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A STUDY OF THE BEHAVIOR

OF ZIRCONIUM IN AQUEOUS SOLUTIONS AND

THE SEPARATION OF RADIOACTIVE ZIRCONIUM

BY ELECTRODIALYSIS

BY

CHARLES WILLIAM BRAUER, JR.

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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

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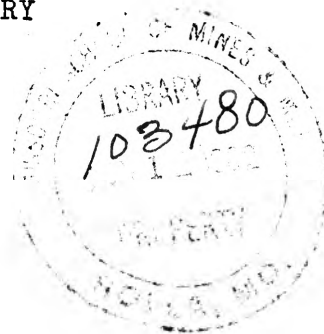
Approved by

William H. Webb (Advisor)   William R. Carroll

Harold Q Fuller

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I. INTRODUCTION

Nuclear reactor installations designed for power production must of necessity operate at higher energy levels than their experimental precursors. As these facilities increase in number, better solutions must be found for both technical and economic problems.

The disposal of waste materials is of primary importance and will require greater effort if satisfactory disposal methods are to keep pace with the increase of waste materials, produced by the increasing number of new nuclear facilities. The radioactive materials present in this waste material may constitute a valuable by-product from these operations if suitable and economic recovery procedures are developed. If the development of recovery methods is sufficiently in advance of nuclear installations, further inducement for installations of this type may be offered. The extent to which nuclear power generation methods will be used will greatly depend upon the economic factors which enhance or hinder competition with conventional power generation methods.

There are many reports of investigations designed to determine methods and conditions for the separation of fission products from various mixtures of isotopes in different solutions. One of the most perplexing phenomena is the behavior of zirconium. Not only is there lack of information, but there are even conflicting reports

regarding the species in various solutions and the extent to which they can be removed by such methods as electrodialysis, precipitation, ion-exchange and liquid-liquid extraction.

This investigation was undertaken primarily to determine the extent to which zirconium could be separated by electrodialysis from solutions of hydrochloric, hydrofluoric, sulfuric, nitric, perchloric or oxalic acid solutions, at various acid concentration ranges with the expectation that the data thus obtained would be of value to those designing facilities for separation of zirconium by electrodialysis. In addition, the information may be useful for determining the nature of the zirconium complex in these solutions where a knowledge of the charge carried serves to eliminate a proposed species or confirm another.

It is, of course, realized that exact determination of the composition of the zirconium species must await further studies along different lines, and this information contributes only to those species which may be accepted or rejected by qualitative arguments relating to the charge carried by the species.

II. LITERATURE REVIEW

The literature review was concentrated along four lines: (1) occurrence of fission products, (2) disposal methods, (3) colloidal nature of radioisotope solutions and (4) solution chemistry of zirconium.

Occurrence of Fission Products

Over three hundred different nuclides result from the fission of U-235, U-233 and Pu-239. The mass numbers of the fission products range from 72 to 161, zinc to terbium [6, 42] with the highest yields occurring in the mass number range of 95 to 139. [28] These high yield components possess the greatest activity and present the more difficult disposal problems.

The used fuel elements are stored under water for ninety to one-hundred twenty days to permit decay of the short half-life fission components and for the Np-239 to decay to Pu-239. Solvent extraction techniques are then employed to effect separation of the unused fissionable material from the remaining fission products. Generally [7] the fuel elements are dissolved in nitric acid and the solution passed through an extraction column.

Organic solvents such as tributyl phosphate (TBP) dissolved in kerosene or methyl isobutyl ketone (hexone) are used to selectively extract uranium and plutonium from the aqueous phase and thus effect their removal from the

cladding and fission products. Nitric acid or aluminum nitrate is added to "salt-out" the remaining minute amounts of fissionable materials from the organic phase. Nearly all (more than 99.9 per cent) of the fission products are left in the aqueous phase containing nitric acid, aluminum nitrate and other inorganic salts.

Zirconium is a very desirable material for use in cladding fabrication where operating temperatures and the ensuing corrosion problems are both greater than many other materials are able to withstand.[38]

Dissolution of zirconium cladding requires the use of about six moles of hydrofluoric acid for each gram atomic weight of zirconium dissolved, leaving a solution which is about one molar in zirconium and over six molar in hydrofluoric acid.

When all desired radioisotopes are removed from the solutions, they are usually concentrated by evaporation for final disposal by storage in underground steel tanks. These solutions may have activities of thousands of curies per gallon.[27]

Publications dealing with processing for disposal are readily available and reference is made thereto.[49, 50] No further pursuit of the subject will be given here in consideration of its slight bearing on the purpose of this investigation.

Disposal Methods

Regardless of the way a material, whether solid, liquid or gas, may become radioactive, the disposal problem challenges the ingenuity of everyone associated with reactors or reactor products. Gases used as cooling agents may absorb neutrons during passage through the reactor; solid materials may become radioactive when used to handle or contain radioactive materials.

The radioactive liquid materials of prime concern here result from dissolution of fission products and are generally discussed in arbitrary terms[27] according to their activity as (1) low level, (2) intermediate level and (3) high level.

At present, the low level waste disposal method is satisfactory but the reactors of sufficiently high power level to be used for commercial power generation present an every increasing supply of high level waste material. It is estimated that around three to four grams of fission products are produced per megawatt day of electrical power generation by nuclear reactions. This high level waste is the aqueous acid phase from the extraction columns in the reprocessing of the irradiated fuel elements.

It is estimated that this source might account for as much as a billion gallons of high level waste by the year 2000.[27, 40] Inability to reduce its activity and the biological hazard which would be created by its release leaves storage in underground steel tanks the only choice

of disposal at the present time. The contemplated increase
in volume of this high level waste decreases the desirabil-
ity of this disposal method. Instability of some of the
solutions to heating prevents concentration by evaporation
and the corrosion resistance of the tanks places a limit
on the time such solutions can be contained. There still is
no permanent disposal method for fluoride waste solutions.

Fixation of radioactive materials on ion exchange
clays, metal oxides or other systems of similar nature is
now receiving considerable attention. Recent developments
along these lines are reveiwed by Dale Harris[33] with
primary emphasis on the work which has been done with clays

One of the greatest disadvantages of ion exchange
fixation is the decreased adsorption caused by non-radio-
active cations such as tri-valent aluminum or hydrogen ions
in the waste solution, as well as the preferential adsorp-
tion of multivalent species. Use of this procedure would
necessitate removal of the aluminum ions from the salting-
out process and removal of the zirconium ions resulting
from dissolution of the cladding, since inert cations have
been reported to decrease the effective capacity of the
resin for adsorption of fission products by as much as
ninety per cent.[24] It has been shown that water rather
effectively leaches alkali and alkaline earth metals from
solid calcined columns, thus making retention of the most
active long half-life Cs-137 and Sr-90 practically impos-
sible when the clays are exposed to ground water. The
characteristic radiation of these two long-lived isotopes,

Cs-137 and Sr-90, makes further discussion of interest here.

Strontium-90 is a pure beta emitter with no gamma radiation present. This quality makes it very desirable for use as a standard beta source in as much as heavy gamma shielding would not be required. Cesium-137 is also a pure beta emitter with a daughter, Ba-137, which emits strong gamma radiation. Due to its availability as a by-product of fission processes, it is a likely replacement for the presently used Co-60 in gamma applications. It is estimated that the price of Cs-137 is only a small fraction of the cost of production of Co-60.

Colloidal Nature of Radioisotope Solutions

Colloidal behavior has been exhibited by nineteen fission product elements under certain conditions. This problem aggravates separation efforts and further discussion of this behavior is pertinent to this work.

Particles of colloidal dimensions, diameters between one and one hundred millimicrons, composed of radioactive material are referred to as "radiocolloids." Other definitions differing somewhat from this one have been given. Paneth[48] was the first to report radiocolloidal behavior. He first noticed that when a solution containing very small amounts of Ra-D (Pb-210), Ra-E (Bi-210) and Ra-F (Po-210) was dialyzed, the lead passed through the parchment or animal membrane used, but the bismuth and polonium did not. Further investigation of diffusion phenomena using these elements revealed that bismuth and

polonium appeared to be colloidal in neutral, ammonical or weak acid solutions. The radioactive lead was ionic in acid solutions but colloidal in ammonical solution.

Radiocolloidal behavior is manifested by: (1) diminished diffusion velocity, (2) stratification in presence or absence of centrifugation, (3) coagulation or peptization by electrolytes, (4) anomolous 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 discontinuous distribution of the radioactive matter as revealed by radioautographs.

Radiocolloids have been detected by use of the following methods: (1) dialysis, (2) filtrations or ultra-filtration, (3) diffusion coefficient studies, (4) electro-phoresis, (5) sedimentation and centrifugation, (6) radio-autographs, (7) adsorption and (8) isotopic exchange. The detection methods are reviewed by Schweitzer and Jackson.[57]

Paneth's discovery has been followed by many discussions leading to wide disagreement. No completely acceptable explanation for radiocolloidal systems has yet evolved. While Paneth regarded them as true colloids, others attributed the behavior to activity adsorbed upon solid impurities in the solutions. The dilemma caused by Paneth's belief that these radiocolloids were true

colloids stems from the seeming violation of the law of
chemical equilibrium in as much as the equilibrium law
requires that the solubility product of the insoluble
compound must be exceeded. Using the known solubility
product of lead II hydroxide, 1.2×10^{-10}, at room temper-
ature, 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 to exceed the
solubility product. Paneth found that the lead isotope,
Thorium-B, exhibited colloidal behavior when present to
the extent of 1×10^{-11} molar in this ammonium hydroxide
solution.

Concentrations of the order of magnitude of the
Thorium-B mentioned above are easily detected by radio-
chemical means.[25] In fact, radiochemical methods can
detect concentrations as low as 1×10^{-20} molar.[18]

Those who did not regard radiocolloids as true
colloids held to the belief that the concentration of many
carrier-free radioisotopes was too low to permit formation
of an independent colloidal phase, and proposed that "the
radioactive ions were adsorbed upon solid impurities
accidently present in the solutions, thereby imitating a
colloidal character and form in the so called radiocol-
loids."[31]

Recent work has provided an explanation acceptable
to both theories, although the dilemma still exists.

The factors known to affect radiocolloidal formation
are: (1) solubility of the radioactive tracers,

(2) presence of foreign particles, (3) electrolytes,
(4) solvents, (5) ionizing radiation, (6) time and (7)
concentration of radioisotopes. (19, 58)

Since radiocolloidal behavior, whenever present,
is superimposed upon the electromigration behavior expected
from the ionic species by virtue of its charge, it is felt
that its relevence to this investigation justifies the
following elaboration of the factors just mentioned.

Solubility of Radioactive Tracers. Radiocolloidal
formation is favored by hydrolysis which yields an
insoluble compound with some component of the solution.
The presence of complexing agents thus tends to prevent
radiocolloidal formation.

Schubert (52) has described the conditions for
radiocolloidal formation in the following manner: "The
principle condition under which a radioelement present in
solution is likely to become radiocolloidal 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."

Radioisotopes of zirconium and other elements which
form insoluble hydrous oxides or hydroxides in macro
concentrations often form radiocolloids. Mayer and
Morton (43) have described stable radiocolloidal solutions

of zirconyl radiophosphate.

The formation of radiocolloids at concentrations much lower than needed to exceed solubility products has been questioned.[3, 45] Those who do not agree believe that the solubility products have not been accurately enough determined. Haissinsky[1], in 1934, reported the following as a result of his work on redetermining the solubility products of some insoluble hydroxides and sulfides. "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. Those who believe that radiocolloids are merely activity adsorbed on impurities performed experiments to prove their theory. Werner[69, 70] tested for existence of radiocolloidal lead and bismuth in water which had been filtered and purified. He found less activity in solutions of this water than in corresponding solutions of doubly distilled water. The presence of foreign particles not removed is the explanation for the greater activity in the solutions made with doubly distilled water. Other investigators[45] have found that the impurities have a negligible effect on radiocolloidal formation.

Schweitzer and Jackson[56] showed that adsorption was not the primary factor in radiocolloidal formation by

showing that soluble anions in low concentration were not adsorbed upon positively charged impurities in acid solutions. They also showed that cations which do not form insoluble hydroxides do not show radiocolloidal behavior in presence of impurities. Broda [20] has stated that impurities facilitate but are not necessary for radiocolloidal formation.

Alimarin and Rudney [3] report that they have found that two groups of particles are present in radiocolloids, one with sizes of the order of some ten microns and others of the order of one micromicron. The suggestion may be made that the coarsely dispersed particles are radioactive elements adsorbed on impurities, while the finely dispersed particles are true colloidal particles. It was found that the radiocolloid did not pass through a membrane and that the larger particles would pass through slowly.

Effect of Electrolytes on Radiocolloidal Formation.

Shortly after the discovery of radiocolloids [29] the effect of the addition of highly charged cations or acids on the direction of migration of polonium and bismuth radioisotopes was noticed.

The addition of strong base caused the migration direction to change. This adsorption with acquisition of a net charge is typical of colloidal behavior.

Schubert and Conn [53] found that addition of nitric or sulfuric acid increased the dialysis of zirconium and niobium. The effect of sodium nitrate or sodium sulfate was negligible. Fluoride, oxalate, phosphate and hydrogen

ions were also found to increase the dialysis of zirconium
and niobium.

