common element separation is accomplished by two mechanisms: (1) the greater affinity of the resin for trivalent ions than for mono- or divalent ions (charge-difference mechanism), and (2) the formation of anionic, neutral, and lower-valent cationic complexes of the ions by chloride ion (complex-formation mechanism). The latter mechanism is primarily responsible for the separation of most of the common elements. in particular the trivalents, from the rare earths. The resin has no affinity for the neutral and anionic chloride complexes, consequently these pass through the resin bed with essentially the flowrate of the solution phase (complexformation mechanism only). Elution of the lower-valent cationic chloride complexes by the charge difference mechanism is facilitated by the introduction of a greater charge difference between these ions and the rare earths, which are complexed to only a slight degree by chloride ion (complex-formation plus charge-difference mechanisms). Chromatographic separation by means of the activity differences between ions of the same valence (activity-difference mechanism) enhances the separation of the trivalent common elements from the rare earths, but its effect is only of minor importance under the exchange conditions used in this work. The activity-difference separation mechanism requires the use of long columns with low flowrates, since the relative affinity differences between members of a given valency series are small in magnitude. Consequently, with the short column used in this work, the activity-difference mechanism aids the separation only during the relatively infrequent instances when ions of the nominally trivalent common elements are present on the resin in trivalent form. Those mono- and divalent common elements which are only slightly complexed by chloride ion are separated from the rare earths primarily by charge-difference only.

2. Column design and operation

The thorium-rare-earth-common element separation is performed by the column in downward flow; the thorium is removed from the column after rare-earth separation by upward flow. This bidirectional flow necessitates the use of a somewhat unconventional column design. A detailed diagram of the critical parts of the column proper is presented in Figure 4. However, in order to appreciate the significance of this design, a discussion of the manual operation of the complete apparatus, which is illustrated in Figure 3, must first be undertaken. As discussed previously, the use of fine-mesh resin results in greater resistance to the passage of solution, hence a lower flowrate. To increase the flowrate so as to decrease the total time for the separation to a reasonable value, hydrostatic pressure was applied to the column. A positive pressure was applied to the top of the resin bed by placing the elutriant reservoirs 2.5 feet above the column; a negative pressure was applied to the bottom of the bed by extending the take-off tubing 3.7 feet below the column. The column itself being 1.5 feet long, the total head for downflow operation was 7.7 feet. With this arrangement, the flowrate for downflow operation was 1.0 liters per hour. The sulfuric acid reservoir was mounted 1.0 feet above the top of the resin bed. Neglecting the height of the column, since this is balanced out, the total head for upflow operation was 4.7 feet; the flowrate being 0.39 liters per hour. The following eight steps describe the manual operation of the column shown in Figure 3:

- (1) 110 + 10 ml of 4M HCl solution containing the ten-gram thorium sample is added to the sample reservoir.
- (2) With the resin bed in the 4M HCl cycle, the three-way stopcocks 3, 4, and 5 and stopcock 6 are adjusted to permit straight-through passage of solution. Since the transfer volume for rare-earth collection is measured from first passage of sample into the column, the effluent is collected in a 2500 ml erlenmeyer flask calibrated to contain 2250 ml.
- (3) While the sample solution is passing into the column, the sample container is washed with approximately 10 ml of 4M HCl from a wash-bottle. Following passage of all but about 0.5 ml of the sample into the column, the 10-ml .sample-container wash is added. This process is repeated with a second 10-ml wash of the sample container, after which the sample reservoir is washed with 4M HCl from a wash-bottle. While the reservoir wash is draining into the column, stopcock 1 from the 4M HCl elutriant reservoir is opened (the flow is still impeded by stopcock 3).
- (4) When only 0.5 ml of sample reservoir wash still remains, stopcock 3 is adjusted to impede the flow from the sample reservoir and conduct the flow from the 4M HCl elutriant reservoir. The column may now run for two hours without operator attention.
- (5) Upon collection of 2250 ± 50 ml of effluent, a 5000-ml beaker calibrated for 4300 ml is substituted for the 2500 ml receiver, which now contains the common impurity fraction. Elution may be permitted to proceed for an additional four hours without operator attention.
- (6) Upon collection of the 4300 ± 100 ml which contains the rare-earth fraction, elution is discontinued by closing first stopcock 1, then stopcock 6. This sequence reduces the pressure on lower stopcocks. The beaker containing the rare-earth fraction is covered with a ribbed watch glass and placed on a hot plate for evaporation to dryness. Subsequent treatment of the rare-earth fraction is described in Section IV B 5.





Column for the Separation of Rare Earths from Thorium





Detail of the Critical Parts of the Column

- (7) After opening stopcock 2, stopcock 5 is adjusted to conduct the 4M H₂SO₄ elutriant from its reservoir up through the column, whereupon stopcock 4 is turned to conduct the elutriant from the top of the column to the side-arm take-off tubing. A ten-liter container is provided for collection of the 4M H₂SO₄ elutriant. The sulfuric acid elution is allowed to proceed for twelve hours.
- (8) Before a subsequent sample may be processed, 200 ml of 4M HCl must be passed through the column to remove the 4M H₂SO₁.

Close operator attention is required in this procedure only when the sample and washings are being sorbed onto the resin bed (steps 3 and 4). To obtain efficient washing, the reservoir must be allowed to drain as much as possible between addition of sample and addition of subsequent washings. However, it is essential that no air be allowed to enter the column, since air in the resin bed causes channeling. Consequently, the operator must be on hand at the propitious moment to wash the sample vessels and to transfer the column from sample feed to elutriant feed. No other operation is critical, although the transfer from common element fraction to rare-earth fraction should be made within 50 ml of the 2250 ml level. The volume at which collection of the rare-earth fraction is terminated is optional, so long as it is greater than 4200 ml. The excess effluent is pure 4M HCl, which is subsequently evaporated away.

To allow the column to be usable during the working hours of each day, elution of the thorium sample from the resin bed is performed overnight. As will be demonstrated in Section IV B 4, complete elution of the thorium requires 4500 ml of 4M H₂SO₄ elutriant. To avoid excessive waste of elutriant, the flowrate was chosen to require fifteen hours for five liters to pass. This was accomplished by reducing the height of the sulfuric acid reservoir above the resin bed.

Upon termination of thorium elution, the column must be converted to the 4M HCl cycle before a subsequent sample may be processed. Otherwise, the leading edge of the subsequent thorium sample may mix with the trailing edge of the sulfuric acid, thereby permitting sulfate complexes of thorium to form which may result in contamination of the rare-earth fraction by this thorium (Section IV C 2).

A variety of considerations were involved in the development of the column design used for the separation here reported. Of primary importance is the elution behavior of thorium. Since the thorium band is moved down the column during the rare-earth separation to only a slight degree (Section IV B 4), its removal by upflow elution is more efficient since it need traverse only a short length of resin bed. Both smaller elutriant volume and less elution time are thereby required. In additon, since the sulfuric acid elutriant is more dense than the hydrochloric acid elutriant, convection currents would result on downflow elution of thorium, thereby causing a further increase in the required elutriant volume and elution time.

A consideration of equal importance is the elimination of contamination of successive samples. The elution behavior of a number of elements--e.g., Zr, Nb, Ta--is similar, at least in low concentrations, to that of thorium under the separation conditions used. The downflow hydrochloric acid elution completely removes from the resin the rare earths and all elements of smaller exchangeability. All elements of greater exchangeability are removed in the opposite direction by the upflow sulfuric acid elution. Consequently, neither thorium no elements similar to it ever come into contact with the lower portions of the resin bed, with the result that non-rare-earth elements from previous samples cannot contaminate the rare-earth fractions of subsequent samples.

A third consideration was the elimination of the tedious washing of the sample reservoir required in conventional column designs. Since only one reservoir is provided in these designs, into which the sample solution is placed followed by the elutriant, failure to completely wash the sample from the large capacity reservoir results in some of the sample solution being dispersed throughout the elutriant. Consequently, small amounts of sample are continuously passing into the resin bed during the course of the elution, resulting in a small but persistent tailing of sample components through the bands of one another. The present design overcomes this problem by providing separate reservoirs for sample and elutriant which are coupled to the exchanger through a capillary stopcock (Figure 3). On sample feed, the elutriant reservoir is isolated from the system, and the sample reservoir is conversely isolated from the system during elutriant feed. The washing in the high flow-velocity capillary system is complete and essentially instantaneous. Consequently, tailing from the abovestated cause is eliminated. Actually, no washing of either sample container or sample reservoir is necessary, since the action of the added yttrium as both rare-earth carrier and spectrographic internal standard compensates for any rare-earth losses (Section IV A), but good analytical technique necessitates it and the procedure therefore provides for it.

Although only one sample can be done per day per column, the method requires so little attention that one operator can easily handle a dozen or more columns. The longest step requiring operator attention is sample sorption and washing, occupying thirteen minutes. By charging the columns successively in sets of two, a dozen columns may be charged in 1.5 hours. Each column will now require five minutes more of operator time; two minutes to change containers at the start of the rare-earth fraction, and three minutes to discontinue rare-earth elution, put the sample on a hot plate, and initiate the thorium elution. The remaining hours of the operator's day may be spent in preparing the samples for the following day's runs and processing the rare-earth residues from the previous day's runs.

A diagram of the column showing the essential constructional details is presented in Figure 4. The factor of greatest importance in the construction of the column is the attainment of a minimal free-volume. Free-volume may be defined as the volume of the column not occupied by resin from the point of sample entry at the top to the point of effluent exit to the receiver at the bottom. In all such free-volumes, convection mixing of solution strata may occur, resulting in a decreased separation efficiency. In the column used in this work, free-volumes exist (1) in all stopcocks and connecting tubing from stopcock 3, Figure 3, to the end of the take-off tubing from stopcock 6 of the same Figure; (2) in the spaces between the fritted glass disc and the capillary tubing of the retaining and the bed support plugs (Figure 4); and (3) in the space between the fritted glass disc of the retaining plug and the top of the resin bed in the exchanger, (Figure 4). The detrimental effects of free-volumes may be minimized by making the cross-sectional area through these volumes as small as is practical, thereby attaining high flow-velocities, and by making the transitions between regions of different cross-sectional area as gradual and smooth as possible.

