A STUDY OF THE METHODS OF DETERMINATION OF THE RARE EARTH ELEMENTS IN A SUBSTANCE WITH A HIGH CONCENTRATION OF CALCIUM AND PHOSPHATES AND THE APPLICATION TO HUMAN BONES

by

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TABLE OF CONTENTS

INTRODUCTION

The rare earth elements are found in many different substances but are usually present in low concentrations. They are found in plants, a large number of minerals, and in bones. Recently it has been discovered that these elements are among the by-products of the atomic fission of some of the heavier elements.

The chief difficulties in the determination of the rare earth content of bones and some minerals are due to the very low concentration of these elements and to the high concentration of calcium which has similar chemical properties. The methods used in the past have been repeated precipitation and spectroscopic analysis. In the precipitation method many steps are involved and the process is long and tedious.

A new quantitative method employing ion-exchange techniques with synthetic resins has shown promise along these lines. It is believed that with a combination of the precipitation methods and ion-exchange techniques a better procedure for the determination may be obtained.

LITERATURE REVIEW

Historical Background

In the periodic table the elements with atomic numbers 57-71 inclusive are referred to as the rare earth elements. They are located between barium and hafnium and generally placed in Group III A. The location of the rare earth elements in the periodic table has long been a puzzling problem. The determination of the unusual electronic structure of these elements has helped to explain their position in the table.

The rare earth elements occur widely scattered in minerals and in a wide range of concentrations(56). Since the rare earths are found in minerals it is to be expected that they would be present in plants and animals. This has been shown to be true with the discovery of varying amounts of rare earths in many plants(47) and in bones(10,25,18). Very little is known about the physiological effects of these elements.

The similarity of the elements and their compounds is great and is responsible for the lack of information about the individual elements. All of the elements of the group form the trivalent oxide and the number of electrons in the valence level is three(11). The position which shows a variation in the number of electrons as indicated by the atomic number is the 4f shell(12). Here the number of electrons in this shell

increases from zero for lanthanum to 14 for lutecium. This would lead to the correct number of elements in the group and would account for the similarity in chemical properties since the number and location of the valence electrons remain unchanged and the atomic radii vary only slightly.

The history of the rare earths begins in the latter part of the eighteenth century with the discovery of ytterbia[28]. Since then it has been a slow process of establishing the identity of the fourteen elements. The elements not included in these fourteen but which are included in this discussion are scandium, yttrium, hafnium, and thorium. These elements often occur in small quantities with the other fourteen and have similar properties.

An interesting thing about this group of elements is that in minerals where one element is found several of the elements are always found and often each member of the group is present. The elements are divided into two subgroups, the cerium and yttrium subgroup. Usually in a mineral one of these groups predominates considerably over the other and it is seldom that any one of the elements makes up over 50% of the total concentration of the group.

The rare earths form insoluble oxalates, hydroxides, and fluorides. Various schemes using these facts have been tried to separate the elements as a group. Also the separation of

the individual elements by fractional precipitation has been attempted. It is known[57] that the rare earth elements are among the fission products of uranium and other of the heavier elements. With increased work and interest in atomic fission a need for better means of determination and separation of the rare earths was needed. This led to spectroscopic analysis, measurement of magnetic properties, use of complexing agents, ion-exchange techniques, and other methods.

Properties of the Rare Earths and Their Compounds

In this group of elements the following are included with their atomic weights and numbers[27].

Element	Symbol	Atomic Number	Atomic Weight
Scandium[1]	Sc	21	45.1
Yttrium[1]	Y	39	88.92
Lanthanum	La	57	138.92
Cerium	Ce	58	140.13
Praseodymium	Pr	59	140.92
Neodymium	Nd	60	144.27
Promethium	Pm	61	146.
Samarium	Sm	62	150.43
Europium	Eu	63	152.0
Gadolinium	Gd	64	157.3
Terbium	Tb	65	159.2
Dysprosium	Dy	66	162.46
Holmium	Ho	67	163.5
Erbium	Er	68	167.64
Thulium	Tm	69	169.4
Ytterbium	Yb	70	173.5
Lutecium	Lu	71	175.0
Hafnium[1]	Hf	72	178.6
Thorium[1]	Th	90	232.12

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[1] Sc, Y, Hf, and Th are included with the rare earths due to their similar chemical properties.

Not a great deal is known about the rare earth metals themselves. The most successful method of preparation of the metals has been the electrolysis of the fused chlorides[29]. The metals show the typical metallic lustre and are usually white, grey, or yellow. The metals have strong reducing properties and have a great affinity for oxygen[30].

The rare earth elements are found widely distributed in nature but usually in low concentration. The most abundant element in the group is cerium which is more abundant than such "common" elements as tin, mercury, antimony, bismuth, or tungsten[58]. The even numbered members of the group are more abundant than the odd numbered members. In the usual qualitative scheme of analysis the rare earth elements are precipitated as the hydroxide with aluminum[66].

All of the elements of the group form the trivalent rare earth oxides R_2O_3. While the rare earths are generally considered to be trivalent it is known that both higher and lower valences exist[17]. Quadrivalent compounds of cerium, praseodymium and terbium are known. Also by electrolytic reduction samarium, europium, and ytterbium show a valence of two. When the carbonates, oxalates, sulfates, and hydroxides are ignited at high temperatures the sesquioxides R_2O_3 are formed with most of the elements. The exceptions are cerium and thorium and possibly terbium and praseodymium which form the dioxide RO_2.

The oxides dissolve in the common acids and the only difficulty is encountered in the case of the cerium oxide which must be converted to the trivalent state. This can be done in hydrochloric acid with heat provided the cerium oxide does not make up over 50% of the group[54]. The oxides R_2O_3 are strong bases showing a decrease in basic properties with an increase in atomic weight[59]. The basic strength of some of the more basic elements is about the same as the alkaline earths. Upon ignition of the oxalates or hydroxides the oxides have a characteristic cinnamon brown color due to the presence of CeO_2 and PrO_2[55].