Various investigators[51, 54] have reported the
unusual phenomena of increase in adsorption of radiocol-
loids of zirconium, niobium and thorium on solids with
increasing electrolyte concentration. This unexpected
behavior in view of the law of mass action was explained by
Schubert and Richter[54] as a result of the electrolyte's
action as a coagulating agent with the ion exchange resin
adsorbing the radiocolloid as a result of its increased
surface area.

Schweitzer and his fellow workers[60, 62] found
contradictory results when non-complexing salts were added
to radiocolloids of lanthanum, yttrium and beryllium and
the activity retained on fritted glass filters was measured
at constant pH.

Schubert and Richter[54] also reported that zirconium
and niobium are the only fission products which exhibit this
anomolous adsorption behavior in the presence of electro-
lytes in one molar hydrochloric acid solutions.

Effect of Solvents on Radiocolloids. To determine
the effect of the solvent on radiocolloidal formation,
studies were made in sealed tubes containing radon and other
gases.[53] The results obtained indicate that radiocolloids
were formed from the decay products of radon when the other
gas in the tube was polar and no radiocolloidal formation
was detected with non polar gases. Aggregates were formed

in moist air, hydrogen chloride and chloroform, but not in dry air or carbon tetrachloride.

Convincing evidence is thus furnished that nuclei, not foreign impurities, are needed to induce radiocolloidal formation. An explanation is that ions and recoil atoms present in the mixture as a result of ionizing radiation or radioactive disentegration tend to remain together upon collision, particularly if the particle would normally exist as a solid. (53) Polar molecules would be expected to be present in the group that forms because of the tendency of such molecules to be adsorbed on solids. The groups, once formed, will continue to grow by further adsorption of polar molecules, recoil atoms or ions.

The small number of recoil atoms present compared to the number of solvent molecules definitely would cause polar molecules to favor, and possibly be essential for, formation of aereoradiocolloids.

An analogous explanation is given for formation of radiocolloids in liquids. Hahn (31) reports that carrier free lead and bismuth tracers do not form radiocolloids in dioxane or acetone, but they do form in methyl alcohol, ethyl alcohol, ether and water. (61) Recent experiments indicate that the lower the dipole moment of the solvent, the greater the repression of radiocolloidal formation.

The Effect of Time on Radiocolloidal Formation. In general, the amount of radioactivity which can be removed

by dialyzing and other methods increases with the age of the
solution.[57] In many cases, however, the amount which can
be removed reaches a maximum in a few minutes. It was
observed also that when the amount removable becomes inde-
pendent of time, very little change is caused by the
addition of non-complexing electrolytes.[56]

Effect of Radiation on Radiocolloidal Formation. The
fact that ionizing radiation tends to decrease the stability
of positively charged colloids and has little effect on
negatively charged colloids is rather well established.

The reactions of the free hydroxyl radicals formed
by the radiation of the charged colloidal particles seem to
be the best explanation for these phenomena.

It was found that gamma radiation[46] from a cobalt-
60 source induced coagulation of a positively charged
colloidal system of silver iodide and increased the sta-
bility of the negatively charged silver iodide, silver and
gold systems.

The Effect of Concentration on Radiocolloidal
Formation. From studies on polonium[45, 57] it was found
that in acid solutions, the per cent of the polonium centri-
fuged from the solutions decreased with an increase in the
polonium concentration. Addition of much greater quantities
of polonium finally resulted in further increase in the
amount centrifuged.

Morrow, et. al.,[45] found that at constant acid
concentration, an increase in polonium concentration in-
creased the amount of isotope removable by filtration and

offered the following explanation: The increase in polonium concentration decreases the time required for colloidal formation and favors the increase in size and number of aggregates.

Schweitzer and Bishop[55] reported opposite results for the gold removable with increasing gold concentration, while other investigators have found no relationship between the concentration of radioisotope in solutions and the fraction removable.

Perhaps some evaluation could be made regarding the effect of concentration of radioisotopes on the amount removable if more details, such as concentrations of gold used, were reported.

Solution Chemistry of Zirconium

Prediction of the behavior of zirconium under various conditions and the intrepretation of accurately made predictions have long been difficult and confusing.

According to Blumenthal[15] one of the most fundamental general assumptions regarding the behavior of zirconium is that zirconium never exists as the terpositive ion either in solution or solid compounds of zirconium.

A charge of +4 would violate the Pauling Electroneutrality Principle. The various methods of bonding lead to groups of atoms with positive or negative electrical charges. This fact leads to an explanation of the oxide according to the formula, $ZrOZrO_3$, a zirconyl zirconate, empirically written as ZrO_2. The extremes of the oxide

structure are given by Blumenthal[12] as

$$\begin{array}{c} O \\ \diagdown \\ O \diagup \end{array} Zr \leftarrow O \qquad \text{and} \qquad O = Zr - O$$
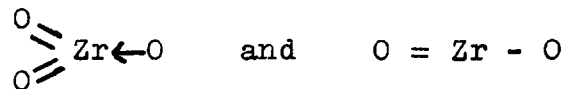
The oxide dissolves in complexing acids such as HF, because of residual surface bonding potential.

Although usually not dissolved by HCl, under some conditions extremely finely divided ZrO_2 has been dissolved in HCl. This is explained by the action of the hydronium ion by the following equation:

$$ZrO_2 + H_3O^+ \longrightarrow ZrO(OH)^+ H_2O$$
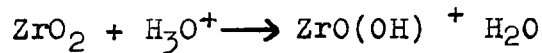
When aqueous solutions of hydrochloric acid in which zirconium oxide has been dissolved are evaporated, $ZrOCl_2 \cdot 8H_2O$ is obtained. X-ray diffraction studies of the crystal have led to the conclusion that the chlorine or bromine atoms are not bound to the zirconium atoms.[10] It is therefore thought that this will also be the case for these substances in solution. Natta's work[10] showed that the Raman Spectra of zirconyl chloride and zirconyl bromide are identical.

It was once thought that the zirconyl ion, ZrO^{+2}, was the predominate species of zirconium solutions. It now seems more likely that ZrO^{+2} exists only in a certain range of acid concentration and that it is the $ZrO(OH)^+$ group which persists during the course of chemical reaction of zirconium compounds.[10] This leads to the designation of compounds of the type $ZrOX_2$, with water of hydration, as zirconyl compounds. In solutions, zirconyl compounds

attain the highest coordination numbers sterically possible, usually 5, 6, or 7. [9]

Reaction of zirconium compounds are usually very slow to reach equilibrium. A freshly prepared 1 formal solution of zirconyl chloride shows a hydrogen ion activity of 0.32 after one minute and a value of 0.60 after 1 hour at 25 degrees centigrade. [10] Small conductivity changes are also observed. The final acid strengths are nearly the same as those of HCl solutions of the same concentration. [10] This information is interpreted to indicate that the net empirical effect of the dissolution and hydrolysis of $ZrOCl_2$ may be represented by the following:

$$ZrOCl_2 + H_2O \longrightarrow ZrO(OH)^+ + H^+ + Cl^-$$
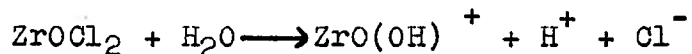
Rayleigh light scattering experiments indicate ionic weights of the order of 8000. [10] This is indicative of association. One explanation is that the tetra zirconium ions of the formula $\left[Zr_4(OH)_8 \right]^{+8}$ with water of hydration pass into the solution phase and are surrounded by anions. Their charge is balanced by a layer of anions such as chloride, bromide or hydroxyl ions. At concentrations of the order of 0.01 to 1 formal with respect to zirconium, the tetramer breaks down almost completely into the basic zirconyl ion, $ZrO(OH)^+nH_2O$. Assuming a value of 4 for n, this can be expressed as follows:

$$Zr_4(OH)_8^{+8} \, 4H_2O + (16\ 4)H_2O \longrightarrow 4\ ZrO(OH)\ 4H_2O^+ + 4H^+$$
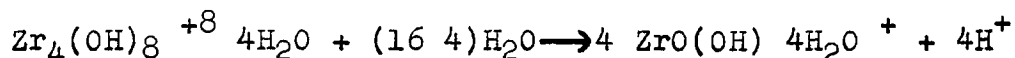
This reaction is considered to be reversible, with an increase of acid favoring the formation of the tetramer.

Further evidence for considering $ZrO(OH)^+$ as the prevailing species at moderate acid concentrations is offered by the work of Konarev and Salorkin[10] as a result of their precipitation of $ZrO(OH)IO_3 \cdot 5H_2O$ from zirconium nitrate solutions upon addition of KIO_3 at pH 2-3. $ZrO(OH)C_2H_3O_2 \cdot nH_2O$ can also be precipitated by adding 2 moles of sodium acetate for each mole of $ZrOCl_2$.

Ionizations which occur may be represented as follows:

1. $ZrA_4 \cdot 4H_2O \xrightarrow{\ H_2O\ } ZrA_{(4-n)}(H_2O)^{+n} + nA^-$

2. $ZrA_4 \cdot 4H_2O \longrightarrow nH^+ + Zr(A-H)_nA_{4-n} \cdot 4H_2O^{-n}$
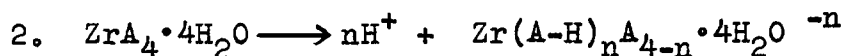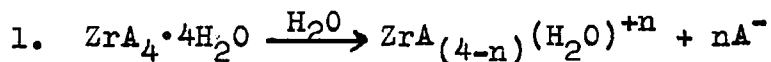
Equation 2 assumes A to be a radical containing an ionizable hydrogen, e.g. HSO_4^-. These equations indicate that whether the zirconium ion is a cationic or an ionic species depends upon the relative bond strengths of atoms or groups in the molecules under the prevailing environmental conditions. If the relative bond strengths are in reverse order, A^- anions and complex zirconium cations will form. Thus if a radical, A^-, is exchanged for an aquo group the complex will be cationic; if it releases a proton and acquires an aquo group, it will be anionic. These exchanges may have superimposed upon them other changes such as replacement of a radical, A^-, by an OH^- group.[10]

The interpretation of hydrous oxides according to Thomas and his co-workers,[5] may apply to zirconium chemistry. They regard the species of these solutions as polymers having ol and oxo linkages. The ol refers to linkage by OH groups and oxo indicates linkage through an O. Hydrous

oxides form by hydration, followed by olation (OH linkage), and oxolation (O linkage), and anion penetration consisting of replacement of a coordinated group such as an anion, hydroxo, hydroxyl or aquo.

Olation is favored by an increase in concentration, increase of temperature and especially by an increase in basicity.[69] Oxolation is favored by the same factors but to a lesser extent.[5] The ol group has a higher electron density and protons react more readily with it than with an oxo group to make depolymerization of olated polymers easier than depolymerization of oxolated polymers.[32]

A study of the foregoing data led Thomas and his co-workers to consider the colloidal metal oxides (sols) to consist of micelles which are polymeric ol or oxo compounds in which a variable fraction of the coordination positions may be occupied by anions rather than ol, oxo or aqua groups. The micelle is regarded as a very large ion whose charge is inherent in its structure, rather than merely adsorbed on the surface.

Thomas and Whitehead[65] noted that aluminum oxychloride sols aged at room temperature became more acidic. They attributed this behavior to hydrolysis (conversion of aqua groups to OH) of the highly polymeric ions. Sols prepared at room temperature were found to become more acidic when heated, and returned to the original acidity only after several weeks. It was suggested that heating promoted hydrolysis followed by olation and oxolation; reversal was attributed to slow conversion of oxo to ol groups.

The fact that sols prepared at higher temperatures slowly became more basic when aged at room temperature was interpreted to indicate that they initially contained oxo groups which slowly reacted with hydrogen ions. Evidence is available to indicate a strong tendency for zirconyl salt complexes to oxolate.[64]

The review of the solution chemistry of zirconium will be continued with a discussion of the systems encountered in this work: (1) the nitrate system, (2) the chloride system, (3) the perchlorate system, (4) the sulfate system, (5) the oxalate system and (6) the fluoride system.

The Nitrate System. Zirconium in nitrate solutions is almost entirely non-ionic, possibly $ZrO(OH)NO_3$.[4] When zirconyl nitrate is dissolved the following may occur: (ignoring water of hydration)

$$ZrO(NO_3)_2 + H_2O \longrightarrow ZrO()H)NO_3 + H^+ + NO_3^-$$
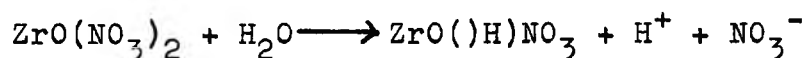
Evidence for this non-ionic species is offered by passage of zirconyl nitrate solutions through amberlite IR-100 cation exchange resin. Only 2 per cent of the zirconium was retained. Only 1 per cent was retained when the sodium salt of the resin was used. Similar low retention was observed using amberlite JR-4 anion exchange resin.

Lister and McDonald[39] reported that below an acid concentration of 0.3 normal large polymerized species predominate and propose $\left[Zr_4O_7\right]^{+2}$ and $\left[Zr_3O_5\right]^{+2}$ as likely species. Increasing acid concentration causes depolymerization with formation of such ions as $\left[(OH)_2-Zr-O-Zr(OH)_2\right]^{+2}$. Lister and McDonald[39] proposed $\left[Zr(OH)_2NO_3\right]^+$

as the most probable species in acid concentrations of the
order of 3 normal in nitric acid.

Schubert and Conn[53] reported a large increase in
the amount of zirconium which can be dialyzed from zirconyl
solutions when nitric acid is added.

