THE SEPARATION OF ALUMINUM AND ZIRCONIUM BY ION EXCHANGE

by

FREND JOHN MINER

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

June 1952
APPROVED:

[Signature]
Assistant Professor of Chemistry
In Charge of Major

[Signature]
Head of Department of Chemistry

[Signature]
Chairman of School Graduate Committee

[Signature]
Dean of Graduate School

Date thesis is presented May 15, 1952

Typed by Evelyn Kanzelmeyer
ACKNOWLEDGMENT

I wish to express my sincere gratitude to Dr. Harry Freund for his invaluable suggestions and assistance in the research described in this thesis.

I also want to thank the Bureau of Mines, Albany, Oregon, for zirconium samples and for permitting me to conduct some of the work in their laboratory.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>THEORETICAL CONSIDERATIONS</td>
<td>7</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>18</td>
</tr>
<tr>
<td>PLANS FOR FUTURE WORK</td>
<td>41</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>42</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>43</td>
</tr>
</tbody>
</table>

## TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Results of Equilibrium Experiments with Aluminum Fluoride Complex</td>
<td>27</td>
</tr>
<tr>
<td>II</td>
<td>Results of Equilibrium Experiments with Zirconium Fluoride Complex</td>
<td>29</td>
</tr>
<tr>
<td>III</td>
<td>Recovery of Aluminum by Itself</td>
<td>34</td>
</tr>
<tr>
<td>IV</td>
<td>Recovery of Aluminum with Zirconium Present</td>
<td>36</td>
</tr>
<tr>
<td>V</td>
<td>Effect of Interferences on Determination of Aluminum</td>
<td>37</td>
</tr>
<tr>
<td>VI</td>
<td>Effect of Potassium Sulfate on Determination of Aluminum</td>
<td>38</td>
</tr>
<tr>
<td>VII</td>
<td>Recovery of Aluminum from Zirconium Hydride</td>
<td>40</td>
</tr>
</tbody>
</table>

## FIGURE

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Distribution Coefficients of Aluminum and Zirconium Fluoride Complexes</td>
<td>31</td>
</tr>
</tbody>
</table>
THE SEPARATION OF ALUMINUM AND ZIRCONIUM BY ION EXCHANGE

INTRODUCTION

Many impurities influence the physical characteristics 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 determinations 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 investigate 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, C₆H₅CHOHCOOH, 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 categories (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°C, zirconium tetrachloride at 330°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 divinylbenzene 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 concentrations indicated the possibility of three types of complexes, \((\text{AlF}_6)^{-3}\), \((\text{Al}_2\text{F}_9)^{-3}\) and \((\text{AlF}_4)^{-1}\) (4, p. 3805).
Sidgwick indicates that \((\text{AlF}_5)^{-2}\) 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 thienoyltrifluoroacetone 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 \(8 \times 10^{-3}\) 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:

<table>
<thead>
<tr>
<th>Hydrofluoric acid concentration</th>
<th>Average number of fluoride ions per zirconium</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \times 10^{-5} \text{ M})</td>
<td>1</td>
</tr>
<tr>
<td>(5 \times 10^{-4} \text{ M})</td>
<td>2</td>
</tr>
<tr>
<td>(10^{-2} \text{ M})</td>
<td>3</td>
</tr>
</tbody>
</table>

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 Radiation 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 summarized 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 exchange 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 complexes, 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 separation 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 calculated 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, however, 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 distribution 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.
APPARATUS.

Ion exchange column. 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 polyethylene plastic, which is unattacked by hydrofluoric.

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

REAGENTS.

