THE SEPARATION OF ALUMINUM AND
ZIRCONIUM BY ION EXCHANGE

by

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A THESIS

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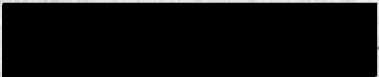
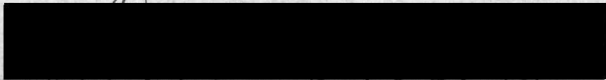in partial fulfillment of
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TABLE OF CONTENTS

TABLES

FIGURE

THE SEPARATION OF ALUMINUM AND
ZIRCONIUM BY ION EXCHANGE

INTRODUCTION

Many impurities influence the physical character-
istics of metallic zirconium. Consequently, the routine
control of the raw materials, as well as the final metal,
necessitates many analyses for minor constituents. The
determination of aluminum in the range below 500 ppm is
often required. While numerous methods for the deter-
minations of small amounts of aluminum are known, none
are successful in the presence of large amounts of
zirconium. Consequently a suitable separation method is
required and it is the purpose of this thesis to investi-
gate the separation of zirconium and aluminum by means of
anion exchange.

Several methods may be found in the literature for
the separation and determination of macro-quantities of
aluminum in zirconium.

The first methods were developed in conjunction
with the determination of zirconium in steel. Since
aluminum also occurred in the steel, it was necessary to
separate the two. Lundell (16, p.563) reviewed the
methods up until 1920 and recommended the use of excess
sodium hydroxide for the separation of aluminum from
zirconium. The procedure depends upon the amphoteric
properties of aluminum. The aluminum will dissolve in a

caustic solution, but zirconium, being non-amphoteric, will precipitate as the hydroxide.

In the same year Lundell published a method for the analysis of zirconium in minerals. He used cupferron, the ammonium salt of phenylnitrosohydroxylamine, which will precipitate zirconium quantitatively in acid solution, but not aluminum (15, p.1447).

Arsonic acids were found to be specific reagents for the quadrivalent metals of Group IV, the group containing zirconium. Based on this, Geist and Chandlee developed a method for the separation of zirconium and aluminum in steel analysis (6, p.169). n-Propyl arsonic acid was used to precipitate zirconium quantitatively, leaving the aluminum in solution.

More recently, investigation of the chemistry of Group IV elements showed that mandelic acid, $C_6H_5CHOHCOOH$, precipitates zirconium quantitatively in strongly acid solutions, separating it from aluminum (13, p.376; 7, p.1579). The zirconium mandelate is ignited to the oxide for weighing, since the zirconium mandelate itself can not be washed free of excess mandelic acid.

This discovery suggested to other investigators that the glycolic acid group (-CHOH-COOH), present in mandelic acid, might be specific for zirconium (18, p.1510). Consequently, a number of glycolic derivatives

were prepared and their reactions with zirconium studied. The results of these studies indicated that the preferable reagents for the determination of zirconium were first, p-bromomandelic acid, then p-chloromandelic acid and finally mandelic acid itself. The halogen derivatives are especially attractive because the compounds they form with zirconium are apparently capable of direct weighing to determine the zirconium, instead of ignition to zirconium oxide before weighing. Results are reported for the successful analysis of iron-zirconium-aluminum alloys.

A report of a very recent investigation (1950) describes the use of phthalic acid as a selective precipitant for zirconium (20, p.684). The zirconium is precipitated quantitatively by the phthalic acid from solutions 0.35 N with respect to free hydrochloric acid. Aluminum is separated in this way from zirconium with a single precipitation.

Another very recent investigation indicates the possibility of using m-nitrobenzoic acid to separate zirconium and aluminum (19, p.382). m-Nitrobenzoic acid appears to be specific for quadrivalent ions: it can precipitate zirconium quantitatively, but leave aluminum in solution.

The methods just described all fail when the concentration of aluminum becomes very low. It is necessary to develop a procedure that will separate the aluminum from the zirconium. Then the aluminum can be determined by conventional methods.

The common separation methods fall into the following catagories (25, p.26-28):

Direct Precipitation of the Desired Minor Constituent. This involves the precipitation of the desired minor constituent from the major. Usually a small amount of the major constituent will be precipitated and a second precipitation will be required to achieve complete separation.

Fractional Precipitation of the Minor Constituent. This method is similar to the preceding one, except that the reagent is capable of precipitating both the major and the minor constituents. Sufficient reagent is added to precipitate all of the minor constituent and a very small amount of the major. This separation is based on the lower solubility of the minor constituent in comparison to that of the major constituent.

Extraction with Immiscible Solvent. Extraction of the minor constituent with an immiscible solvent is possible in many cases. The general procedure for metals is to add a reagent capable of forming a complex ion

which is preferentially soluble in an immiscible solvent. An example of this is the extraction of various heavy metals as dithizonates with carbon tetrachloride or chloroform.

Distillation or Sublimation. Complete separations of minor constituents are often possible by distillation. Traces of arsenic can be separated from large amounts of copper, antimony or tin by distillation of the arsenic trichloride from a hydrochloric acid solution.

The separation of minor quantities of aluminum from zirconium by any of the preceding methods is not feasible. Reagents that will precipitate aluminum will also precipitate zirconium. And invariably the zirconium compounds are more insoluble. It is possible that an organic reagent could be found that would complex aluminum and not zirconium, and so permit the use of solvent extraction, but apparently no adequate reagent is yet known. It is possible that aluminum and zirconium could be separated by sublimation of their chlorides. Under anhydrous conditions, aluminum chloride sublimes at about $200^{\circ}C.$, zirconium tetrachloride at $330^{\circ}C.$ (24, p.480). But this procedure would require special apparatus to maintain anhydrous conditions. And it might be very difficult to quantitatively sublime a very small amount

of aluminum chloride from a large quantity of zirconium tetrachloride.