McVey[23] reported $Zr(NO_3)^{+++}$ and $Zr(NO_3)_2^{++}$ as the
ionic species in a 4 normal nitric acid solution.

Connick and McVey[23] reported that nitric acid
solutions in the pH range of -0.4 to 2 contain a mixture of
the tetravalent zirconium ions and $Zr(OH)^{+3}$.

The Chloride System. There is some evidence which
might lead to the postulation of a monochloro complex but the
small magnitude of migration of zirconium either to the
cathode or anode cells during electrodialysis might favor
regarding the species as neutral.

Adolf and Pauli[2] by conductance, pH, freezing
point lowering and electromigration studies have suggested
the following possibilities for the formula of the species
present in hydrochloric acid solutions:

$$\left[Zr()H)_4ZrO\right]^{+2}, \left[Zr(OH)_2Cl_4\right]^{-2}, \left[Zr(OH)_4Cl_2\right]^{-2}$$
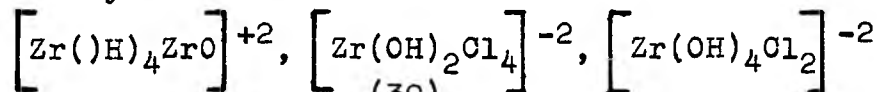
Lister and McDonald[39] consider the hydrochloric
acid system to be composed of anionic, cationic and neutral
species.

Connick and McVey[23] concluded that polymeric
species exist in zirconyl chloride solutions and found that
the complexes contain one chloride ion in two normal hydro-
chloric acid solution.

The Perchlorate System. Little if any complexation occurs with zirconium and perchlorate ion.[16] The species is usually considered to be $Zr(OH)_2^{+2}$ in strong perchloric acid solutions.[52] The existence of the tetrapositive zirconium ion has been claimed by Connick and Reas[24] from the results of their extraction methods using one to two normal perchloric acid solutions. This behavior seems unlikely in light of the fact that uptake from perchloric acid solutions is slower than from nitric acid solutions.[30]

Perchloric acid is a good solvent for hydrous zirconia. One mole of zirconia per 2 moles of perchloric acid was found to be the limiting proportions if solution of the zirconia was to be effected within a few weeks.[16] Evaporation of the solution over calcium chloride gave crystals of the empirical formula $4ZrO(ClO_4)_2 \cdot HClO_4$.

Electromigration and anion exchange experiments have indicated anionic complexes in perchloric acid solutions but no explanation of the nature of these complexes has been made. The following formula: $\left[Zr(OH)_{3.4} \right]_n^{+0.6}$ has been reported at a pH of 2.77.[37]

The tetravalent zirconium ion has been reported to exist in solutions of low zirconium concentration which were two normal with respect to perchloric acid; at lower acidities, $Zr(OH)_3^+$ and $Zr(OH)_2^{+2}$ are considered to be the predominate species.[24] Connick and McVey[23] also report $Zr(OH)^{+3}$ and $Zr(OH)_2^{+2}$ as the predominate species at lower perchloric acid concentration.

<u>The Sulfate System.</u> Complex ion formation depends upon the relative strengths of the complexing group bonds compared to the strength of the Zr-O bond. Chloride, nitrate and perchlorate bonds with zirconium are weaker than Zr-O bonds.[14] and fluoride bonds are stronger than Zr-O bonds.[14]

The sulfate ion more closely resembles fluoride than chloride ions with respect to zirconium chemistry. It has a greater affinity than water for the zirconium atoms as shown by the following equation:[14]

$$Zr(SO_4)_2 + 4H_2O \longrightarrow 2H^+ + ZrO(SO_4)_2 \cdot 3H_2O^{-2}$$
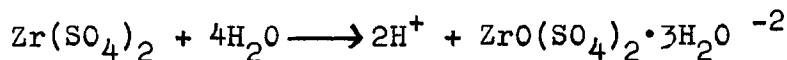
There is, at ordinary temperatures, very little tendency for water to displace sulfate, but hydroxyl ions compete strongly.[14]

In strong acid (low hydroxyl ion concentration) more sulfate groups may be attached:[14]

$$ZrO(SO_4)_2 \cdot 3H_2O^{-2} + SO_4^{-2} \longrightarrow ZrO(SO_4)_3 \cdot 2H_2O^{-4} + H_2O$$
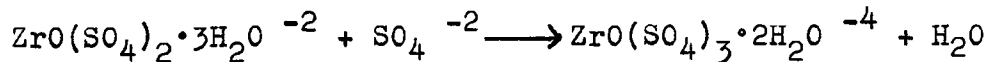
The zirconyl or oxo oxygen atom appears to react reversibly with hydrogen ions to form hydroxo complexes:[14]

$$ZrO(SO_4)_2^{-2} + H^+ \longrightarrow ZrO(OH)(SO_4)_2^{-1}$$

but in presence of suitable hydroxyl ion concentration, the following occurs:[14]

$$ZrO(SO_4)_2^{-2} + OH^- \longrightarrow ZrO_2 \cdot xH_2O + 2SO_4 + (1-x)H_2O$$
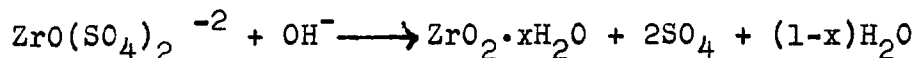
It then appears that the sulfate ion has practically no tendency to displace oxo groups and a negligible tendency to displace hydroxyl groups, but has a strong tendency to displace aquo ligands from zirconium.

In strongly acid solution, $Zr(SO_4)_4^{-4}$ can be made.[14] Sulfate ions are covalently bound in all compounds of

zirconium and more correctly named as sulfato zirconic
acids, rather than zirconium sulfates. They may be thought
of as derivates of the hypothetical metazirconic acid, [14]
$H_2ZrO_3(ZrO(OH)_2)$ in which one, two, three or even four of
the zirconium bonds with O or OH are replaced by bonds to
the sulfate ion. [14]

Lister and McDonald [39] consider the sulfate system
to contain anionic, cationic and neutral species in
equilibrium. At an acid concentration of 1.5 normal with
respect to sulfuric acid, they report that the cationic
species has disappeared.

Schubert and Conn [52] report an increase in the rate
of dialysis of zirconium from zirconyl solutions when sul-
furic acid is added, but no increase for the addition of
sodium sulfate.

Connick and McVey [23] suggest an equilibrium system
consisting of the following species: $ZrSO_4^{+2}$, $Zr(SO_4)_2$
and $Zr(SO_4)_3^{-2}$.

The Oxalate System. Oxalate complexes are easily
prepared from zirconyl nitrate or chloride solutions. [66]
The presence of sulfate ions would result in competition
with the oxalate ions for the bonding orbitals. [17]

The addition of oxalate ions to zirconium solutions
results in formation of a precipitate which redissolves up-
on further addition of oxalate ions. [66] Precipitation from
solution by addition of oxalate ions yields $ZrO(C_2O_4) \cdot 4H_2O$.
The compounds are best regarded as derivatives of oxalato
zirconic acid. [17] Various proposals for the species

existing in oxalic acid solutions consist of complex anions.

The following species constitute the equilibrium system:

$$\left[\begin{array}{c} O = C - O \searrow \overset{\overset{O}{\downarrow}}{\underset{\underset{HOH}{\uparrow}}{Zr}} \diagup O - C = O \\ O = C - O \diagup \qquad \diagdown O - C = O \end{array} \right]^{-2}$$

$$\left[\begin{array}{c} \overset{O}{\overset{\cdot\cdot}{}} \quad \overset{O}{\overset{\cdot\cdot}{}} \qquad \overset{\overset{O}{\downarrow}}{} \\ - O - C - C - O - \underset{\underset{H\overset{\cdot}{O}H}{\uparrow}}{Zr} \diagdown O - C = O \\ \diagdown O - C = O \end{array} \right]^{-2}$$

$$\left[\begin{array}{c} \overset{O}{\overset{\cdot\cdot}{}} \quad \overset{O}{\overset{\cdot\cdot}{}} \qquad \overset{O}{\overset{\cdot\cdot}{}} \qquad \overset{O}{\overset{\cdot\cdot}{}} \quad \overset{O}{\overset{\cdot\cdot}{}} \\ - O - C - C - O - \underset{\underset{HOH}{\uparrow}}{Zr} - O - C - C - O \end{array} \right]^{-2}$$
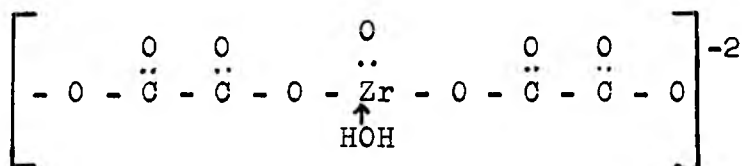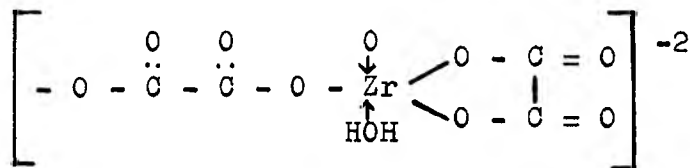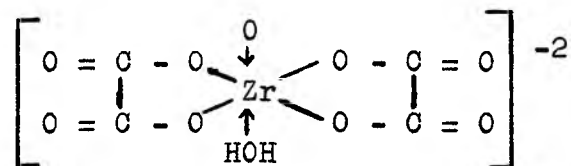
The Fluoride System. A one per cent water solution
of potassium hexafluorozirconate has a pH of about 4 at room
temperature.[11] The acidity is assumed to be due to the
removal of an OH^- ion from the water of the solution as
expressed by:[11]

$$ZrF_6^{-2} + H_2O \longrightarrow HOZrF_6^{-3} + H^+$$
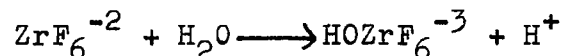
If KF is added the pH rises, indicating formation of
the heptafluorozirconate ion according to:

$$HOZrF_6^{-3} + F^- \longrightarrow ZrF_7^{-3} + OH^-$$

When ammonium hydroxide is added to the potassium hexa-
fluorozirconate solution, a precipitate is obtained, which
after drying has the composition $H_3ZrO_2F_3 \cdot 3H_2O$.

These observations indicate a coordination number of
seven for zirconium in aqueous fluorozirconate solutions
and that the Zr-F bond is more stable than the Zr - OH_2

bond but generally not more stable than the Zr-OH bond.

Moffat[44] suggests the following species:

$$\left[-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle OH}{|}}{Zr}} - O - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle OH}{|}}{Zr}} - O - \right]_n \; , \; \left[-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{Zr}} - O - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle OH}{|}}{Zr}} - O - \right]_n \; ,$$

$$\left[-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{Zr}} - O - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{Zr}} - O - \right]_n$$
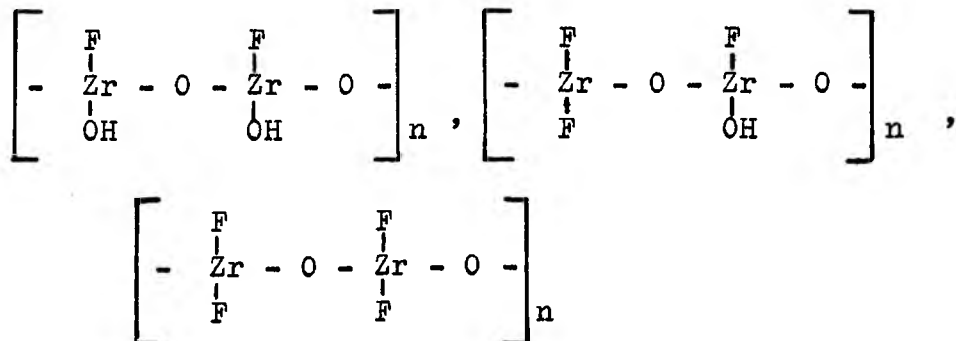
to indicate the effect of increasing HF concentration.

Connick and McVey[23] found that there is an average of one fluoride ion per zirconium atom at an HF concentration of 2×10^{-5} molar; an average of two fluoride ions per zirconium atom in 3×10^{-4} molar HF; three fluoride ions per zirconium atom in 1×10^{-2} molar HF.

Ion Exchange Membranes

Ion exchange membranes also called ion transfer membranes, electric membranes, cation or anion permeable membranes and permselective membranes, may be of two general types, homogeneous or heterogeneous, as determined by the method of preparation.

The hetereogeneous ion exchange membranes are more widely used for industrial processes because of its greater mechanical strength. Hetereogeneous ion exchange membranes consist of finely divided granular resins held together by an inert plastic binder on a flexible insoluble matrix such as polyethylene or glass cloth.[41] The imbedded ion exchange resin makes the cation membranes permeable only to

cations and the anion membranes permeable only to anions, although there is no actual exchange of ions with the membranes. The term ion exchange refers only to the composition of the membrane resin.

An ideal permselective membrane[35, 36] is a membrane which, when subjected to a potential gradient, permits passage of cations and the exclusion of anions or vice versa, depending on the membrane employed. Theories of ion exchange resins also apply to permselective membranes.

An easily understood explanation may be obtained from the Donnan membrane theory from consideration of its postulate that the product of the ion concentrations on both sides of the membrane's interface must be the same.[68]

A permselective membrane contains easily displaced ions loosely bound to fixed groups of opposite charge. The fixed groups may be ionic and of opposite charge with respect to the loosely bound groups. Electrical repulsion thus seeks to exclude ions of the same charge as the fixed groups.