Dowex 1 and Dowex 2. 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 condition 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 opalescence. 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 dissolving 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$_2$·6H$_2$O, 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-hydroxyquinoline). The oxine quantitatively precipitates aluminum as Al(C_9H_6O_3N)_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 hydrofluoric 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 complexes 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 distribution 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>
<thead>
<tr>
<th>Run #</th>
<th>Millimoles Al Taken</th>
<th>Millimoles moles Al Recovered</th>
<th>Kd</th>
<th>Acid Concentration (molar)</th>
<th>HF</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.652</td>
<td>0.659</td>
<td>-***</td>
<td>0.5</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.730</td>
<td>0.734</td>
<td>-***</td>
<td>0.5</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.726</td>
<td>0.730</td>
<td>-***</td>
<td>0.5</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.726</td>
<td>0.716</td>
<td>0.0137</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.688</td>
<td>0.678</td>
<td>0.0145</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.700</td>
<td>0.675</td>
<td>0.0357</td>
<td>0.5</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.704</td>
<td>0.678</td>
<td>0.0369</td>
<td>0.5</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.672</td>
<td>0.663</td>
<td>0.0136</td>
<td>0.1</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.723</td>
<td>0.718</td>
<td>0.0079</td>
<td>0.1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.738</td>
<td>0.707</td>
<td>0.0420</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>0.723</td>
<td>0.760</td>
<td>-***</td>
<td>0.8</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>0.775</td>
<td>0.808</td>
<td>-***</td>
<td>0.8</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.742</td>
<td>0.744</td>
<td>-***</td>
<td>0.8</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>121</td>
<td>0.656</td>
<td>0.626</td>
<td>0.0457</td>
<td>0.8</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>0.808</td>
<td>0.718</td>
<td>0.111</td>
<td>0.8</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>0.786</td>
<td>0.688</td>
<td>0.125</td>
<td>0.8</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>0.674</td>
<td>0.533</td>
<td>0.209</td>
<td>0.8</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>0.822</td>
<td>0.645</td>
<td>0.216</td>
<td>0.8</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

*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

<table>
<thead>
<tr>
<th>Run #</th>
<th>Millimoles Zr Taken</th>
<th>Millimoles Zr Recovered</th>
<th>Acid Concentration (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kd</td>
</tr>
<tr>
<td>18</td>
<td>1.007</td>
<td>0.5601</td>
<td>0.798</td>
</tr>
<tr>
<td>19</td>
<td>1.023</td>
<td>0.2666</td>
<td>2.808</td>
</tr>
<tr>
<td>22</td>
<td>1.012</td>
<td>0.1304</td>
<td>6.785</td>
</tr>
<tr>
<td>15</td>
<td>1.030</td>
<td>0.6632</td>
<td>0.553</td>
</tr>
<tr>
<td>20</td>
<td>1.023</td>
<td>0.2763</td>
<td>2.707</td>
</tr>
<tr>
<td>16</td>
<td>1.030</td>
<td>0.1337</td>
<td>6.676</td>
</tr>
<tr>
<td>17</td>
<td>1.007</td>
<td>0.6632</td>
<td>0.503</td>
</tr>
<tr>
<td>21</td>
<td>1.012</td>
<td>0.4626</td>
<td>1.186</td>
</tr>
<tr>
<td>151</td>
<td>1.065</td>
<td>0.8277</td>
<td>0.166</td>
</tr>
<tr>
<td>145</td>
<td>1.044</td>
<td>0.5964</td>
<td>0.752</td>
</tr>
<tr>
<td>146</td>
<td>1.065</td>
<td>0.2105</td>
<td>3.578</td>
</tr>
<tr>
<td>147</td>
<td>1.021</td>
<td>0.0526</td>
<td>18.42</td>
</tr>
<tr>
<td>148</td>
<td>1.085</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>149</td>
<td>1.093</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>150</td>
<td>1.074</td>
<td>0.0</td>
<td>-</td>
</tr>
</tbody>
</table>

*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 coefficient increases, indicating that the zirconium complex is exchanging more completely with the resin. At very low hydrochloric acid concentrations, this exchange is complete, 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 concentration.