The use exclusively of 2 mm I.D. capillary tubing and stopcocks essentially eliminates mixing effects in the connecting tubing. Although mixing effects in the retaining and bed support plugs could not be entirely eliminated, they were minimized by making the free-volumes between the fritted discs and capillary bores as small as possible (approximately 0.1 ml). To reduce the freevolume between the retaining plug and the top of the resin bed, the resin bed was carefully equilibrated in the bed packing operation, to be discussed shortly, so that the resin level remained in the neck of the exchanger during the course of an analysis.

Butt joints between stopcocks and connecting tubing were made with one-half inch lengths of 3/16" I.D. Tygon tubing which had been dipped briefly in concentrated ammonium hydroxide. Very serviceable pressure-proof connections were made in this manner. The retaining plug was similarly attached to the neck of the exchange section with 3/8" I.D. Tygon tubing.

Only the critical dimensions of the exchanger are listed in Figure 4. However, all other dimensions may be determined by measurement, since Figure 4 is a scale drawing of the column used for this work. Two capillary stopcocks--4 and 6 of Figure 3-- were intentionally omitted from Figure 4 to simplify the drawing. The lengths of their leads are the same as for the two stopcocks shown.

The packing of the resin bed into the exchange section is accomplished by attaching a large funnel to the neck of the section with Tygon tubing, then filling the column with 6M HCl. A spirit level is used to adjust the column to be perfectly vertical. This is required to obtain a uniform density of packing of the resin particles. A column which is non-vertical when packed yields a greater resin density on the lower side. The flowrate will then be faster through the less dense side, consequently a lamina of solution which is horizontal when passing into the resin bed will be tilted downward toward the less densely packed side upon emergence from the bed. Non-uniform packing thus results in decreased separation efficiency.

A slurry of 100-200 mesh Dowex-50 resin, 12% DVB, which has been previously washed repeatedly with 6M HCl followed by equilibration in 6M HCl overnight, is added to the funnel. Since fine-mesh resin settles very slowly, the process may be hastened by opening the stopcock of the column sufficiently to yield a flowrate of about 15 ml per minute. The 6M HCl-resin slurry is periodically added to the funnel until the resin settles in the funnel stem, indicating that the column is filled. With a water aspirator and collection bottle, the excess resin is siphoned to the top of the column neck. After passage of two liters of 1M HCl through the column, the resin bed is allowed to expand and settle overnight. The excess resin in the funnel stem may then be again siphoned to the top of the column neck, whereupon the column is ready for incorporation into the assembly of Figure 3. The column must again be mounted perfectly vertical. If at any time during this procedure the column runs completely or partically dry, the added resin must be removed and the procedure restarted. Air must be completely excluded from the resin bed to prevent channeling.

After the incorporation of the exchange section into the complete assembly of Figure 3, air must be removed from all lines. With the 4M HCl and 4M H_2SO_4 elutriant reservoirs filled, stopcocks 3 and 4 are adjusted to allow the 4M HCl elutriant to enter the sidearm of 3 and pass from the sidearm of 4 to the receiver. By opening stopcock 1, sufficient elutriant is permitted to remove all air bubbles, whereupon stopcock 1 is closed. Stopcocks 5 and 6 are next adjusted to allow the 4M H_2SO_4 elutriant to enter the sidearm of stopcock 5 and pass through stopcock 6 to the receiver. By opening stopcock 2, elutriant is again permitted to pass until the line is free from air bubbles. Finally, to remove the air in the retaining plug, stopcocks 4 and 5 are adjusted to pass 4M H_2SO_4 elutriant up through the column and out to the receiver, whereupon stopcock 2 is closed. The assembly is now free from air and ready for use.

Precaution must be taken with this enclosed type of column to add no solutions whose concentrations are less than the equivalent of four normal acid. Since the resin is considerably contracted in such high ionic strength solutions, the use of more dilute solutions will cause the resin to expand. Since, however, there is no room for the resin to expand, pressure will build up until either stopcocks blow out or the column explodes. It is for this reason that 4M HCl is used as the sample solution base, and also as the wash solution in the sample sorption step. This is also the reason why 4M H₂SO₄, which is equivalent to 4N H₂SO₄ at this concentration, is used as the elutriant for the thorium.

3. Choice of column parameters

The ultimate goal when designing an ion exchange column for any separation problem is the attainment of a proper balance between high separation efficiency and short analysis time. The factors affecting both of these criteria were considered at length in Section III. They will be reviewed here briefly in the light of the requirements of the present problem. The parameters affecting both separation efficiency and analysis time are resin type, degree of crosslinkage, particle size, elutriant concentration, bed dimensions, sample volume, elutriant flowrate, and reaction temperature. a. Resin type. It was shown in the previous section that the rare-earththorium separation is accomplished by the charge-difference mechanism. Consequently, thorium ions must be present in solution in the tetravalent state. Since hydrolysis of thorium commences at pH = 1.5 (28), the separation must be conducted in a strong acid medium. Sulfonated polystyrene resins, being strong acids, have the same exchange efficiency and capacity in strong acid media as in neutral or alkaline media, and are also highly resistant to reagent attack. Thus they are ideal for strong acid work. Dowex-50 was chosen since it is available in a variety of degrees of cross-linkage, and because the particles are spherical, which provides for closer, more uniform packing and less void space. The closer packing of spherical particles than of irregularly shaped particles increases the exchange capacity of the column, and the more uniform packing provides for better liquid flow characteristics. The importance of uniform packing was discussed in the preceding section.

b. Degree of cross-linkage. Since the separation is to be accomplished by the charge-difference mechanism, a high cross-linkage resin is preferred since it magnifies the absolute differences in relative affinity between ions of different valence (Section III A 5). However, since the resin is to be used in strong acid media where its swelling properties cause it to contract, too high a cross-linkage may inhibit the rate of diffusion through the resin particle, thereby decreasing the separation efficiency. For this work, a 12% crosslinkage resin was chosen.

c. <u>Resin particle size</u>. Separation efficiency in chromatographic columns is a function of the degree of approach to equilibrium which can be attained. The use of a small particle size facilitates approach to equilibrium since the diffusion paths into and out of the particle are shorter (Section III A 6). However, too small a particle size seriously decreases the flowrate. Since means are available for counteracting this affect on flowrate, a rather low particle size (100 - 200 mesh) was used.

d. Elutriant concentration. As previously mentioned, the separation must be performed in strong acid media to prevent thorium hydrolysis. Hydrochloric acid was chosen because it is a strong acid, is available in high purity at low cost, is easy to evaporate and thus remove from the eluate, and will not oxidize the exchanger. The concentration used (μ M HCl) was chosen because it was recommended in the literature (Section III A μ), and because preliminary experiments using 2M HCl and 6M HCl indicated these to yield poorer rare-earth-common element separations.

e. Resin bed dimensions. A high capacity column was required because of the large sample size needed to obtain sufficient rare-earth sensitivity (Section IV B 5). For a given resin in a given solution system, exchange capacity is dependent, to a first approximation, only on exchanger volume. Consequently, both a long column of small diameter and a short column of large diameter have the same total capacity if they have the same volume. As discussed in Section III B 5, however, a minimum column length is required for a given separation under given conditions. Excess column length over the minimum yields no better separation, since the separation of the bands of the elements is complete with the minimum length. The bands of the elements are only moved farther apart. Excess length is, in fact, undesirable since a greater elutriant volume is then required to remove the elements from the column and the flowrate is further decreased by the increased impedance of the excess resin, with the concomitant result that analysis time is increased.

The minimum bed length for the rare-earth-common element separation was determined in preliminary experiments. Adequate length was provided for the separation from the rare earths of all common elements except the alkaline earths. As discussed in Section III A 5, the alkaline earth-rare-earth separation is based on the charge-difference mechanism alone, neither group being appreciably complexed by chloride ion. Column separation of these groups would have almost doubled the minimum length, with consequent doubling of the analysis time. Since provision could easily be made for the efficient removal of alkaline earths in the subsequent rare-earth hydroxide precipitation step, their incomplete separation by the column is of little consequence.

Using the minimum column length, sufficient exchange capacity for the proposed sample size was provided by increasing the diameter of the column. Since the flowrate, which is calculated on unit area basis, remains unchanged upon increase of the cross-sectional area of the column, this procedure permits large samples to be separated with the same speed and separation efficiency as small ones.

f. Flowrate. It was pointed out in Section III B 4 that elution time may be decreased by increasing the flowrate, but only to the point where the resin diffusion process becomes the rate determining factor. Beyond that point, analysis time is independent of flowrate. Because of the uncommonly small resin particale size chosen, the flowrate may therefore be increased, without impairment of separation efficiency, to a value greater than that normally used in chromatographic separations. However, the large impedance to flow of high-mesh resin tends to decrease the flowrate attainable. To overcome this effect, the elutriant is supplied to the column under pressure (Section IV B 1). The consequent increase in flowrate so-obtained permits the separation to be made in a shorter time without excessive loss of efficiency.

g. <u>Sample solution volume</u>. Normally in chromatographic work of this kind the sample is sorbed onto the column in neutral or dilute acid media (e.g., 0.01-0.1N), then eluted with strong acid. Under such conditions, the volume of the sample solution is essentially immaterial.¹ However, when the sample solution must be more acidic (e.g., 1N), the effect of its volume on the minimum bed length must be considered. To illustrate, let us compare two general cases; (1) the concentration of the elutriant species (e.g., HCl) in the sample solution is nil or very low, and (2) the concentration of the elutriant species is high.

¹A greater degree of element partition occurs in the sorption step when dilute solutions are used rather than concentrated solutions (29), but this is distinctly a second order effect.

For case (1), the only reaction taking place in the resin bed is the displacement of resin counter ions by sample ions. This reaction involves only the probability that a sample ion will diffuse into a resin particle, and so is not concentration dependent. Consequently, whether the sample solutions are of small volume and high sample concentration, or of large volume and low sample concentration, the sample after sorption is present in the same small volume of resin at the top of the column. Therefore, the "band length" (Section III B 5) is the same regardless of the volume of the sample solution, so that the same minimum bed length is adequate for the separation in either case.