Many electrodialysis applications of membranes have been used. Their design is reviewed by Mason and Kirkham[42] and by Winger.[72]

Their properties of high selectivity to electrical transfer of anions and cations, high electrical conductivity and low permeability to the passage of water are the primary virtues of these membranes which have attracted attention for use in processes involving deacidification, electrolytic reduction, conversion of salts to acids and

bases (called salt-splitting) and separation and concentration or dilution of ions of like charge.

III. EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was to determine the extent to which zirconium could be separated by electrodialysis from acid solutions of varying strengths and add to the knowledge of its solution chemistry.

Plan of Experimentation

This investigation was conducted so as to determine by electrodialysis the extent to which zirconium could be separated from solutions of hydrochloric, hydrofluoric, sulfuric, nitric, perchloric and oxalic acids of varying strengths.

Materials

The materials used in this investigation, their specifications, manufacturers and suppliers along with the purpose for which they were used are listed.

Hydrochloric Acid. CP, meets ACS specifications, lot number D509032, assay 37.0 - 38.0% HCl. Specific gravity 1.19. Manufactured by General Chemical Division, Allied Chemical and Dye Corp., New York, New York. Used in preparation of the zirconium HCl solutions.

Hydrofluoric Acid. Analyzed reagent, meets ACS specifications, lot number 20061, assay 49.3% HF. Manufactured by J. T. Baker Chemical Co., Phillipsburg, New

Jersey. Used to prepare the zirconium HF solutions.

Isotope. Zirconium and Niobium-95, carrier free as the oxalate in 0.30 normal oxalic acid. Zirconium concentration, 7.80 microcuries per milliliter; niobium concentration, 9.82 microcuries per milliliter, obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Membrane. Cation exchange membrane 3142, anion exchange membrane 3148. Membranes are eight mils thick, wet bursting strength ca 200 psi. Excellent acid resistance. Transport number in 0.15 normal sodium chloride: Cation 0.995, anion 0.962. Manufactured by the Permutit Co., New York, New York.

Nitric Acid. CP, meets ACS specifications, lot number D505111, assay 70% HNO_3. Specific gravity 1.42. Manufactured and distributed by the J. T. Baker Chemical Co., Phillipsburg, New Jersey. Used to prepare the zirconium containing nitric acid solutions.

Oxalic Acid. Analytical reagent. Meets ACS specifications. Manufactured by Mallinckrodt Chemical Works, St. Louis, Missouri. Used to prepare the zirconium oxalic acid solutions.

Perchloric Acid. CP, meets ACS specifications, lot number G034, assay 60% $HClO_4$, specific gravity 1.54. Manufactured by the General Chemical Division, Allied Chemical and Dye Co., New York, New York. Used to prepare the zirconium perchloric acid solutions.

Phenolphthalein. Reagent, meets ACS specifications. Lot number 42753. Manufactured by Merck and Co., Rahway,

New Jersey. This reagent was dissolved in an equal volume mixture of alcohol and water and used as an indicator solution.

Sodium Hydroxide. Reagent grade, lot number N3430, meets ACS specifications, minimum assay 97.0% NaOH. Manufactured by General Chemical Division, Allied Chemical and Dye Co., New York, New York. Used to prepare a solution of standard base for titration.

Sulfuric Acid. CP, lot number D407092, meets ACS specifications, assay 95.5 - 96.6% H_2SO_4. Specific gravity 1.84. Manufactured by General Chemical Division, Allied Chemical and Dye Co., New York, New York. Used to prepare the zirconium sulfuric acid solutions.

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

Zirconyl Chloride. Basic, purified, lot number 762666. Obtained from Fisher Scientific Co., New York, New York. Used to prepare the zirconium hydrochloric acid solutions and for pH studies.

Zirconyl Nitrate. Purified, lot number 782716. Obtained from Fisher Scientific Co., New York, New York. Used to prepare the zirconium acid solutions and for pH and nitrate ion studies.

Apparatus

The apparatus used in this investigation, specifications, manufacturer and supplier (where different from the manufacturer) along with the purpose for which each was used is 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. D.C. Model 280, No. 140938, 0-10 amp. MSM Property No. 13744. Manufactured by Weston Electric Instrument Corp., Newark, New Jersey. Used to measure current during electrodialysis.

Balance. Analytical, Type LCB No. 31447, MSM Property No. 131181, weighing 0 to 100 grams, to nearest 0.1 milligrams. 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 formality of solutions used.

Counter. Geiger-Muller tube, Model 10106, No. 588, 2.0 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 inches deep. Manufactured by Radiation Counter Laboratories, Inc., Skokie, Illinois.

Dosimeters. Type 541/A, direct reading, No. 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 3 inch diameter cylinder "Plexiglas," acrylic plastic material. Consists of three cells of approximately 75 milliliters capacity each. The electrodes were made from platinum and are 12.25 square centimeters in area. Similar model described by Bub and Webb.[21]

Electrodialyzer. Made of glass by Ace Glass Co., Vineland, New Jersey on special order. Capacity about the same as the electrodialyzer described above, provided with glass stopcocks for draining. Same size electrodes. Used for carrying out the electrodialysis of all but HF solutions.

Glassware. Assorted sizes of standard laboratory glassware obtained from the Quantitative Analysis Stockroom, Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used for their intended individual purposes.

Heat Lamp. Infrared, type 7A-N, 110 volts, A.C. or D.C., 2 amp. Manufactured by Prometheus Electric Corp., New York, New York. Used to dry samples.

Plastic Laboratory Equipment. An assortment of polyethylene graduated cylinders, beakers and bottles. Obtained from Fisher Scientific Co., Chicago, Illinois. Used for

preparing HF solutions.

Platinum. Metal sheet. Obtained from Storeroom, Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used to make electrodes for the electrodialyzers.

Power Source. D.C. Rectifier, MSM Property No. 13296, 0-40 volts, approximately 8 amps. Used to provide current for electrodialysis.

Power Source. A.C. motor driven D.C. generator installed in Chemical Engineering Building, Missouri School of Mines and Metallurgy, Rolla, Missouri. 0-220 volts, 15 amps. Used to supply current for electrodialysis where demand was in excess of supply capacity of other power source.

Scaler. Automatic counting scaler, Model B-1601, MSM Property No. 21651, 105-135 volts, 50-60 cycle, 100 watts. Maximum counting rate, 100,000 counts per minute. Manufactured by NRD Instrument Co., St. Louis, Missouri. Used to record activity of samples.

Shield. Lead well "pig" MSM Property No. 21642. Manufactured by NRD Instrument Co., St. Louis, Missouri. Used to shield counter from stray radiation.

Stirrer. No. 18835, MSM Property No. 13310, 110 volts, 50-60 cycle, 0.06 amp. Purchased from Central Scientific Co., Chicago, Illinois. Used to stir contents of middle cell of the three cell electrodialyzer during electrodialysis.

Thermometer. Range 0-200 deg. C., obtained from stockroom, Chemical Engineering Department, Missouri School

of Mines and Metallurgy, Rolla, Missouri. Used to measure temperature of various cells during electrodialysis.

Thermostat. Large glass container with copper coil for circulation of water. Obtained from storeroom of Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used to effect temperature control during electrodialysis.

Timer. Precision "time-it", divisions to 0.1 seconds, 115 volts, 60 cycle, 5 watts. Manufactured by Precision Scientific Co., Chicago, Illinois. Used to measure time intervals during electrodialysis.

U-Tube. Fabricated from various pieces of glassware obtained from storerooms of the Chemical Engineering Department, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used for electrodialysis through a fritted glass membrane.

Method of Procedure

The following procedure was used in performing the experimental work: (1) preparation of the acid solution of the desired normality, (2) assembling the electrodialyzer, (3) introduction of the radioisotope into the solution to be electrodialyzed, (4) preparation of the samples to determine recovery, (5) electrodialyzing the solution, (6) withdrawing the solution from the cells, (7) sampling the solutions from the cells to determine the activity, (8) counting the samples and (9) calculation of the per cent migration of the zirconium during electrodialysis.

Preparation of Acid Solutions. The desired acid
concentration was prepared by dilution of stock solutions
to the approximate normality and then establishing the exact
normality by titration with a standard base solution using
phenolphthalein indicator. The standard base was prepared
by titration of an oxalic solution prepared gravimetrically
from primary standard grade oxalic acid, $H_2C_2O_4 \cdot 2H_2O$.

Assembling the Electrodialyzer. Four steel rods of
about one-eighth of an inch in diameter, threaded on both
ends were passed through the two end pieces of the electro-
dialyzer. The three cells with their gaskets and membranes
between cells one and two and two and three were placed
between the end blocks and the nuts placed on each end of
each rod were tightened to secure the cells and prevent
leakage around the gaskets. The same assembly procedure was
used on both cells. Connection to the electrodes, fixed in
the end of cells one and three, was made by alligator clips.

The fritted glass membrane cell was assembled by
insertion of the anode and cathode tubular cells, with
membranes attached, into the plastic tubing extending from
each side of the U-tube center cell. Electrical connection
was made by alligator clips to the lead wires extending
through the small glass tube placed in the hole of the
stoppers which covered the anode and cathode cells.

Addition of Radioisotope. The radioisotope used was
transferred by pipette from the stock solution to the center
cell of the three compartment electrodialyzer and the desired
quantity of acid was added. This stock solution was

thoroughly refluxed with nitric acid to assure removal of oxalate ions before electrodialysis. In all electrodialysis work except in nitric acid solutions, the nitrate ion was destroyed and the radioisotope mixture was prepared in other containers and added to the center cell.

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

Electrodialyzing. After filling and placing stirrer in operation and the lapse of a few minutes time for thorough mixing of the contents of the center cell when zirconium-95 solution was added directly, a two milliliter sample was withdrawn from the center for activity and acid analysis. No sample was withdrawn from the anode or cathode cells at the beginning, since they were filled with an acid solution of known concentration. However, frequently a sample was withdrawn to assure the absence of activity from preceding electrodialysis experiments. The current was then turned on and quickly adjusted to the value which would establish a current density of 114.29 milliamperes per square centimeter. Adjustment was made as needed in the resistance of the circuit so as to maintain the desired current density.

The same general procedure was used in filling the fritted glass membrane cell, except that there was no provision for stirring the center cell contents.

Withdrawing Solutions. Samples were withdrawn from each cell at the end of the dialyzing interval. One milliliter was used for activity analysis by evaporation to dryness in a counting dish, a second one milliliter sample was withdrawn for acid analysis.

Sampling the Solution. The one milliliter sample to be analyzed for acid concentration was diluted to about 40 milliliters with distilled water, throughly mixed and titrated with a standard base solution. Phenolphthalein solution was used as the indicator. The one milliliter sample for activity determination was placed in a counting dish and dried under the infra red heat lamp.

Radioactive Counting. The throughly dried sample was subjected to standard beta counting procedures, consisting of placing the sample under a shielded Geiger-Mueller counter 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.[26, 34] The difference was the activity due to the beta emissions of Zr-95. Periodic checks were made to insure that the absorbers and other apparatus inserted into the counting chamber did not become contaminated. The same geometry was used for all counting.

The voltage applied to the G-M tube was as prescribed by the manufacturer from a knowledge of the voltage plateau for the tube.

The background count was determined for a one hour

counting time. The counting time used in all cases was of sufficient length to make the counting error less than one per cent. The same counter, G-M tube, and scaler were used throughout in order to eliminate the need for correction due to geometry, dead time and efficiency.

Calculations. From the data taken, the per cent of the zirconium dialyzed to the anode and cathode and the per cent remaining in the center cell are calculated, along with the per cent recovery.

Use will be made of the fictictious data in the table below in order to illustrate the method of calculation. The activities here, as in the experimental work, are corrected for background activity.

Cell	Volume (ml)	cps/ml using 28 mg/cm^2 absorber	cps/ml using 139 mg/cm^2 absorber	cps/ml due to Zr-95
Anode	80	200	100	100
Center	80	600	200	400
Cathode	80	450	150	300
initial*	80	1200	300	900

* activity of center cell at beginning.

Per cent dialyzed to anode cell: $\dfrac{100 \times 80 \times 100}{900 \times 80}$

Per cent dialyzed to cathode cell: $\dfrac{300 \times 80 \times 100}{900 \times 80}$

Per cent remaining in center cell: $\dfrac{400 \times 80 \times 100}{900 \times 80}$

Per cent recovered: $\dfrac{80 \times (100 + 400 + 300)}{900 \times 80}$

Data and Results

The data and results of this investigation are
presented in the form of tables and graphs. Graphical
presentation of the results for each of the different acid
solutions used is obtained from figures 1 through 12. The
tabulated data appears in Tables 1 through 12.

The values reported in the tables are average values
obtained by at least two separate determinations. The data
were not treated statistically, owing to the already
mentioned erratic behavior of radiocolloidal systems. The
agreement of data from various determinations was, however,
within a few per cent of the values reported in the higher
percentage ranges and within several one-hundredths of a
per cent at lower values. Results for one system (the
nitric acid system) without the use of absorbers in the
counting are included to serve as a possible explanation for
the somewhat higher values reported by some observers. The
total recovery was determined by washing the cells with an
oxalic or hydrofluoric acid solution and combining the
activity of the wash solutions with the other cell contents.
For this reason, the figures given for the relative pro-
portion in the three cells will not total 100.