The rare earths are precipitated by ammonium or alkali hydroxide as $R(OH)_3$ which is insoluble. The hydroxides are white gelatinous precipitates which are readily soluble in mineral acids. The estimated solubility products for the rare earth hydroxides are[60]:

lanthanium	1×10^{-19}
cerium and praseodymium	1×10^{-20}
gadolinium	1×10^{-22}
lutecium	1×10^{-24}

The chemical property most used in the separation of the rare earths from the common elements is the insolubility of the oxalates in water, excess of oxalic acid, and dilute mineral

acids. Oxalic acid, ammonium oxalate or alkali oxalate can be used as the precipitating agent. These oxalates are best precipitated from a warm solution. The solubility of the decahydrated oxalates in water is about 1×10^{-6} moles per liter(61).

The fluorides are very slightly soluble in water and are precipitated quantitatively from slightly acidic solutions of hydrofluoric acid(15). The other halides and nitrates of the rare earth group are soluble in water. Phosphates and silicates are found widely distributed in nature and other compounds such as molybdates, uranates, columbates, formates, acetates, benzoates, citrates, succinates, tartrates, tungstates, and carbonates are known(62).

By dissolving the hydroxides, carbonates, or oxides in dilute sulfuric acid the hydrated sulfates crystallize out with varying amounts of water of crystallization(31). With the alkali sulfates the rare earths form double sulfates. This is important and interesting because part of the rare earths form nearly insoluble double sulfates while other members of the group form readily soluble double sulfates. This has been the chief means of separating the elements into two groups. Those insoluble double sulfates are the cerium group and the soluble group is the yttrium group. The members of the groups are

as follows:

Cerium Group	Atomic Number	Yttrium Group	Atomic Number
Lanthanum	57	Scandium	21
Cerium	58	Yttrium	39
Praseodymium	59	Europium	63
Neodymium	60	Gadolinium	64
Promethium	61	Terbium	65
Samarium	62	Dysprosium	66
		Holmium	67
		Erbium	68
		Thulium	69
		Ytterbium	70
		Lutecium	71

The uses of the rare earth metals or their compounds are few. Cerium was widely used in the gas mantle industry which was quite important several decades ago(32). This industry through its support and supplies of concentrates has increased the interest and knowledge of rare earth chemistry. Ceric salts are used as an oxidizing agent in analytical chemistry and cerium alloys are used in cigarette lighters, tracer bullets, and luminescent shells due to their pyrophoric properties(63). Of the other members of the group lanthanum sesquioxide is used in optical glass, didymium in glass blowers

goggles, and mixed rare earth fluorides and oxides for core mixture in cored graphite rods in search lights(63). Recently rare earths have been used in preparation of high temperature alloys for jet engines.

The rare earth elements and their compounds show strong paramagnetism. This phenomenon has been used to determine the purity of samples and also has given information as to the electronic configurations. The paramagnetism is believed to arise from the 4f electrons which are shielded from the chemically bonded groups(64). The measured magnetic susceptibilities agree well with the calculated values of the various ions when the calculations are made assuming that the 4f shell is built from 1 to 14 for the group(64).

Also spectroscopic examination of these elements has been valuable. The colored solutions of the rare earths show absorption in the visible range of the spectrum. The three elements which give the strongest and most characteristic absorption bands are praseodymium, neodymium, and erbium(33). These can be identified easily but a quantitative determination is not very successful. Emission spectroscopic work is widely used to determine the presence of the elements in a sample and some quantitative analysis of individual elements has been done.

The Use of Ion-Exchange in Analytical Chemistry

The application of ion-exchange has been known for at least one hundred years. However the development of a wide variety

of applications of ion-exchange and the study and knowledge of the theoretical considerations involved are very new developments.

Until the last 20 years the application of ion-exchange had been almost entirely limited to water softening processes. The first applications involved the use of naturally occurring silicates to treat water[37]. The next exchangers used were sulfonated carbonaceous materials such as peat, coal, or wood. In 1935 two Englishmen, Adams and Holmes, condensed phenol sulfonic acid with formaldehyde to form a resin which showed considerably higher capacity than the naturally occurring products used before.

The applications of ion-exchange can be divided into five divisions[26]. These include:

a. Transformation of ionic constitutents.

b. Fractionation of ionic substances.

c. Concentration of ionic substances.

d. Removal of ionic substances.

e. Miscellaneous applications.

Ion-exchange can also be separated into two main divisions i.e. cation exchange and anion exchange. In cation exchange one cation which forms an insoluble salt with the anion of the resin is replaced by a different cation which also forms an insoluble salt. A general formula for this exchange is:

$$A^+ + BR \rightleftharpoons B^+ + AR$$

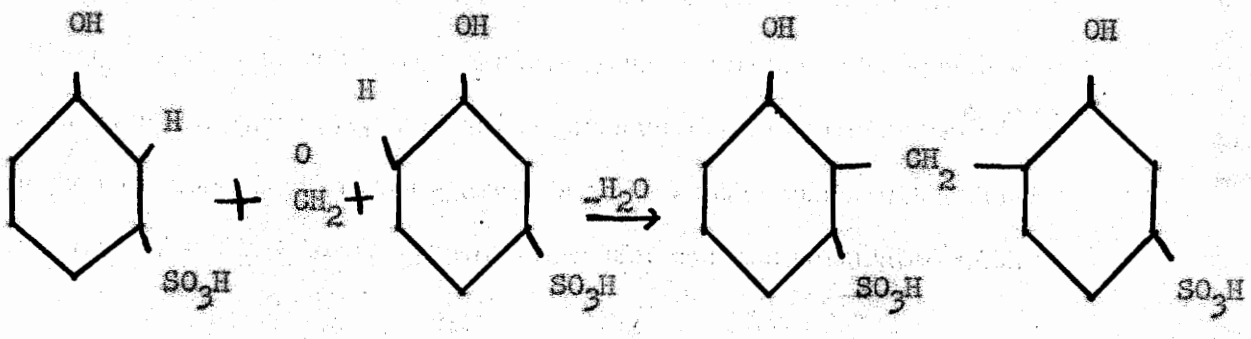
Here R refers to the anion of the resin and A and B refer to the cations which are competing to form the insoluble salt. Although there is still some question as to the mechanism of an anion exchange it is believed to be similar to the cation exchange.