Ion exchange appears to be a practical method for the separation of aluminum and zirconium. It is not hampered by having the aluminum present in very small amounts. It completely separates the zirconium from the aluminum, so that conventional methods may be used to determine aluminum.

This thesis reports the development of the ion exchange method for the separation of aluminum and zirconium. Both of these elements form negatively charged fluoride complex ions. The zirconium fluoride complex is exchanged and retained on the resin. The aluminum fluoride complex passes on through the resin column and the aluminum is determined in the eluate.

THEORETICAL CONSIDERATIONS

DEVELOPMENT OF ION EXCHANGE. Ion exchange has had a curious history. It has been known for at least a hundred years, but the diversity of its applications as well as the complexity of its theoretical aspects are only a few decades old (17, p.1).

The discovery of ion exchange is credited to two English soil scientists, Way and Thompson (17, p.1). They noticed, in 1850, that water-soluble fertilizer salts such as ammonium sulfate and potassium chloride could not easily be leached out of the soil by the action of rain water. Nothing more was done with the phenomenon until a German chemist, Gans, in 1910, showed that ion exchange could be applied to the softening of hard water. From this time until 1935 the little work that was done on ion exchange used natural products such as alumino-silicates and sulfonated coals as exchangers.

In 1935, Adams and Holmes, in England, condensed phenolsulfonic acids with formaldehyde and obtained an ion exchange material that was suitable for hydrogen interchange. They went one step further and produced anion exchange resins by condensing polyamines with formaldehyde (17, p.1).

With this development of synthetic resins, which soon could be tailor made to have almost any desired characteristics, the applications of ion exchange became legion. The separation of the rare earth elements that was accomplished at Iowa State College during the last war is an indication of the type of problem that can be solved by ion exchange methods (2, p.1200). Until this time, the separation of even some of the rare earths was at best a tedious job. But now ion exchange methods can produce pound lots of these elements.

Until the last three or four years, most of the ion exchange separations involved cations because strongly basic anion exchangers were not available. The anion exchange resins that were available had extremely low exchange capacities which were very sensitive to pH (17, p.23). Recently, high capacity anion exchange resins have appeared that can be used under wide conditions of pH, so that it is now possible to conduct anion exchange reactions under almost any pH condition.

DESCRIPTION OF ANION EXCHANGE RESIN. The resins used in this work were Dowex 1 and Dowex 2. Both of these resins are of the quaternary amine type (R R' R'' R''' N^+ A^-) (23, p.1088). One of the R's is derived from polystyrene, which in turn has been linked with divinyl-benzene for maximum exchange capacity and to render the

resin insoluble in aqueous and nonaqueous media. In the case of Dowex 1, three of the R groups in the structure mentioned above are methyl groups, whereas in Dowex 2, one of the methyl groups is replaced by hydroxy ethyl. The chief difference between these two is that Dowex 1 is somewhat more basic in character.

Chemically, the resin behaves as if it were a strongly dissociated electrolyte. Fundamentally, the only difference between a resin and an electrolyte is that in the former the cation is insoluble and non-mobile while in the latter the cation is soluble and mobile (14, p.1086). To preserve electrical neutrality in the resin, the anion is confined to the vicinity of the non-mobile cation. But when another anion approaches, and conditions are favorable, the anions can be exchanged.

Equilibrium conditions exist in the partition of the anions between the external liquid phase and the resin. Much work has been done on the study of this equilibrium. Numerous and unexplained difficulties have arisen, however, so there is no generally applicable theory that can be applied to all ion exchange equilibria conditions (21, p.324). The attempts to interpret the equilibrium partition of the anion between the liquid and solid phase may be classified under several headings (21, p.324): a) as analogous to a reversible double

decomposition reaction, to which the law of mass action
may be applied; b) as analogous to an ionic adsorption
reaction, capable of being described by the Langmuir
isotherm; c) as a problem in the behavior of ions at a
charged surface; or d) as a Gibbs-Donnan distribution
between two homogeneous phases. For the type of study
being made in this thesis, it is not necessary to know
the exact mechanism of the equilibrium process: it would
nevertheless be interesting to see which of the above
mechanisms best describes the equilibrium.

FLOURINE COMPLEXES OF ALUMINUM AND ZIRCONIUM.
Soluble complex fluoride ions of both aluminum and
zirconium are known. They are very stable complexes:
the covalent bond between the aluminum and zirconium and
the fluoride ion is very strong (22, p.435; 5, p.3183).

A whole series of complexes is formed by changes
in the metal-fluoride ratio. In solutions, this ratio is
seldom known with certainty. In fact, there are usually
several species present in a given solution at the same
time.

Of the two metals, the least information was found
on aluminum fluoride complexes. Cryoscopic measurements
of solutions of aluminum fluoride of various concentra-
tions indicated the possibility of three types of com-
plexes, $(AlF_6)^{-3}$, $(Al_2F_9)^{-3}$ and $(AlF_4)^{-1}$ (4, p.3805).

Sidgwick indicates that $(AlF_5)^{-2}$ is also known (22, p.435).

