1962

A study of the colloidal properties of zirconium and promethium by electrodialysis and liquid-liquid extraction

James N. Click

Recommended Citation

Click, James N., "A study of the colloidal properties of zirconium and promethium by electrodialysis and liquid-liquid extraction" (1962). *Masters Theses*. 2734.
https://scholarsmine.mst.edu/masters_theses/2734

A STUDY OF THE COLLOIDAL PROPERTIES
OF ZIRCONIUM AND PROMETHIUM
BY ELECTRODIALYSIS AND LIQUID-LIQUID EXTRACTION

BY

JAMES N. CLICK

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMISTRY

Rolla, Missouri

1962

Approved by

William H. Webb (Advisor) M. R. Strunk

D. S. Eppelsheimer Donald J. Siehr

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Since the end of World War II, nuclear chemistry has become of increasing importance and today it is a major field of scientific investigation. The advent of nuclear energy opened an era of almost unlimited power and countless problems. One of these problems which arose and is of extreme importance is the recovery of unburned nuclear fuel and the claiming of transmutation products from the irradiated fuel elements. The chemical processing of these elements must separate the fission products from the fissionable material if the fuel is to be used again. Once the fission products are separated from the fissionable material, their disposal becomes a difficult problem and at the present a very costly one.

The irradiated fuel elements are stored from 90 to 120 days to allow the intense short half-life activity to decay. After "cooling down" the nuclear fuels are separated from the fission products and inert components of the reactor element by solvent extraction. Once the wastes are isolated from the fuel element, they are concentrated by evaporation and stored in underground steel tanks. Since the storage facilities are limited and the method costly, a method must be developed for the permanent disposal of the fission products. If certain commercially and medically useful radioisotopes could be separated from the waste solutions, this would be an economical means of obtaining the isotopes as well as minimizing the amount of material which must be disposed of or permanently stored.

The commercial possibilities of zirconium and its occurrence as a fission product in the nuclear reactors have created a demand for a better understanding of its behavior in aqueous solutions. For a number of investigations, including fundamental studies of radiation effects on living tissues and the therapeutic utilization of radioisotopes, it is valuable to have methods for obtaining pure radioisotopes. This necessitates the need for a more intimate understanding of the solution chemistry of zirconium, one of the most widely therapeutically used radioisotopes.

One of the least understood aspects of the solution chemistry of zirconium is its occurrence as a colloid in solution of certain pH values. A better understanding of the colloidal chemistry of zirconium would aid in the understanding of the solution chemistry, and also in studying the optimum conditions for obtaining the pure isotope.

The purpose of this investigation was to study the solution chemistry of zirconium by investigating the colloidal behavior of natural zirconium and zirconium-95, utilizing electrodialysis and liquid-liquid extraction techniques. Also incorporated into this study was the investigation of optimum conditions for the extraction of the natural zirconium and zirconium-95 with thenoyl trifluoracetone. A limited amount of work was done on the colloidal nature of promethium-147.

II. LITERATURE REVIEW

The literature review is divided into four parts: (1) the occurrence and uses of the elements zirconium, cesium-137 and promethium-147, (2) solution chemistry of zirconium, cesium-137 and promethium-147, (3) colloidal nature of radioisotopes and (4) use of dialysis and liquid-liquid extraction as a means of study.

Occurrence and Uses of the Elements Zirconium, Cesium-137 and Promethium-147

Zirconium. Compounds of zirconium are widely distributed and fairly abundant in nature.(4) Clarke and Washington(4) have estimated that zirconium constitutes about 0.017% of the lithosphere, about the same as carbon. The element does not occur in the free state as a consequence of its vigorous chemical activity at the temperatures of its environment during the solidification of the earth's crust. The chief occurrences are in the mineral zircon, $ZrO_2 \cdot SiO_2$, baddeleyite, ZrO_2 and a variety of complex minerals, particularly the silicates. Zircon is the most common zirconium mineral. It occurs in all types of rock but chiefly in granitic and syenitic rocks. Zirconium-95 occurs chiefly in nuclear reactors as a fission product.(3)

The need for obtaining the element zirconium in pure form for use as a cladding material in nuclear reactors has become of great importance today. Zirconium is used as a cladding material because of its resistance to corrosion at high operating temperature. Zirconium finds many uses as a component in certain alloys in which specific properties induced by zirconium are desired.

Zirconium-95, because of its low toxicity and short half-life, is widely used in medicine as a means of studying radiation effects and in the treatment of cancer and other diseases.(21)

Cesium-137. Cesium-137 occurs as a fission product in nuclear reactors and has varied and important uses.(17) Cesium-137 is a very suitable gamma radiographic source. Dutli and Taylor(16) compared its radiographic characteristics with those of cobalt-60 and found it to be very good. It is expected that cesium-137 will replace cobalt-60 in many applications requiring gamma radiation since the daughter product of cesium-137, barium-137, is a strong gamma emitter.

Cesium-137 is useful for the treatment of some cancers. Gauwerky(18) describes the preparation and use of cesium-137 applicators for the treatment of cancer by local application.

Promethium-147. Promethium-147 occurs only as a fission product of uranium(50) and due to its scarcity, has found few practical uses. It is felt, however, that it might have possibilities as a radioactive source for the treatment of certain diseases where a longer half-life radioisotope is desired.

Some Aspects of the Solution Chemistry of Zirconium,

Cesium-137 and Promethium-147

Zirconium. The behavior of zirconium under various conditions and the interpretation of accurately made predictions have long been difficult and confusing.

In the earlier studies of zirconium nitrates, the investigators were not clear as to whether they were dealing with zirconyl nitrate or with zirconium tetranitrate, and they are prone to regard a solution containing 4 molecules of nitric acid per zirconium atom as tetranitrate solution. The clarification of the problem of molecular species in systems containing zirconium and nitrate ions or radicals has progressed somewhat in recent years, but much remains to be learned in order to permit a sound delineation of the structures of zirconium species in solution.(7)

Zirconyl nitrate of composition $ZrO(NO_3)_2 \cdot 2H_2O$ is the phase most commonly obtained from aqueous solutions containing zirconium and nitrate ions. Solutions which yield zirconyl nitrate can be prepared by mixing zirconium chlorides with nitric acid by dissolving hydrous zircona in nitric acid.(8)

When an aqueous solution of zirconyl nitrate was passed through Amberlite IR-100 resin cation exchanger and Amberlite JR-4 anion exchanger, only 2% of zirconium was retained. Only 1% was retained when the sodium salt of the resin was used. This indicates that the zirconium ion in solution is almost entirely in a nonionic state, probably $ZrO(OH)NO_3$ or ignoring hydration, $ZrO(NO_3)_2 + H_2O$

$ZrO(OH)NO_3 + NO_3^- + H^+$.

No complex nitrates of zirconium are known, aside from the acid $H_2Zr(NO_3)_6 \cdot 4H_2O$ which was identified by M. Fabuski(5) as a phase separating from a solution of hydrous zirconia in very strong, fuming nitric acid. No salts of this compound are known.(6)

Perhaps the most detailed investigation to date on the composition of zirconium solutions was reported by Connick and McVey in 1949.(15) They made up dilute solutions of zirconyl chloride in 2.00M perchloric acid solution and shook the solutions with a benzene solution of thenoyl trifluoracetone, a complexing agent for tetravalent zirconium. The complex carries the zirconium into the benzene phase as an uncharged molecular chelate which is in equilibrium with the ionic forms of zirconium in the aqueous phase. They investigated the very dilute range--from the carrier free activity supplied by the United States Atomic Energy Commission to 10^{-3} molar. Their work in 2M perchloric acid shows that the ion $ZrOH^{+3}$ predominates and that polymerization effects are negligible. Results also pointed out that Cl^- and NO_3^- ions form only weak zirconium complexes of nearly equal stability.

Dewell and Voigt(15) studied the composition of zirconium ions in solution by ion exchange. They found that a time dependency of the exchange of zirconium existed and in attempting to discover its nature, conductance measurements at 10^{-4} M zirconium were made as time studies. Unfortunately, the results were not subject to analysis in terms of the probable species present.

Larsen and Gammill(27) performed electrometric titrations of zirconium and hafnium solutions in order to determine the effects of concentration on the pH of precipitation and coagulation. They found that in all cases the hafnium solutions had a higher pH of precipitation than the zirconium solutions. Since Zr^{+4} is slightly smaller than hafnium, one would expect the zirconium to have a lower pH of precipitation values; and since the difference is only 0.01Å, one would not expect to find large differences in the pH of precipitation. It is interesting to note that they found the differences in the pH of precipitation in perchlorate very small while in nitrate and chloride solutions the difference much larger. They also found that increasing the anion concentration increases the pH of precipitation in all cases.

Lister and McDonald(28) studied the solution chemistry of zirconium in nitric, hydrochloric, perchloric and sulphuric acid solutions utilizing ion exchange techniques in addition to diffusion studies, pH determinations and electromigration studies. The results in nitric acid solutions are interpreted as indicating the presence at lower acid concentrations of polynuclear hydrolysis products, and at higher acidities such complexes as: $Zr(NO_3)_2(H_2O)_4^{+2}$, $Zr(OH)_2(NO_3)(H_2O)_3^{+1}$, $Zr(OH)_2(NO_3)_2(H_2O)_2^{+2}$, and $Zr(OH)_2(NO_3)_4^{-2}$. Their results also indicate great differences between the behavior of ionic species of zirconium and thorium in comparable solutions.

Cesium-137. Due to the very limited amount of work done on cesium-137 the review of its chemistry in solution will be limited to specific points which are directly associated with this investigation.

Most of the chemistry of cesium has been investigated in connection with its separation as a fission product. Cesium concentration and purification are affected by preparing cesium and ammonium alum and performing a fractional crystallization. Cesium-137 precipitated in this process with a purity greater than 99%.(13)

Finston and Kinsley(17) have reported one of the most extensive studies of cesium in which they give a review of the features of cesium chemistry which is of interest to radiochemists.

Promethium-147. The solution chemistry of promethium is meager and most investigations have dealt strictly with its separation as a fission product. The promethium-147 and europium fractions of fission products are separated by ion-exchange techniques. The promethium is sorbed on a steam heated cation exchange column and eluted with ammonium citrate.(12)

Colloidal Nature of Radioisotopes

It has been known for many years that some radioactive isotopes behave in a manner resembling colloids. Recently it has been observed that some of the radioisotopes produced by fission, zirconium for example, possess a colloidal nature. To date, nineteen fission elements have displayed colloidal behavior under selected conditions.