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 explained previously, the conditions at this point are those that are most suited for an efficient column separation 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 1

DISTRIBUTION COEFFICIENT

HCl CONCENTRATION (molar)

10^{-2} 10^{-1} 1 10 10^{2}

1

10^{-2} 10^{-1} 1 10 10^{2}

AL: 0.5 M HF

Zr: 0.5 M HF

Zr: 0.8 M HF

AL: 0.8 M HF
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 zirconium came through the column.

Two hundred fifty milliliters of eluate were collected for this first run and all subsequent runs. This volume was determined by the consideration of the following. 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 conditions. The results are tabulated in Table III.

Recovery of Aluminum with Zirconium Present. Difficulty 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 separations 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>
<thead>
<tr>
<th>Run Number</th>
<th>Mg. of Aluminum Taken</th>
<th>Mg. of Aluminum Recovered</th>
<th>% of Aluminum Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>76(a)</td>
<td>41.8</td>
<td>41.7</td>
<td>99.7</td>
</tr>
<tr>
<td>116</td>
<td>41.0</td>
<td>40.0</td>
<td>97.5</td>
</tr>
<tr>
<td>86</td>
<td>7.0</td>
<td>6.8</td>
<td>97.1</td>
</tr>
<tr>
<td>106</td>
<td>8.7</td>
<td>7.5</td>
<td>86.2</td>
</tr>
<tr>
<td>126</td>
<td>8.4</td>
<td>8.3</td>
<td>98.8</td>
</tr>
</tbody>
</table>
The alternative source of zirconium was the purified zirconium oxychloride. This oxychloride was used in several runs, but high, inconsistent results were obtained. The oxine precipitate did not have the crystalline 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 zirconium 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 zirconium 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

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Source of Zirconium</th>
<th>Mg. of Al Added</th>
<th>Mg. of Oxine Precipitated</th>
<th>Mg. of Al Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>14C</td>
<td>Metal</td>
<td>37.3</td>
<td>125</td>
<td>36.8</td>
</tr>
<tr>
<td>16C</td>
<td>Metal</td>
<td>38.6</td>
<td>132</td>
<td>38.9</td>
</tr>
<tr>
<td>42C</td>
<td>ZrOCl₂</td>
<td>0.5</td>
<td>8.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
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 oxy-chloride 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

<table>
<thead>
<tr>
<th>Run number</th>
<th>Interference expressed as</th>
<th>ppm Al found when weight ratio of interference to Al is:</th>
</tr>
</thead>
<tbody>
<tr>
<td>540, 430</td>
<td>Fe</td>
<td>660 670</td>
</tr>
<tr>
<td>460</td>
<td>Sn</td>
<td>--- 516</td>
</tr>
</tbody>
</table>

(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) *

<table>
<thead>
<tr>
<th>Run number</th>
<th>G. of K2SO4 taken</th>
<th>Mg. of oxine precipitated</th>
<th>Mg. of oxine precipitated (corrected)</th>
<th>ppm Al found</th>
</tr>
</thead>
<tbody>
<tr>
<td>50C</td>
<td>4</td>
<td>2</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>48C *</td>
<td>3</td>
<td>10.6</td>
<td>9.1</td>
<td>530</td>
</tr>
<tr>
<td>49C *</td>
<td>2</td>
<td>9.3</td>
<td>8.3</td>
<td>490</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th>Run number</th>
<th>Mg. of oxine ppt.</th>
<th>Mg. of oxine ppt. -corrected for iron</th>
<th>ppm of Al added</th>
<th>ppm Al found in hydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>256</td>
<td>9.9</td>
<td>3.9</td>
<td>150</td>
<td>80</td>
</tr>
<tr>
<td>240</td>
<td>9.9</td>
<td>3.9</td>
<td>150</td>
<td>80</td>
</tr>
<tr>
<td>270*</td>
<td>3.7</td>
<td>3.7</td>
<td>150</td>
<td>70</td>
</tr>
<tr>
<td>280*</td>
<td>1.0</td>
<td>1.0</td>
<td>0</td>
<td>60</td>
</tr>
</tbody>
</table>

*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 hafnium has many of the same chemical and physical properties 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.