For case (2), however, where the sample solution contains a high concentration of elutriant species, the elutriant species in subsequent portions of the sample solution tend to elute the sample ions absorbed from previous portions down the column. If the volume of sample solution is small, only a small quantity of elutriant species passes through the sample band; consequently, the band is lengthened only slightly. If the sample is contained in a large volume, however, the large quantity of elutriant species passing through the sample band lengthens it appreciably. Consequently, for solutions containing high concentrations of elutriant species, the "band length" is directly proportional to sample solution volume; hence, so also is the minimum bed length for separation (Section III B 5).

The partial elution of the band during sorption in the latter largevolume case contributes very little to the separation of the sample, which occurs mainly during elution. Since the inflowing sample solution is homogeneous, the last mililiter entering the bed has the same composition as the first, so that it is still necessary to move the ions of the less exchangeable element in the tail of the sample band past the ions of the more exchangeable element in the head to achieve separation.

For the column used in this work, the sample solution must contain the same concentration of hydrochloric acid as is present in the elutriant (Section IV B 1). A small sample volume (100 ml) was therefore chosen to keep the band length small, thereby allowing the use of a short resin bed to achieve the desired separations.

Although more fully discussed in Section IV C 2, it should be mentioned here that an advantage exists in using elutriant as the base for the sample solution whenever separations of kind are to be performed by the complexformation mechanism (Section IV B 2). By forming the desiring complexes in the elutriant environment of the sample solution before addition to the column (pre-complexing), the elements so-complexed will act, upon entry into the resin bed, as if elution were already taking place. This results in increased separation efficiency since the elutriant need not now both displace from the resin and then complex these elements (post-complexing), as would be the case were the conventional operations of sorption and elution followed.

h. <u>Temperature</u>. Studies on chromatographic separations at elevated temperatures (30) indicate that the use of elevated temperatures greatly increases the separation efficiency, as is to be expected since diffusion is the basic rate determining factor in ion exchange kinetics (Section III A 6). However, serious practical problems arise in the design, construction, and operation of such columns, especially for analytical work. Room temperature was chosen for the present study since it was felt that longer columns, slower flowrates, and increased analysis time could be endured more easily than troublesome high temperature technique.

4. Elution curves for rare earths, thorium, and common elements

Before chromatographic separations can be achieved for elements lacking a sufficiently rapid and sensitive spot test, elution curves must be determined to study the behavior of such elements on the column under given experimental conditions. An elution curve, which is a plot of effluent concentration vs. effluent volume, may be determined by measuring any property of an element which, in a given experiment, is peculiar to that element alone. For the elements in question in this investigation, the rare-earth behavior was studied by radiotracer technique; thorium and the common elements aluminum, bismuth, calcium, cadmium, cobalt, chromium, copper, iron, lead, magnesium, manganese, nickel, uranium, and zinc were studied by gravimetry plus spectrographic examination.

The elution curve for yttrium is reproduced in Figure 5. In order that it indicate the behavior of yttrium under actual analytical conditions, the separation procedure for this study, as well as for the elution studies of thorium and the common elements, was identical with that presented in the recommended procedure for analysis (Section IV B 5). For this particular experiment, a 200,000 cpm charge of radioactive Y^{90} , freshly separated from its Sr^{90} parent (31), was added to the sample before sorption onto the column. Effluent fractions were collected in volumetric flasks, quantitatively transferred to beakers, then taken to dryness and counted for Y^{90} content. The experimental data are summarized in Table 1. Collection of yttrium is seen to be quantitative in the 2400 ml-6100 ml effluent volume range.

The assumption is made that the other members of the rare-earth group will also be quantitatively collected within this range. Theoretical considerations and experimental evidence both justify this assumption. Although slight differences in exchangeability exist among the rare earths, significant separations can be achieved in systems of this type (activity-difference mechanism) only by the use of very long columns and very low flowrates (Section IV B 2). Fractionation of an equimolar mixture of rare earths in the short and relatively high-flowrate column used in this investigation would be very slight. In addition, however, fractionation of a mixture composed preponderantly of one rare earth is more difficult yet, since the band of the preponderant rare earth spreads out and overlaps all of the others (Section III B 5). Since the rare-earth mixture being separated in this analysis is always at least 90%





Elution Behavior of Yttrium and Thorium Decay Products

Table	1

Data for the Determination of the Yttrium Elution Curve

Fraction	Volume Collected (ml)	cpm/ml/fraction	% Y ⁹⁰ /fraction
1	200	0.00	
2	200	13.00	
3	200	16.50	
4	200	0.40	
5	200	0.50	
6	200	0.40	
7	200	1.50	
8	200	0.55	
9	200	0.70	
10	200	0.40	0.03
11	200	0.40	
12	200	0.65	
13	200	1.96	0.26
14	200	5.88	0.79
15	200	21.78	2.94
16	200	45.70	6.17
17	200	71.80	9.69
18	200	93.60	12.62
19	500	100.10	33.73
20	500	69.60	23.49
21	500	20.90	7.06
22	500	7.84	2.63
23	500	1.57	0.53
24	500	0.00	0.00

yttrium, and generally 99% yttrium, no detectable fractionation would be expected on theoretical grounds, and this expectation can be verified by a recovery experiment (Section IV B 6).

Spectrographic examination of the yttrium fraction residues failed to detect the presence of thorium. In an attempt to determine the thorium breakthrough volume, three additional four-liter fractions of effluent were collected from this run. Spectrographic examination of these residues--primarily silicon from the beaker attack--again indicated the absence of thorium. No further attempts were made to elute the thorium, since demonstration that a 200% excess of 4M HCl elutriant over that required for complete elution of rare earths satisfactorily indicated the ability of the method to completely separate rare earths from thorium.

The rare-earth elution curve was checked twice during the course of subsequent experiments. In each case the results verified the original curve, indicating breakthrough at 2400 ml and complete collection at 6100 ml. Elution curves for a given column will be constant and reproducible so long as the experimental conditions are reproduced, and meither the column nor the resin bed are altered.

To study the simultaneous separation of the common element impurities present in the thorium sample from the rare-earth impurities, the elution behavior of a group of common elements was studied under the same conditions as were used for the rare-earth study. The elements were chosen to include those whose chemical properties would be representative of a number of elements, as well as those likely to be found in thorium. No monovalent elements were chosen, since they are known to be much more rapidly eluted than trivalent elements (Section III A 5). The group consisted of aluminum, bismuth, calcium, cadmium, chromium(III), cobalt, copper(II), iron(III), lead(II), magnesium, manganese(II), nickel, uranium(VI), and zinc. Five hundred milligram quantities of each of these elements were added to a normal thorium-rare-earth sample. Thirty-two 200 ml fractions of effluent were collected, which were then evaporated to dryness, ignited, weighed, and examined spectrographically. The results are summarized in Figure 6. The values listed refer to the percentage of the total element added which was found in the indicated fraction. Significant amounts of calcium and uranium, as well as small amounts of chromium, magnesium, copper and iron, were observed to contaminate the rare earths. In order to achieve sufficient sensitivity to detect these elements in those fractions where their concentration is low, it was necessary to add an unrealistically large amount of each element to the sample. If present as an impurity in thorium, the quantity of each element added would be equivalent to a concentration of five per cent, making the total impurity content of the thorium seventy per cent. Taking this factor into consideration, and recognizing that thorium intended for use as reactor fuel is rarely less than 99% pure, it is readily apparent that, of the elements investigated, only calcium, and to a slight extent uranium, would contaminate the rare earths.





Elution Behavior of some Representative Common Elements

Several of the elements tested passed through the column much more rapidly than would correspond simply to their elution as cations by 4M HCl. This behavior may be attributed to the formation of the chloride complexes of these elements (Section IV B 2). Most notable is the behavior of lead which, although only sparingly soluble in dilute chloride solutions, dissolves with ease in 4M HCl probably with the formation of the complex ion PbCl₁. Bismuth behaves similarly. Because of its poor complexing power, the behavior of calcium may be taken as indicative of the elution behavior of a divalent cation under the conditions existing in the column.

An interesting development which dramatically demonstrates the ability of an ion exchange column to quantitatively separate trace amounts of impurities is the separation from thorium of its radioactive decay products, as shown in Figure 5. While counting the fractions for their radioactive Y^{90} content in the determination of the rare-earth elution curve, activity was observed to be present in all fractions. To identify the radioactive species, half-life determinations were made. The relatively intense activity in fractions 2 and 3 was found to be due entirely to Pb^{212} ($t_1 = 10.6$ hr.). Calculation of the amount of Pb^{212} present in equilibrium with ten grams of natural thorium indicated that the ion exchange column had quantitatively separated 8 µpg of Pb^{212} from the thorium parent. It is of interest to note the similarity between the elution behavior of the 8 µpg of lead shown in Figure 5 with the elution behavior of 500 mg of lead shown in Figure 6. This example illustrates admirably the nonconcentration dependency of separation efficiency which makes ion-exchange columns ideal for trace impurity determinations.

Half-life determinations on the residues from fractions 13 and 23 indicated the emitter to be Y^{90} ($t_1 = 62 \text{ hr.}$), as expected. Attempts to determine the radioactive species present in fractions 4-12 were unsuccessful because the half-lives were too short (<1 hr). However, these species are probably the short-lived members of the thorium decay series (32).

After the downflow elution of the rare earths, the thorium sample is removed from the column by upflow elution with $4M H_2SO_4$ elutriant. To determine the volume required for complete removal of the thorium, the elution curve of Figure 7 was determined. The data are presented in Table 2. The thorium content of each fraction was determined gravimetrically by precipitation with ammonia. Thorium removal is seen to be essentially complete after passage of four liters of $4M H_2SO_4$ elutriant through the column. No explanation can be given for the unusual shape of this elution curve. However, since thorium sulfate has a limited solubility in $4M H_2SO_4$, effects due to the kinetics of crystallization and dissolution of thorium sulfate salt in the resin bed may be postulated to be the cause.