The definition of radiocolloids varies considerably from one investigator to another. Kurbatov(26) defines a radiocolloid as any radioactive material which can be removed by filtration from a very dilute solution, 10^{-9} molar or less. Schubert(39) defines them more generally, radiocolloids are "radiotracers which are present in minute concentrations and exhibit colloidal behavior." The definition most accepted is: radiocolloids are "particles of colloidal dimensions, diameter between 1 and 100 millimicrons, composed of radioactive materials."

Paneth(36) was the first investigator to report evidence of radiocolloidal behavior. He first noticed that when a solution containing very small amounts of RaD(Pb-210), RaE(Bi-210) and RaF(Po-210) was dialyzed, the lead passed through the membrane but bismuth and polonium did not. He further investigated this phenomena using the same elements and revealed that bismuth and polonium appeared to be colloidal in neutral, ammonical or weak acid solutions. The lead was ionic in acid solutions but colloidal in ammonical solutions.

Schubert and Conn proposed that radiocolloidal formation is increased(39) by (1) diminished diffusion velocity (2) stratification in presence or absence of centrifugation (3) coagulation or peptization by electrolytes (4) anomalous adsorption by ion exchangers (5) adsorption, generally irreversible upon finely divided matter or upon the walls of containing vessels (6) incomplete or lack of equivalence between radioactive and non-radioactive isotopes of the same element (7) inability to dialyze through membranes permeable to ions in general and (8) a discontinous distribution of the radioactive matter as revealed by radioautographs.

Radiocolloidal formation has been detected by the following methods:(9) (1) dialysis (2) filtration or ultrifiltration (3) diffusion coefficient studies (4) electrophoresis (5) sedimentation and centrifugation (6) radioautographs (7) adsorption and (8) isotopic exchange. The detection methods are reviewed by Schweitzer and Jackson.(43)

Factors Affecting the Formation of Radiocolloids

An acceptable explanation of radiocolloidal formation does not exist at the present time.(39) Paneth's discovery of radiocolloidal formation and his belief that they were true colloids caused an upset, in that, according to the laws of chemical equilibrium, the formation of a colloid requires that the solubility product constant of the insoluble compound must be exceeded. It was known that the solubility product (K_{sp}) of $Pb(OH_2)$ is about 1.2×10^{-10} at room temperature. Using the known solubility product of lead hydroxide at room temperature, in a dilute ammonium hydroxide solution of hydroxyl ion concentration of 1×10^{-3} molar, the minimum lead concentration would have to be 1×10^{-4} molar in lead ions to exceed the solubility product. Paneth found that the lead isotope, ThB, exhibited colloidal behavior when present to the extent of 1×10^{-11} molar in the ammonium hydroxide solution.

Other investigators did not share Paneth's belief that radiocolloids were true colloids and were convinced that the concentrations of many carrier-free radioisotopes were too low to permit formation of an independent colloidal phase. Hahn theorized that "the radioactive ions were adsorbed upon solid impurities accidentally present in solutions, thereby imitating a colloidal character and form the so-called radiocolloids."(23)

Other investigators have proposed explanations acceptable to both theories.(46)

Known factors which affect radiocolloidal behavior are: (1) solubility of radioactive tracers (2) presence of foreign particles (3) electrolytes (4) ionizing radiation (5) time and (6) concentration of radioisotopes.(10, 44)

Solubility of Radioactive Tracers. The hydrolysis of a tracer in aqueous solution to form an insoluble compound with some component of the solution favors radiocolloidal formation. The presence of a complexing agent which will form a soluble complex with the tracer prevents radiocolloidal formation.(10)

Schubert(38) has described the condition for radiocolloidal formation as follows: "the principle condition under which a radioelement present in solution is likely to become a radiocolloid is through a reduction of the solubility to such a point that if the radioelement were present in macroscopic concentration, precipitation would be observed. The requisite reduction in solubility can be effected by a variety of methods, but most frequently by adding a precipitating anion or cation, or, in the case of radiotracers whose hydroxides are insoluble, by raising the pH."

Mayer and Morton(32) describe stable colloidal solutions of zirconyl radiophosphate giving rise to the belief that zirconium and other elements which form insoluble hydrous oxides or hydroxides in macro quantities often form radiocolloids.

The belief that radiocolloids form at concentrations much lower than the solubility products of the compounds is not shared by all investigators.(2, 34) Those who disagree feel that the solubility products have not been accurately determined. Haissensky(1) reported that "one is dealing with polydispersed systems containing both simple and complex ions, and colloidal micelles of various dimensions in a slow state of evolution. The ordinary principles of solubility and solubility products are not applicable."

Presence of Foreign Particles. Investigators(52, 53) who believe that radiocolloids are not true colloids have performed many experiments to prove this theory. Other investigators(34) have found the action of impurities to be negligible in comparison to the amount of radiocolloid present.

Schweitzer and Jackson(42) felt that the primary factor in radiocolloidal formation was the adsorption phenomenon. However, by experimentation, they discovered that adsorption was not the primary factor and state that impurities facilitate radiocolloidal formation, but are not necessary for their presence.

Effects of Electrolytes on Radiocolloidal Formation. After the discovery of radiocolloids,(21) it was noted that the addition of highly charged cations or acids changed the direction of migration of certain radioisotopes. This adsorption of a highly charged ion, with the acquisition of a net charge, is typical of colloidal behavior.

The effects of the presence of various electrolytes on the radiocolloidal formation of zirconium,(39, 40) niobium(40) polonium(34, 45) and yttrium(25, 47) have been studied. These studies have pointed out that electrolytes play an important role in radiocolloidal formation.

Effects of Solvents on Radiocolloids. Past experiments have indicated that the effect of solvents on radiocolloidal formation may be of fundamental importance.

Experiments reported by Hahn(23) and Bouissieres(11) indicate that a polar solvent aids or may be necessary for the formation of radiocolloids in liquids.

The Effect of Time on Radiocolloids. The age of a radiocolloidal solution has a vast effect on the amount of radioactivity that can be removed by physical means. In general, the older the solution, the more radioactivity that can be removed.(45) The effect of time upon this phenomena is found to reach a maximum value in most cases in three to five days.(26, 47)

The Effect of Concentration of Radioisotopes. Studies of the effect of radioisotopic concentration on radiocolloidal formation is limited. The most extensive investigation was done on polonium by Morrow.(34, 45) He found that increasing the concentration of polonium while holding the acid concentration constant increases the amount of activity which could be removed by filtration.

Other investigators have found no correlation between radiocolloidal formation and the concentration of the radioisotope.

Effect of Radiation on Radiocolloids. Recent investigations(22) have pointed out that ionizing radiation coagulates or diminishes the stability of positively charged colloids, but has little or no effect on negatively charged colloids.

Preparation of Radiocolloids. The preparation of pure radiocolloids has become of importance for a number of investigations, including fundamental studies of radiation effects on living tissue and therapeutic utilization of radioisotopes. It is valuable to have methods for the selective localization of radioisotopes in certain tissues. Finely dispersed anhydrous chromic phosphate has been found useful by Jones, Wrobel, and Lyons(21) in selective irradiation of the liver and spleen with P^{32} beta particles. For these types of investigations, colombium, yttrium, zirconium and lanthanum colloids are particularly suitable because of their short half-lives. Gofman(21) prepared several types of colloids of the above radioisotopes, varying in size and charge, stability toward flocculation with electrolytes, chemical structure and in particle size.

Colloidal suspensions of differing particle size of radioactive nuclides of zirconium, yttrium, colombium or lanthanum were prepared by varying the mol proportions of tartrate, lactate, or citrate ions at a given pH. Zirconium colloids of relatively large particle size were prepared by peptizing zirconium oxide or zirconyl chloride in dilute nitric acid, disodium acid phosphate or sodium lactate solution. Precise ranges of particle sizes were not determined.

Use of Dialysis and Liquid-Liquid Extraction as a Means of Investigation

Dialysis has been used quite extensively as a means of study in radioisotopic chemistry where the rate of diffusion, ion size and particle size were determined.

The diffusion coefficients of zirconium species in solutions of various acidities were measured by Jander and Jahr(28) and they found a decrease in the rate of diffusion with decrease in acidity. Their results were in agreement with the postulate that highly aggregated hydrolysis products were formed. The diffusion coefficient was determined by measuring the rate of diffusion of an ion from a radioactive solution contained in a cell into an external solution of the same composition but with no tracer added.

Schubert and Conn(39) dialyzed a solution of uranyl nitrate at its natural pH and containing most of the fission products and found that zirconium and colombium were the only fission products which did not dialyze completely. They also studied the effects of different reagents on the dialysis of zirconium, colombium, and lanthanum and found that the results were compatable with the known complexing action of the various reagents with zirconium.

Paneth and Havesky(39) utilized dialysis to study the diffusion coefficient for the purpose of determining the electrovalence of the radioelements in solution and of detecting radiocolloidal behavior.

Several investigators have attempted to determine size of various ions of radiocolloids in solution utilizing dialysis through permselective membranes. The limiting factor in their investigations has been that either the membrane pore size was not known or that the pore size was not uniform.

Electrodialysis, a direct current potential applied across an arrangement of permselective membranes, has been used by many investigators. Applications investigated by Mason,(29, 31) Willard(54) and Parsi(37) include: (1) deacidification, (2) electrolytic reduction of uranium VI to uranium IV, (3) conversion of salts to acids and bases, (4) separation of ions of like c arge, and (5) concentration or dilution of electrolyte solutions.

Various investigators have utilized extraction with complexing resins as a means of studying the chemistry of various radioisotopes. As was previously mentioned, Connick and McVey(15) utilized a two phase equilibrium system to study the chemistry of zirconium, in the +4 oxidation state, in dilute acid solutions. The equilibrium studied was between the various zirconium species in the aqueous phase and the thenoyl-trifluoracetone chelate of zirconium in the benzene phase.

Moore(33) studied the extraction of zirconium-95, at both tracer and macro concentrations, from aqueous solutions of nitric acid, hydrochloric acid, and oxalic acid into 0.5 molar thenoyl-trifluoracetone in xylene.

Other ion exchange resins have been used by investigators to determine extraction coefficients, ion size and ion charge.(28)

III. EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was: (1) to prepare and purify radiocolloids of zirconium-95 and promethium-147 (2) to study the extractibility of zirconium-95 and natural zirconium in nitric acid solution with thenoyl trifluoracetone and (3) to determine the pH of precipitation of promethium-147 in the presence of the nitrate ion.

Plan of Experimentation

A study of the preparation and purification of the radiocolloids of zirconium-95 and promethium-147 was planned. The application of electrodialysis was considered as a means of purification.