The activity due to zirconium-95 in the center cell
at the beginning of each determination was approximately
150 counts per minute per milliliter.

TABLE I

The Electrodialysis of Zirconium[95] from Nitric Acid Solution
Using Permselective Membranes

Time (Hrs.)	Normality Center Cell	Relative Proportion[a]			Recovery[b] Per Cent
		Anode	Center Per Cent	Cathode	
1	3.28	0.12	45.6	0.13	96.7
1	2.22	0.12	38.3	0.15	97.1
1	1.04	0.13	30.4	0.17	96.2
1	0.81	0.13	26.3	0.17	93.8
1	0.66	0.14	20.8	0.15	94.7
1	0.39	0.17	15.8	0.19	95.6

[a] The temperature of the center cell varied from 25 deg. C to 31 deg. C.

[b] Recovery after washing cells with HF solution.

Figure 1. The Effect of Nitric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes.

TABLE II

The Electrodialysis of Zirconium[95] from Nitric Acid Solution
Using Fritted Glass Membranes

Time[ab]	Normality (Center Cell)	Per Cent Dialyzed			Recovery[c] Per Cent
		Anode	Center	Cathode	
2 Hrs.	3.14	1.4	83.8	2.5	93.6
2 Hrs.	2.22	0.9	95.1	2.1	90.2
2 Hrs.	1.00	0.6	84.4	0.9	85.4

[a] The temperature varied from 24 deg. C to 63 deg. C.

[b] Each time interval is a separate determination.

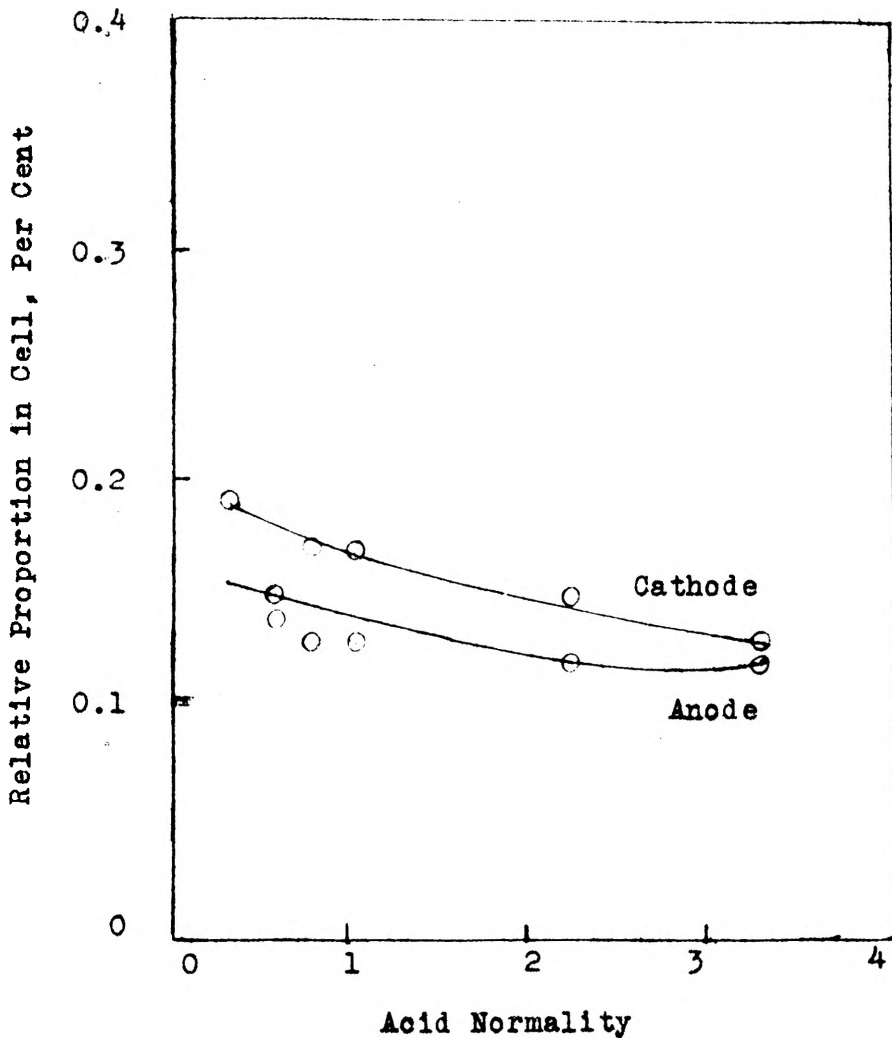[c] After washing with HF solution.

Figure 2. The Effect of Nitric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Fritted Glass Membranes.

TABLE III

The Electrodialysis of Zirconium^{95} from Nitric Acid Solution
Using Permselective Membranes and Measuring Total Activity.

Time (Hrs.)	Normality (Center Cell)	Relative Proportion[a]			Recovery[b] Per Cent
		Anode	Center	Cathode	
1	3.20	2.1	93.0	3.8	95.3
1	2.97	3.1	91.0	4.1	95.2
1	2.88	4.6	81.0	5.1	93.4
1	2.78	4.2	67.0	5.9	91.1
1	2.63	4.5	66.5	6.95	90.7
1	2.52	4.1	61.0	7.9	90.8
1	2.39	4.1	52.0	9.6	89.2
1	2.29	4.1	49.0	10.2	89.1

[a] The temperature varied from 28 deg. C to 36 deg. C.

[b] After washing with HF solution.
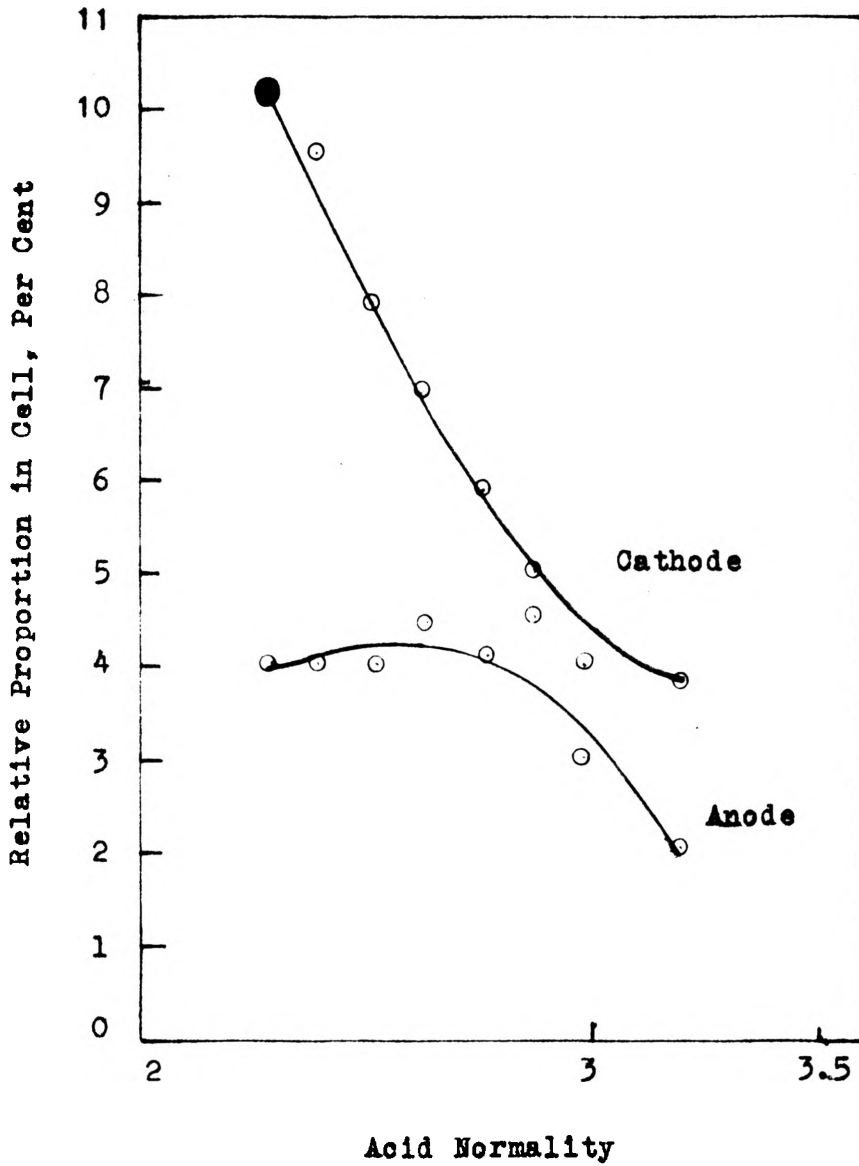
Figure 3. The Effect of Nitric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes,
Measuring Total Activity.

TABLE IV

The Electrodialysis of Zirconium[95] from Hydrochloric Acid
Solution Using Permselective Membranes[a]

Time (Hrs.)	Normality (Center Cell)	Relative Proportion[a]			Recovery[b] Per Cent
		Anode	Center Per Cent	Cathode	
1	3.30	0.14	49.2	0.15	98.2
1	2.11	0.12	41.6	0.14	97.1
1	1.06	0.11	33.4	0.16	93.8
1	0.68	0.13	21.9	0.19	92.8
1	0.41	0.16	18.7	1.20	89.9
1	0.20	0.80	16.3	3.80	82.3

[a] The temperature varied from 22 deg. C to 53 deg. C.

[b] The decreasing per cent recovery is attributed to
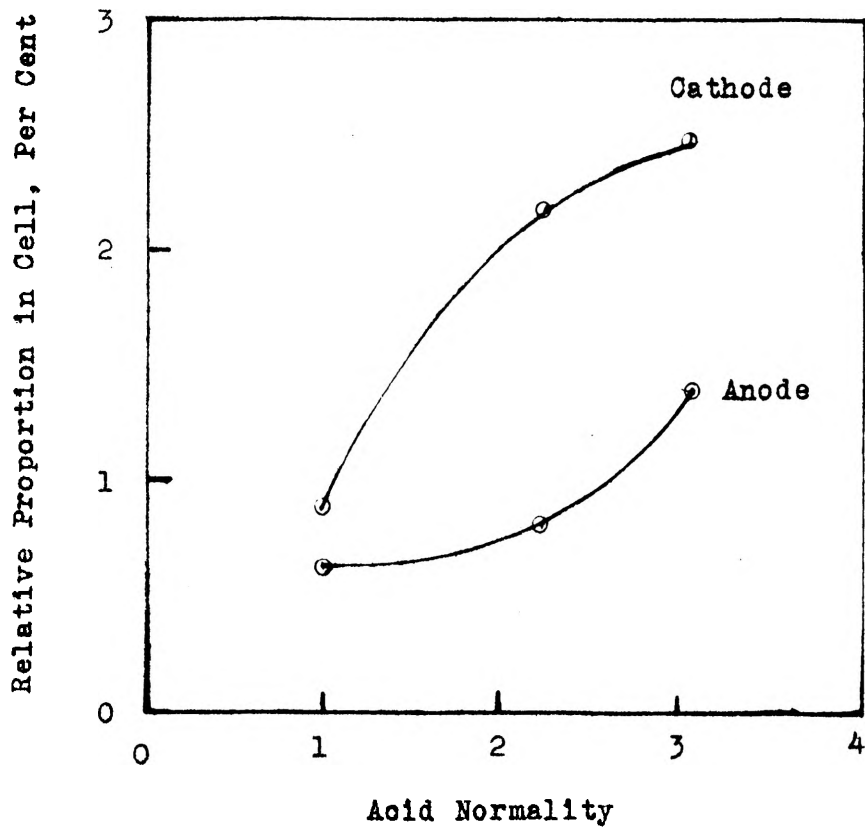adherence of the zirconium species to the membranes
and cell walls.

Figure 4. The Effect of Hydrochloric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes.

TABLE V

The Electrodialysis of Zirconium[95] from Hydrochloric Acid
Solution Using Fritted Glass Membranes[a]

Time	Normality	Relative Proportion[a]			Recovery[b]
(Hrs.)	(Center Cell)	Anode	Center	Cathode	Per Cent
			Per Cent		
1	3.08	0.3	78.3	0.8	94.2
1	2.10	0.2	74.4	0.9	95.3
1	0.50	0.4	63.9	3.9	89.7

[a] The temperature varied from 22 deg. C to 68 deg. C.