Zirconium fluoride complexes have been more thoroughly investigated. Connick and McVey (5, p.3189), working in a 2.0 molar perchloric acid solution and using a two phase distribution equilibrium with thenoyltrifluoroaceton as a chelating agent, reached the following conclusion, which indicates the great stability of the complex: in 10^{-5} molar hydrofluoric acid, 78% of the zirconium is complexed and in 8×10^{-3} molar hydrofluoric acid all but 0.0012% of the zirconium is complexed.

By the same type of experiment, these men were also able to obtain some information on the composition of the fluoride complex. Their results indicated the following:

Hydrofluoric acid concentration	Average number of fluoride ions per zirconium
2×10^{-5} M	1
5×10^{-4} M	2
10^{-2} M	3

These authors indicate, however, that these are only the average number of fluoride ions per zirconium ion, and that any solution would contain several of these different species.

ANION EXCHANGE STUDIES OF THE ZIRCONIUM FLUORIDE
COMPLEX. Anion exchange, involving the fluoride complex
of zirconium, had been reported before this thesis was
begun. The first report, by Kraus and Moore at the Oak
Ridge National Laboratory, concerned the anion exchange
separation of zirconium and hafnium. It appeared in
1949. By using Dowex 1, and an eluent containing 0.5 M
hydrofluoric acid and 1 molar hydrochloric acid, a
separation of zirconium (IV) and hafnium (IV) on a tracer
scale was feasible, although the separation achieved was
by no means quantitative (12, p.3263).

In the same year, Huffman and Lilly, at the Radia-
tion Laboratory, University of California, succeeded in
separating milligram quantities of zirconium and hafnium,
using essentially the same process as Kraus and Moore,
and getting about the same results (9, p.4147).

Both of these articles indicated that a separation
of zirconium and hafnium, using the fluoride complex, was
possible. Since their publication, other work has been
reported on zirconium and hafnium (8, p.2902) as well as
zirconium and niobium (11, p.9). The portions of these
later works that are related to zirconium can be sum-
marized as follows:

1) At high hydrochloric acid concentrations
(above 3 molar) and at hydrofluoric acid concentrations

studied (0.004 to 6.9 molar) there was very little ex-
change between the chloride form of the anion exchange
resin and the zirconium fluoride complex.

2) At lower hydrochloric acid concentrations,
the zirconium fluoride complex becomes more completely
exchanged. At very low hydrochloric acid concentrations,
this exchange is quantitative (11, p.12).

In order to determine whether aluminum and
zirconium could be separated using their fluoride com-
plexes, it was necessary to determine the exchange
characteristics of the aluminum fluoride complex. If
these characteristics were sufficiently different from
the zirconium fluoride complex characteristics, a separa-
tion would be possible.

EQUILIBRIUM STUDIES. In a liquid-resin system,
there is a partition of ions between the liquid and the
resin phases. A distribution coefficient can be cal-
culated which will express this partition. The technique
used in determining the distribution coefficient consists
of combining a weighed quantity of resin with a solution
containing the ions to be studied. The mixture is shaken
until equilibrium has been attained. Then an aliquot of
liquid is withdrawn and analyzed. From this analysis the
distribution coefficient, K_d, can be calculated.

This coefficient is defined as the concentration
of an ion in the resin phase divided by its concentration
in the liquid phase. When the weight of the resin and
the volume of the liquid are kept constant,

$$K_d = \frac{M_s}{M_l}$$

where M_s and M_l are the millimoles of the metal ion, M,
in the resin and liquid phases, respectively.

The distribution coefficient indicates the extent
of exchange of an ion with a resin. If the value of the
distribution coefficient is high, it indicates that the
ion has exchanged extensively with the resin. If it is
low, it indicates that there has been little exchange and
that the concentration of the ion is high in the liquid
phase.

The distribution coefficient for a particular metal
ion remains constant for any change in the ratio of the
resin mass to the volume of the solution containing the
ion. This distribution coefficient remains constant, how-
ever, only as long as the species of the metal ion in the
solution does not change.

When there is a change in the species of the metal
ion in the solution, there will be a change in the dis-
tribution coefficient. Since the distribution coefficient
is a measure of the ratio of the millimoles of metal on

the resin to the millimoles of metal in the liquid, it follows that an increase in the distribution coefficient will indicate an increase in the amount of metal on the resin.

If it is desirable, therefore, to put a metal on the resin, some method can be used to alter the ion species so that the partition of the metal between the resin and the liquid will leave most of the metal on the resin.

One method by which a metal ion species can be altered is by complexing the ion. This can be accomplished by keeping the concentration of the metal ion being studied constant and varying the concentration of the complexing ion. For example, in nine molar hydrochloric acid, three different species of the niobium fluoride complex ion are observed. Two of these species occur at low fluoride ion concentration, the third at a higher fluoride ion concentration (11, p.13).

The particular effect that any new ion species has on the partition of the metal between the liquid and the resin can be determined by equilibrium experiments and expressed as distribution coefficients. In the case of the three niobium fluoride ion species, it was found that the distribution coefficient was high at hydrofluoric acid concentrations ranging from 0.004 to 0.05 molar,

indicating that most of the metal was on the resin. At hydrofluoric acid concentrations ranging from 0.1 to 0.5 molar, the coefficient was low, indicating that most of the metal was in the liquid phase. The coefficient was high again at hydrofluoric acid concentrations ranging from 1.0 to 6.9 molar, indicating that most of the metal again was on the resin.

It has been shown that the greater the separation between the distribution coefficients of two different ion species, the most easily can these species be separated in a column of resin (1, p.8). This is easily understood. A solution going through a column of resin receives the same treatment as if it had gone through many batch equilibrium runs. If the distribution coefficient of one of the ion species is high, and the distribution coefficient of the other ion species is low, the species having the higher coefficient will concentrate on the resin, while the species having the lower coefficient will concentrate in the solution and so be carried through the resin column.