Regeneration Behavior of Thorium

Table 2

Fraction	Volume Collected (ml)	Weight ThO2 (mg)	mg Th O₂/ml/fraction
1	1000	4061	4.061
2	1000	3098	3.098
3	1000	2788	2.788
4	200	83.4	0.417
5	200	122.5	0.613
6	200	180.6	0.903
7	200	39.8	0.199
8	200	21.3	0.107

Data for the Determination of the Thorium Elution Curve

5. Analytical procedure

The flow sheet diagram presented in Figure 8 outlines the procedure developed for the separation of rare earths from thorium. To a ten gram sample of thorium metal is added 75 ml of distilled water, followed by 50 ml of concentrated hydrochloric acid in successive small portions to control the dissolution reaction. To the hot solution, 20.0 mg of pure Y_{203} is added as a carrier. After cooling, the 110 \pm 10 ml resultant sample solution is sorbed onto the cation exchange column, through which is then passed 6500 ml of LM HCl elutriant. The effluent from the column is collected in a 2500 ml erlenmeyer flask calibrated for 2250 ml.

Upon collection of 2250 \pm 50 ml, the 2500-ml receiver is replaced by a 5000-ml beaker calibrated for 4300 ml. Upon collection of 4300 \pm 100 ml of effluent, the column is adjusted for 4M H₂SO₁ backwash overnight, and the beaker is transferred to a hot plate for evaporation to dryness overnight.

With the specific column used in these experiments, rare-earth breakthrough occurs at 2300 ml total effluent volume, and rare-earth collection is complete at 6100 ml total effluent volume. The 0-2250 ml fraction contains the mono- and divalent common element impurities present in the thorium, together with those trivalent ions which are complexed to either the negative, neutral, monopositive, or dipositive state by four molar chloride ion. The rare earths are quantitatively collected in the 2250-6500 ml fraction, essentially free from common element impurities. The tetravalent thorium is completely retained by the exchanger. It is removed from the column by overnight elution with 4M H₂SO₄ by means of the formation of its sulfate complexes.



Figure 8

Flow Sheet Diagram for the Separation of Rare Earths from Thorium To dehydrate the silica which has been leached from the beaker by the long evaporation, as well as to dehydrate any other earth acids which may be present, the dried residue is allowed to bake for one hour at $200-250^{\circ}$ C. The rare earths plus any other hydrochloric acid solubles which may be present are dissolved in 50 ml of lel0 hydrochloric acid and filtered to remove the insoluble earth acids. To remove any iron, calcium, or magnesium which may have been introduced by the beaker attack, the filtrate is treated with hydroxylamine hydrochloride to reduce the iron to the ferrous state, followed by 1,100-phenanthroline to complex and stabilize the ferrous iron. To accomplish a carbonate-free ammonium hydroxide precipitations of the rare earths, ammonia gas is passed into the filtrate until the phenolphthalein endpoint is reached (pH = 9). At this pH the rare earths are quantitatively precipitated, whereas the alkaline earth elements are soluble. The now-pure rare-earth residue is ignited to oxide and analyzed spectrographically.

The spectrographic analysis determines the concentration of the individual rare earths present in the pure yttrium carrier added at the beginning of the procedure. The rare earths originally present in the thorium sample move through the concentration and separation procedure in consort with the pure yttrium carrier. Consequently, the rare-earth residue after separation consists of the original yttrium carrier which now contains the rare earths originally present in the thorium are now present in twenty milligrams of yttrium, the rare-earth impurities may be said to have been concentrated, hence the designation "concentration procedure". Individual rare earths--e.g., gadolinium--may be determined in yttrium down to 400 ppm within the normal spectrographic error of $\pm 5\%$ of the amount present. Consequently, the sensitivity of this method for the determination of gadolinium in thorium is:

$$\frac{100 \pm 20 \text{ ppm } \text{Gd}_2 \text{O}_3}{10^6 \text{ ppm } \text{Y}_2 \text{O}_3} \times 20 \text{ mg } \text{Y}_2 \text{O}_3} \times \frac{314 \text{ mg } \text{Gd}}{362 \text{ mg } \text{Gd}_2 \text{O}_3} \times \frac{10^{-3} \text{g}}{\text{mg}}}{10.0 \text{ g } \text{Th}} \times 10^6 = 0.068 \pm 0.004 \text{ p.p.m.} \frac{\text{Gd}}{\text{Th}} (4)$$

As was discussed in Section IV A, the use of yttrium as both the carrier for the separation procedure and the matrix material for the spectrographic analysis incorporates the additional feature that any errors that may be made in the separation procedure are automatically compensated. Therefore, although with good technique the method yields quantitative recovery of rare earths, the use of sloppy technique will not invalidate the results. Consequently, technicians can be employed to perform this analysis.

6. Purity and recovery data

The data presented in Section IV B 4 demonstrate the ability of this procedure to quantitatively separate yttrium from thorium. During the developmental stages, it was assumed that all of the rare earths would behave similarly to yttrium. To prove this, a recovery experiment was performed.

Four hundred grams, as metal, of thorium nitrate tetrahydrate were dissolved to form a homogeneous solution, which was divided into four equal aliquots. Similarly, 80.0 mg of pure yttrium oxide were dissolved to form a homogenous solution, following which each of its four equal aliquots were added to the four thorium-sample aliquots. Four samples -- A, B, C, D, -of identical composition were thus prepared. To these samples were added volumes, in the ratio 0:1:2:4 respectively, of a synthetic rare-earth "impurity" solution containing known amounts of samarium, gadolinium, terbium, dysprosium, and erbium. After separation and purification according to the recommended analytical procedure, the residues were analyzed spectrographically. Since no test impurities were added to sample A, the values reported for it represent the rare-earth impurity content of the thorium and yttrium used. Following subtraction of this "blank" from the values for samples B, C, and D, the resultant values should be in the ratio of 1:2:4, corresponding to the ratio of the volumes of the homogenous test solution which were added.

The results of the spectrographic analyses of the four separated rareearth residues are presented in Table 3. To conclusively prove the absence of fractionation, the ratios of the values for samples C and B (C/B) and samples D and C (D/C) should equal 2:0, and the ratio of the values for samples D and B (D/B) should equal 4:0, within the limits of normal spectrographic error. Since normal spectrographic error for a single determination is \pm 5% of the amount present at a 95% confidence level, and since each ratio is composed of two such values, the experimental ratios should fall within \pm 10% of the actual ratios added. Inspection of the results presented in Table 3 indicates that only for dysprosium does this occur. The failure of the remainder of the rare earths tested to satisfy this criterion may be due to either of two causes: (1) the occurrence of fractionation in the column, and (2) errors in the spectroanalytical procedure. It is felt that the erratic results were due to the latter cause.

The following arguments are presented to support this contention. Assuming for the moment that the spectroanalytical values are correct, consider the data shown in Table 3. The ratios C/B and D/B for samarium are too low, indicating losses of samarium for the higher concentration standards. However, the ratio D/C is too high, indicating greater loss from sample C than from sample D. This is inconsistent with fractionation behavior in ion exchange columns, since the percentage loss should be progressively greater as the concentration is increased. Consequently, fractionation is not indicated because the deviations are random.

Table	3
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Recovery H	Experiment	Results
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Test Element	Test Run	Concen- tration added	Spectro- graphic Analysis	Average Minus A	Couple	Ratio	Per- missable Range
Sm	A	0.00	∠0.05	·	a / D		2.0.0.0
	В	0,30	0.16	0.17	C/B	1.3	1.0-2.2
	С	0.60	0.21	0.22	D/C	2.6	1.8-2.2
	D	1.20	0.57 0.58	0.575	D/B	3.4	3.6-4.4
Gd	A	0.00	< 0.02				
	В	0.10	0.070	0.073	C/B	1.9	1.8-2.2
	С	0.20	0.138	0.138	D/C	1.6	1.8-2.2
	D	0.40	0.22 0.23	0.225	D/B	3.1	3.6-4.4
 ТЪ	A	0.00	< 0.05				
	B	0.30	0.32	0.31	C/B	1.6	1.8-2.2
	C	0.60	0.46	0.48	D/C	2.4	1.8.2.2
	ם	1.20	1.12 1.18	1.15	D/B	3.7	3.6-4.4
Dy	A	0.00	0.01				
	В	0.30	0.20	0.18	C/B	2.0	1.8-2.2
	С	0.60	0.36	0.36	D/C	1.9	1.8-2.2
	D	1.20	0.50 0.68 0.70	0.68	D/B	3.8	3.6-4.4

Table 3 (continued)

Recovery	Experiment	Results
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Te s t Eleme n t	Test Run	Concen- tration added	Spectro- graphic Analysis	Average Minus A	Couple	Ratio	Per- missable Range
Но	A B C D	0.00 0.00 0.00 0.00	<0.02 <0.02 <0.02 <0.02 <0.02				
Er	A B C D	0.00 0.30 0.60 1.20	<0.005 0.34 0.34 0.58 0.60 1.12	0.34 0.59 1.10	C/B D/C D/B	1.7 1.9 3.2	1.8-2.2 1.8-2.2 3.6-4.4

For gadolinium, the ratio C/B falls within the permissable range, but the ratios D/C and D/B do not. Since only the D value is common to the errant ratios, this value is spurious and is too low. Consequently, it must be concluded that, if fractionation occurred, it occurred only for sample D.

For terbium, only the ratio D/B falls within the permissable range. Therefore, C--the value common to the errant ratios--is spurious and is too high. Fractionation in this case is indicated in samples B and D, but not in C.

Fractionation is not indicated for dysprosium since all ratios fall well within the permissable range. No conclusions can be drawn from the holmium data since no holmium was added to any of the samples, and its concentration in all samples was below the determinable range.

Since, for erbium, only the ratio D/C falls within the permissable limits, the value for sample B which is common to the deviant errors must be spurious, and is too high, indicating fractionation in samples C and D.

Correlation of the above fractionation behaviors indicated by the data yields the following conclusions:

Sample A: no fractionation since no test impurities were present

Sample B: fractionation only for terbium

Sample C: fractionation only for samarium and erbium

Sample D: fractionation for samarium, gadolinium, terbium, and erbium

Such random behaviour is inconsistent with the reproducible and predictable behavior of ions in ion-exchange columns. The random nature of the results indicates, instead, errors due to some insufficiently controlled variable or variables in the spectroanalytical procedure.