[b] The low recovery is attributed to adherence of the
zirconium species to the glass membranes or cell walls.
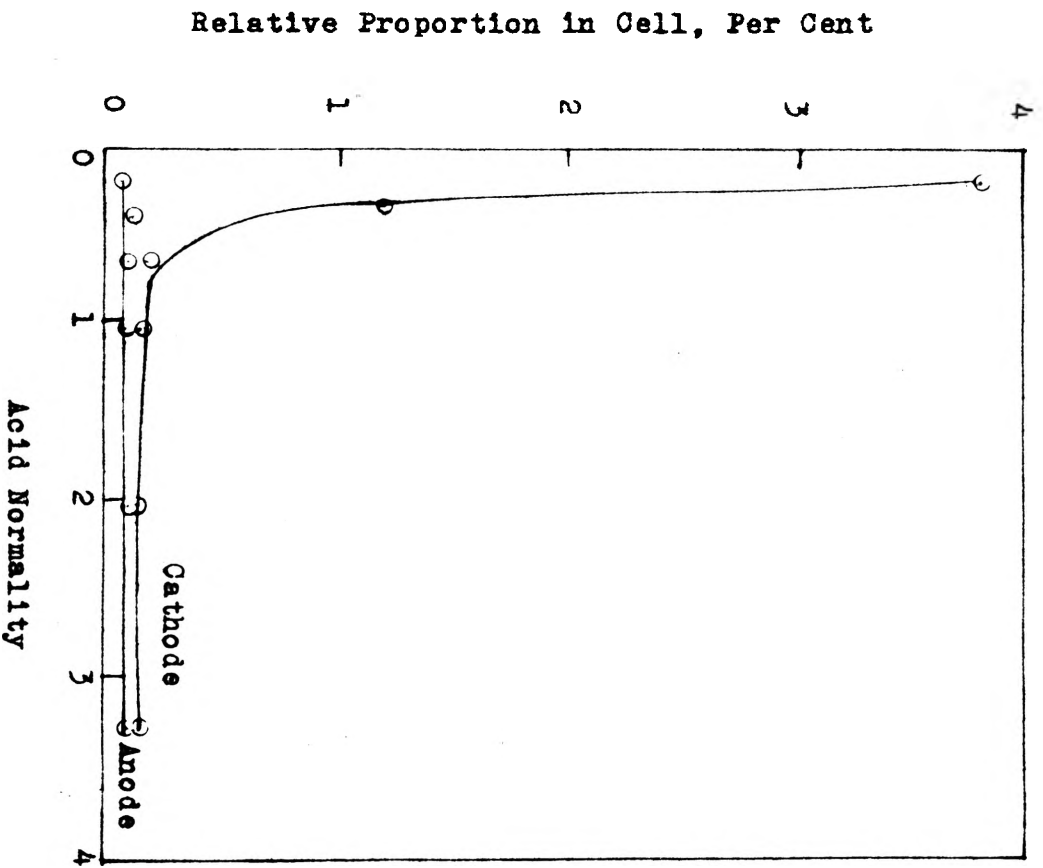
Figure 5. The Effect of Hydrofluoric Acid

Concentration on the Electrodialysis

of Zirconium-95 through Fritted Glass Membranes.

TABLE VI

The Electrodialysis of Zirconium[95] from Perchloric Acid
Solution Using Permselective Membranes[a]

| Time (Hrs.) | Normality (Center Cell) | Relative Proportion[a] | | | Recovery[b] |
		Anode	Center Per Cent	Cathode	Per Cent
2	6.27	0.2	73.1	0.30	94.8
2	3.97	0.18	69.3	0.30	93.2
2	2.07	0.11	54.6	0.13	94.6
2	1.12	0.12	33.2	0.11	91.8
2	0.43	0.08	28.9	0.07	92.4

[a] The temperature varied from 23 deg. C to 38 deg. C.

Figure 6. The Effect of Perchloric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes.

TABLE VII

The Electrodialysis of Zirconium[95] from Perchloric Acid
Solution Using Fritted Glass Membranes[a]

Time (Hrs.)	Normality (Center Cell)	Relative Proportion[(a)]			Recovery[(b)] Per Cent
		Anode	Center Per Cent	Cathode	
1	6.27	0.20	75.4	0.20	93.1
1	4.11	0.20	61.2	0.21	94.4
1	3.02	0.18	54.3	0.19	89.7
1	1.98	0.19	41.7	0.19	88.3
1	1.06	0.12	31.9	0.11	89.6
1	0.48	0.09	34.5	0.08	88.7

[a] The temperature varied from 24 deg. C to 66 deg. C.

[b] The low recovery is attributed to adherence of the
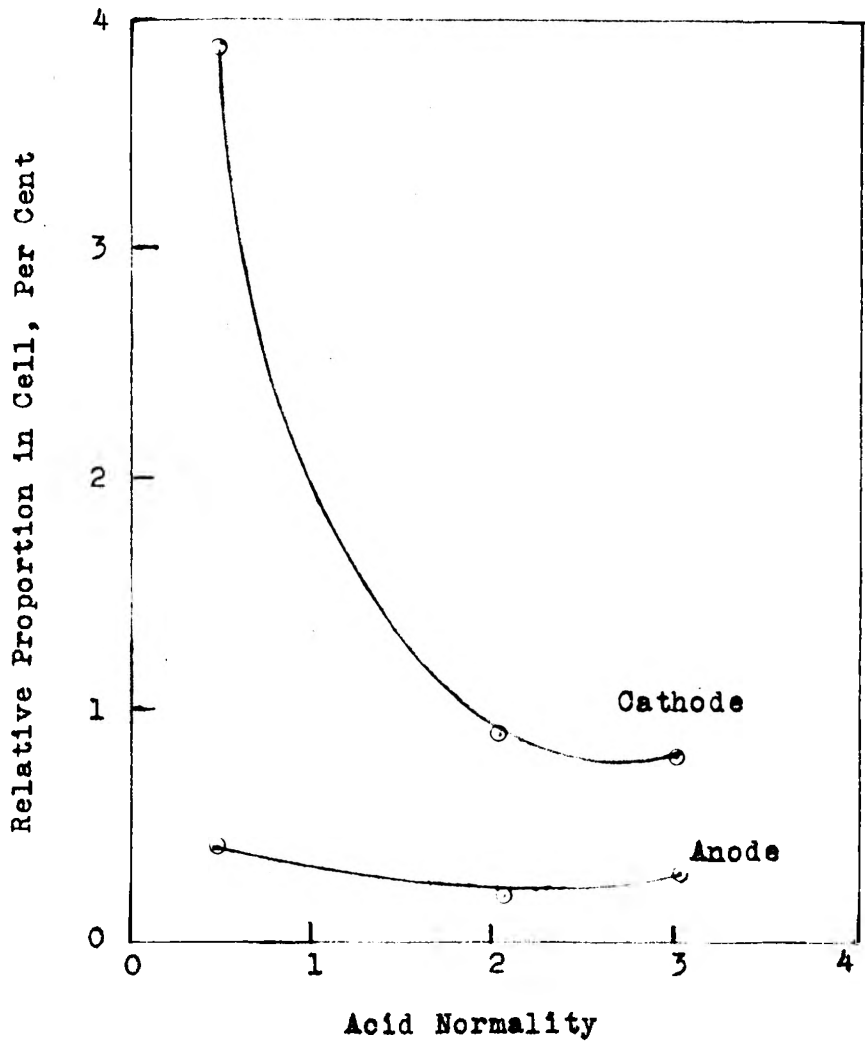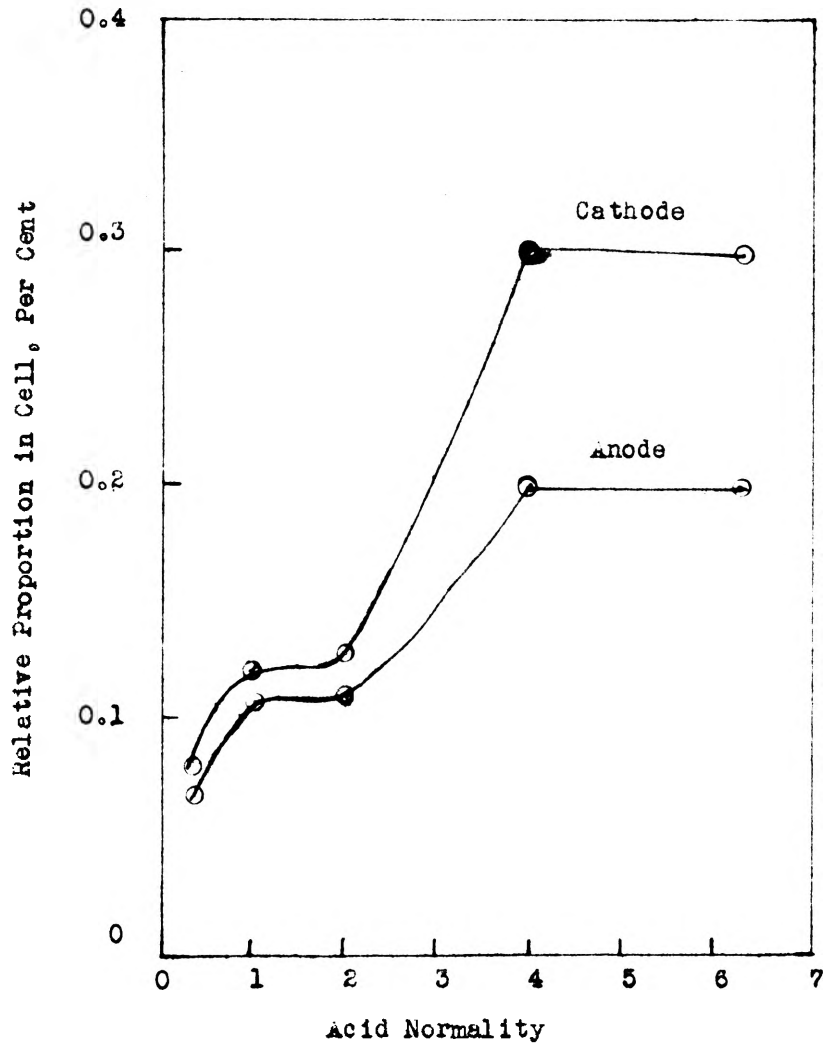zirconium species to the glass walls or membranes.

Figure 7. The Effect of Perchlòric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Fritted Glass Membranes.

TABLE VIII

The Electrodialysis of Zirconium[95] from Sulfuric Acid
Solution Using Permselective Membranes[a]

| Time | Normality | Relative Proportion[a] | | | Recovery[b] |
| (Hrs.) | (Center Cell) | Anode | Center | Cathode | Per Cent |
			Per Cent		
1	3.00	14.42	90.8	1.34	101.5
1	2.14	15.8	81.7	0.83	98.2
1	1.00	11.3	79.1	0.37	92.5
1	0.50	5.1	72.3	0.8	93.3

[a] The temperature varied from 23 deg. C to 44 deg. C

[b] The low recovery is attributed to adherence of the
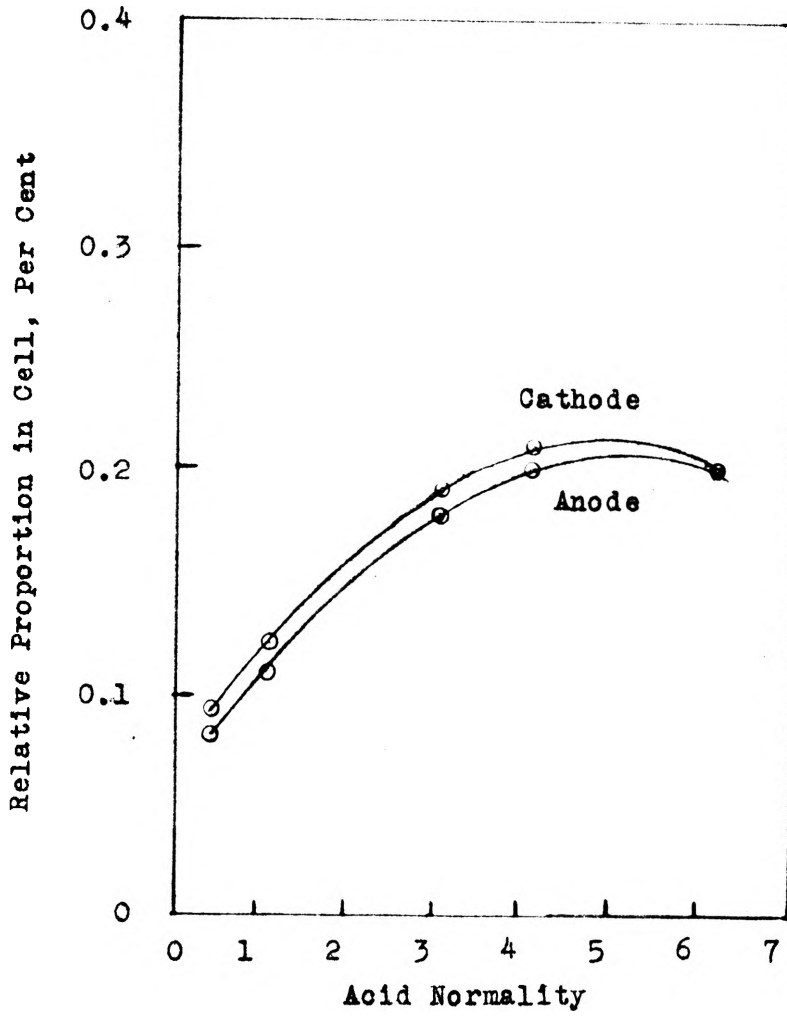zirconium species to the glass walls or membranes.

Figure 8. The Effect of Sulfuric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes.

TABLE IX

The Electrodialysis of Zirconium[95] from Sulfuric Acid
Solution Using Fritted Glass Membranes[a]

Time (Hrs.)	Normality (Center Cell)	Relative Proportion[a]			Recovery[b] Per Cent
		Anode	Center Per Cent	Cathode	
1	3.08	6.2	98.1	0.9	102.3
1	2.00	3.9	98.9	0.7	103.5
1	1.00	3.1	98.5	1.1	102.7
1	0.50	4.8	70.4	3.6	81.5

[a] The temperature varied from 23 deg. C to 68 deg. C.

[b] Erratic recovery is possibly due to adherence of the
species to the glass.

Figure 9. The Effect of Sulfuric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Fritted Glass Membranes.