The pH of precipitation of promethium-147 in the presence of the nitrate ion was to be determined. Dialysis was considered as a means of study.

The investigation consisted also of a study of the colloidal nature of natural zirconium and zirconium-95 in nitric acid by comparing the extractibility of each with thenoyl trifluoracetone.

Materials

The materials used in this investigation, their specifications, the manufacturer or supplier and their uses are listed.

Ammonium Hydroxide. USP Aqua Ammonia 26° Baume.

Manufactured and distributed by E. I. DuPont De Nemours and Co., Inc., Wilmington, Delaware. Used to prepare basic solutions.

Dextrose. USP Dextrose (hydrous). Manufactured by Mallinckrodt Chemical Works, St. Louis, Missouri. Used to prepare colloidal zirconium phosphate.

Gelatin. USP, lot No. 793923. Purchased from Fisher Scientific Company, New York, N. Y. Used in colorimetric analysis of zirconium.

Hydrochloric Acid. CP, meets ACS specifications, lot No. D509187, assay 37.0-38.0% HCl. Specific gravity 1.19. Manufactured by General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in preparation of zirconium solutions.

Isotope (Cesium and Barium-137). Carrier free as CsCl in 0.965 normal hydrochloric acid, concentration: 6.94±10% mc/ml, radiochemical purity greater then 99%. Obtained February 6, 1958, from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. Used to prepare solutions of the radionuclides.

Isotope (Zirconium and Niobium-95). Carrier free as the oxalate in 0.60 normal oxalic acid. Zirconium concentration: 4.49± 5% mc/ml, niobium concentration: 4.35 mc/ml. Obtained April 1°, 1961, from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. Used to prepare solutions of the radionuclides.

Isotope (Promethium-147). Carrier free as the chloride in 0.42 normal hydrochloric acid. Promethium concentration: 1183.0±10% mc/ml. Obtained May 17, 1961, from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. Used to prepare solutions of the radionuclides.

Membrane, Cellophane. "Visking", seamless cellulose tubing, size "C", No. S-25275-C. Purchased from E. H. Sargent and Co., Chicago, Illinois. Used as a dialyzing membrane.

Membranes, Permselective. Cation exchange membrane 3142, anion exchange membrane 3148. Membranes are 8 mils thick; wet bursting strength, ca 200 psi. Excellent acid resistance. Limited mechanical ability in strong bases. Transport number in 0.15 normal sodium chloride; cation 0.995, anion 0.962. Manufactured by the Permutit Company, New York, N. Y. Used as electrodialyzing membrane.

Nitric Acid. CP, meets ACS specifications, lot No. D708011, assay 70% HNO_3. Specific gravity 1.42. Manufactured by J. R. Baker Chemical Company, Phillipsburg, New Jersey. Used to prepare zirconium solutions.

Perchloric Acid. CP, meets ACS specifications, lot No. G034, assay 60% $HClO_4$. Manufactured by Allied Chemical and Dye, General Chemical Division, New York, N. Y. Used in colorimetric analysis of zirconium.

Phenolphthalein. Reagent, meets ACS specifications, lot No. 42753. Manufactured by Merck and Company, Rahway, New Jersey. An equal water and alcohol solution used as indicator.

Potassium Hydrogen Phthalate. Reagent grade, lot No. 545805, meets ACS specifications, assay 99.93% potassium hydrogen phthalate. Purchased from Fisher Scientific Co., New York, N. Y. Used as primary standard in preparation of standard base solutions.

Pyrolcatechol Violet. CP, meets ACS specifications, lot No. 7589. Purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York. Used in colorimetric analysis of zirconium.

Resin, LA-1 Amberlite. Lot No. 3179. Purchased from Rohm & Haas Company, Philadelphia 5, Pennsylvania. Used for extraction experiments with zirconium.

Resin, LA-2 Amberlite. Lot No. 6120. Purchased from Rohm & Haas Company, Philadelphia 5, Pennsylvania. Used for extraction experiments with zirconium.

Sodium Acetate. Fisher Certified Reagent Grade, lot No. 545635. Purchased from Fisher Scientific Co., New York, N. Y. Used in colorimetric analysis of zirconium.

Sodium Hydroxide. Reagent grade, lot No. N353C, meets ACS specifications, minimum assay 97.0% NaOH. Manufactured by General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used to prepare standard base solutions.

Sodium Nitrate. Meets ACS specifications, analytical grade, assay 99.97% sodium nitrate, lot No. 7608. Purchased from Mallinckrodt Chemical Works, St. Louis, Missouri. Used as carrier in electrodialysis of promethium-147.

Sodium Phosphate Dibasic. Analytical reagent grade, pH range 1/15 molar solution - 9.0-9.3, lot No. 7917. Manufactured by Mallinckrodt Chemical Works, St. Louis, Missouri. Used in the preparation of colloidal zirconium phosphate.

Sulfuric Acid. CP, lot No. D407092, meets ACS specifications, assay 95.5-96.5% H_2SO_4. Specific gravity 1.84. Manufactured by General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in colorimetric analysis of zirconium.

Thenoyl Trifluoracetone. Purified. Purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York. Used to extract zirconium.

Thioglycollic Acid. 80% in water, analytical grade, lot No. 2249, purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York. Used in colorimetric determination of zirconium.

Water, Distilled. Obtained from Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used to prepare aqueous solutions.

Xylene. Analytical reagent grade, boiling range: 137-140°C, lot No. 8668. Purchased from Mallinckrodt Chemical Works, St. Louis, Missouri. Used as solvent for thenoyl trifluoracetone.

Zirconyl Chloride. Basic, purified, lot No. 762666. Purchased from Fisher Scientific Company, New York, N. Y. Used in the preparation of colloidal zirconium.

Zirconyl Nitrate. Purified, lot No. 782716. Purchased from Fisher Scientific Company, New York, N. Y. Used in the preparation of zirconium nitrate solutions for extraction.

Apparatus

The apparatus used in this investigation, the specifications for use, the manufacturer or supplier, and the use of the apparatus are given.

Absorber. Aluminum beta type, MSM property No. 21883, 28 milligrams per square centimeter and 139 milligrams per square centimeter. Used to distinguish between zirconium and niobium beta rays.

Ammeter. DC. Model 280, No. 140938, 0-10 amp. MSM property No. 13744. Manufactured by Weston Electric Company Instrument Corp., Newark, New Jersey. Used to measure current during electrodialysis.

Balance. Analytical, Type LCB, No. 31447, MSM property No. 13191, weighing 0 to 100 grams, to nearest 0.1 mg. Manufactured by William Ainsworth and Sons, Inc., Denver, Colorado. Used to weigh primary standard for titrating solutions and to weigh zirconium compounds for the exact normality of the solutions used.

Centrifuge. Clinical, Model CL, No. 50204H, 115 volts, 1 amp. Manufactured by International Equipment Company, Boston, Massachusetts. Used to separate zirconium precipitates from aqueous solution.

Counter. Geiger-Muller Tube, Model 10106, No. 589, 3.3 milligrams per square centimeter mica end window. Manufactured by Radiation Counter Laboratories, Inc., Skokie, Illinois. Used to measure activity of the radioisotopes.

Counting Dishes. Stainless steel, one inch diameter, 5/8 inch deep. Manufactured by Radiation Counter Laboratories, Inc., Skokie, Illinois. Used as containers for the radioisotopes to be counted.

Dosimeters. Type 541/A, direct reading, Nos. 07646, 0-200 milliroentgens. Manufactured by Victoreen Instrument Co., Cleveland, Ohio. Used to determine radiation dosage received by investigator.

Electrodialyzer. Constructed in Chemical Engineering Department Shop, Missouri School of Mines and Metallurgy, Rolla, Missouri. Built from sheet and 2 inch diameter cylinder "PVC" polyvinyl chloride plastic material. Consists of three cells of approximately 50 milliliters capacity each. The electrodes were made from platinum. Similar model described by Bub and Webb.(14)

Electrodialyzer. Made of glass by Ace Glass Company, Vineland, New Jersey on special order. Consists of 3 cells of approximately 100 ml capacity each. The electrodes were platinum. Used for carrying out the electrodialysis experiments.

Glassware. An assortment of standard glassware was used, including flasks, pipettes, funnels, crucibles, etc. Obtained from Quantitative Analysis Stockroom, Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri.

Heat Lamp. Infrared, type 7A-N, 110 volts, AC-DC, 2 amp. Manufactured by Prometheus Electric Corp., New York, N. Y. Used to dry samples for counting.

Oven. "Thelco", Model 15, Serial No. N-1, Temperature range to 150°C, 115 volts, 750 watts. Obtained from Precision Scientific Company, Chicago, Illinois. Used to dry samples for counting.

pH Meter. Leeds and Northrup Company, Model No. 7664-A1. 120 volts, 50 or 60 cycles. pH range 0 to 14 using L & N electrodes voltage ranges 0 to ± 1400 millivolts. Manufactured by Leeds and Northrup, Philadelphia 44, Pennsylvania. Used in measuring pH.

pH Meter. Beckman Zeromatic, Model No. 9600, with standard electrodes and holder. Operates on 110 to 250 volts, at frequencies of 40 to 60 cycles. pH range 0-14, millivolt range 0 to ± 700. Accuracy 0.1pH. Manufactured by Beckman Instruments, Inc., Fullerton, California. Used to measure pH.

Platinum. Metal sheet. Obtained from storeroom, Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used as electrodes for the three cell electrodialyzer.

Power Source. D.C. rectifier, MSM property No. 13296, 0-40 volts, approximately 8 amps. Used to provide current for electrodialyzer.

Scaler. Automatic counting scaler, Model B-1601, MSM property No. 21641, 105-135 volts, 50-60 cycle, 100 watts. Maximum counting rates, 100,000 counts per minute. Manufactured by NRD Instrument Co., St. Louis, Missouri. Used to record activity of samples.

Shaker. Burton Clinical Shaker, Model No. 1450, 60 cycle, voltage AC 110-120, Manufactured by Burton Manufacturing Company, Los Angeles 64, California.

Shield. Lead well "pig", MSM property No. 21641. Manufactured by NRD Instrument Company, St. Louis, Missouri. Used to shield counter from stray radiation.

Spectrophotometer. Beckman "Model B". Serial No. 13214. MSM property No. 21764. Manufactured by Beckman Instruments, Inc., Fullerton, California. Used in colorimetric analysis.

Thermometer. Range 0-150°C; obtained from stockroom, Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used to measure temperature of solutions.