Additional arguments from ion-exchange theory may be cited to show the improbability of fractionation occurring in this system. First, as discussed in Section IV B 4, the activity-difference mechanism requires very long columns and low flowrates for significant separations since the relative affinity differences between adjacent rare earths are very small. The short column used in this work provides only a small fraction of the bed length required for separations in such systems.

Secondly, because of its preponderance among the rare earths in this system, the yttrium band is so wide that it overlaps any small rare-earth bands which may form.

The third and most conclusive argument concerns the relation between the band width of each element on the column after separation and the number of theoretical plates required for separation. The concept of theoretical plates in ion-exchange work is derived by analogy of the ion-exchange separation mechanism to the mechanism of separation by means of boiling point differences in fractionation towers. The smaller the boiling point differences between two liquids in such towers, the greater is the number of condensation plates required to affect a given degree of separation. Similarly in ion-exchange columns, the smaller the activity difference between two elements, the greater will be the number of thin resin laminae ("plates") required for separation. Whenever the amount of two elements on a column is so small that each occupy less than the thickness of a theoretical "plate", no separation of the elements can ever be achieved regardless of the column length used. This is exactly the situation occurring with the trace rare earths in the large diameter column used for this work. Plate thickness is independent of plate diameter, but the capacity of the plate is directly proportional to the square of its diameter. Whenever it is desired to separate elements present in microgram quantities, capillary bore columns must be used so that the band width of the elements on the column will be greater than the thickness of the theoretical plate. Since this was not the case in the column used, fractionation among the rare-earth impurities in this system is theoretically impossible.

The recovery experiment here reported was designed to indicate whether all rare earths are collected in the same effluent-volume-interval as is yttrium. The above discussions indicate that this is probably the case, in spite of the results of the recovery experiment. However, even if any fractionation among the rare earths should occur on the bed, this effect is easily overcome by increasing the effluent-volume-interval collected to include those rare earths which break through before and after yttrium. Such an increase would result in a reduced degree of separation of some common elements from the rare earths, but if necessary these elements could be subsequently separated from the rare earths by standard chemical procedures. The separation of the rare earths from thorium, however, would still be complete since it was demonstrated that even after a 200 per cent excess of effluent was collected, thorium still could not be detected in the effluent. Consequently, it is certain that this procedure can accomplish the mutual complete separation of rare earths and thorium.

To test the efficiency of the method for separating common elements from rare earths, 100 mg amounts of each of the common elements studied in Section IV B 4 were added to a normal thorium-rare-earth mixture. After processing the sample according to the recommended analytical procedure, a spectrographic qualitative analysis was performed on the rare-earth residue. The results are presented in Table 4. From these results the residue is estimated to be at least 99.90% pure rare earths, and probably 99.99% pure. The ability of the method to yeild a pure rare-earth residue suitable for spectrographic analysis is thus demonstrated.

Table 4

Test Impurity	Concentration Present (%)	Test Impurity	Concentration Present (%)
Al	0.005-0.015	Fe	0,005-0,05
Bi	∠0 <u>,</u> 002	Mg	0,001-0,005
Ca	0.005-0.025	Min	0.005-0.05
Cd	<0.005	Ni	0.001-0.01
Co	<0.00 5	Pb	0.001-0.01
Cr	0.001-0.005	Si	0.001-0.005
Cu	0.001-0.005	Zn	< 0.01

Purity of the Separated Rare-Earth Residue

C. Separation of Rare Earths from Uranium and Zirconium

The separation of rare earths from thorium was first attempted by the method to be developed in this section. Although this method failed to yield a sufficiently complete separation of rare earths from thorium, it was found to be applicable to the mutual complete separation of trace amounts of rare earths from uranium and zirconium. It is for this reason that a method for the separation of rare earths from uranium and zirconium has been included in a report concerning the determination of rare earths in thorium. For the sake of completeness, data concerning the work done on thorium will be included also.

It must be pointed out--indeed, stressed--that only the separation of rare earths from uranium and zirconium has been studied. Concerning rare earths in thorium, a complete method for their determination is presented. No such procedure is presented here for rare earths in uranium and zirconium. The sole purpose of the following discussion is to indicate the feasibility of such a method. The separation step, which is the heart of the procedure, has been developed.

To provide guidance for the possible future development of a method for the determination of trace rare earths in uranium and zirconium, a proposed procedure will be presented in the following section for the purification of the column-separated rare earths. Except that the mode of separation employed is based on a different ion-exchange principle, the proposed method for the determination of trace rare earths in uranium and zirconium is identical in its theory with that previously described for the determination of trace rare earths in thorium.

1. Separation mechanism in the resin bed

The separation of rare earths from thorium discussed previously utilizes the ability of a cation exchanger to differentiate between cations possessing different degrees of exchangeability -- ion exchange chromatography. The principle underlying the separation of rare earths from thorium, uranium, and zirconium discussed here is the ability of an ion exchanger to differentiate between exchangeable ions and non-exchangeable ions -- the ion-exchange method. To achieve a separation of rare earths from thorium, uranium, or zirconium in this latter manner, it is necessary to find a complexing agent which will convert the three matrices to the neutral or anionic state, while leaving the rare earths in cationic form. Sulfate ion was found to be the only complexing agent capable of achieving this. Formation constants for the sulfate complexes of thorium (33), uranium (34), zirconium (35), and the rare earths (36) are summarized in Table 5. Spedding and Jaffe (36) found no evidence of the formation of anionic sulfate complexes of the rare earths in concentration range investigated $\sum <0.1 \text{ N RE}_2(SO_4)_3$. Since the rare earth concentrations in this work are never greater than 0.001 molar, no rareearth loss due to anionic complex formation need be feared.

Table	5
TUNTO	- 2

$Th^{+l_{4}} + HSO_{l_{4}}^{} ThSO_{l_{4}}^{+2} + H^{+}$ $Th^{+l_{4}} + 2HSO_{l_{4}}^{} Th(SO_{l_{4}})_{2} + 2H^{+}$	<u>Kf</u> 157 2850
$UO_2^{+2} + SO_1^{=} UO_2 SO_1$	56
$UO_2^{+2} + 2SO_4^{-1} - UO_2(SO_4)_2^{-1}$	450
$UO_2^{+2} = 3SO_{11}^{-1} = UO_2(SO_{11})_3^{-1}$	2500
$2r^{+1_4} + HSO_{1_4}^{} 2rSO_{1_4}^{+2} + H^{+}$	590
$2r^{+1_4} + 2HSO_{1_4}^{} 2r(SO_2)_2 + 2H^+$	31300
$Zr^{+l_4} + 3HSO_{l_4}^{-} Zr(SO_{l_4})_3 = + 3H^+$	31300
$RE^{+3} + SO_{\mu} =RESO_{\mu}^{+}$	$(3.0 - 3.8) \times 10^3$
(Neutral + Anionic) Th U Zr	
(Cationic) 168 1340 5150	

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Formation Constants for Sulfate Complexes of Th, U, Zr, R. E.

Since the matrix element is non-exchangeable when in the form of neutral or anionic complexes, an indication of the relative ease of elution of the three matrices may be provided by calculation, at equilibrium in $0.75 \text{ M} (\text{NH}_{1})_2 \text{SO}_4$ solution (pH = 3), of the ratio of the concentration of each element present in the neutral plus anionic form to the concentration present in cationic form. The values derived from such calculations and presented in Table 5 indicate that the ease of elution decreases in the order zirconium, uranium, and thorium. It must be emphasized here that no greater significance can be attached to these values than what is deduced above, since the conditions under which they were derived are decidedly not the conditions existing in the resin bed.

The sample solution consists of five grams, as metal, of matrix element dissolved in 100 ml of 0.75 M $(NH_{1})_{2}SO_{1}$ solution, pH = 3. Following sorption, elution ensues using 0.75 M $(NH_{1})_{2}SO_{1}$ (pH = 3) elutriant. The pH of the solution phase must be high enough to reduce the bisulfate ion concentration to a small value, yet low enough to prevent the precipitation of the matrix elements as hydroxides. A pH of 3.5 \pm 0.5 was found to be satisfactory.

In the following discussion concerning the behaviour of complex ions on a cation resin bed, thorium is used as a concrete example. However, the description applies equally well to the behavior of uranium and zirconium under the same conditions. Before sorption of the 100 ml sample solution onto the column, the relative concentrations of thorium existing as $Th(SO_{1})_{2}$, $ThSO_{1}^{+2}$ and Th^{+4} are 168 : 1 : 0.00067, as given by the formation constants cited in Table 5. Following sorption, the sample solution passes through the column in a band whose volume is 100 ml. Since the solution phase volume present in the resin bed is 225 ml, the band length is 9/20 of the column length. As the sample first enters the column, the resin bed adsorbs the Th^{+4} and $ThSO_{1}^{+2}$ cations while the neutral $Th(SO_{1})_{2}$ ions pass along with the flowrate of the solution. However, the leading edge of the sample band, having had its cationic content removed, is now no longer in equilibrium. In an attempt to reestablish the equilibrium, $Th(SO_1)_2$ complexes decompose to form $ThSO_1^{+2}$. As soon as these cationic complexes form, however, the resin absorbs them. The process therefore repeats itself continously until the leading edge breaks through the bottom of the column. The prevailing reaction occurring as the sample band passes through the resin bed is, therefore, the deposition and distribution of a fraction of the thorium throughout the resin bed.

The conditions prevailing at the trailing edge of the sample band are exactly the reverse. Since $(NH_{1})_2SO_{1}$ elutriant is added immediately after the last of the sample solution enters the bed, a given resin lamina after passage of the trailing edge is immersed in complexing agent containing no thorium. The Th⁺¹⁴ and ThSO₁⁴² cations previously formed in the sample band and retained by the column now tend to reestablish equilibrium by the formation of Th(SO₁)₂ complexes. When formed, these pass down the column with the flowrate of the solution. The prevailing reaction following passage of the sample band is, therefore, the removal of the absorbed thorium by

the ammonium sulfate elutriant. However, the efficiency of removal of thorium from a given lamina by successive equal volumes of elutriant is not constant. Rather, it decreases as the concentration of thorium in the lamina decreases since, although the percentage removal of the amount present is constant in successive equal elutriant volumes, the absolute amount present continuously decreases, thereby decreasing the absolute amount removed.