There are two general methods of application of ion-exchange. This includes batch technique and the column technique. In the batch method the solution and the resin are stirred together in a beaker until equilibrium is reached and then the resin and solution are separated by decantation or filtration. This process is limited to cases where small volumes are handled and where the equilibrium is very favorable. In the column method the solution is passed down through a column which is packed with the desired resin, at a predetermined pH, and the treated solution is collected at the bottom of the column. When a large volume of solution is to be treated and where there is a moderately favorable equilibrium the column technique is used. Most applications of ion-exchange use the column method.

When certain ions from a solution are being adsorbed by a resin the resin will approach a state of saturation for the ion. Then the resin can be regenerated or returned to its original form and used over again. As an example of regeneration consider the water softening process. The calcium and magnesium ions in the water are adsorbed by the resin with the release of sodium ions. When the resin becomes saturated with

the calcium and magnesium ions the bed is treated with a sodium chloride solution and converted back to its original form and is ready to use again.

In the past few years a large number of good quality synthetic resins have been produced. The synthetic resins are organic acids or bases which form salts by the replacement of an ion for the hydroxyl or hydrogen ion. For the cation exchange resins the active group is generally the phenolic (OH), carboxylic (COOH), or sulfonic (SO_3H)(1). The anion exchangers have as their active group the NH_2, NHR, or NR_2. Some of these resins may have two different type groups present. An example of the formation of a specific cation exchange resin is the synthesis of a phenol-formaldehyde polymer containing nuclear sulfonic acid groups(38). This is formed by condensing m-phenol sulfonic acid with formaldehyde. Two molecules of the acid react with one molecule of formaldehyde to form the first stage of the condensation(39).



This condensation continues to give a long chain. A large number of these chains are cross linked to form a high molecular weight polymer. This forms a large mesh like structure with the anion groups bound together and the acid group exhibiting nearly the same properties as in the monomer. The hydrogen of the acid group behaves as in the monomer and can be replaced by another ion such as sodium or calcium to form an insoluble salt.

The application and theory of the anion exchange resins have not been studied as much as the cation exchangers. An example of the mechanism of anion exchange is given where you have an exchange between chloride and hydroxide ions(40).

$$Cl^- + RNH_3^+ OH^- \rightleftharpoons RNH_3^+ Cl^- + OH^-$$

Some of the desirable properties of the new synthetic ion-exchange resins are(49):

1. Good stability with resistance to heat, acids, oxidation, organic solvents, and mechanical abrasion.
2. High capacity per unit volume.
3. High exchange velocity and sharp break through.
4. Good variety of properties for various problems such as mesh size and active groups.

The most extensive use of ion-exchange other than the softening of water is probably the separation of certain metals. To accomplish this you need to adsorb certain cations from a

solution without adsorbing others or you must adsorb all of the cations and then desorb certain of them. The affinity of a cation for a cation exchanger increases with increasing valence[41]. The order of adsorption affinity is then: monovalent < divalent < trivalent. For the cations of the same valence the affinity increases with increasing basicity. The sequence of adsorption for the alkali metals would be: $Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+$; for the alkaline earth cations: $Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++}$; and for the rare earth cations the order is: $La^{+++} > Ce^{+++} > Pr^{+++} > Nd^{+++} > Sm^{+++} > Eu^{+++} > Y^{+++} > Sc^{+++}$.

The greater affinity a cation has for the cation exchanger the more difficult it will be to desorb or elute that cation from the exchanger. The competition of two cations for the cation exchanger can be given:

$$A^{+n} + nBR \rightleftharpoons AR_n + nB^+$$

where R is the resin, B^+ its original cation, and A^{+n} the cation brought into contact. The final equilibrium depends principally upon the activities of the two cations and the respective affinity of each for the resin[52]. If the affinity for the resin and/or the concentration of the ion introduced is greater than that of the ion originally combined the replacement will be nearly complete[53]. The formation of complexes

to lower the ionic concentrations is common in ion-exchange applications.

W. C. Bauman and J. Eichhorn have summarized the properties of a synthetic cation exchange as[3]:

1. Ion-exchange rate and equilibrium for Dowex 50 have been shown to be consistent with the hypothesis that the resin phase is equivalent to a highly ionized salt solution.

2. Assuming activity coefficients equivalent to those in strong chloride solutions, the ion-exchange equilibrium data may be interpreted by the Donnan concept of membrane diffusion.

3. At low concentrations the exchange rate for Dowex 50 is controlled by the mass action reaction rate between the ions at the surface of the particle.

4. The diffusion rate of HCl and NaCl in the resin phase is about one fifth as great as in the dilute aqueous solution. This rate indicates that the interdiffusion of ions in the resin phase should be controlling in the exchange rate at solution concentrations above about 0.1 molal.

In the Plutonium Project it was necessary to isolate the major fission products for the study of physical, chemical, and biological problems raised by the production of plutonium[53].

Since the rare earths were included among these products a method was needed for the separation of these elements. The use of ion-exchange techniques to separate the rare earths has been one of the high points of this work. The most successful work has been done using a nuclear sulfonic cation exchange resin.

This investigation brought out the value of the complexing agents such as citric acid. The dissociation of citric acid proceeds as follows[42]:

$$H_3Cit \overset{-H^+}{\rightleftharpoons} H_2Cit^- \overset{-H^+}{\rightleftharpoons} HCit^{=} \overset{-H^+}{\rightleftharpoons} Cit^{\equiv}$$

The percent of the particular ions present in a solution of citric acid varies greatly with the pH. At a pH of 7 the trivalent citrate ion is predominant while at a pH of 3 the ion H_2Cit^- is predominant. The rare earths are strongly complexed by citrate solutions at a pH of approximately 3[43]. The predominant rare earth complex present at this pH is $M(H_2Cit)_3$ where M is the trivalent rare earth cation.