Each of the metal ion species present in a given liquid-resin system will have a unique distribution coefficient. Equilibrium experiments will furnish information for the calculation of each of these distribution coefficients. From these data, it will be possible to

determine the conditions at which there is the greatest difference between the distribution coefficients of the different ions. These are the conditions that would be used for a column separation of the ions.

EXPERIMENTAL

APPARATUS.

<u>Ion exchange column</u>. The ion exchange column was made from Pyrex tubing, 19 millimeters in diameter and a meter long. There was a constriction at one end of the tube to which was attached a piece of Tygon tubing. A pinch clamp was used on this tubing to help regulate the rate of flow of solution through the column.

Suction was used to produce the rapid flow rates that were desired. A small suction flask was attached to the Tygon tubing. Suction was applied through a safety bottle by a water aspirator. The pressure was regulated by a bleeder valve on the safety bottle.

To prevent hydrofluoric acid from attacking glass and introducing aluminum into the solution, all glass-ware coming in contact with the acid was coated with Tygon or paraffin. Beakers were used that were made from poly-ethylene plastic, which is unattacked by hydrofluoric.

<u>Plastic bottles</u>. Experiments to study the equilibrium between the fluoride complexes and the resin were conducted in 250 milliliter polyethylene plastic screw-cap bottles.

REAGENTS.

<u>Dowex 1 and Dowex 2</u>. These anion exchange resins

were supplied by Microchemical Specialties Co., 1834
University Avenue, Berkeley 3, California. The resin
used was 200 to 400 mesh. It arrived in a moist condi-
tion and was treated with concentrated hydrochloric acid
to convert it all to the chloride form. It was then
washed with water until the eluate, when treated with a
silver nitrate solution, showed only a slight opales-
cence. The resin was oven-dried at 80°C. This chloride
form of the resin was used for all of the experiments.

Zirconium metals. Metal turnings were obtained
from the Bureau of Mines in Albany, Oregon. The metal
was impure.

Zirconium oxychloride. Zirconium oxychloride was
used as a source of pure zirconium. It was prepared by
James Kanzelmeyer from zirconium tetrachloride by dis-
solving the tetrachloride in water and crystallizing the
oxychloride out of an 8 normal hydrochloric acid solution.
The composition was approximately that of the hexahydrate,
$ZrOCl_2 \cdot 6H_2O$, having an analysis of 31.20% zirconium.

Zirconium hydride. Zirconium hydride was prepared
at the Massachusetts Institute of Technology by the
hydrogenation of zirconium salts. The samples used in
this work were obtained from the Bureau of Mines at
Albany, Oregon.

Aluminum metal. Aluminum foil was used. It was free from iron by the thiocyanate test.

Boric acid. Reagent grade crystals were used.

Hydrofluoric acid. J. T. Baker Chemical Company's c.p. reagent was used. It was about 48% hydrogen fluoride.

Ammonium acetate solution, 2 normal. This solution was prepared by dissolving 77 grams of reagent grade ammonium acetate crystals in 500 milliliters of distilled water.

Oxine (8-hydroxyquinoline) reagent. This solution was prepared by dissolving 5 grams of Eastman's White Label 8-hydroxyquinoline in 10 milliliters glacial acetic acid, filtering and diluting to 100 milliliters with boiling distilled water. The solution was kept out of direct light.

Elutriant solution for column runs. This solution was prepared by diluting 10 milliliters 3 molar hydrochloric acid and 15 milliliters 27 molar (concentrated) hydrofluoric acid to 500 milliliters with distilled water.

Potassium sulfate. Mallinckrodt's Analytical Reagent grade potassium sulfate, powdered, was used.

All of the other chemicals used were of reagent grade.

METHODS FOR DETERMINING ALUMINUM.

Oxine Method for Determining Aluminum. Aluminum

was determined by precipitation with oxine (8-hydroxy-quinoline). The oxine quantitatively precipitates aluminum as $Al(C_9H_6ON)_3$ from an acetic acid solution buffered with acetate (19, p.327). The favorable gravimetric factor, due to the low aluminum content of the precipitate, is a distinct advantage of the oxine method for determining small amounts of aluminum. The gravimetric factor for aluminum in the oxine is 0.05874.

Procedure. The eluate from an equilibrium run or a column run is combined with 2 or 3 milliliters of concentrated sulfuric acid in platinum dishes and then evaporated on a steam bath. In order to remove the small amount of resin that is present in the solution, the sulfuric acid is heated to fuming and nitric acid is added dropwise until all of the resin is oxidized. This fuming aids also in removing the hydrofluoric acid from the solution.

After fuming, the sample is transferred from the platinum dishes into a glass beaker and diluted to approximately 100 milliliters. Methyl red indicator is added to this acid solution and it is heated to boiling. In order to completely remove any fluoride ions remaining in the solution, crystalline boric acid is added. If all of the fluoride ions are not removed, it is impossible later to quantitatively precipitate the aluminum with

oxine. About 10 grams of boric acid are necessary for every 10 milligrams of aluminum present.