Timer. Precision "Time-it", divisions to 1/10 second, 115 volts, 60 cycle, 5 watts. Manufactured by Precision Scientific Company, Chicago, Illinois. Used to determine flow rate through electrodialyzer.

Method of Procedure

The methods of procedure will be divided into four parts: (1) preparation of radiocolloids, (2) electrodialysis, (3) dialysis and (4) extraction.

Preparation of Radiocolloids

Preparation of Colloidal Zirconium-Oxide. Ten ml of 0.1 molar zirconium exychloride solution, mixed with an amount of zirconium-95 tracer solution to give the activity desired, was titrated to the phenolphthalein end-point with one normal sodium-hydroxide solution, resulting in the quantitative precipitation of the zirconium. The hydrated oxide precipitate was centrifuged out and the supernatant was discarded. The precipitate was suspended in 50 ml of 0.04 molar nitric acid and then shaken for 12-18 hours in a mechanical shaker to peptize the zirconium oxide. Following this, the mixture was centrifuged. The supernatant from this centrifugation was the final colloidal solution. This method of preparation is similar to that outlined by Gofman.(21)

Preparation of Colloidal Zirconium Phosphate Containing Zirconium-95. Two ml of 0.1 molar zirconium oxychloride was mixed with 46 ml of 5% dextrose solution and to this mixture was added 2 ml of 0.6 molar disodium acid phosphate.

Immediately a colloidal solution of zirconium oxide formed.

Glucose was used as a stabilizer. Should foreign ions flocculate the colloid, repeated extraction of the precipitate with the original volume of 5% glucose solution containing disodium acid phosphate, results in resuspension of the colloidal zirconium phosphate.(21) Gelatin can be used in place of glucose but is not as effective.

Preparation of Colloidal Zirconium Oxide-Promethium-147 Oxide. This radiocolloid was prepared in exactly the same manner as that outlined for colloidal zirconium oxide with the exception that the 0.1 molar zirconium oxychloride was mixed with promethium-147 instead of zirconium-95.

Zirconium serves as a carrier for the promethium-147 as promethium is an artificial element and does not exist in the natural form.

Preparation of Colloidal Zirconium - Promethium-147 Phosphate. Colloidal zirconium - promethium-147 phosphate was prepared in the same manner as that outlined for colloidal zirconium phosphate with the exception that the 0.1 molar zirconium oxychloride solution was mixed with promethium-147 instead of zirconium-95. Zirconium was used as a carrier for the promethium-147.

Method of Procedure for Electrodialysis Experiments

The following procedure was used in performing the electrodialysis experiments: (1) preparation of solutions, (2) assembling the electrodialyzer, (3) introduction of solutions to the electrodialyzer, (4) preparation of standard sample to determine recovery, (5) electrodialyzing the solution, (6) sampling, (7) radioactive counting and (8) calculation of radioisotope migration during electrodialysis.

Preparation of Solutions. The desired nitric acid concentration was obtained by diluting the required calculated volume of concentrated nitric acid with water in a volumetric flask. The nitric acid was measured with a burette and the volume required was calculated from the specific gravity of the acid. The exact normality of the solution was determined by titration with a standard base. Other materials needed to prepare blanks for the anode and cathode cells were weighed on an analytical balance or measured with a volumetric pipette.

Assembling the Electrodialyzer. The three cells with their membranes and rubber gaskets were bolted together by means of end blocks on the cells. The nuts were tightened evenly to prevent leakage around the gaskets. Connections to the electrodes were made by means of alligator clips and lead wires.

Introduction of Solutions to the Electrodialyzer. A feed solution, previously mixed with the radioisotope to give the desired activity, was then added to the center cell, Blanks containing the same materials as the feed cell less the radioisotope were added to the cathode and anode cells.

Preparation of Sample to Determine Recovery. To prevent error in calculated recovery due to adherence of zirconium on the membranes and cell walls, a sample was taken directly from the solution and placed in the center cell before electrodialysis was started. This sample was placed in a counting dish, dried, and counted.

Electrodialyzing the Solution. The electrodialysis was begun immediately after the addition of the solutions. The current was turned on and adjusted to give a current density of 90 milliamperes per square centimeter, when possible. Adjustment was made as needed in the resistance of the circuit in order to maintain a constant current density.

Sampling. One milliliter samples were pipetted from each cell at selected time intervals, dried, and counted. At the end of the experiment, a 10 ml sample was drawn from each cell and titrated with a standard base to determine the acid concentration.

Radioactive Counting. The 1 milliliter sample was dried in a stainless steel counting dish by means of an infrared heat lamp or oven. The samples were then counted with a Geiger-Muller tube.

The voltage applied to the Geiger-Muller tube was determined by obtaining a voltage plateau for the tube.

The background count was determined for a one-hour counting time. The samples were counted for a time to make the counting error less than 1.3 per cent. The same Geiger-Muller tube and scaler was used throughout in order to eliminate the need for correction due to dead time and tube efficiency.

Calculations. The values determined for each experiment were the total recovery of the radioisotope and the relative proportions of radioactivity in each cell. The total recovery was calculated as the combined activity from the cells compared to the standard sample. The relative proportion of radioactivity in each cell was calculated as the amount of radioactivity in each cell divided by the total activity. Both total recovery and relative proportion were expressed in percentage.

Method of Procedure for Dialysis Experiments

A solution containing the desired activity of promethium-147 was adjusted to a predetermined pH with a pH meter and was then checked for accuracy against a second pH meter. A blank solution, less the promethium-147, was adjusted to the same pH and the solutions were added to separate cells of a two cell dialyzer. The solutions were dialyzed until a constant activity was attained in each cell indicating that equilibrium was reached.

Sampling, sample preparation, radioactive counting and calculations were carried out in the same manner as that outlined in the electrodialysis procedure.

Method of Procedure for Extraction of Zirconium

The following procedure was used in the extraction of the zirconium: (1) preparation of solutions, (2) extraction of the solutions, (3) sampling, (4) analysis of zirconium and (5) calculations.

Preparation of Solutions. A 0.5 molar thenoyl trifluoracetone (TTA) solution in xylene was prepared by dissolving 11.1950 grams of thenoyl trifluoracetone in 100 milliliters of xylene.

Natural zirconium solutions in various nitric acid solutions were prepared as follows: A nitric acid solution containing the desired acid concentration was prepared by diluting the required amount of concentrated nitric acid with distilled water in a volumetric flask. The nitric acid was measured with a burette and the amount required was calculated from the specific gravity and concentration of the acid. The exact normality was then determined by titrating a sample with a standard base. To the prepared acid solution an amount of zirconium oxynitrate was then added to give a zirconium concentration ranging from 0.23-0.25 milligrams per milliliter.

Zirconium-95 solutions containing varying quantities of nitric acid were prepared as follows: A zirconium-95 tracer solution in 9.56 normal nitric acid was diluted to give an activity of 135-160 counts per second per milliliter. To this solution, concentrated nitric acid was added to give the approximate normality desired. The exact normality was then determined by titrating with standard base.

Solutions of a mixture of zirconium-95 and natural zirconium in nitric acid were prepared as follows: A zirconium-95 tracer solution of the desired acid normality was prepared as above and to this solution zirconium oxynitrate was added to give a natural zirconium content of 0.23-0.25 milligrams per milliliter.

These solutions were analyzed for zirconium content before extraction to check the error in preparing the solutions.

Extraction. Ten milliliter samples of the zirconium solutions were shaken with an equal volume of 0.5 molar TTA in xylene for 30 minutes in a mechanical shaker. The aqueous phase and organic phase were then separated by means of a separatory funnel.

The extraction was carried out at a temperature of 22± 1°C.

Sampling. One milliliter samples of the organic phase and the aqueous phase from the extraction of the radioactive solutions were pipetted into stainless steel counting dishes, dried, and counted.

In the case of the natural zirconium solutions, 5 milliliter samples were pipetted from the aqueous and organic phases and placed in separate 50 milliliter beakers.

Analysis of Zirconium. The amount of radioactive zirconium-95 in the samples was analyzed by a standard beta counting procedure. This procedure consists of placing the sample under a shielded Geiger-Muller tube and recording the activity through two aluminum absorbers by consecutive use of an absorber containing 139 milligrams of aluminum per square centimeter and a second containing 28 milligrams of aluminum per square centimeter.(24) The difference is the activity due to the beta emissions of zirconium-95. Periodic checks were made for contamination of the absorbers and counting chamber. The same geometry was used in all counting.

The voltage applied to the Geiger-Muller tube was that determined from a voltage plateau of the tube. The counting time used in all cases was of sufficient length to insure a counting error of less than 1.3 per cent.

The natural zirconium content in the samples was analyzed by the pyrolcathechol violet spectrophotocolorimetric method.

Calculations. From the data, the per cent of zirconium extracted, per cent not extracted, and total recovery were calculated.

As an example of the calculations involved in the analysis of the radioactive zirconium, use will be made of the table of ficticious data given below. The activities in this table, as in the experimental work, are corrected for background activity and tube efficiency.

Solution	cps/ml using 28 mg/cm^2 absorber	cps/ml using 139 mg/cm^2 absorber	cps/ml due to Zr-95
Feed	330	30	300*
Organic	270	20	250
Aqueous	60	10	50

*Activity of solution before extraction.

Per cent extracted $= \frac{250 \times 100}{300}$

Per cent not extracted $= \frac{50 \times 100}{300}$

Per cent recovery $= \frac{(250 + 50) \times 100}{300}$

A standard curve in which the optical density was plotted against the micrograms of zirconium per milliliter was used to determine the natural zirconium content of the sample. The calculations are common to those necessary for any colorimetric analysis.

Data and Results

The data and results obtained for this investigation are presented in the form of tables and graphs.

Tables I and II are the data and results obtained in the electrodialysis and dialysis of colloidal zirconium.

Table III is the data and results obtained in the separation of cesium-137 from colloidal zirconium phosphate by electrodialysis.

Table IV is the data and results obtained from the dialysis of promethium-147 at different pH values in the presence of the nitrate ion. Graphical representation of the results is presented in figure 1.

Tables V through XXIV are the data and results obtained from the extraction of natural zirconium and zirconium-95 at different nitric acid concentrations. Figure 2 is a graphical representation of the results and each point on the figure is the average of 20 separate determinations. The values presented in Tables V through XXIV have been treated statistically and the average standard deviation for all the values was found to be 1.6 per cent. The standard deviations varied from 1.30 to 1.80 per cent.