The exchange and complexing reactions of the rare earth ion and the resin and the citrate at a pH of about 3 are:

$$M^{+3} + 3NH_4R \rightleftharpoons MR_3 + 3NH_4^+$$

and

$$M(H_2Cit)_3 \rightleftharpoons M^{+3} + 3H_2Cit^-$$

By careful control of the pH and concentration of the citrate solution it is possible to elute the rare earths individually since each rare earth is eluted only when the pH reaches a critical value[44].

The pH at which citric acid solutions appreciably complex cations of different valences varies considerably[45]. Therefore it is possible to separate the alkaline earths from the rare earths by controlling the pH of the solution.

Spectroscopic Analysis

Considerable spectroscopic work has been done in analysis of the rare earths. In emission spectroscopy the lines are very numerous and are best studied in the violet and ultraviolet region of the spectrum. The most characteristic spectra are given by the colorless salts[34]. The qualitative analysis of a sample is valuable for determining the elements present and for the identification of impurities. Considerable quantitative spectroscopic work has been done on the individual elements[13,14,18,34]. This is particularly valuable in studying the progress of other means of separation. In qualitative work it is suggested that the well known spectrum for iron be used to locate the lines of the rare earths.

Johnson[19] did considerable spectroscopic work in his thesis on determination of rare earths in bones. He identified eleven of the rare earth elements in human bones by means of emission

spectroscopy. He also determined the quantity of yttrium in human bones by emission spectroscopy. In the determination of the concentration of yttrium he used chromium as an internal standard and obtained the value of 3.3 p.p.m. of yttrium in human bone ash.

The Composition of Human Bone

Morse[36] gives the following analysis of bone ash:

	Percent
CaO	51.31
MgO	00.77
K_2O	00.32
Na_2O	01.04
H_2O (Crys.)	02.46
H_2O (Comp.).....	01.32
P_2O_5	36.65
CO_2	5.86
Cl	00.01

It has been demonstrated by Hevesy[16] that bones of animals are in a state of dynamic equilibrium with respect to their surroundings. There have been various references to the rare earth content of bones. Cossa[10] found 15 mgr. of rare earth oxide per kilogram of bone. Herman Lux[35] obtained a 3 mgr. concentration of the rare earths from 6 kilograms of fresh bone.

Johnson[20] determined the concentration of rare earth oxides in human bone ash. He reported the concentration to be 19.6 p.p.m. of rare earth oxide in human bone ash. The bones he used in this determination were several femurs and the method he used is given in the following section.

Analytical Procedures

In the determination and isolation of the rare earth elements in a sample such as bones, rocks, or plants there are certain obvious difficulties. First the concentration of the rare earths is usually very low and the number of necessary steps are numerous. Also in these substances there is a large concentration of calcium and often a high concentration of phosphates. Calcium shows many of the same chemical properties as the rare earth elements and the phosphates precipitate as calcium phosphate from neutral and basic solutions.

W. O. Robinson, Senior Chemist for the U. S. Bureau of Plant Industry, has done a large amount of work on the determination of rate earth content in plants and soils. The procedure used by Robinson for determining the rare earth content of phosphate rocks consists of the following steps[48]: Solution of the sample and removal of the phosphates as phosphomolybdate. This is followed by two ammonia precipitations, then two oxalate precipita-

tions with an intervening ammonia precipitation. The final oxalate precipitate is ignited and the residue is reported as rare earth oxides.

A second method reported for the analysis of bone ash or similar substances involves the precipitation of calcium as calcium sulfate[21]. The sample is brought into solution as in the W. O. Robinson method and then by addition of sulfuric acid, calcium sulfate is precipitated. The filtrate is then treated with ammonium hydroxide and the rare earth hydroxides are precipitated. This residue is dissolved in hydrochloric acid and the rare earths precipitated as the oxalate by the addition of oxalic acid. The oxalates are ignited to the oxides by ignition and reported as such.

A third method of determining the rare earth content of bones or similar substances is the oxalic acid method[22]. The sample is brought into solution and the pH is adjusted to 1.6 using thymol blue as the indicator. The solution is heated to 60°C and the rare earths and some of the calcium are precipitated as the oxalate upon addition of an excess of oxalic acid. This oxalate is dissolved in nitric acid and a second oxalate precipitation is carried out under the same conditions. The oxalate precipitate is dissolved and the solution is treated with ammonium hydroxide. The hydroxides are filtered and ignited and the residue i s reported as rare earth oxides.

Johnson[23] applied these three procedures for isolation of rare earths from bones. By the W. O. Robinson method he obtained a 74.5% recovery and from the calcium sulfate method he obtained a 63.4% recovery using a synthetic sample with a known concentration of rare earths. These low returns were assumed to be due to methodical loss in the many steps and to co-precipitation of the rare earths in the precipitation of the interfering ions. In the oxalic acid method Johnson[24] obtained an 84.2% recovery from a sample of known concentration.

In the determination of the rare earth content of phosphate rocks, C. W. Bondurant[5] used a modified form of the oxalic acid method and included ion-exchange techniques in the procedure. His procedure includes the following steps: First the sample is brought into solution and the pH adjusted to 1.6. The rare earths are precipitated as oxalates with efforts being made to reduce the calcium and phosphate concentration. The precipitate was ignited and dissolved in hydrochloric acid and the quantity of calcium remaining was further reduced by precipitating rare earth hydroxides with ammonia in the presence of a 1 molar ammonium ion concentration. Then he made use of an anion exchanger to reduce the remaining phosphate concentration. This was followed by removal of the remaining calcium by employing a cation exchanger. The rare earths were precipitated as the oxalates and ignited to the oxides and reported as such. On the basis of four artificial samples with 100 mgr. of rare earth oxides added

he reports a recovery of 89.2 mgr. On the basis of four phosphate rock samples enriched with a known quantity of rare earths he reported a concentration of 190 p.p.m. for the brown phosphate rock and 510 p.p.m. for the blue phosphate rock. The residue had a color characteristic of the rare earth oxides and gave a positive test for cerium. The residue also gave a negative test for calcium and phosphates.