The solution is removed from the heat, and sodium hydroxide is added until the indicator changes color. A slight excess of oxine reagent is added, allowing about one milliliter of reagent for every 3 milligrams of aluminum present. Slowly, 2 normal ammonium acetate solution is added. If more than 5 milligrams of aluminum is present, the ammonium acetate is added until a precipitate begins to form, and then 25 milliliters more is added for each 100 milliliters of solution. If less than 5 milligrams of aluminum is present, the precipitate forms so slowly that the above method is impractical. Instead, 25 milliliters of the ammonium acetate solution is added for every 100 milliliters of the original solution. Enough reagent has been added, if, at this point, the supernatant liquid is yellow. The solution is set aside for an hour without further heating, and then is filtered, using suction, through a weighed, sintered glass crucible. The precipitate is washed thoroughly with cold water and then dried at 130-140°C. for at least an hour and weighed.

As mentioned in the procedure, it is impossible to quantitatively precipitate aluminum with oxine if any fluoride ions are present. The usual procedure for

removing fluoride ions is by fuming with sulfuric acid. Apparently, however, this does not completely remove all of the fluoride ions, for enough remain in the solution to prevent the complete precipitation of aluminum by oxine.

The effect of fluoride ions on the precipitation of aluminum by oxine was observed by Vasilier (26, p.523). He suggested the use of boric acid to complex the fluoride ions. By doing this he was able to quantitatively precipitate the aluminum with oxine.

By combining the sulfuric acid fuming with the addition of boric acid, it was possible in these determinations to completely remove the fluoride ions and so precipitate aluminum quantitatively with oxine.

Although no direct reference was found for the type of complex formed by the fluoride ion and boric acid, it is probable that the structure is that of one of the fluoroboric acids (22, p.385).

Fluorescent Method for Determining Aluminum. White and Weissler describe a fluorescent method for determining very small amounts of aluminum (24, p.532). They used Pontachrome Blue Black R, a dye giving a red fluorescence with aluminum. The method was of interest to us, for it permitted determination of much smaller amounts of aluminum than it was possible to determine by

the oxine precipitation method.

A great deal of time was spent in trying to adapt this fluorescent method for our use. Using pure aluminum metal dissolved in hydrochloric acid as a source of aluminum, very good results were obtained. But it proved impossible to get consistent results if the aluminum first went through a column separation.

METHOD FOR DETERMINING ZIRCONIUM. The determination of zirconium was necessary only in the equilibrium studies. In the method developed for the separation of aluminum from zirconium, the zirconium remains on the resin, so the determination of it as a part of the separation procedure is unnecessary.

For the equilibrium studies, zirconium was determined by precipitating it as the hydroxide, igniting it to the oxide and weighing.

Procedure. The zirconium metal is dissolved in hydrochloric and hydrofluoric acids and the equilibrium runs are made as described previously. After equilibrium has been attained, the solution is filtered to remove the resin. Two or three milliliters of concentrated sulfuric acid is added and the solution is evaporated in platinum dishes on a steam bath. The small amount of resin that has come through the filter paper is removed by fuming with sulfuric acid and adding nitric acid dropwise until

the resin is all oxidized.

This fuming is sufficient to remove the hydro-
fluoric acid so that the zirconium may be precipitated
as the hydroxide, ignited and weighed.

RECLAMATION OF THE RESIN. After each run, the
resin is reclaimed and returned to its original chloride
form by eluting with 3 normal hydrochloric acid. This
elution is carried out in a Büchner funnel fitted on a
suction flask. The acid is passed through the resin until
a sample of the eluate, when neutralized with sodium
hydroxide, gives no zirconium hydroxide precipitate. The
resin is then washed with distilled water until silver
nitrate, when added to the eluate, gives only a slight
opalescence. Suction is then applied to partially dry
the resin. The drying is completed in an oven at about
80°C.

EQUILIBRIUM EXPERIMENTS. Since the fluoride com-
plexes of aluminum and zirconium are to be used in the
separation of the two metals, equilibrium experiments
were run to furnish data for the calculation of the dis-
tribution coefficients of their fluoride complexes.

Procedure for Equilibrium Experiments. Two grams
of oven dried resin is placed in a 250 milliliter plastic
bottle. The aluminum or zirconium metal is dissolved in
predetermined quantities of hydrochloric and hydrofluoric

acids and this solution is diluted to 100 milliliters with water. The bottle is then mechanically shaken for one to three hours.

After the shaking, the solution is filtered to remove the resin, 2 or 3 milliliters of concentrated sulfuric acid is added and the solution is evaporated in platinum dishes on a steam bath. To remove the small amount of resin that has come through the filter, the sulfuric acid solution is heated to fuming and concentrated nitric acid is added dropwise until all of the resin is oxidized. This fuming also aids in removing the hydrofluoric acid remaining in the solution.

The quantity of zirconium and the aluminum are determined as previously described.

Results of Equilibrium Experiments. The data from the equilibrium experiments of the aluminum fluoride complex are tabulated in Table I. The distribution coefficients, calculated from these data, are also included in the table.

The concentration of the hydrochloric acid has a marked effect on the distribution coefficient of the aluminum complex. In three, six and nine molar hydrochloric acid and 0.5 molar hydrofluoric acid there is no exchange of the complex with the resin. But as the concentration of the hydrochloric acid decreases, the

TABLE I

RESULTS OF EQUILIBRIUM EXPERIMENTS WITH
ALUMINUM FLUORIDE COMPLEX

Run * Number	Millimoles Al Taken	Milli- moles Al Recovered	K_d	Acid Concentration (molar)	
				HF	HCl
1	0.652	0.659	—**	0.5	9.0
2	0.730	0.734	—**	0.5	6.0
4	0.726	0.730	—**	0.5	3.0
5	0.726	0.716	0.0137	0.5	1.0
6	0.688	0.678	0.0145	0.5	0.5
8	0.700	0.675	0.0357	0.5	0.2
9	0.704	0.678	0.0369	0.5	0.1
3	0.672	0.663	0.0136	0.1	3.0
7	0.723	0.718	0.0079	0.1	0.5
10	0.738	0.707	0.0420	0.1	0.1
125	0.723	0.760	—**	0.8	1.0
124	0.775	0.808	—**	0.8	0.5
120	0.742	0.744	—**	0.8	0.2
121	0.656	0.626	0.0457	0.8	0.05
122	0.808	0.718	0.111	0.8	0.02
123	0.786	0.688	0.125	0.8	0.01
132	0.674	0.533	0.209	0.8	0.005
134	0.822	0.645	0.216	0.8	0.0

*Runs from 1 to 10 were made with Dowex 2. The remaining runs were made with Dowex 1.