Another factor of importance in this process is that the resin must be made to release its divalent and tetravalent thorium ions by the inefficient eluting action of the monovalent ammonium ions. This effect tends to further decrease the efficiency of removal of thorium from the resin by the elutriant. It is the combination of these two effects which causes the "tailing" observed in Figure 9, Section IV C μ .

Still, if sufficient elutriant were allowed to pass, the thorium could be quantitatively removed from the resin. But unfortunately, for a given column, there is a limiting volume of elutriant which may be used to accomplish the "clean-up" of the resin bed. This limit is set by the breakthrough volume of the rare earths. As seen in Table 5, the rare earths are present in sulfate solutions as RESO, complexes. These monopositive complexes are also retained by the resin bed as the sample band passes through the column, but being monopositive, they are simultaneously and continuously eluted down the column by the 1.5 molar ammonium ion concentration associated with the $0.75 \text{ M} (\text{NH}_1)_2 \text{SO}_1$ elutriant. Since the receiver must be changed to collect the rare-earth fraction at the rareearth breakthrough volume, this is the maximum volume of elutriant which can be used to remove absorbed thorium from the resin. The success of the separation depends on whether this volume is sufficient to quantitatively remove the thorium from the column. If not, some thorium will pass into the rare-earth fraction. Unfortunately, as will be seen in Section IV C 4. the latter is the case for thorium. However, successful separations can be made from uranium and zirconium.

2. Column design and operation

Although lacking sufficient efficiency for the mutual complete separation of rare earths from thorium, the two-section column shown in Figure 10 proved capable for separating rare earths from uranium and zirconium. To protect the resin bed from the convection currents generated by the addition of solutions to the reservoir, a circle of orlon filter cloth of column diameter was placed over the packed bed and held in place by a slightly oversize neoprene O-rings. The capillary stopcocks and the construction of the bed support plugs are identical with those shown in Figure 4 for the chromatographic column. No retaining plug is placed between the sections since all elution is performed downflow. To increase the flowrates (cf. Section IV B l), a negative pressure was applied to the bottom of each section by extending the capillary take-off tubing (identical with Figure 3) 4.1 feet below the bed support plug of the second section.



Elution Behavior of Thorium, Uranium, and Zirconium





Column for the Separation of Rare Earths from Uranium and Zirconium The operation of the column for single section separations will be described in Section IV C 5. The following procedure presents the two-section operation:

- (1) With the column in the 0.75 M elutriant cycle, the sample solution is added to the empty reservoir.
- (2) Sorption is commenced by adjusting stopcock 1 to conduct the effluent through the side arm to a one-liter volumetric flask. While sorption proceeds, the sample container is washed with 10 ml of 0.75 M elutriant from a wash bottle.
- (3) As the last lamina of sample solution enters the resin bed, the samplecontainer wash is added, and then the reservoir is thoroughly washed with 0.75 M elutriant. Improper washing of the reservoir will seriously reduce the separation efficiency, as discussed in Section IV B 1.
- (4) As the last laminus of wash solution enters the bed, 1600 ml of 0.75 M elutriant is added to the reservoir.
- (5) Upon collection of 100 ml of effluent from Section One, stopcock l is adjusted to impede the flow through the side arm and conduct the flow through Section Two. The effluent from Section Two is collected in a one-liter volumetric flask.
- (6) When approximately 10 ± 5 ml of 0.75 M elutriant remain in the reservoir, 2000 ml of 2.0 M elutriant is added.
- (7) Upon collection of the first 100 ml of effluent from Section Two, the receiver is replaced by another one-liter volumetric flask. The rare earths are quantitatively collected in this second 100-ml fraction.
- (8) To convert the column to the 0.75 M elutriant cycle in preparation for a subsequent sample, the excess 2.0 M elutriant is siphoned from the reservoir, after which 2500 ml of 0.75 M elutriant is passed through both sections.

It is most important that air never be permitted to enter the resin bed. If this should occur, the bed must be backwashed into the reservoir and repacked. No other procedure yields satisfactorily packed columns.

To facilitate the packing of the second section, a large funnel is attached to its neck with Tygon tubing. A spirit level is used to adjust both sections to be perfectly vertical. This is required to obtain a uniform density of packing of the resin particles (cf. Section IV B 1). Upon filling the barrels of both sections with 2.0 M $(NH_{1})_{2}SO_{1}$ solution, a slurry of resin equilibrated overnight in the same solution is added to the reservoirs. Since fine-mesh resin settles very slowly, the process may be hastened by opening the stopcock of each section sufficiently to yield a flowrate of about 15 ml per minute. The 2.0 M elutriant-resin slurry is periodically added to the reservoirs until the desired bed lengths (Table 6 of Section IV C 3) are obtained. Following passage of two liters of $0.75 \text{ M} (\text{NH}_{\text{L}})_2 \text{SO}_{\text{L}}$ solution through each section, the resin beds are permitted to expand and settle overnight. Upon removal of the excess resin, the sections may be mounted, again perfectly vertical, as shown in Figure 10.

The enclosed second section has now been equilibrated for 0.75 M elutriant. As 2.0 M elutriant passes through for the rare-earth elution, the resin bed will contract creating a large free-volume (Section IV B 1). Since the separation has already occurred, however, this free-volume does not affect the separation efficiency; it affects only the rare-earth elution efficiency. This effect is not serious. Upon conversion to the 0.75 M elutriant cycle, the bed will re-expand to its original length, thereby re-minimizing the free-volume for the subsequent separation. However, care must be taken never to pass solutions of lower ionic strength through this section, lest the additional expansion of the resin cause the section to explode (cf. Section IV B 1).

3. Choice of column parameters

Since, as just stated, the mutual separation of rare earths and matrix depends on whether the matrix can be completely eluted before rare-earth breakthrough, conditions must be found which will maximize the complex-formation mechanism of separation while minimizing the activity-difference and chargedifference mechanisms (Section III A 5). Studies were made to find the optimum values for elutriant concentrations, flow rate, column length, column design, pH, equilibration time, and sample solution volume. The results of these studies are summarized in Table 6.

Parameter .	Optimum Value
Elutriant concentration	0.75 molar
Flow rate	0.7 ml/cm ² /minute (section #1) 0.5 ml/cm ² /minute (section #2)
pH	3.5 ± 0.5
Equilibration time	One hour
Sample solution volume	100 ml
Column size	5.0 cm I.D. x 35 cm long (section #1) 5.0 cm I.D. x 30 cm long (section #2)
Column design	Two sections

Table 6 Optimum Values of Column Parameters

Resin particle size and degree of cross-linkage were not studied. Before these could be performed, preliminary experiments on the chromatographic rareearth-thorium separation indicated the superiority of that method. The particle size used, 100-200 mesh, is probably optimum since it is necessary to displace the absorbed matrix cations before they can be complexed by the elutriant. However, the degree of cross-linkage used (12% DVB) is probably not optimum, since high cross-linkage enhances the relative affinity differences between monovalent ions (RESO₁⁺) and divalent ions (TbSO₁⁺²), thereby making the elutriant (NH₄⁺) more efficient for the elution of rare earths than thorium.

The change of the column design from the conventional single-section type to the multiple-section type produced the largest single increase in the degree of separation of the rare earths from the matrix elements. As described in Section IV C 2, the predominant reaction as the sample band passes through the exchanger is the deposition of cationic thorium sulfate complexes throughout the resin bed. A short resin bed is therefore desirable since less cationic thorium will be retained by the exchanger. However, to permit the passage of the large volumes of elutriant required to remove these, a long resin bed is desirable since it provides a larger breakthrough volume for the rare earths. The use of a split column (Figure 10) provides a degree of satisfaction of both. The sample band may be collected from the first section until the rare-earth breakthrough volume is reached. The flow may then be directed into the second section, which the sample band has not contaminated, providing the longer bed length required for the larger rare-earth breakthrough volume. Theoretically, the more sections into which a given exchanger is split, the greater will be its efficiency for separations of this type. However, the increased free volume of multiple-section columns establishes a point of diminishing returns. In addition, the separation efficiency of each succeeding section decreases rapidly since successively smaller quantities of thorium pass through each section and successively smaller quantities are therefore separated. To illustrate, for the threesection column studied, the observed separation efficiences were 98.0%, 1.48%, and 0.34%. However, the efficiency of multiple section columns over single section columns of the same total bed volume is shown by the 99.8% separation of the three-section column compared to the 86.7% separation of the equal-volume singlesection type.

4. Elution behavior of rare earths and matrix elements

The elution behavior of yttrium was studied by radiotracer technique. Thorium, uranium, and zirconium were studied by gravimetric procedure. In all cases, the experiments were run under actual analytical conditions. The yttrium study was performed using thorium as the matrix constituent. For this study, a 200,000 cpm charge of Y^{90} was added to the thorium sample whose composition is described in Section IV C 4. The behavior of yttrium, as indicated in Tables 7 and 8, was determined by two experiments. The breakthrough volumes for the two sections (Table 7) were determined by following the operational procedure of Section IV C 1, except that fifteen successive 100-ml fractions were taken from each section and 0.75 M elutriant only was used. The complete collection volume for two-section operation (Table 8) was determined using the same operational procedure, except that the 1000-ml rare-earth fraction was divided into five 200-ml fractions. Examination of the data indicates that the breakthrough volumes for the two sections are 1000 ml and 1100 ml respectively, and that complete collection is obtained within 700 ml following second section breakthrough. The transfer volumes cited in the two-section operational procedure of Section IV C 1 were specified on the basis of these results. Although 1100 ml could have been collected in the matrix fraction from section two and the rare earths could have been collected in a subsequent 700-ml fraction, 100-ml transfer volumes were chosen both to provide a margin of safety, and to permit the convenience 'afforded by the use of one-liter volumetric flasks as receivers.

Having determined the maximum volumes collectible from each section, samples containing only the matrix constituent were processed, the effluent from each section being collected in 200-ml fractions. The matrix content of each fraction was determined gravimetrically by precipitation with ammonium hydroxide. The data so-obtained are presented in Tables 9, 10, and 11 for thorium, uranium, and zirconium respectively. The separation efficiencies tabulated refer to the percentage of the total matrix which was separated in each section. In each case fractions 1 and 6 consist of the solution phase volume (225 ml) of the respective section. Since this volume must be displaced before the sample band can break through the bed, these fractions can possess no matrix content. Elution curves depicting the behavior of thorium, uranium, and zirconium are presented in Figure 9.