EXPERIMENTAL

Method of Attack

It is desired to establish a procedure for the determination of the rare earth elements in a substance such as human bone ash. The human bone ash has a high concentration of calcium and phosphates with a very low concentration of rare earths. The efficiency of the procedure can be determined by working with a synthetic bone ash sample containing a known amount of rare earths.

Of the methods reviewed[1] the oxalic acid method and the modified oxalic acid method appear to be the most desirable. The precipitation of the calcium as calcium sulfate and of the phosphates as ammonium phosphomolybdate is undesirable due to the loss of rare earths by co-precipitation. It is desirable to effect the separation by precipitating the rare earths and leaving the interfering ions in solution and thus eliminate the loss due to co-precipitation. The oxalic acid method follows this principle and the results reported are better than for the other methods. It was thought that this method with possible modifications could be used in this problem.

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[1] Literature Review, page 23.

The Elimination of the Phosphate Ion

The precipitation of the rare earth hydroxides by the addition of ammonium hydroxide to the solution with a high ammonium ion concentration is the most desirable method of separating the rare earths from a large portion of the calcium. This however is impossible when there is a large amount of phosphate present since calcium phosphate precipitates from basic solution. This leads to the problem of first removing the phosphate which is present in high concentration in bone ash.

Johnson(25) reports that if the rare earths and calcium are precipitated as the oxalate from an acid solution the phosphate ion concentration can be greatly reduced. He reports that if two successive oxalate precipitations are carried out at a pH of 1.6 the ammonium phosphomolybdate test for phosphates is negative using a small portion of the solution. Bondurant(6) in working with phosphate rock which has about the same amount of phosphate present found that two successive oxalate precipitations at a low pH did not completely eliminate the phosphate ion. He accounts for this as being due to larger samples and thus higher concentrations. Bondurant reports that two oxalate precipitations with an intervening ammonium phosphomolybdate precipitation completely eliminated the phosphate concentration. He also reports that the phosphate ion concentration in a solution

can be reduced by using an anion exchange resin but that the resin does not have a high capacity for the phosphate ion.

When the rare earths are precipitated as the oxalates at a low pH the calcium is not completely precipitated as the oxalate. A check of this point was made by treating a calcium chloride solution at a pH of 0.7 with an excess of oxalic acid. Approximately 59 percent of the calcium was precipitated within 30 minutes. Due to the reduction in calcium concentration in the oxalate precipitation and possible loss of rare earths using the molybdate precipitation the oxalate precipitation appears to be the most suitable as a means of elimination of a large portion of the phosphate concentration. Experiments by several investigators[7,46] have shown that thirty minutes is sufficient for complete precipitation of the rare earth oxalates from a warm solution. These experiments also showed that upon standing longer the precipitate is contaminated with more phosphate and calcium.

The Elimination of Calcium

If the phosphate ion is completely removed the elimination of the large amount of calcium remaining is accomplished by precipitation of the rare earth hydroxides with ammonia. The solubility products of the rare earth hydroxide ranges from 10^{-19} to 10^{-24}[65]. Due to the very large concentration of the calcium some calcium hydroxide is precipitated upon addition

of NH_4OH. This can be greatly decreased by the addition of enough NH_4Cl to make the solution approximately 1 molar. This salt greatly increases the NH_4^+ concentration and thus decreases the hydroxide ion concentration with a decrease in the calcium hydroxide precipitate. Two successive hydroxide precipitations with NH_4OH in the presence of a high concentration of ammonium ions should eliminate the calcium present provided the phosphate ions have been completely removed.

The Application of Ion-Exchange to This Problem

The two constituents of a sample of bone ash which are the most difficult to remove in the analysis of the rare earths are calcium and phosphates. Of the other constituents reported, a combination of oxalate precipitation from an acidic solution and hydroxide precipitation from a solution with a high ammonium ion concentration should completely remove them.

The possibility of using ion-exchange techniques in this problem was considered. Shearin and Bleicher(50) attempted the separation of calcium and the rare earths by the use of ion-exchange. In their experiments they dissolved the rare earths and calcium in a citrate buffer solution with a pH of 3.4. They passed the solution through a column 10 cm long and 1 cm in diameter which contained the resin Amberlite IR-120 in the hydrogen form. The calcium was adsorbed and the rare earths were not adsorbed. The solutions which they used were much lower in

calcium ion concentration than the original bone ash solution would have been. Their experiments show that a large portion of the calcium will have to be removed before the use of ion-exchange. Bondurant[8] uses ion-exchange techniques to remove the last traces of calcium and phosphates. He uses the same conditions in the separation of calcium from the rare earths as Bleicher and Shearin used. In the removal of the last traces of phosphate ions he used the anion exchanger Amberlite IRA-410. The resin was placed in the chloride form by passing .1 N HCl solution through the column until the effluent reached a pH of 2. It is believed that the methods used could be adopted in this procedure for the removal of the last traces of calcium and phosphates.

The Establishment of Procedure With a Synthetic Sample

In order to establish a procedure for the analysis of a sample of human bone it was necessary to work with a synthetic sample with a known amount of rare earths added. This was done by preparing a synthetic bone ash containing the percent of constitutents found in animal bone ash as given earlier. The standard rare earth solution was prepared using a rare earth oxalate sample obtained from the University of Illinois. A weighed amount of the rare earth oxides were dissolved in a hydrochloric acid solution and evaporated nearly to dryness. Then the moist residue was diluted to the desired volume with one-tenth normal

hydrochloric acid. The weight of rare earth oxides per liter was known and a known amount of the rare earths could be added to the synthetic ash by measuring the desired volume.