TABLE I

Electrodialysis of Colloidal Zirconium-95 Oxide in Nitric Acid Solutions

Acid Normality	Dialyzing Time (Hrs.)	Feed Solution (cps/ml)	Activity of Solutions after Electrodialysis Per Cent of Total: Feed Cell	Anode Cell	Cathode Cell	Total Recovery(1)
0.020	1.0	485	54.5	0.4	0.5	55.4
0.040	1.0	601	51.5	0.4	0.4	52.3
0.059	1.0	872	54.2	0.3	0.3	54.8
0.079	1.0	631	51.0	0.5	0.4	51.9
0.099	1.0	570	51.1	0.4	0.4	51.9

(1) Total recovery is low because of large deposit of colloidal zirconium-95 on cation membrane.

TABLE II

Dialysis of Colloidal Zirconium-95 Oxide in 0.06 Normal Nitric Acid Solution

Dialyzing Time (Hrs.)	Feed Solution (cps/ml)	Activity of Solution after Dialysis Per Cent of Total after Dialysis			
		Feed Cell	Anode Cell	Cathode Cell	Total Recovery
1	240	79.5	0.9	0.9	81.3

TABLE III

Electrodialysis of Colloidal Zirconium and Cesium-137 Mixture

Colloid	Time (Hrs.)	Feed Solution (cps/ml)	Activity of Solutions after Electrodialysis Per Cent of Total			
			Feed Cell	Anode Cell	Cathode Cell	Total Recovery
Zirconium Oxide	1.5	2850	34.5	0.5	67.0	102.0
Zirconium Oxide	3	2700	27.0	0.5	73.0	100.5
Zirconium Phosphate	3	99	59.0	7.5	22.8	89.3
Zirconium Phosphate	4	99	48.4	6.2	33.0	88.6

TABLE IV

Dialysis of Promethium-147 in Presence of Nitrate Ion through Nalfilm D-30 Membrane

pH	Dialyzing Time (Hrs.)	Feed Solution (cps/ml)	Activity of Solutions after Dialysis Per Cent of Total		
			Feed Cell	Blank Cell	Total Recovery(1)
3.00±.05	128	1500	34.0	34.0	68.0
6.00±.05	128	1450	4.6	6.5	11.1
6.50±.05	128	1400	7.6	6.2	13.8
7.00±.05	128	1496	8.4	6.0	14.4
7.10±.05	128	1510	8.6	2.9	11.5
7.20±.05	128	1500	8.7	1.5	10.2
7.30±.05	128	1410	9.6	1.6	11.2
7.50±.05	128	1490	8.8	1.3	10.1

(1) High activity of membrane after dialysis indicates that the promethium-147 was deposited upon them.

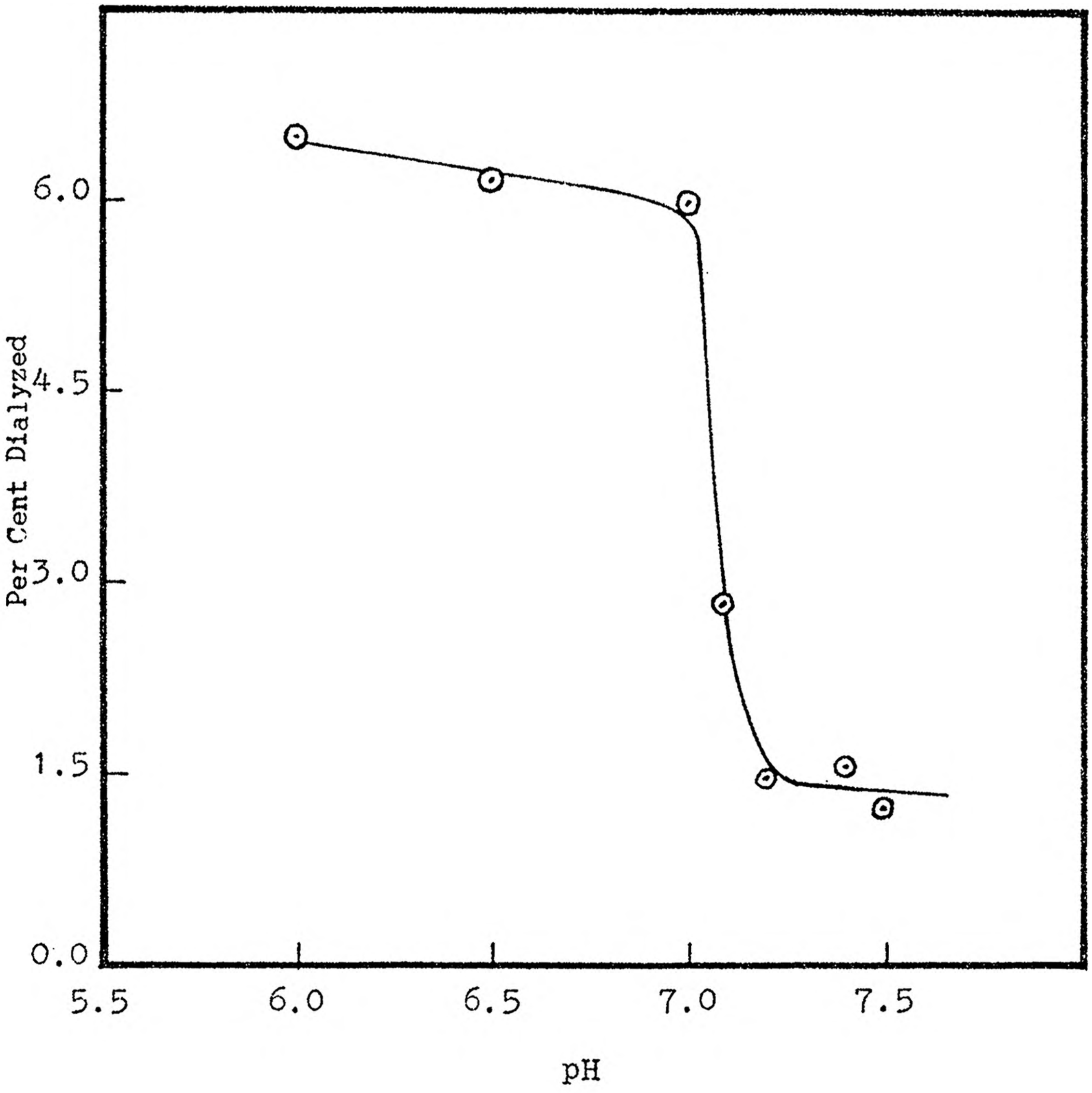

Figure 1. The Effect of pH on the Dialysis of Promethium-147 in the Presence of the Nitrate Ion.

TABLE V

TTA Extraction of Zirconium-95 in 0.9803 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	90.6	6.0	96.6
2	90.9	5.9	96.8
3	90.3	5.9	96.2
4	91.7	6.2	97.9
5	91.5	6.6	98.1
6	86.7	6.9	93.6
7	92.1	6.4	98.5
8	87.2	7.8	95.0
9	91.0	6.8	97.8
10	89.4	5.8	95.2

(1) Activity of feed solution for each run was 198 cps/ml.

TABLE VI

TTA Extraction of Zirconium-95 in 1.398 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	93.8	4.7	98.5
2	97.1	3.6	100.7
3	92.1	7.5	99.6
4	93.8	7.2	101.0
5	94.2	8.4	102.6
6	94.5	5.4	99.9
7	93.0	8.2	101.2
8	92.6	4.7	97.3
9	92.5	7.6	100.1
10	94.0	7.4	101.4

---

(1) Activity of feed solution for each run was 156 cps/ml.

TABLE VII

TTA Extraction of Zirconium-95 in 1.860 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	98.5	5.2	103.7
2	98.2	4.6	103.8
3	96.0	5.4	101.4
4	101.6	5.2	106.8
5	96.0	6.7	102.7
6	98.1	5.4	103.5
7	96.8	4.9	101.7
8	98.8	3.2	102.0
9	96.7	5.9	102.6
10	98.8	4.4	103.2

(1) Activity of feed solution for each run was 135 cps/ml.

TABLE VIII

TTA Extraction of Zirconium-95 in 2.4515 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	98.7	1.7	100.4
2	97.9	1.9	99.8
3	98.8	3.2	102.0
4	98.8	1.4	100.2
5	97.9	0.7	98.6
6	97.8	1.8	99.6
7	98.5	6.0	104.5
8	98.9	1.2	100.1
9	99.5	1.1	100.6
10	96.3	1.8	98.1

---

(1) Activity of feed solution for each run was 155 cps/ml.

TABLE IX

TTA Extraction of Zirconium-95 in 2.9356 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	98.0	4.2	102.2
2	98.0	4.2	102.2
3	98.9	0.2	99.1
4	101.0	1.6	102.6
5	99.2	1.6	100.8
6	99.7	0.0	99.7
7	97.9	2.7	100.6
8	100.0	0.7	100.7
9	99.6	1.9	101.5
10	99.9	0.0	99.9

(1) Activity of feed solution for each run was 157 cps/ml.

TABLE X

TTA Extraction of Natural Zirconium in 0.9991 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	103.9	0.0	103.9
2	99.6	0.9	100.5
3	99.6	0.0	99.6
4	94.4	1.3	95.7
5	99.6	0.4	100.0
6	99.6	0.9	100.5
7	100.0	0.0	100.0
8	93.1	0.3	94.4
9	98.7	0.9	100.6
10	102.7	0.9	103.6

---

(1) Concentration of feed solution for each solution was 0.23 mg/ml.

TABLE XI

TTA Extraction of Natural Zirconium in 1.4832 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	99.6	0.8	100.4
2	100.0	0.0	100.0
3	97.1	0.0	97.1
4	95.8	0.8	96.6
5	101.0	0.0	101.0
6	97.9	1.3	99.2
7	98.3	0.0	98.3
8	100.8	0.4	101.2
9	99.0	1.8	101.8
10	98.8	1.2	100.0

---

(1) Concentration of feed solution for each solution was 0.24 mg/ml.

TABLE XII

TTA Extraction of Natural Zirconium in 1.9596 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	99.3	0.9	100.2
2	97.8	0.9	98.7
3	99.1	0.4	99.5
4	100.9	0.0	100.9
5	99.1	0.9	100.0
6	100.4	0.0	100.4
7	100.0	0.9	100.9
8	100.0	0.4	100.4
o	98.2	0.0	98.2
10	101.8	0.0	101.8

---

(1) Concentration of feed solution for each solution was 0.23 mg/ml.