**The values of this distribution coefficient are zero.

distribution coefficient increases, indicating that an exchange is beginning to take place between the aluminum fluoride complex and the resin.

The concentration of the hydrofluoric acid also has an effect on the distribution coefficient. If the concentration of the hydrofluoric acid is kept at 0.8 molar and the hydrochloric acid concentration is increased, beginning with a solution that contains no hydrochloric, the amount of the aluminum complex that exchanges decreases, until at 0.2 molar hydrochloric acid, all of the aluminum complex is in the liquid phase. If the concentration of the hydrofluoric acid is kept at 0.5 molar, there is exchange between the resin and the aluminum complex until the hydrochloric acid concentration reaches three molar.

The data from the equilibrium experiments on the zirconium fluoride complex and the distribution coefficients calculated from these data are given in Table II.

Equilibrium data were not determined at high hydrochloric acid concentrations for the zirconium fluoride complex because the behavior of this complex in high hydrochloric acid concentrations is described in the literature (11, p.10).

When the hydrofluoric acid concentration is held constant, and the hydrochloric acid concentration varied,

TABLE II

RESULTS OF EQUILIBRIUM EXPERIMENTS
WITH ZIRCONIUM FLUORIDE COMPLEX

Run # Number	Millimoles Zr Taken	Milli- moles Zr Recovered	K_d	Acid Concentration (molar)	
				HF	HCl
18	1.007	0.5601	0.798	1.0	0.5
19	1.023	0.2686	2.808	1.0	0.2
22	1.012	0.1304	6.785	1.0	0.1
15	1.030	0.6632	0.553	0.5	0.5
20	1.023	0.2763	2.707	0.5	0.2
16	1.030	0.1337	6.676	0.5	0.1
17	1.007	0.6632	0.503	0.1	0.5
21	1.012	0.4626	1.186	0.1	0.2
151	1.065	0.8277	0.166	0.8	1.0
145	1.044	0.5964	0.752	0.8	0.5
146	1.065	0.2105	3.578	0.8	0.2
147	1.021	0.0526	18.42	0.8	0.05
148	1.085	0.0	-	0.8	0.02
149	1.093	0.0	-	0.8	0.01
150	1.074	0.0	-	0.8	0.005

*Runs from 15 to 22 were made with Dowex 2. The remaining runs were made with Dowex 1.

there is a marked change in the distribution coefficient
of the zirconium fluoride complex. As the hydrochloric
acid concentration decreases, the distribution coeffi-
cient increases, indicating that the zirconium complex is
exchanging more completely with the resin. At very low
hydrochloric acid concentrations, this exchange is com-
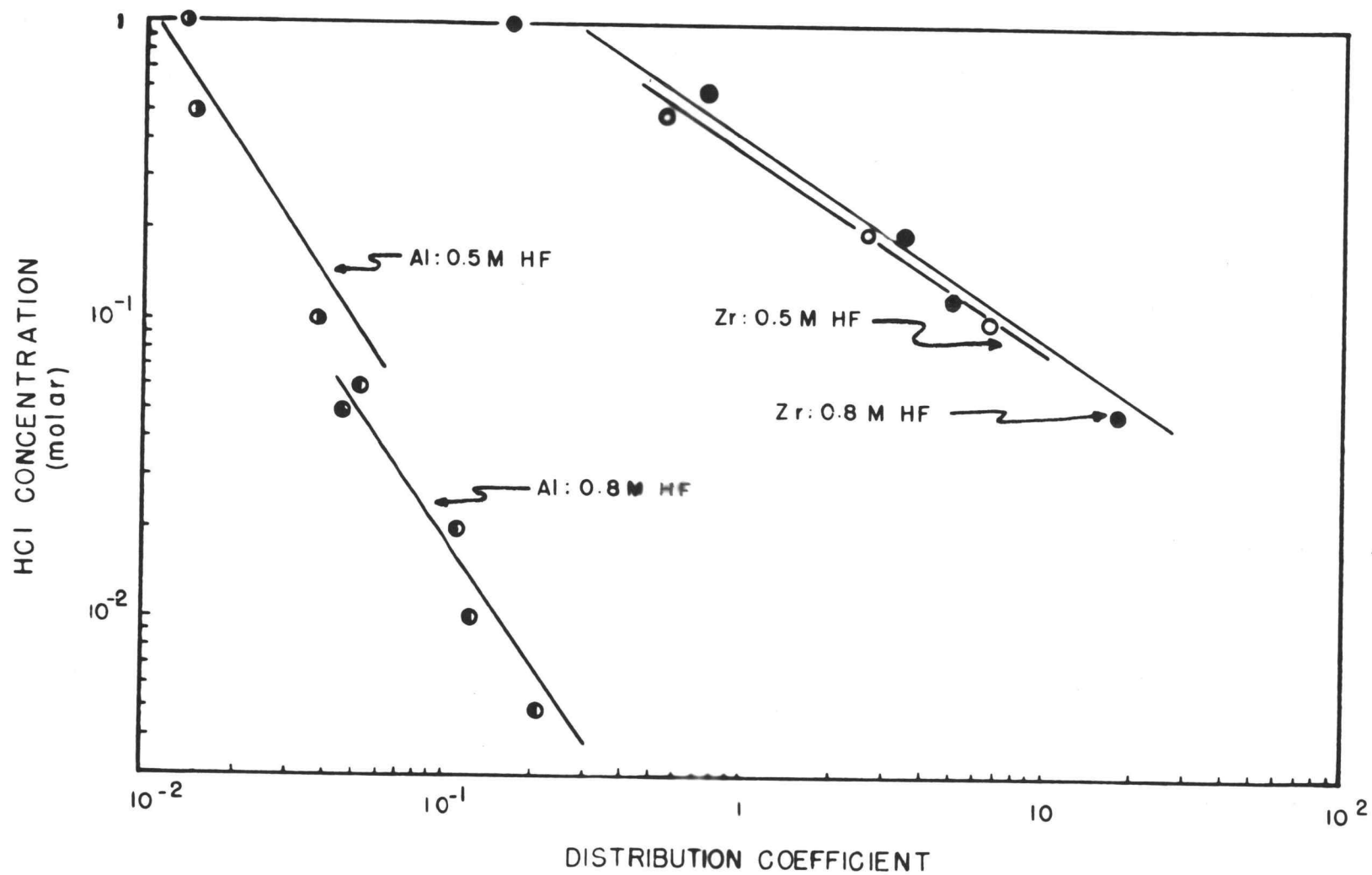plete, so that no zirconium remains in the liquid phase.