At first a rare earth oxalate sample rich in the cerium group elements was used as the standard rare earth solution. After using this solution to establish a procedure it was found that the loss due to solubility was high and variations in the results of different samples was considerable. This variation and loss was great enough to make the analysis of a sample of bone ash unreliable. A sample of rare earth oxalates which were rich in the yttrium group elements was available. A standard solution of this sample was prepared and used in the synthetic ash sample. The results of a number of samples showed that the solubility losses and variations in results were much less than with the other standard solution. For all of the following work on establishment of the procedure this rare earth chloride solution rich in the yttrium group was used. By adding a known amount of this standard rare earth chloride solution to a weighed quantity of the synthetic ash it was hoped that a satisfactory procedure for the determination of the rare earths could be established.

A. Solution of the Synthetic Sample

In preparing the synthetic samples forty grams of the synthetic ash was weighed and placed in a beaker. To this

was added enough of the standard rare earth chloride solution to contain 25.0 milligrams of rare earth oxides. The sample was dissolved by slowly pouring 150 ml of 1-1 HCl into the beaker. The solution was then slowly evaporated nearly to dryness on a hot plate. The volume was increased to 250 ml by adding distilled water to the moist residue which dissolved completely.

B. The Oxalate Precipitation

From preceding work it appeared that an oxalate precipitation was the best means of eliminating a large portion of the phosphate concentration. The pH of the sample solution was adjusted to approximately 0.7 by adding either NH_4OH or HCl. The solution was heated to 65°C on a hot plate and 200 ml of a saturated oxalic acid solution was added. This was allowed to stand for thirty minutes with occasional stirring and then filtered on a glass funnel using Qualitative Filter Paper. The residue was washed with forty ml of five percent oxalic acid solution. The oxalate precipitate was burned for two hours in the muffle furnace at approximately 850°C in an evaporating dish.

To further reduce the phosphate ion concentration a second oxalate precipitation was carried out. The oxide was dissolved in 30 ml of water and forty-five ml of

hydrochloric acid with heat and transferred to a 400 ml beaker. The solution was diluted to 200 ml with distilled water. The pH was adjusted to 0.7 as before. The solution was filtered to remove any insoluble residue, mostly silicon dioxide. This residue has been tested for rare earths and found negative each time when working with bones. The residue was washed with a small amount of distilled water. The filtrate and wash water were combined and heated to 65°C on the hot plate and 150 ml of a saturated oxalic acid solution was added. This solution was allowed to stand for 30 minutes with occasional stirring, filtered, and washed as before and again ignited for two hours in the muffle furnace at approximately 850°C. This oxide was dissolved as before and diluted to 100 ml. A few drops of the solution at this point gave a negative[1] test for phosphates in all of the samples.

C. The Hydroxide Precipitation

The solution from the two oxalate precipitations is diluted to 100 ml with distilled water. To this is added enough NH_4Cl to make the solution 1 molar with respect to NH_4Cl. Then NH_4OH is added until a precipitate is formed

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[1] Colormetric test of Fiske and Subarrow(4).

and a few drops in excess are added. This is heated on a hot plate in order to form a coarser precipitate and to drive off excess ammonia. The solution is cooled and filtered on a glass funnel using Filco Brand Filter Paper. The residue is washed with 25 ml of dilute ammonia water.

Due to the large amount of calcium originally present a second hydroxide precipitation was carried out. The hydroxide residue on the filter was dissolved by pouring 50 ml of 1-1 HCl over the precipitate and collecting the filtrate. The paper was washed with distilled water and the wash water was collected and added to the acid filtrate. This was diluted to 100 ml by adding distilled water. Ammonium chloride was added as before and the rare earth hydroxides precipitated with a slight excess of NH_4OH. The solution was warmed as before. The precipitate was filtered on the same funnel with the same filter paper and washed with dilute ammonia water.

If the phosphate and the calcium have been both removed the precipitate should be entirely rare earth hydroxide. However for several samples the hydroxide was filtered on a quantitative filter paper and converted to the oxide by ignition. By igniting the hydroxide in a weighed crucible and weighing the resulting crucible and residue the amount of oxide was determined. It was evident that the interfering

ions had not been completely removed because the resulting oxide was greater than the rare earth oxide originally added. The amount of interfering ions was small because the final oxide was not more than 5 mgr. heavier than the original rare earth oxide for any of the samples. Not only were the results too high but they varied several milligrams.

The results indicated that there was some calcium phosphate in the final residue. This could be true due to co-precipitation of a small amount of phosphate with the calcium oxalate precipitates which were very large. This phosphate would have precipitated as calcium phosphate in the hydroxide precipitation of the rare earths. It became evident that some method was required to remove the last traces of calcium and phosphates.

D. The Use of Ion-Exchange

To eliminate these interfering ions the use of ion-exchange techniques was believed desirable. Bondurent[9] in his thesis, "The Estimation of Rare Earth Elements in Phosphate Rock," which is a closely related problem reports the successful use of ion-exchange resins to remove the phosphate and calcium. He employed an anion exchanger to remove the phosphate and a cation exchanger to remove the calcium. He was able to use these techniques only after the major portion of the calcium and phosphates had been

removed. From the samples run through the oxalate and hydroxide precipitation it was evident that the concentration of the interfering substances was small. It was believed that if the calcium could be adsorbed on a high capacity cation exchanger and the resulting solution treated with oxalic acid to precipitate the rare earths as oxalates the interfering ions could be eliminated.

In applying ion-exchange techniques where a column is used usually there is a large volume of solution to treat and also the loss of the ions is appreciable. For these reasons the use of a batchwise technique was considered. In using the batch method the amount of substance to be adsorbed must be small and the final equilibrium must be very favorable. The volume of solution is small and remains small because a great deal of washing is not necessary as in the column method.

To test the applicability of this method a 30 gram sample of the synthetic ash with no rare earths added was treated with two oxalate precipitations and two hydroxide precipitations as previously described. Upon adding the NH_4OH in the second precipitation a small amount of white precipitate formed which was believed to be calcium phosphate.