5. Separation procedure

The sample solution to be added to the column consists of five grams, as metal, of matrix element dissolved in 100 ml of $0.75 \text{ M} (\text{NH}_4)_2 \text{SO}_4$ solution, pH = 3. The sample solutions used in the experimental work were prepared as follows:

a. Thorium. To 12.0 grams of thorium nitrate tetrahydrate dissolved in 25 ml of water is added 5 ml of 0.001 M hydrochloric acid solution containing 20.0 ± 1.0 mg of pure yttrium oxide. The resultant solution is mixed, with stirring, into a 60 ml solution containing 15.7 grams of ammonium sulfate. The sequence of mixing is important, since thorium sulfate will precipitate in the absence of excess complexing agent. Upon dilution to volume in a 100-ml volumetric flask, the pH will be 3.5 ± 0.5 .

b. Uranium. Five grams of uranium metal or its oxide equivalent is dissolved in a ten per cent over stoichiometric quantity of nitric acid followed, after addition of 20.0 ± 1.0 mg of pure yttrium oxide, by evaporation of the solution almost to dryness to remove excess acid.

A pH of 3.0 ± 0.5 results when this sample, dissolved in 30 ml of water, is added to 60 ml of solution containing 16.9 grams of ammonium sulfate, and the mixture subsequently diluted to 100 ml in a volumetric flash.

Table	7
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Second Section		
) cpm		
• ===		
40 60		
90 .40		

Determination of Yttrium Breakthrough Volumes

Table 8

Determination of Yttrium in the Complete Collection Volume

Fraction	Volume (ml)	Y ⁹⁰ cpm
1 2 3 4 5	200 200 200 200 200	50 240 120,000 370

Table	9
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		First Castion	· · ·
Fraction	Volume (ml)	<u>First Section</u> Weight (mg)	Wt. Vol.
1 2 3 4 5	200 200 200 200 200	5117.7 431.3 73.8 44.2	25.59 2.16 0.37 0.22
		Second Section	
Fraction	Volume (ml)	Weight (mg)	Wt. Vol.
6 7 8 9 10	200 200 200 200 200	19.5 29.7 14.8 9.5	0.10 0.15 0.07 0.05
		Rare-Earth Fraction	
Fraction	Volume (ml)	Weight (mg)	Wt. Vol.
11 12 13 14 :	500 500 500 500	22.3 9.7 4.3 1.2	0.04 0.02 0.01 0.006
		Separation Efficiency First Section - 98.08% Second Section - 1.27% Unseparated - 0.65%	

Determination of Thorium Elution Behavior

Table 10 .

First Section Wt.				
Fraction	Volume (ml)	Weight (mg)	Vol	
1 2 3 4 5	200 200 200 200 200	5123.7 568.0 128.2 50.4	25.62 2.84 0.64 0.25	
Fraction	Secon Volume (ml)	d <u>Section</u> Weight (mg)	Wt. Vol.	
6 7 8 9 10	200 200 200 200 200	5.1 5.6 3.0 0.6	0.026 0.028 0.015 0.003	
	Rare-Ea	rth Fraction		
Fraction	Volume (ml)	Weight (mg)	Wt. Vol.	
11 12 13 14	500 500 500 500	0.4	0.001	
<u>Separation Efficiency</u> First Section - 99.75% Second Section - 0.24% Unseparated - 0.007%				

Determination of Uranium Elution Behavior

Table	11
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Fraction	<u>First Sectio</u> Volume (ml)	n Weight (mg)	Wt. Vol.
1 2 3 4 5 6 7 8 9 10	100 100 100 100 100 100 100 100 100 100	4296.2 2084.1 348.0 5.7	42.96 20.84 3.48 0.06
	Done Forth Fre	ation	
Fraction	Volume (ml)	Weight (mg)	Wt. Vol.
11 12 13 14	500 500 500 500		
	Separation Ef First Section Unseparated	ficiency - 100.00% - 0.00%	

Determination of Zirconium Elution Behavior

c. Zirconium. To 17.7 grams of zirconyl chloride octahydrate in 35 ml of solution is added 5 ml of 0.001 M hydrochloric acid solution containing 20.0 \pm 1.0 mg of pure yttrium oxide. The resultant solution is mixed, with stirring, into a 150 ml solution containing 38.0 grams of ammonium sulfate. Upon dilution to volume in a 200-ml volumetric flask, the pH will be 2.0 \pm 0.5. Because of the limited solubility of zirconium sulfate, the sample solution volume must be 200 ml.

With the column in the 0.75 M (NH₁)₂SO₁ (pH = 3) cycle, the sample solution is added to the column reservoir, whereupon sorption is commenced. While sorption proceeds, the sample container is washed with 10 ml of 0.75 M (NH₁)₂SO₁ (pH = 3) elutriant from a washbottle. As the last lamina of sample solution passes into the resin bed, the 10 ml sample-container wash is added, following which the column reservoir is thoroughly washed with 0.75 molar elutriant. As the last lamina of wash solution passes into the bed, 600 ml of 0.75 M elutriant is added to the reservoir. When only 10 \pm 5 ml of 0.75 molar elutriant remain in the reservoir, 1500 ml of 2.0 M (NH₁)₂SO₁ elutriant is added.

Upon collection of the first 1000 ml of effluent, the one-liter-volumetricflask receiver is replaced by another. The rare earths are quantitatively collected in the second 1000-ml fraction. To return the column to the 0.75 molar cycle for separation of a subsequent sample, the excess 2.0 molar elutriant is siphoned from the reservoir with a water aspirator and collection bottle, after which two liters of 0.75 molar elutriant are passed through the column.

The 0.75 molar elutriant consists of 99 grams of ammonium sulfate per liter of solution, to which is added 4.5 ml of 1.0 molar hydrochloric acid to adjust the pH to 3.5 ± 0.5 . The 2.0 molar elutriant consists of 264 grams of ammonium sulfate per liter of solution. To this is added 12.0 ml of 1.0 molar hydrochloric acid to keep the ammonium ion - hydronium ion ratio constant between the two elutriants. If this addition is not made, the equilibration of the bed will be disturbed.

The pH of both sample solution and elutriant must be high enough to reduce the bisulfate ion concentration to a small value, yet low enough to prevent the precipitation of the matrix elements as hydroxides. A pH of 3.5 ± 0.5 was found to be satisfactory. In those cases where practical problems prevent the attainment of a pH of 3 in the sample solution, the effect of the lower pH on the sulfate concentration is compensated by the high capacity of the resin bed. Shortly after entering the bed, exchange between the excess hydronium ions and the equilibrated resin quickly raises the pH to 3, which is the pH of the equilibrated ammonium bed.

The values specified above for the rare-earth breakthrough and complete collection volumes pertain only to the particular column used in this work. For any column constructed to duplicate this separation, these values must be newly determined as described in Section IV C μ .

To separate the rare earths from the 2.0 molar ammonium sulfate effluent, precipitation was effected with an equal volume of concentrated ammonium hydroxide. Following digestion and settling overnight, much of the supernatant liquid could be removed before filtration by slowly and carefully siphoning it out with a water aspirator and collection bottle. To check for losses by this procedure, the supernatant liquid so-removed from one experiment was treated with aqua regia to destroy the ammonium salts. The resultant sulfuric acid was fumed to dryness and the residue examined spectrographically. No yttrium could be detected, indicating that the loss was less than 0.001 milligram.

The preceding discussion described the separation procedure used in this work. The remainder of this section is devoted to the presentation of notes and suggestions for the benefit of anyone desiring to build an analytical method around this separation.

Unlike the chromatographic separation of rare earths from thorium, this procedure does not separate the common element impurities present in the sample from the rare earths. If it is intended to use the emission spectrometric method for the determination of the individual rare-earth content of the yttrium carrier, the common element impurities must be separated from the rare earths by subsequent chemical treatments. The following proposed procedure has been adapted from a method by Hettel and Fassel (37) for the purification of similarly-obtained rare-earths residues.

Treatment of the rare-earth fraction with excess ammonium bifluoride will quantitatively precipitate the rare earths, simultaneously separating them from the many elements whose fluorides either are soluble or are solubilized by fluoride complexing. Following filtration, the ignited fluorides are dissolved by fuming 25 ml of concentrated sulfuric acid to dryness, followed by dissolution in dilute hydrochloric acid. Subsequent treatment with hydroxylamine hydrochloride, 1,10 o-phenanthroline, and ammonia gas to pH = 9 (Section IV B 5) will remove (1) elements soluble at pH = 9, (2) elements complexed by ammonia, and (3) elements reduced and complexed by the above-specified reagents. Of the elements interfering with the spectrographic procedure, only rhodium, lead, and thallium are not separated (37).

A two-section column was used in this work (Figure 9). As was shown in Section IV C 4, mutual complete separation of rare earths and zirconium was obtained using only the first section, whereas 0.25% of the uranium sample remained unseparated from the rare earths when only the first section was used. Since a fluoride separation of the rare earths has already been proposed in the purification procedure, separation of the residual uranium will be accomplished here. Consequently, the use of only the first section of the column is suggested in any method subsequently developed for the determination of fractional ppm amounts of rare earths in uranium and zirconium.

6. Discussion of results

Mutual complete separation of rare earths from zirconium is observed to be easily obtained using the first section alone. Although only 99.993% separation of uranium is effected using, as transfer criterion, 1000 ml from section two, mutual complete separation could have been attained had the full 1100 ml available been collected from this section. For thorium, however, only 99.35% separation was achieved, indicating that 0.65% of the original sample was collected in the rare-earth fraction. This corresponds to the presence of 37.5 mg of thoria in the 20-mg rare-earth residue.

Since thorium is a line interference in the spectroanalytical procedure, no more than 0.1 mg of thoria can be tolerated. Although many methods are available for the subsequent separation of this residual thorium from the rare earths (38), the protracted time and effort required would negate two of the advantages of this method -- fast separation and easy operation. Consequently, the method is unsatisfactory for the mutual complete separation of thorium and the rare earths.