In Figure 1 the distribution coefficients for the
aluminum and zirconium fluoride complexes have been
graphed as a function of the hydrochloric acid concen-
tration.

From this graph it is possible to choose the
hydrochloric and hydrofluoric acid concentrations that
will be used in the column separation of aluminum and
zirconium. The acid concentrations that are chosen are
the concentrations at the point at which there is the
greatest difference between the distribution coefficients
of the aluminum and the zirconium complexes. As ex-
plained previously, the conditions at this point are
those that are most suited for an efficient column separa-
tion of the metals.

The greatest difference between the distribution
coefficients for the aluminum and zirconium fluoride
complexes occurs at a hydrochloric acid concentration of
0.06 molar and at a hydrofluoric acid concentration of

DISTRIBUTION COEFFICIENTS OF ALUMINUM AND ZIRCONIUM FLUORIDE COMPLEXES
FIGURE I

0.8 molar. This is the concentration of the elutriant that will be used in the column separation of aluminum from zirconium.

COLUMN EXPERIMENTS. After determining the hydrofluoric and hydrochloric acid concentrations to be used in the column separation, the determination of the physical dimensions of the column was a prerequisite to performing column exchange experiments.

It was intended to vary the flow rate of solution through the column and determine the fastest rate that could be used before zirconium came through. The amount of resin was also to be varied and the same rate of flow studies made on each new quantity of resin.

One gram of zirconium was used as a basis for calculating the initial quantity of resin to be used in a column. This amount of zirconium was chosen because it would approximate the size of the zirconium samples when the column was used for actual separations. Equilibrium experiments had indicated it would require two grams of resin to completely exchange 100 milligrams of zirconium. Twenty grams of resin would be the minimum to exchange one gram of zirconium. To allow a margin of safety, 30 grams of resin were used.

Fortunately, the conditions chosen for the first run - 30 grams of resin and a flow rate of five

milliliters per minute - proved adequate, for no zir-
conium came through the column.

Two hundred fifty milliliters of eluate were col-
lected for this first run and all subsequent runs. This
volume was determined by the consideration of the follow-
ing. The sample was added in a volume of 100 milliliters.
The volume of liquid associated with 30 grams of wet
resin (the so-called "free volume" of the resin) was
about 50 milliliters. Two hundred milliliters would be
the minimum that could be expected to remove all of the
solution containing the sample. The extra 50 milliliters
was a safety factor. Also, it was shown that no zirconium
came through even after 500 milliliters of solution had
passed through the column.

Recovery of Aluminum by Itself. Several column
runs were made with aluminum alone under the above con-
ditions. The results are tabulated in Table III.

Recovery of Aluminum with Zirconium Present. Dif-
ficulty was encountered in finding a source of pure
zirconium. The zirconium turnings used in the equilibrium
experiments were too impure to use in those column separa-
tions which involved very small amounts of aluminum. The
turnings could be used, however, when relatively large
amounts of aluminum were involved. It was impossible to
obtain any pure zirconium metal.

TABLE III

RECOVERY OF ALUMINUM BY ITSELF

Run Number	Mg. of Aluminum Taken	Mg. of Aluminum Recovered	% of Aluminum Recovered
7C(a)	41.8	41.7	99.7
11C	41.0	40.0	97.5
8C	7.0	6.8	97.1
10C	8.7	7.5	86.2
12C	8.4	8.3	98.8

The alternative source of zirconium was the puri-
fied zirconium oxychloride. This oxychloride was used
in several runs, but high, inconsistent results were
obtained. The oxine precipitate did not have the crys-
talline character it had had previously, rather it was
gelatinous, more like a hydroxide precipitate.