The residue and the filter paper were placed in a beaker with 20 ml of 1-1 HCl. To this was added 50 ml of an ammonium citrate-citric acid buffer solution with a pH

adjusted to 3.3. The pH of the solution was adjusted to 3.3 by adding NH_4OH. Approximately 2 grams of wet cation exchange resin were added to the beaker. The contents were slurried in the beaker and after 30 minutes the contents were filtered on a glass funnel using Filco Brand Filter Paper. The paper and the resin were washed with 30 ml of the ammonium citrate-citric acid buffer with a pH of 3.3. The filtrate and wash liquid were collected, combined, and heated to 65°C. To this was added 30 ml of saturated oxalic acid solution. This was allowed to stand for 30 minutes and then filtered on a glass funnel using a Whatman No. 30 filter paper. This paper was charred and burned in a weighed porcelain crucible for two hours at approximately 850°C. The crucible was cooled for 45 minutes in a desiccator charged with calcium chloride and reweighed. There was no weighable residue. This shows that the calcium had been adsorbed on the resin.

The resin used was Amberlite IR-120 which was donated by Rohm and Haas Company. This is a high capacity sulfonic acid type cation exchanger(2). The resin was converted to the hydrogen cycle by first treating the resin with a ten percent sodium chloride solution followed by a 3 normal hydrochloric acid solution.

A number of synthetic bone ash samples with 25 mgr. of rare earth oxides rich in the yttrium group were carried

through the two oxalate and two hydroxide precipitations as described earlier. The second hydroxide precipitate and the filter paper were placed in 20 ml of 1-1 HCl. The residue dissolved readily and was treated with the resin, batchwise, as just described. The citric acid-ammonium citrate buffer was prepared by adding NH_4OH to to a five percent citric acid solution until the pH was raised to 3.3. A small amount of phenol was added to make the solution one-tenth of one percent phenol. The phenol was added to the buffer to prevent the growth of molds in the citrate solution which would change the pH[51]. The purpose of the citric acid at a pH of 3.3 was to lower the concentration of the rare earth ions by formation of the complex $M(H_2Cit)_3$ where M is the trivalent rare earth cation. This is the predominant citrate complex at a pH of 3.3[43]. At this pH the calcium should be adsorbed on the resin while the rare earths are in the form of the rare earth citrate complex. The filtrate and wash solution were collected for the following step.

E. <u>The Final Oxalate Precipitation and the Ignition to the Oxide</u>

The solution which was approximately 150 ml from the ion-exchange treatment was heated to 65°C on a hot plate. To this was added 30 ml of a saturated oxalic acid solution. This was allowed to stand for 30 minutes and then filtered on

a glass funnel using Whatman No. 30 filter paper. The precipitate was washed with 30 ml of 5% oxalic acid solution. The paper and residue were charred and burned at approximately 850°C to a constant weight in a muffle furnace in a previously weighed porcelain crucible. The crucible and contents were cooled for 45 minutes in a desiccator charged with calcium chloride and weighed. The original synthetic ash samples contained 25.0 mgr. of rare earth oxides rich in the yttrium group. The weight of rare earth oxides recovered and the average recovery was determined. The mgr. of rare earth oxides recovered from eight samples were: 23.1; 22.6; 22.7; 22.8; 22.7; 24.0; 21.9; and 21.9. This gives an average recovery of 22.7 mgr. of rare earth oxides for the eight synthetic samples each containing 25.0 mgr. of rare earth oxide.

Solution of the Human Bone Sample

The bones used in the analysis were obtained through the generous cooperation of Dr. H. L. Osterud, Professor of Anatomy, Medical College of Virginia. They included several of most of the bones of the body. The only information that was known about the source was that they came from people between the ages of forty and seventy. The bones had been dried in the air for at least 3 years.

The bones that were analyzed were cut into small pieces to aid burning. Approximately 80-100 grams of the air dried bone were taken for each analysis. They were burned thoroughly to drive off the organic matter so that solution of the bones would be possible. First the bones were heated with a Bunsen burner with a low flame in a large porcelain casserole. Gradually the heat was increased and the bones were burned for a total of 10 hours over the flame. Then the casserole with the bones was placed in the muffle furnace for 4 hours at approximately 850°C. At the end of this time the bones were nearly white and were easily dissolved in dilute hydrochloric acid. Upon complete ignition of the bones they lost from 40 to 60 percent of their original weight. They were weighed after ignition and placed in a beaker and dissolved in 150 ml of 1-1 HCl with heat.

Application of the Proposed Procedure to a Human Bone Sample

The solution containing the bone ash was enriched with 25 mgr. of the rare earth oxides rich in the yttrium group. This solution was then slowly evaporated nearly to dryness on a hot plate. The residue was then dissolved in distilled water and diluted to 250 ml with distilled water. This solution was carried through the same steps as used in the establishment of procedure with the synthetic samples.1/ Two successive oxalic acid precipitations

1/ Complete procedure given in Summary.

were made at a pH of 0.7. The hydroxides were precipitated from a solution with a high concentration of ammonium ions. The ion-exchange resin IR-120 was employed at a pH of 3.3 using the batch-wise method. The final oxalate precipitate was burned to a constant weight in the muffle furnace at approximately 850°C.

The bones available included a few of most of the bones of the body. There was not enough of any one bone to run more than two or three analyses. Since it was necessary to take the average of a large number of samples it was impossible to determine the rare earths in any one bone. Therefore it was necessary to use several different bones to make a determination. The bones chosen were a hip bone, several collar bones, a femur, two humeri and a heel bone. The size of the air dried sample was from 80 to 100 grams.

In the synthetic samples the average recovery from the originally added 25.0 mgr. was 22.7 mgr. This is an average recovery of 90.8% of the rare earths. Twenty-five mgr. of the rare earth oxides were added to both the synthetic sample and to the bone ash. To estimate the rare earth content in the human bone ash it was assumed that the percentage loss in the synthetic ash would be the same as in the bone ash. Whether or not this assumption that the percentage recovery would be constant for samples with different amounts of rare earths was not determined. However for small differences in the concentration of the rare

earths originally present it was believed that this was the best way to estimate the rare earth content in the enriched bone ash.