TABLE XIII

TTA Extraction of Natural Zirconium in 2.4102 Normal Nitric Acid Solution$^{(1)}$

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Recovery
1	100.4	0.0	100.4
2	100.0	0.9	100.9
3	97.4	0.0	97.4
4	100.9	0.9	101.8
5	100.0	0.0	100.0
6	98.7	0.9	99.6
7	101.7	0.0	101.7
8	98.3	0.0	98.3
o	100.9	0.9	101.8
10	100.4	1.3	101.7

---

(1) Concentration of feed solution for each solution was 0.23 mg/ml.

TABLE XIV

TTA Extraction of Natural Zirconium in 2.9356 Normal Nitric Acid Solution(1)

Run No.	Per Cent Extracted	Per Cent Not Extracted	Per Cent Total Pecovery
1	100.4	0.0	100.4
2	100.0	0.4	100.4
3	99.2	0.0	99.2
4	99.6	0.8	100.4
5	100.8	0.0	100.8
6	100.0	0.0	100.0
7	100.8	0.4	101.2
8	98.8	0.4	99.2
9	98.8	0.0	98.8
10	100.0	0.0	100.0

---

(1) Concentration of feed solution for each solution was 0.24 mg/ml.

TABLE XV

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 0.9723 Normal Nitric Acid Solution(1)

Run No.	Zirconium-95 Per Cent Extracted	Zirconium-95 Per Cent Not Extracted	Zirconium-95 Per Cent Total Recovery
1	89.5	8.8	98.3
2	89.1	10.6	99.7
3	88.1	6.8	94.9
4	91.4	9.0	101.4
5	91.2	5.6	96.8
6	92.4	10.3	102.7
7	91.8	8.7	100.7
8	86.7	10.5	97.2
9	91.0	9.2	100.2
10	90.2	8.9	99.1

---

(1) Activity of feed solution for each run was 135 cps/ml.

TABLE XVI

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 1.4523 Normal Nitric Acid Solution(1)

Run No.	Zirconium-95 Per Cent Extracted	Zirconium-95 Per Cent Not Extracted	Zirconium-95 Per Cent Total Pecovery
1	93.3	6.7	100.0
2	91.9	9.2	101.1
3	91.5	10.1	101.6
4	93.1	7.4	100.5
5	95.6	8.6	104.2
6	92.2	7.5	99.7
7	91.3	8.6	99.9
8	91.4	10.3	101.7
9	89.9	7.6	97.5
10	93.7	6.7	100.4

---

(1) Activity of feed solution for each run was 148 cps/ml.

TABLE XVII

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 1.9725 Normal Nitric Acid Solution(1)

Run No.	Zirconium-95 Per Cent Extracted	Zirconium-95 Per Cent Not Extracted	Zirconium-95 Per Cent Total Recovery
1	95.2	6.5	101.7
2	96.7	7.9	104.6
3	98.4	2.7	101.1
4	95.1	1.6	96.7
5	96.1	3.4	99.5
6	94.7	4.0	98.7
7	98.2	6.2	104.4
8	95.3	7.1	102.4
9	96.1	3.7	99.8
10	96.5	2.7	99.2

---

(1) Activity of feed solution for each run was 144 cps/ml.

TABLE XVIII

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 2.3690 Normal Nitric Acid Solution(1)

Run No.	Zirconium-95 Per Cent Extracted	Zirconium-95 Per Cent Not Extracted	Zirconium-95 Per Cent Total Recovery
1	97.1	0.2	97.3
2	98.3	0.2	98.5
3	97.8	2.2	100.0
4	99.3	2.7	102.0
5	98.5	1.5	100.0
6	99.7	5.3	105.0
7	98.1	1.5	99.6
8	98.5	1.8	100.3
9	98.5	1.8	100.3
10	98.2	2.0	100.2

---

(1) Activity of feed solution for each run was 150 cps/ml.

TABLE XIX

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 2.7604 Normal Nitric Acid Solution(1)

Run No.	Zirconium-95 Per Cent Extracted	Zirconium-95 Per Cent Not Extracted	Zirconium-95 Per Cent Total Recovery
1	98.5	1.6	100.1
2	97.2	2.1	99.3
3	100.1	0.4	100.5
4	99.4	0.6	100.0
5	99.9	0.5	100.4
6	98.6	0.8	99.4
7	96.6	2.2	98.8
8	100.2	0.0	102.0
9	98.1	1.1	99.2
10	99.4	0.6	100.0

---

(1) Activity of feed solution for each run was 158 cps/ml.

TABLE XX

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 0.9723 Normal Nitric Acid Solution(1)

Run No.	Zr-Natural Per Cent Extracted	Zr-Natural Per Cent Not Extracted	Zr-Natural Per Cent Total Recovery
1	99.2	0.00	99.2
2	100.0	0.00	100.0
3	100.0	0.40	100.4
4	99.2	0.40	99.6
5	100.8	0.40	101.2
6	98.4	0.40	98.8
7	100.0	0.40	100.4
8	98.0	0.40	98.4
9	99.6	0.80	100.4
10	100.4	0.80	101.2

---

(1) Concentration of feed solution for each solution was 0.24 mg/ml.

TABLE XXI

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 1.4523 Normal Nitric Acid Solution(1)

Run No.	Zr-Natural Per Cent Extracted	Zr-Natural Per Cent Not Extracted	Zr-Natural Per Cent Total Recovery
1	99.1	2.4	101.5
2	98.1	2.4	100.5
3	98.0	3.1	101.1
4	99.6	0.0	99.6
5	99.2	0.4	99.6
6	96.5	0.4	96.9
7	99.6	0.4	100.0
8	100.0	0.0	100.0
9	99.6	0.4	100.0
10	100.8	0.0	100.8

---

(1) Concentration of feed solution for each solution was 0.25 mg/ml.

TABLE XXII

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 1.9725 Normal Nitric Acid Solution(1)

Run No.	Zr-Natural Per Cent Extracted	Zr-Natural Per Cent Not Extracted	Zr-Natural Per Cent Total Recovery
1	98.8	2.1	100.9
2	97.5	2.9	100.4
3	100.4	0.0	100.4
4	100.0	0.0	100.0
5	99.1	0.0	99.1
6	100.0	0.0	100.0
7	99.1	0.0	99.1
8	99.1	4.7	103.8
9	100.0	0.0	100.0
10	98.7	6.6	105.3

---

(1) Concentration of feed solution for each solution was 0.23 mg/ml.

TABLE XXIII

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 2.3690 Normal Nitric Acid Solution(1)

Run No.	Zr-Natural Per Cent Extracted	Zr-Natural Per Cent Not Extracted	Zr-Natural Per Cent Total Recovery
1	99.6	1.8	101.4
2	100.0	0.0	100.0
3	100.0	1.8	101.8
4	99.1	0.9	100.0
5	100.4	0.9	101.3
6	100.0	0.0	100.0
7	102.2	0.0	102.2
8	99.6	1.8	101.4
9	100.1	1.0	101.1
10	99.0	0.9	99.9

---

(1) Concentration of feed solution for each solution was 0.23 mg/ml.

TABLE XXIV

TTA Extraction of Zirconium in Zirconium-95 and Natural Zirconium Mixture in 2.7604 Normal Nitric Acid Solution(1)

Run No.	Zr-Natural Per Cent Extracted	Zr-Natural Per Cent Not Extracted	Zr-Natural Per Cent Total Recovery
1	98.7	1.4	100.1
2	100.9	1.4	102.3
3	100.0	1.7	101.7
4	99.2	0.0	99.2
5	99.2	1.7	100.9
6	99.6	2.5	102.1
7	101.6	0.8	102.4
8	100.0	0.0	100.0
9	97.5	1.7	99.2
10	100.8	0.0	100.8

---

(1) Concentration of feed solution for each solution was 0.24 mg/ml.

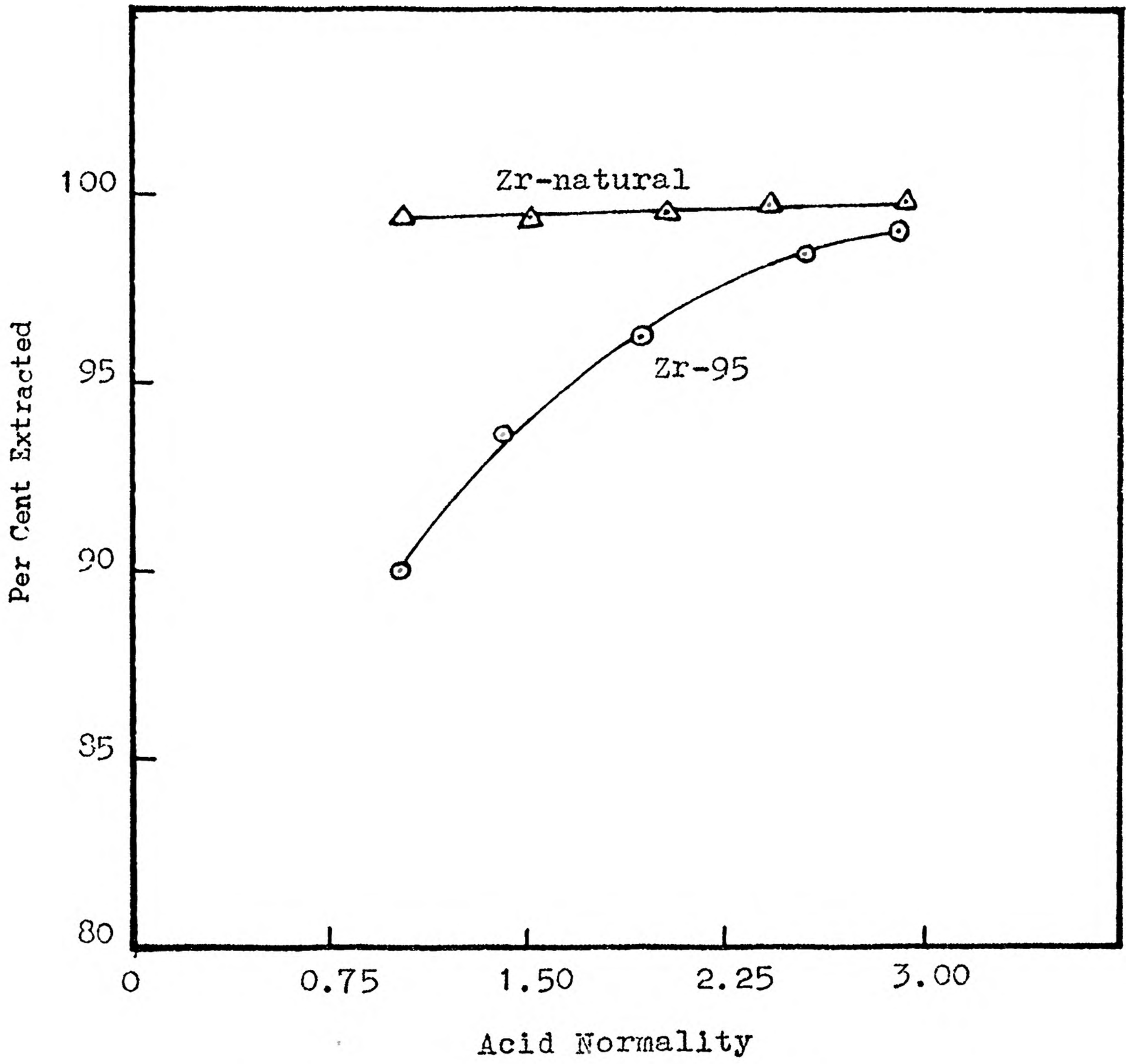

Figure 2. Comparison of the Extraction of Zirconium-Natural and Zirconium-95 in Nitric Acid with Thenoyl Trifluoracetone in Xylene.