These erratic results were explained when it was
realized that zirconium oxychloride hydrolyzes in water,
with the production of basic ions. Evidently, fluoride
does not complex the zirconium when it is in this form
so the zirconium goes through the column. This zir-
conium is precipitated as oxine when the pH is adjusted
to precipitate the aluminum with oxine.

To eliminate this zirconium, the eluate from the
column was evaporated in platinum dishes and fumed with
sulfuric acid in the usual manner. Then sodium hydroxide
was added until the solution was very basic. This caustic
solution was heated to its boiling point and kept at this
temperature for 15 minutes. By this treatment, the zir-
conium that had come through the column was precipitated
as the hydroxide and the aluminum remained in solution.
This solution was filtered, acidified, and the aluminum
was precipitated in the usual manner with oxine.

Results of the separation runs are shown in Table
IV.

TABLE IV

RECOVERY OF ALUMINUM WITH ZIRCONIUM PRESENT

Run Number	Source of Zirconium	Mg. of Al Added	Mg. of Oxine Precipitated	Mg. of Al Recovered
14C	Metal	37.3	125	36.8
16C	Metal	38.6	132	38.9
42C	$ZrOCl_2$	0.5	8.5	0.5

INVESTIGATION OF INTERFERENCES. Before this method of separation can be applied in practical analysis, the effect of interfering ions must be investigated. The following ions were picked for study because of their probable occurrence in zirconium samples.

One gram of zirconium in the form of zirconium oxychloride was used in each run. The run through the column and the precipitation of aluminum by oxine were carried out as before, except that the caustic treatment was introduced before the aluminum was precipitated.

TABLE V

EFFECT OF INTERFERENCES ON DETERMINATION OF ALUMINUM

Run number	Interference expressed as	ppm Al found when weight ratio of interference to Al is:	
		1:1	10:1
54C, 43C	Fe	660	670
46C	Sn	---	516

(500 ppm of Al taken)

The aluminum oxine precipitate from both of the experiments with iron was green (pure aluminum oxine is yellow), indicating that not all of the iron had been removed by the caustic treatment.

No one to one ratio was run with tin, because the ten to one ratio indicated acceptable recovery of aluminum.

Potassium sulfate was studied as a possible source of interference because potassium bisulfate is often used to fuse zirconium containing samples that are impossible to dissolve in acids.

The procedure for these runs was the same as for the other interference runs.

TABLE VI

EFFECT OF POTASSIUM SULFATE ON
DETERMINATION OF ALUMINUM

(500 ppm of Al taken) *

Run number	G. of K$_2$SO$_4$ taken	Mg. of oxine precipitated	Mg. of oxine precipitated (corrected)	ppm Al found
500	4	2	---	---
480 *	3	10.6	9.1	530
490 *	2	9.3	8.3	490

The potassium sulfate contains an appreciable amount of oxine precipitable material. But if a blank is run, and a correction is made, potassium sulfate offers no serious interference.

ANALYSIS OF ZIRCONIUM HYDRIDE. Zirconium hydride was obtained from the Bureau of Mines in Albany, Oregon. The aluminum content of the hydride had been determined spectrographically at the Bureau.

A gram of this hydride was dissolved, run through

the column and the aluminum in the eluate determined in the usual manner. The oxine precipitate from the first two runs was green, indicating the presence of iron. In the next run, the caustic treatment, described above for the separation of zirconium from the eluate, was used to remove the iron in the eluate. The iron hydroxide precipitated in this way was ignited and the amount of iron determined. A correction for this iron was applied to the previous runs.

The results reported in Table VII were obtained by weighing the oxine precipitate in a sintered glass crucible. Weighing by difference was the method used in obtaining the weights of the precipitate. Sixty ppm of aluminum is equivalent to only one milligram of oxine precipitate. The weight of the sintered glass crucibles used was about 13 grams. The error involved in weighing a milligram in these crucibles could easily amount to half a milligram, and half a milligram of the oxine precipitate is equivalent to 30 ppm of aluminum. The results in Table VII should be considered in light of these possible errors.

Another, more sensitive method for the analysis of these small quantities of aluminum must be developed before accurate and consistent results can be expected.

TABLE VII

RECOVERY OF ALUMINUM FROM ZIRCONIUM HYDRIDE

(Hydride contains 40 ppm Al,
as determined spectrographically)

Run number	Mg. of oxine ppt.	Mg. of oxine ppt. -corrected for iron	ppm of Al added	ppm Al found in hydride
250	9.9	3.9	150	80
240	9.9	3.9	150	80
270*	3.7	3.7	150	70
280*	1.0	1.0	0	60

*Iron removed by caustic treatment before oxine
 precipitation.

PLANS FOR FUTURE WORK

A more thorough investigation of interferences
is necessary. Included in this investigation will be
calcium, wolfram, lead, bismuth, manganese, chromium,
silicon, cadmium, cerium, beryllium, titanium, vanadium,
niobium, tantalum, thorium, nickel and cobalt.

There is no method at present for the separation
of small amounts of aluminum from hafnium. Since haf-
nium has many of the same chemical and physical proper-
ties as zirconium, it would be reasonable to assume that
this method could be used to separate aluminum from
hafnium.

SUMMARY

A method is presented for the quantitative separation of aluminum from zirconium using anion exchange.

The fluoride complexes of aluminum and zirconium were the anions used in the separation. A study was made of the distribution of these complexes between the liquid and the resin phases. Optimum distribution was attained at a 0.8 molar hydrofluoric acid and 0.06 molar hydrochloric acid concentration.

Interference caused by iron, tin and potassium sulfate was determined.

Synthetic aluminum and zirconium mixtures and zirconium hydride were analyzed for their aluminum content.

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