The grams of rare earth oxides recovered from the enriched sample were divided by 0.908 and the resulting value was subtracted by 25.0 to give the estimated weight of rare earth oxides in the bone ash. From this the estimated p.p.m. of rare earth oxides in human bone ash for the various samples were as follows:

Sample	p.p.m.
Femur	25.6
Femur	7.5
Humerus	33.3
Humerus	7.4
Collar Bone	0.0
Hip Bone	27.2
Hip Bone	35.1
Hip Bone	8.4
Heel Bone	46.2
Average	21.2

The Reagents Used

The reagents used in the establishment of the procedure and the determination of the rare earth content of the bones were marked "A. C. S." or "U. S. P.". Chemicals that meet the specifications published by the Committee of Analytical Reagents of the American Chemical Society are marked "A. C. S.". Chemicals that fully meet the requirements of the United States Pharmacopoeia are marked "U. S. P.". These reagents were tested for the presence of rare earths or other interfering impurities. No rare earths or other interfering impurities were detected in the reagents using chemical tests.

DISCUSSION

A method of determining the rare earth content of bones is presented. This procedure was developed by a study of methods previously used and contains many of the steps previously reported[5,18] with a number of modifications.

The average concentration of rare earth oxides in human bone ash was estimated as being 21.2 p.p.m. This value was obtained by analyzing nine bone ash samples enriched with 25.0 mgr. of rare earth oxides rich in the yttrium group. The same procedure was applied to the bone ash as was applied to the eight synthetic ash samples containing 25.0 mgr. of rare earth oxides rich in the yttrium group. It was assumed that the percentage loss due to methodical error and solubility would be the same for the synthetic sample as for the enriched bone ash sample.

The number of steps in the procedure is still high. This fact and the low concentration of the rare earth oxides make it necessary to take the average value for a number of samples to arrive at any result. This was necessary in both the determination of the loss in a synthetic sample containing a known amount of rare earths and the determination of the rare earth content in the enriched human bone ash.

CONCLUSIONS

1. By using a combination of precipitation and ion-exchange steps an analysis for the rare earth content of a sample with a high calcium and phosphate content can be made. A procedure was developed using a synthetic sample and this procedure was applied to a number of human bone samples.

2. By precipitation of the rare earths as oxalates at a low pH the phosphate concentration can be nearly eliminated and the calcium content can be reduced.

3. After the removal of the phosphate ion concentration, the calcium can be eliminated by the precipitation of the rare earths with NH_4OH in the presence of a high concentration of ammonium ions.

4. At a pH of 3.3 the resin IR-120 will adsorb calcium and not the rare earths from a 5% citric acid buffer solution. The batchwise technique is satisfactory if the calcium concentration is very low.

5. The analysis of the rare earths is difficult due to the low concentration of rare earths and the very high concentration of calcium and phosphates. The results of the analysis of a number of human bone samples gives an estimated 21.2 p.p.m. of rare earth oxides in human bone ash.

SUMMARY

A method for determining the rare earth elements in bones and similar materials includes these steps:

1. Burn from 80-100 gr. of the air dried bones at 900°C for four hours to eliminate the organic matter. Weigh the bone ash to the nearest one-tenth gram.

2. Transfer the bone sample to a 600 ml beaker and dissolve in 150 ml of 1-1 HCl with heat. Add to this a measured volume of the standard rare earth chloride solution which is rich in the yttrium group. Evaporate this solution almost to dryness and dilute to 250 ml with distilled water.

3. Adjust the pH of the solution to 0.7 by adding HCl or NH_4OH and heat to 65°C on a hot plate. Then add 200 ml of a saturated oxalic acid solution. Allow this to stand for 30 minutes and filter. Wash the residue with 40 ml of 5% oxalic acid solution. Then burn in an evaporating dish at 900°C for two hours in the muffle furnace.

4. Dissolve the residue with 30 ml of H_2O and 40 ml of HCl with heat. Dilute to 200 ml with distilled water. Adjust the pH to 0.7 and filter off any insoluble residue, mostly silicon dioxide. This residue is washed with a

small amount of distilled water and the filtrate is combined with the wash water. Heat the solution to 65°C and add 150 ml of a saturated oxalic acid solution. Allow this to stand for 30 minutes and filter and wash as before. Burn the residue in an evaporating dish at 900°C for 2 hours in the muffle furnace.

5. Dissolve the residue in 30 ml of H_2O and 40 ml of HCl with heat. Then dilute to 100 ml with distilled water. Add enough NH_4Cl to make the solution one molar with respect to the ammonium ion. Add NH_4OH until a precipitate forms and add a small amount in excess. Heat to drive off excess ammonia and to form a coarser precipitate. Allow the solution to cool, then filter and wash with dilute ammonia water.

6. Dissolve the residue by pouring 50 ml of 1-1 HCl through the filter and wash with distilled water. Collect the filtrate and wash water and combine and dilute to 100 ml with distilled water. Add NH_4Cl and reprecipitate as before. Heat, filter, and wash as before on the same paper.

7. Transfer the paper and residue to a beaker with 20 ml of 1-1 HCl. Add 50 ml of the 5% citric acid solution which has the pH adjusted to 3.3 by adding NH_4OH. Adjust the pH of the solution to 3.3 and add approximately

2 grams of the wet resin, Amberlite IR-120. Allow to stand for one-half hour with occasional stirring and filter and wash with 30 ml of the citric acid-ammonium citrate buffer. Collect both the filtrate and the wash liquid and combine.

8. Heat the solution to 65°C and add 30 ml of a saturated oxalic acid solution. Allow to stand for one half hour and then filter and wash with 5% oxalic acid on a Whatman No. 30 filter paper. The precipitate is burned at 900°C to a constant weight and weighed as the rare earth oxides.

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