IV. DISCUSSION

The discussion is comprised of three parts: (1) discussion of results, (2) limitations, and (3) recommendations.

Discussion of Results

The results of the investigation are discussed in the same order as the data were presented.

Preparation of Radiocolloids. The procedures for the preparation of the radiocolloids of zirconium-95 and promethium-147 are presented, in detail, in the experimental section of this thesis.

Preparation of radiocolloids by these methods has several advantages over previous methods of preparation. For one, the activity of the final colloidal solution is controlled by the amount of tracer solution added to the zirconyl chloride solution. Secondly, radiocolloids of other nuclides can be prepared by the same procedures. For example, radiocolloids of all the zirconium and promethium nuclides can be prepared by this method as well as radiocolloids of nuclides with chemistry similar to zirconium and promethium. These include the nuclides of niobium, lanthanum, yttrium, samarium, europium and other nuclides which exist in the same atomic series as zirconium and promethium. Of particular importance is that these series include nuclides of short, intermediate, and long half-life, some of which emit only beta particles, some, only gamma rays, and others, both beta and gamma rays.

In the case of the colloidal zirconium-oxide, the effective peptizing agent is probably the zirconyl ion produced by the reaction of the zirconium oxide with the hydrogen ions.(21) It is suspected that this same type of mechanism is the method by which many other nuclides, similar to zirconium, will form radiocolloids.

The glucose used in the preparation of the colloidal zirconium phosphate is present for the purpose of rendering the solution nearly isotonic. Inorganic salts are not used since weak saline solutions have produced immediate flocculation of colloidal zirconium phosphate in some cases.(21) Gelatin would probably serve the same purpose as glucose in stabilizing the radiocolloid but is not as desirable for therapeutic uses.

In Table I, the effect of increasing acid concentration on the amount of colloid formed has been studied. In the low nitric acid range, increasing the acid concentration has very little effect on the amount of colloid formed. The effect of acid concentration on particle size, stability, and charge cannot be predicted from the results obtained; however, it is known to affect all three of these variables to some extent.

Purification of Radiocolloids by Electrodialysis. The results of separating colloidal zirconium from cesium-137 indicate that a better separation is achieved with colloidal zirconium-oxide in a shorter length of time than with colloidal zirconium phosphate. This can be explained in that the colloidal zirconium phosphate is negatively charged and deposits on the cation membrane preventing the passage of the cesium-137. The colloidal zirconium oxide is neutral and does not migrate to either membrane.

In both cases, time seems to be a limiting factor. Also, in the case of colloidal zirconium phosphate, the deposition of the colloid on the cation membrane limits the amount of separation possible. The amount of colloidal zirconium phosphate present in solution is continually being reduced due to the tendency of the colloid to deposit itself on the cation membrane.

This difference in results between colloidal zirconium-oxide and the phosphate points out that purification of radiocolloids by electrodialysis is feasible in some cases and not in others.

<u>Dialysis of Promethium-147</u>. The pH of precipitation of promethium-147 in the presence of the nitrate ion was determined to be 7.10±.05. This is in close agreement with the value one might predict based on the pH of precipitation of samarium and neodynium in the presence of the nitrate ion. The pH of precipitation of promethium should lie between the values known for samarium and neodynium, which are 6.90 and 7.30, respectively. The increase in the rate of dialysis with increasing hydrogen ion concentration is

attributable to the fact that the size of the promethium species in nitric acid solution decreases with acid normality.

Results obtained from electrodialysis experiments performed at various hydrogen ion concentrations were erratic. It is possible that this is due to fluctuations in the current density.

Extraction of Zirconium in Nitric Acid Solution. The extraction of zirconium-95 in nitric acid solution, with the complexing agent thenoyl trifluoracetone, is dependent on the acid concentration. The amount of zirconium-95 extracted increases with increasing acid normality and a maximum is reached in the vicinity of 3 normal nitric acid solution. At this acid concentration, practically 100 per cent of the zirconium-95 is extracted.

The results of the extraction of natural zirconium under the same conditions indicates that while it is dependent upon acid concentration, it is dependent to a much lesser degree. Only about a 0.5 to 1.0 per cent difference in extraction between 1 normal and 3 normal acid strengths is noted with natural zirconium while a difference of about 10 per cent is observed with the zirconium-95.

The difference in the extraction of zirconium-95 and natural zirconium increases with decreasing acid concentration. (Note figure 2) However, in the 3 normal acid range, both the zirconium-95 and natural zirconium are almost 100 per cent extractable. This difference in extraction can be explained by the supposition that the zirconium-95 is more colloidal in nature than the natural zirconium at nitric acid concentrations below 3 normal. It has been pointed out by a number of investigators(28) that as the nitric acid concentration decreases, zirconium species in solution become more highly hydrated, resulting in the formation of a more highly aggregated or polymerized hydrated product. One could then theorize that the zirconium-95 is more easily hydrated than the natural zirconium owing to the effect of ionizing radiation furnishing energy to the water molecules. While both the natural and radioactive zirconium would be forming larger, more aggregated, hydrated products with decreasing acid concentration, the radioactive zirconium would be doing so to a greater extent. If this were true, radioactive zirconium would exhibit a more colloidal nature than would the natural zirconium in the same acid concentration and would be extracted to a lesser extent.

This theory can be supported further in that the difference in ion size and charge between zirconium-95 and natural zirconium is not great enough to explain the large difference in extraction between the two; therefore, the difference must be due to radiation effects and very possibly to the radiation effect previously mentioned.

The optimum acid concentration for the extraction of both natural and radioactive zirconium under the conditions outlined is 3 normal. The mixing of natural zirconium and zirconium-95 has little effect on their extraction.

Extractions were performed on solutions of zirconium in various acids using Amberlite Resins, LA-1 and LA-2, as the extracting agent. Results indicated that these agents do not extract zirconium.

Limitations

The limitations which might have effected the results are discussed below.

Sampling. The samples for counting and for the colorimetric analysis were removed with a volumetric pipette. Small volume errors could cause error in the activity counted and in the colorimetric determination of the zirconium concentration.

Sample Preparation. The samples used for counting were dried beneath an infrared heat lamp, and a motor-driven rotary platform was utilized to aid in distributing the sample uniformly over the counting dish. This does not, however, guarantee that every sample will be evenly distributed over the dish, and a variation in sample thickness can cause considerable error.

Radiocounting. The random nature of radioactive disintegrations leads to error which is inversely proportional to the counting time.

The results in this investigation have a standard deviation, due to radioactive counting, of less than 1.3 per cent.

Overman and Clark(35) list the following errors as being characteristic of radioactive measurements:

(1) Random disintegration process and, therefore, random emission of radiation.

(2) Failure of the detector to resolve events at higher counting rates.

(3) Variation in performance of scalers due to changes in temperature, applied voltage and efficiency.

(4) Changes in the detectors (Geiger-Muller tubes) due to aging.

(5) Erratic performance of electronic equipment and the mechanical register.

Colorimetric Analysis. The results in this investigation have a standard deviation of less than 1.4 per cent. Willard, Merritt and Dean(55) list the following errors as common to colorimetric analysis:

(1) Nonlinearity of response of the light sensitive devices and the associated measuring circuits.

(2) Variations in intensity of the source.

(3) Stray light striking the cells.

(4) A rise in temperature of the measuring photocells.

(5) Dust, scratches, and imperfections in the optical system.

In spite of these errors, the precision of measurement of a carefully designed instrument is greater than the precision attained by reproducing colors.

Recommendations

The results of the investigation indicate that valuable results could be obtained by extending the work on the extraction of zirconium to include acid normalities below the 1 normal range. This effect should also be studied in regard to other nuclides and their natural element.

The information concerning the purification of radiocolloids by electrodialysis could be extended by applying this method to the purification of other colloids and their probable contaminants. Purification of colloids of lanthanum, yttrium, and colombium should be investigated.

V. CONCLUSIONS

This investigation makes possible the following conclusions:

Preparation of Radiocolloids. The following conclusions concerning the preparation of radiocolloids can be made:

(1) Radiocolloids of zirconium and promethium in the form of their oxides and phosphates can be prepared. It is also possible that radiocolloids of many other nuclides can be prepared in the same manner as the zirconium and promethium colloids.

(2) In the low concentration of nitric acid, .02 to .10 normal, increasing the acid concentration has little effect on the amount of radiocolloid formed.

Purification of Radiocolloids by Electrodialysis. The following conclusion concerning the purification of radiocolloids by electrodialysis can be made:

(1) Purification of radiocolloids by electrodialysis is feasible in some instances and not in others. The purification of radiocolloids by electrodialysis is dependent on the nature of the radiocolloid and its contaminant.

(2) Time is a limiting factor in the purification of radiocolloids by electrodialysis. The amount of contaminant electrodialyzed from radiocolloidal solutions is time dependent.

Dialysis of Promethium-147. The following conclusions regarding the dialysis of promethium-147 can be made:

(1) Dialysis can be used as a means of determining the pH of precipitation.

(2) The pH of precipitation of promethium-147 in the presence of the nitrate ion as determined by dialysis is 7.10±.05.

(3) Electrodialysis cannot be used for the determination of pH of precipitation because the fluctuating current density gives erratic results.

Extraction of Zirconium. The following conclusions regarding the extraction of zirconium in nitric acid solution with thenoyl trifluoracetone can be made:

(1) The extraction of zirconium-95 is dependent upon the acid concentration. The amount of zirconium-95 extracted increases with increasing acid normality.

(2) The extraction of natural zirconium is dependent upon acid concentration but to a much lesser degree than is zirconium-95.