TABLE X

The Electrodialysis of Zirconium[95] from Oxalic Acid Solution
Using Permselective Membranes[a]

Time (Hrs.)	Normality (Center Cell)	Relative Proportion[a]			Recovery Per Cent
		Anode	Center	Cathode	
			Per Cent		
2	1.98	67.5	12.5	2.4	95.4
2	1.30	63.5	18.0	2.0	92.9
2	0.69	51.2	10.1	1.7	96.2

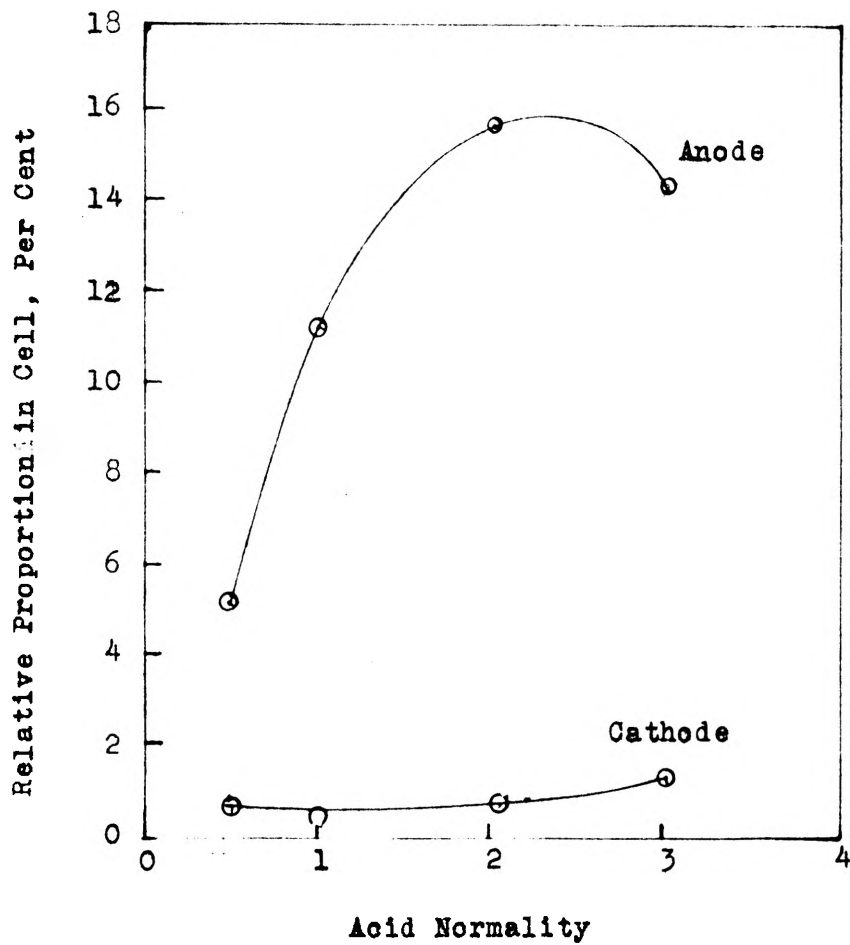[a] The temperature varied from 21 deg. C. to 70 deg. C.

Figure 10.   The Effect of Oxalic Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes.

TABLE XI

The Electrodialysis of Zirconium[95] from Oxalic Acid Solution
Using Fritted Glass Membranes[a]

Time	Normality	Relative Proportion[a]			Recovery[b]
(Hrs.)	(Center Cell)	Anode	Center	Cathode	Per Cent
			Per Cent		
2	2.00	28.3	90.2	0.3	101.3
2	1.06	15.1	41.3	0.7	94.3
2	·0.50	0.7	31.1	0.9	93.3

[a] The temperature varied from 22 deg. C to 71 deg. C.

[b] The low recovery is attributed to adherence of the
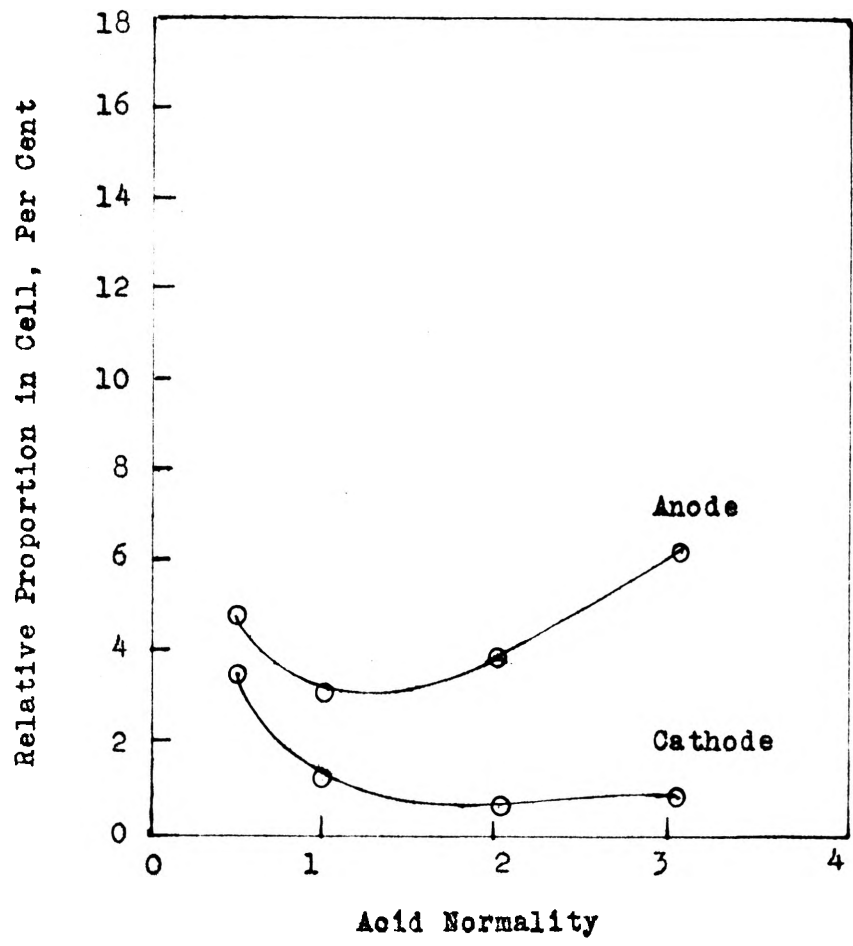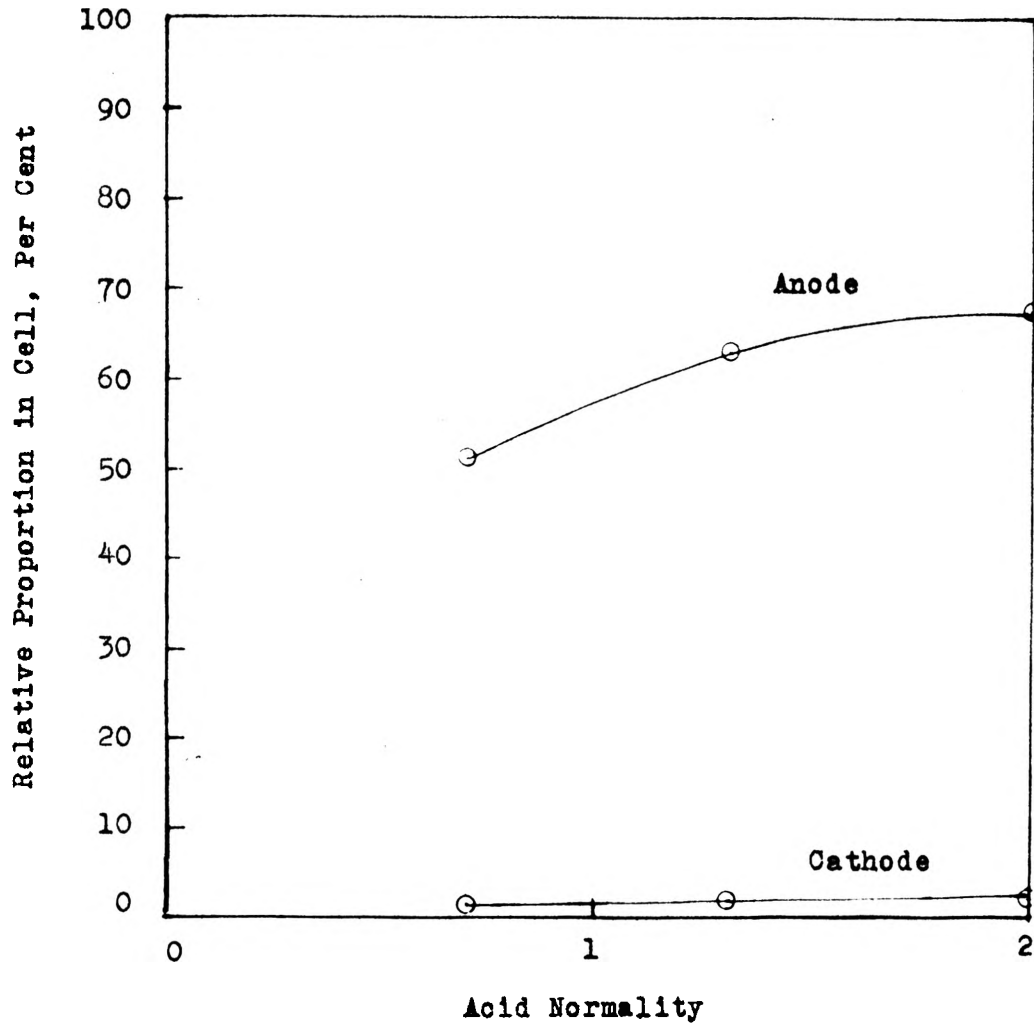zirconium species to the glass walls or membranes.
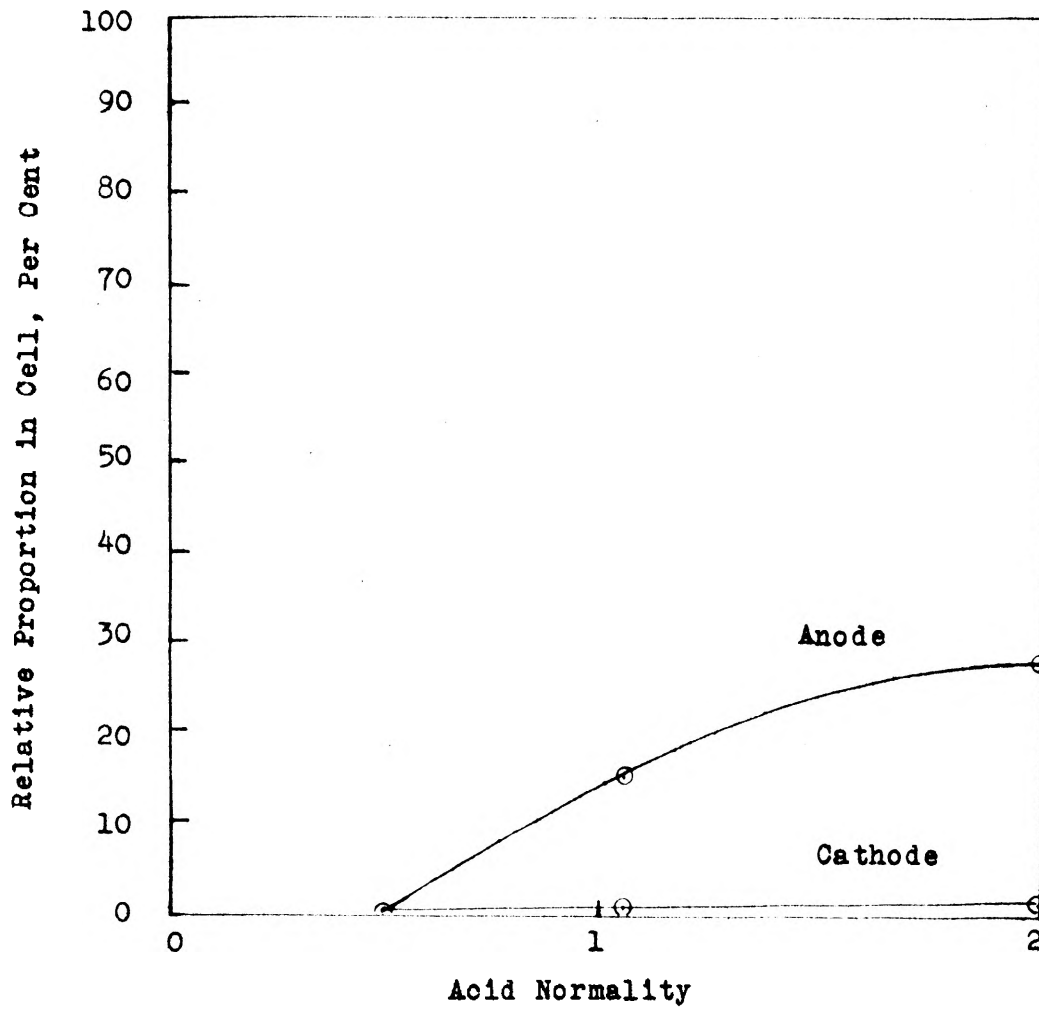
Figure 11. The Effect of Oxalic Acid
Concentration on the Electrodialysis
of Zirconium-95 through Fritted Glass Membranes.