As a concentration procedure, however, the method is quite satisfactory since a 50-fold concentration of rare earths in thorium can be accomplished, using only the first section of the column, with little effort in $l\frac{1}{2}$ hours without loss of rare earths.

D. Spectrographic Determination of Rare Earths in Yttrium

The spectrographic determination of the samarium, gadolinum, terbium, dysprosium, holmium, and erbium contents of the yttrium oxide carrier is performed by a method originally developed for the determination of these rare earths in yttrium purified by F. H. Spedding and associates at the Ames Laboratory. The over-all procedure is patterned after methods previously reported (39-42) for the determination of rare-earth impurities in other purified rare earths. The method is based on the direct current carbon arc excitation of yttrium oxidegraphite mixtures. Selected yttrium lines are used as internal standards. The line pairs employed for the determinations are summarized in Table 12. Pertinent experimental details are summarized in Table 13.

Photographic processing, photometry, and intensity ratio determinations. follow standard practices (43).

Table	12
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Spectroanalytical Line Pairs

Line Pairs	Concentration Range
Tb 3218.43 Y 3182.42	0.04 to 2.0% of Tb_40_7 in Y_20_3
Tb 4318.85 Y 4315.46	0.1 to 2.0% of Tb_10_7 in Y_20_3
Gd 3350.48 Y 3377.71	0.04 to 2.0% of Gd_2O_3 in Y_2O_3
Gd 4327.10 Y 4291.03	0.1 to 2.0% of Gd_2O_3 in Y_2O_3
Dy 3407.80 Y 3469.43	0.02 to 2.0% of Dy_2O_3 in Y_2O_3
Dy 3407.80 Y 3450.95	0.05 to 2.0% of Dy_2O_3 in Y_2O_3
Ho 3453.14 Y 3469.43	0.02 to 0.2% of Ho_2O_3 in Y_2O_3
Ho 3453.14 Y 3450.95	0.06 to 2.0% of Ho_2O_3 in Y_2O_3
Sm 4334.14 Y 4291.03	0.1 to 2.0% of Sm_2O_3 in Y_2O_3
Er 4007.97 Y 3955.09	0.01 to 2.0% of Er_2O_3 in Y_2O_3
Er 4007.97 Y 3987.50	0.01 to 2.0% of Er_2O_3 in Y_2O_3

Table 13

Operating Details for Analysis of Rare Earths

Composition of sample charge	One-half of the yttrium-rare-earth oxide concentrate, blended with 8 mg. of 200-mesh powdered graphite
Spectrograph	Jarrell-Ash, 3.4-meter stigmatic grating spectrograph
Upper electrode (cathode)	Graphite rod, 1/8-inch diameter, pointed at one end
Lower electrode (anode)	Shallow thin-walled graphite electrode (1/4-inch diameter graphite with 2-mm. deep cavity and wall thickness of 1/2 mm.). Anode is supported on 1/8-inch graphite pedestal (39-42)
Analytical gap	Li nm.
Excitation source	D.c. arc, 250 volts, 17-18 amperes (between clean graphite electrodes in air)
Length of exposure	Sample arced to complete consumption
Emulsion	Spectrum analysis No. 1 (3200-3800 A.). Kodak M (3800-4400 A.).
Wave-length region	3200-4400 A., second order
Filter	No. 7740 Corning
Slit	0.040 mm.
Development	Four minutes at 21 ⁰ C. in Eastman Kodak D-19 with continuous agitation
Densitometry	Applied Research Laboratories Comparator-Densitometer
Emulsion calibration	Two-step sector, preliminary curve method (44)

V. OTHER APPLICATIONS

A. Determination of Other Trace Impurities in Thorium

The procedure described for the determination of traces of rare earths in thorium should be equally applicable for the separation and determination of traces of common elements in thorium. These are present in the first fraction collected from the column which, for the purposes of the present method, is simply discarded.

The procedure, as described herein, should also be applicable to the determination of traces of rare earths in other elements which are tetravalent in strong hydrochloric acid solutions; e.g., uranium(IV) and zirconium.

B. Separations in the Normal Range

Since the ion-exchange procedure is not concentration dependent, it may be used with equal efficiency for the separation of common elements and rare earths from thorium in any range. A relatively long column was used in this work to provide a simultaneous separation of common elements from the rare earths. For simple separation of both common elements and rare earths together from thorium, a column one-tenth as long would have been sufficient, thereby requiring only one-tenth as much time. Consequently, by this method analytical separations of rare earths and common elements from thorium may be effortlessly made by technicians in approximately thirty minutes with far greater accuracy than provided by current conventional procedures.

C. Production of High Purity Thorium

Chromatographic elution of the thorium sample by 4 molar hydrochloric acid completely removes from the thorium all less exchangeable elements, regardless of the concentrations of these elements. This classification includes all nominally monovalent, divalent, and trivalent elements, together with all elements which are complexed by 4 molar chloride ion in anionic, neutral, or lowervalent cationic complexes. Consequently, with the possible exception of the acid insoluble elements whose action under these conditions is unknown, it should be possible to prepare high purity thorium by this simple procedure. The purity attainable will be limited only by such factors as the purity of the water and reagents used, and the degree of acid attack of the vessels.

D. Isolation of Thorium Fission Products

At present, Pb^{212} is separated from thorium by carrier precipitation procedures. This same separation has been accomplished by acid chromatographic elution with the added advantages that the separation is easier, more complete, and the isotope can be obtained carrier-free. Separation of the other fission products of thorium can also be accomplished, and similar separation of the fission products of uranium is feasible by reduction of the sample to uranium(IV) before sorption.

- 1. Fassel and DeKalb, "Spectrographic Analysis of Thorium", To appear in book entitled "Thorium" to be published by American Society of Metals, (1956).
- 2. Gordon and Shaver, United States Atomic Energy Document NYO-3555, (January 1, 1953).
- 3. Gordon, Firsching, and Shaver, Anal. Chem., 28, 1476 (1956).
- 4. Lerner and Petretic, Anal. Chem., 28, 227 (1956).
- 5. Atwell, Pepper, and Stukenbroeker, United States Atomic Energy Document FMPC - 505 (January 15, 1955).
- 6. Kember, Analyst, 77, 78 (1952).
- 7. Williams, Analyst, 77, 297 (1952).
- 8. Center, Henry, and Householder, United States Atomic Energy Document BMI-260, (May 15, 1952).
- 9. Feldman and Ellenburg, Oak Ridge National Laboratory Methods 1 00705 and 9 00650. (March 23, 1955).
- 10. Radhakrishna, Anal. Chim. Acta, 6, 351 (1952).
- 11. Ahrens, "Spectrochemical Analysis", Cambridge, Massachusetts, Addison-Wesley Press, Inc., (1950).
- 12. Samuelson, "Ion Exchange in Analytical Chemistry", New York, John Wiley and Sons, (1953).
- 13. Bauman, Anderson, and Wheaton, Ann. Rev. Phys. Chem., 3, 109 (1953).
- 14. Boyd, Ann. Rev. Phys. Chem., 2, 309 (1951).
- 15. Dimler, Trans. Am. Assoc. Cereal Chemists, 12, 1 (1954).
- 16. Karnofsky, Chem. Eng., 61, 189 (1954).
- 17. Kunin and McGarvey, Ind. Eng. Chem., <u>45</u>, 83 (1953).
- 18. Kunin and McGarvey, Anal. Chem., 26, 104 (1954).
- 19. Kunin and McGarvey, Ind. Eng. Chem., 47, 565 (1955).
- 20. Osborn, Analyst, 78, 220 (1953).
- 21. Pepper, Reichenberg, and Hale, J. Chem. Soc., 1952, 3129-36.

- 66
- 22. Wells, Quart. Revs. (London), 7, 307 (1953).
- 23. Hale and Reichenberg, Discussion, Faraday Soc., 1949, 79.
- 24. Kunin and Myers, J. Phys. & Colloid Chem., <u>51</u>, 1111 (1947).
- 25. Samuelson, Dissertation, Tekn. Högskolan, Stockholm, (1944).
- 26. Djurfeldt and Samuelson, Acta Chem. Scand., 4, 165 (1950).
- 27. Kniseley, Fassel, Tremmel, Gordon, and Hayles, Ames Laboratory of the Atomic Energy Commission, Ames, Iowa. Papper to be submitted for publication to Spectrochimica Acta. Cca 1956 3
- 28. Hietanen, Acta Chem. Scand., 8, 1626 (1954).
- 29. Wiklander, Svensk Kem. Tid., 57, 54 (1945).
- 30. Ketelle and Boyd, J. Am. Chem. Soc., 69, 2800 (1947).
- 31. Tompkins, Khym, and Cohn, J. Am. Chem. Soc., 69, 2771-2 (1947).
- 32. Friedlander and Kennedy, "Introduction to Radiochemistry", New York, John Wiley and Sons, Inc., (1949).
- 33. Zebroski, Alter, and Heumann, J. Am. Chem. Soc., 73, 5646 (1951).
- 34. Ahrland, Acta Chem. Scand., 5, 1151 (1951).
- 35. Connick and McVey, J. Am. Chem. Soc., 71, 3188 (1949).
- 36. Spedding and Jaffe, J. Am. Chem. Soc., 76, 882 (1954).
- 37. Hettel and Fassel, Anal. Chem., 27, 1311 (1955).
- 38. Levine and Grimaldi, Geological Survey, Bulletin No. 1006. (Feb. 1950).
- 39. Fassel, J. Opt. Soc. Amer., 39, 187 (1947).
- 40. Fassel, Cook, Krotz, and Kehres, Spectrochim. Acta, 5, 201 (1952).
- 41. Fassel, Quinney, Krotz, and Lentz, Anal. Chem. 27, 1010 (1955).
- 42. Fassel and Wilhelm, J. Opt. Soc. Amer., 38, 518 (1948).
- 43. Nachtrieb, "Principles and Practices of Spectrochemical Analysis", Chapter 6, New York. McGraw-Hill, (1950).
- 44. Churchill, Ind. Eng. Chem., Anal. Ed., 16, 653 (1944).
- 45. Spedding and Powell, J. Am. Chem. Soc., 76, 2550 (1954).