(3) There is a marked difference in the extraction of natural zirconium and zirconium-95 and this difference increases with decreasing acid normality.

(4) The optimum acid concentration for the extraction of zirconium-95 and natural zirconium is 3.0 normal.

(5) Amberlite Resins, LA-1 and LA-2, will not

extract zirconium from nitric, hydrochloric, or sulfuric acid solutions.

VI. SUMMARY

Procedures for the preparation of radiocolloids of zirconium-95 and promethium-147 in the form of their oxides and phosphates have been outlined. It has been shown that electrodialysis can be used as a means of purifying certain radiocolloids.

The pH of precipitation of promethium-147 in the presence of the nitrate ion was found to be 7.10±.05.

A difference in the extraction of zirconium-95 and natural zirconium was found. The extraction of both zirconium-95 and natural zirconium were found to be dependent upon acid concentration. The optimum acid concentration for the extraction of both zirconium-95 and natural zirconium is in the 3 normal range.

VII. BIBLIOGRAPHY

1. Adler, I. and J. Steigman: Adsorption of UX_1 and RaE by an Aqudag Coated Dipping G-M Tube, J. Phy. Chem., 56, 493 (1952).

2. Alimarin, I. P. and N. A. Rudney: Use of Radioactive Isotopes in Analytical Chemistry, Zhurnal Analitcheskoi Khimii, 12, 5--587 (1957); A.E.R.E. Lib/Trans., No. 788.

3. Benedict, Manson and T. H. Pigford: "Nuclear Chemical Engineering," p. 6. McGraw-Hill Book Company, Inc., New York, N. Y., 1957.

4. Blumenthal, W. B.: "The Chemical Behavior of Zirconium," p. 56. D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958.

5. ibid, p. 243.

6. ibid, p. 245.

7. ibid, p. 285.

8. ibid, p. 286.

9. Bonner, N. A. and Milton Kahn: Behavior of Carrier-free Tracers, "Radioactivity Applied to Chemistry" (A. C. Wahl and N. A. Bonner, Editors), p. 102. John Wiley, Inc., New York, N. Y., 1951.

10. ibid, p. 145.

11. Bouissieres, George, Raymond Chasted, and Leopold Vigneron: States of Dispersion of Polonium in Water, Alcohol, and Acetone, Compt. Rend., 224, 43 (1947): C. A., 41, 2676 (1947).

12. Bruce, F. R., J. M. Fletcher, H. H. Hyman, and J. J. Katz: "Process Chemistry," Series III, Vol. 1, p. 350. Pergamon Press Ltd., London, England, 1956.

13. ibid, p. 351.

14. Bub, G. J. and W. H. Webb: Electrodialysis Unit for Fission Product Separation, The Review of Scientific Instruments, 32, 7, 857 (1961).

15. Connick, R. E. and W. H. McVey: The Aqueous Chemistry of Zirconium, J. A. C. S., 71, 3182-92 (1949).

16. Dutli, J. W. and C. M. Taylor: J. Soc. Non-Destructive Testing XII, No. 2, pp. 35-38 (1954).

17. Finston, H. L. and M. T. Kinsley: The Radiochemistry of Cesium, NAS-NA 3035, Office of Technical Services, Department of Commerce, Washington 25, D. C. (1961).

18. Gauwerky, R.: Proc. U. N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, 26, P. 974, pp. 372-373 (1958).

19. Glasstone, Samuel: "Principles of Nuclear Reactor Engineering," p. 116. D. Van Nostrand Co., Inc., Princeton, New Jersey, (1955).

20. Godlewski, Tadeusz: Solutions of Radioactive Products, Le Radium, 10, pp. 250-264 (1913); C. A., 8, p. 298 (1914).

21. Gofman, J. W.: Studies with Colloids Containing Radioisotopes of Yttrium, Zirconium, Niobium, and Lanthanum, AECD-2057, (1948).

22. Haissinsky, M. and W. J. Gluzbarg: Action of Ionizing Radiations on Colloidal Solutions, Compt. Rend., 233, pp. 1192-1194 (November 12, 1951); C. A., 46, 3367 (1952).

23. Hahn, Otto: "Applied Radiochemistry," pp. 50-63. Cornell University Press, Ithaca, N. Y., (1936).

24. Huffman, E. H. and L. J. Beaufait: The Fractional Separation of Zirconium and Hafnium by Extraction with Thenoyl trifluoracetone. J. A. C. S., 71, p. 3179 (1949).

25. Kurbatov, J. D. and J. H. Kurbatov: Isolation of Radioactive Yttrium and Some of its Properties in Minute Concentrations, J. Phys. Chem., 46, pp. 441-457 (1942).

26. ______________________________: Target Chemistry of Zirconium and Yttrium, J. Chem. Phy., 13, p. 208 (1945).

27. Larsen, E. M. and A. M. Gammill: Electrometric Titrations of Zirconium and Hafnium Solutions. J. A. C. S., 72, p. 3615 (1950).

28. Lister, B. A. and L. A. McDonald: Some Aspects of the Solution Chemistry of Zirconium, J. Chem. Soc., p. 4315 (1952).

29. Mason, E. A. and Walter Juda: Applications of Ion Exchange Membranes in Electrodialysis, Chemical Engineering Progress Symposium Series, No. 24, Vol. 55, pp. 155-162, (1959).

30. Mason, E. A. and E. J. Parsi: Applications of Ion Transfer Membranes in Nuclear Chemical Processing, A/Conf 15/P/502, (1958).

31. _____________, E. J. Parsi, and A. S. Giuffrida: Ion Transfer Membranes Remove Bulk Electrolyte in Radioactive Waste. Chemical Engineering Progress, 54, 2--93, (1958).

‾2. Mayer, S. W. and M. E. Morton: Colloidal Zirconyl Radio-phosphate, Nucleonics, 13, 11--98, (1955).

33. Moore, F. L.: Separation of Zirconium from Other Elements by Liquid-Liquid Extraction, Anal. Chem., 28, p. 997, (June, 1956).

34, Morrow, P. E., R. J. Della Rosa, L. J. Casarett, and G. J. Miller: A Preliminary Investigation of Some Radiocolloidal Properties of Po^{210} using Molecular Filters, UR-363, (1954).

35. Overman, R. T. and H. M. Clark: "Radioisotope Techniques," pp. 98-130. McGraw-Hill Book Company, Inc., New York, N. Y., (1960).

36. Paneth, F.: Colloidal Solutions of Radioactive Substances, Kolloid Zhur., 13, 1-4 (1914); C. A., 8, 297, (1914).

37. Parsi, E. J.: The Electrochemical Utilization of Ion Exchange Membrane in AEC Operations, ORNL-1812, (1955).

38. Schubert, Jack: The Colloidal Behavior of Some Fission Products, AECD-1910, (1948).

39. Schubert, Jack and E. E. Conn: Radiocolloidal Behavior of Some Fission Products, Nucleonics, 4, 6--2, (1949).

40. ibid, p. 5.

41. ______________ and J. W. Richter: The Use of Ion Exchangers for the Determination of Physicochemical Properties of Substances, Particularly Radiotracers in Solution. III. Radiocolloids of Zirconium and Niobium, J. Coll. Science, 5, pp. 376-385, (1950).

42. Schweitzer, G. K. and W. M. Jackson: Studies in Low Concentration Chemistry. VII. The Role of Adsorption in Radiocolloid Formation, J. Am. Chem. Soc., 76, pp. 941-944, (1954).

43. _________________ and Morrison Jackson: Radiocolloids, J. Chem. Ed., 29, p. 513, (1952).

44. ibid, p. 514.

45. ibid, p. 515.

46. ibid, pp. 518-519.

47. Schweitzer, G. K. and J. W. Nehls: Low Concentration Chemistry. IV. The Radiocolloidal Properties of Beryllium, J. Am. Chem. Soc., 75, pp. 4353-4356, (1953).

48. _________________, B. R. Stein, and W. M. Jackson: Studies in Low Concentration Chemistry. III. The Radiocolloidal Properties of Yttrium-90, J. Am. Chem. Soc., 75, pp. 793-795, (1953).

49. Steinberg, E. P. and L. E. Glendenin: Survey of Radiochemical Studies of the Fission Process, "Nuclear Chemistry and the Effects of Irradiation," Vol. 7, Proceedings of the International Conference of the Peaceful Uses of Atomic Energy, held in Geneva, August 8-20, pp. 3-14, (1955).

50. Vickery, R. C.: Chemistry of the Lanthanons, p. 55. Academic Press, Inc., New York, N. Y., (1953).

51. ibid, p. 51.

52. Werner, O. Z.: Nature of the So-Called Radiocolloids, Z Physik. Chem. A., 156, p. 89, (1931); C. A., 26, p. 112, (1932).

53. ______________: The State of Subdivision of Dissolved Substances in Extreme Dilution, Mikrochemir, 4, pp. 360-368, (1931); C. A., 26, p. 358, (1932).

54. Willard, H. H. and J. J. Finley: An Evaluation of Selective Electrodialysis, K-1219, (1956).

55. Willard, H. H.,L. L. Merritt, and J. A. Dean: Instrumental Method of Analysis, D. Van Nostrand Company, Inc., Princeton, New Jersey, pp. 45-47. (1958).

VIII. ACKNOWLEDGMENTS

The author wishes to thank Dr. William H. Webb for his generous help and encouragement throughout the investigation.

He is grateful for the financial assistance provided by the Atomic Energy Commission's Grant No. AT(11-1) - 770.

He also wishes to thank his wife for her help in typing this thesis.

IX. VITA

James N. Click, son of James M. and Iva C. Click, was born December 19, 1937 in Blytheville, Arkansas.

He attended public elementary and secondary schools in West Plains, Missouri and received his high school diploma from West Plains High School in May, 1955.

He attended Missouri University at Columbia, Missouri from September, 1955 to June, 1957.

He was married to the former Janis R. Rickman, daughter of James R. and Frances C. Rickman on August 18, 1957 at which time he moved to Springfield, Missouri and enrolled at Southwest Missouri State College. He received the Bachelor of Science degree from this institution in May, 1960.

He was employed as a chemist at Hoffman-Taff, Inc., Springfield, Missouri from February, 1958 to June, 1960.

In September, 1960, he entered the Graduate School of the Missouri School of Mines and Metallurgy to complete the requirements for the Master of Science Degree in Chemistry. During his pursuit of graduate work at the Missouri School of Mines and Metallurgy, he served as a graduate assistant from September, 1960 to June, 1961 and as an NDEA fellow beginning in September, 1961, which position he still holds.