TABLE XII

The Electrodialysis of Zirconium[95] from Hydrofluoric Acid
Solution Using Permselective Membranes[a]

Time	Normality[b]	Relative Proportion			Recovery
(Hrs.)	(Center Cell)	Anode	Center	Cathode	Per Cent
			Per Cent		
1	1.72	72.0	11.5	2.9	101.3
1	1.21	76.1	12.3	2.0	95.4
1	0.94	85.0	5.6	1.8	96.0

[a] The temperature varied from 22 deg. C to 69 deg. C.

[b] The increased reactivity of HF with the cell at the
higher temperatures encountered in the lower acid
concentrations prevented dialysis at lower acid
concentrations.

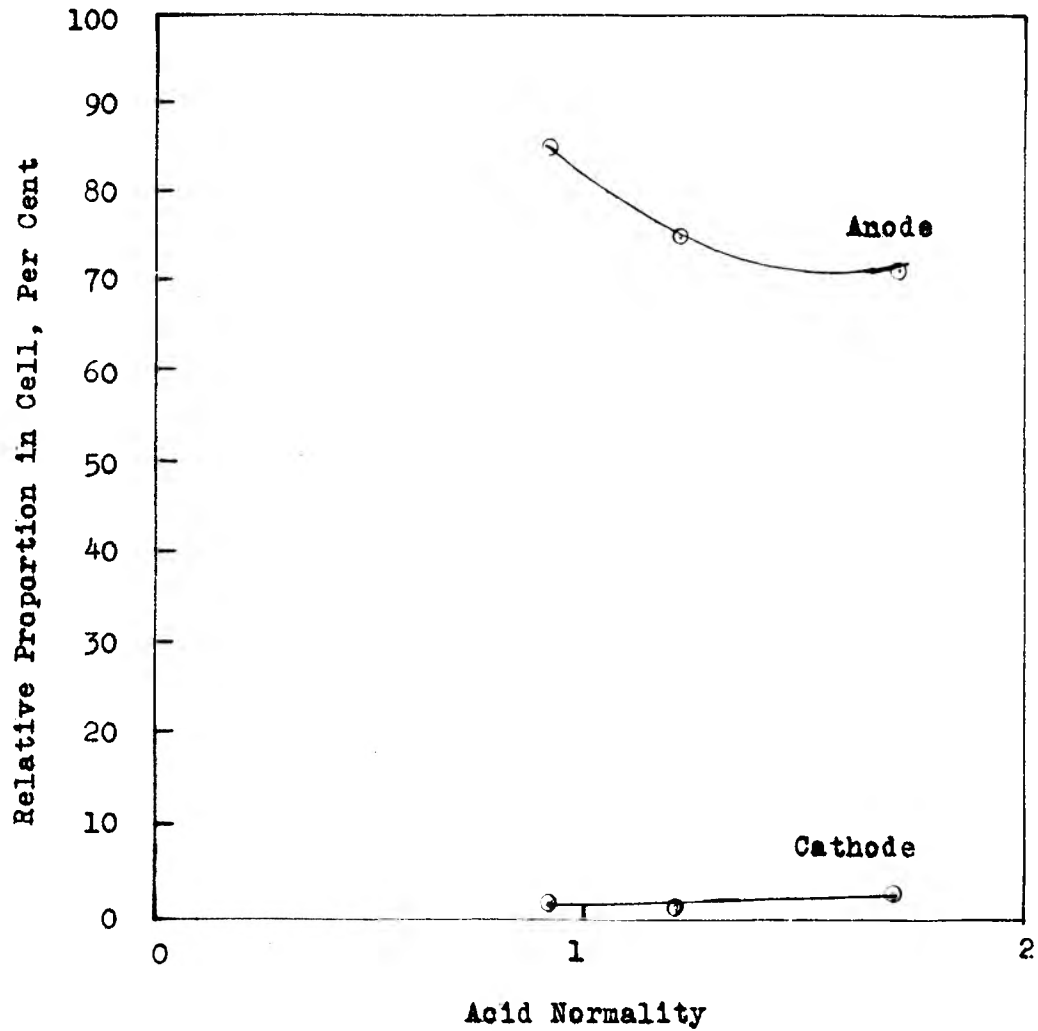Figure 12. The Effect of Hydrofluoric Acid
Concentration on the Electrodialysis
of Zirconium-95 through Permselective Membranes.

IV. DISCUSSION

The discussion consists of three parts: (1) dis-
cussion of results, (2) limitations and (3) recommendations.

Discussion of Results

The results of the investigation are discussed in the
order of data presentation.

The Nitrate System. Below a nitric acid concentration
of about 2 normal, very small per cents of zirconium dialyzed
to the anode and cathode cells. Above an acid concentration
of about 2 normal, even less electromigration was observed.
These results seem to indicate a small number of species of
both positive and negative charge or polymeric species with
charged groups attached. If a neutral dissocating species
is assumed to be present, one is lead to exclude the nitrate
group from it on the basis that the nitrate ion concen-
tration of a 0.1 formal zirconyl nitrate solution is the
same as the nitrate ion concentration of a 0.2 formal sodium
nitrate solution. J. N. Click[22] found that nearly 100 per
cent of the zirconium is extractable from nitric solutions
up to a concentration of 3 normal with respect to nitric
acid by using theonyl trifluoroacetone. An equally credible
explanation for this extraction is found by considering that
the chelating ability of the theonyl trifluoroacetone is
sufficient to break the oxo linkages of a neutral species
or a polymeric species.

The Chloride System. Very little electromigration
was observed in the hydrochloric solutions investigated.
The reported cationic complexes cannot be refuted, but the
small percentage electrodialyzed to the cathode cell is
suggestive of a polymeric species.

The Perchlorate System. Very little separation of
zirconium from perchloric acid solutions was achieved.
Although several cationic species are claimed to exist in
this system, the finding that there is practically no
electromigration of zirconium in these systems makes the
presence of these species doubtful. It is quite likely
that the zirconium in these systems is contained in oxolated
polymers.

The Sulfate System. At Sulfuric acid concentrations
of around 3 normal, about 15% of the zirconium can be
electrodialyzed to the anode cell during a time interval of
one hour. This indicates a negatively charged species. As
the acid concentration is decreased, less can be removed.
This is suggestive of the behavior of nitric and hydrochloric
acid solutions of zirconium. It appears likely that
oxolated polymers exist.

The Oxalate System. The data obtained by electro-
dialysis studies of zirconium in oxalic acid solutions
consistently indicated that the species was anionic. This
data furnishes no basis for disagreement with the species
proposed. The greater electromigration would lead one to
believe that if there was much polymeric nature to these
systems the length of the polymer is certainly less than

the lengths of the polymers in systems such as the nitrate.
Rather good separation of zirconium is possible from
oxalate solutions.

The Fluoride System. It was found that zirconium
can be very effectively separated from hydrofluoric acid
systems by electrodialysis. Data obtained during this
study clearly indicates the anionic character of the complex
but does not provide a basis for accepting or rejecting the
proposed species.

Limitations

The limitations which might have affected the results
are discussed.

Consistency of Membranes. Inhomogeneity of the
membranes would result in greater penetration of the dif-
fusible species when membranes are changed. The membrane
material used was cut from a large sheet and no information
was available regarding its uniformity.

Sampling. The samples for counting were removed with
a one milliliter pipet and placed in the counting dishes.
Small volume errors could thus cause error in the activity
counted, especially for solutions where the activity is high.

Sample Preparation. After pipeting into the counting
dishes, the samples were dried by placing the counting
dishes under a heat lamp. There is no assurance that the
sample was uniformly distributed over the bottom of the
counting dish after drying, although a motor-driven rotating
platform was used. In some cases the acid solution reacted

slightly with the dish, leaving a deposit which could serve as an absorber. If this deposit were not uniform or if the thickness varied in the various samples, considerable error could be introduced.

Radiocounting. The random nature of radioactive disentegrations leads to error which is inversely proportional to the counting time. Standard deviations of 6.6 per cent and 7.3 per cent were obtained[66] for the background count using two different scalers. The magnitude of these deviations correspond to a standard deviation of less than 0.02 counts per second. These results were calculated from forty-four determinations.

The majority of the results (except for samples of very low activity) in this work have a standard deviation of less than one per cent.

Overman and Clark[56] list the following errors as being characteristic of radioactive measurements:

(1) Failure of the detector to resolve events at high counting rates.

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

(3) Random disentegration process and, therefore, random emission of radiation.

(4) Variation in natural background activity during the course of the counting.

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

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

Current Density. The power supply used had no provision for constant current regulation and changes in the resistance of the solutions necessitated changes in the output voltage of the power supply by manual operation. The current was kept as constant as possible, but no adjustment could be made for small fluctuations of line voltage. Comparison of results with others obtained at slightly different values of current density indicated that small current changes of this nature had immeasurable effects on the final results.

Recommendations

Subsequent to the design of equipment to separate zirconium from acid solutions where separation appears feasible, it would be desirable to conduct further electro-dialysis experiments using solutions containing greater concentrations of zirconium in the presence of any other materials which might be anticipated to be present in the solutions. It is quite possible, and highly desirable, that continuous processes of electrodialysis might be devised. Information should be determined regarding the relative complexing strengths of oxalic and hydrofluoric acids in the presence of high concentrations of non-complexing acids such as nitric and perchloric.

The information concerning the charge carried by various species obtained by these experiments does not permit

valid conclusions regarding the actual species present in the colutions. Information which could result in determination of the actual species present might be gained from a study of these complexes by the method of Job[67] if specific absorption bands can be found for the various ligands.

V. CONCLUSIONS

This investigation of the electrodialysis of zirconium from various acid solutions makes possible the following conclusions.

Separation of Zirconium by Electrodialysis. Zirconium can be readily and quantitatively separated by electrodialysis from hydrofluoric acid solutions. The best separation was attained from solutions which were about 1 normal hydrofluoric acid. Most likely, competition of other ions, such as fluoride ion, diminished the electro-migration of the zirconium species at higher acid concentrations.

Separation of zirconium by electrodialysis from oxalic acid solutions can be done, but results are not as good as those obtained from the hydrofluoric acid system.

As much as 15 per cent of the zirconium can be dialyzed from solutions 3 normal in sulfuric acid within one hour.

The time of dialysis is stated for all the solutions for which percentages dialyzed are given.

Separation of zirconium by electrodialysis from hydrochloric, nitric or perchloric acid solutions is not feasible in any concentration range studied.

Species Present in the Solutions. It has already been mentioned that these data do not permit unequivocable designation of the exact composition of the species present

in any of the solutions. The discussion to follow will thus concern the manner in which these data tend to support various proposed configurations.

The low diffusibility of zirconium in hydrochloric, nitric and perchloric acid solutions at all concentrations studied and in the sulfuric acid solutions less than 0.5 normal favor the belief of those who regard these solutions to contain zirconium in a highly polymeric form, but do not refute explanations based on the presence of neutral molecules.

The behavior of zirconium in sulfuric acid solutions of moderate concentration is sufficient to establish the existence of an anionic species.

The magnitude of the diffusion of zirconium from oxalic and hydrofluoric acid solutions certainly supports the proposal of anionic species as the predominate ions of these solutions. The decrease in quantity diffused with increasing acid concentrations may be explained by the greater competition from other ions for carrying the current.

The separation of zirconium by electrodialysis is best accomplished from hydrofluoric or oxalic acid media.

VI. <u>SUMMARY</u>

The purpose of this investigation was to obtain information concerning the electromigration of zirconium species through permselective and fritted glass membranes, and to gain whatever knowledge these data permitted concerning the particular species present. Electrodialysis of zirconium was investigated by using solutions of hydrochloric, nitric, perchloric, sulfuric, hydrofluoric and oxalic acid solutions.

It is established by this work that the most effective separation of zirconium by electrodialysis is accomplished by electrodialyzing from hydrofluoric or oxalic acid solutions.

Although the exact formula of the species was not determinable from these data, it is quite clear that zirconium exists in hydrofluoric and in oxalic acid solutions predominately as anions. Sulfuric acid solutions of zirconium also contain anionic species but these species are not nearly as predominate as those in hydrofluoric and in oxalic acid solutions.

Zirconium species in hydrochloric, in nitric and in perchloric acid solutions are primarily polymeric, making separation of zirconium from these solutions feasible only by removal of other ions which are present, if they are diffusible by electrodialysis.

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VIII. <u>ACKNOWLEDGMENTS</u>

IX. <u>VITA</u>

Charles William Brauer, Jr., son of Charles W. and Mary J. Brauer, was born November 22, 1929, in Mexico, Missouri.

He attended public elementary and secondary schools in Mexico, Missouri and received his high school diploma from Mexico High School in May, 1947.

He received a Bachelor of Science degree from Central Missouri State College, Warrensburg, Missouri, in June, 1951.

Immediately following graduation from college, he entered the United States Air Force and served as an Electronics Officer until October, 1953.

He has been employed as a high school teacher in the Rolla High School, Rolla, Missouri, from September of 1954 until June of 1956. He served as an Instructor of Chemistry in the Jefferson City Senior High School and Junior College, Jefferson City, Missouri until February, 1959. In February, 1959, he joined the faculty of the Missouri School of Mines and Metallurgy as an Instructor of Chemistry. During the summer of 1956, he worked as a chemist with the United States Bureau of Mines, Rolla, Missouri. He worked as a chemist with the Missouri State Highway Patrol, Jefferson City, Missouri during the summer of 1959.

In February, 1959, 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 an Instructor of
Chemistry, which position he still holds.