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APPLICATION OF LIQUID-LIQUID EXTRACTION
FOR THE SEPARATION OF ZIRCONIUM FROM
HAFNIUM

By
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APPLICATION OF LIQUID-LIQUID EXTRACTION FOR THE
SEPARATION OF ZIRCONIUM FROM HAFNIUM*

by

R. A. Foos and H. A. Wilhelm

ABSTRACT

The use of liquid-liquid extraction for the separation of zirconium from hafnium was demonstrated. Hafnium spectrographically free of zirconium was prepared in quantity on a continuous basis. High purity fractions of zirconium were also prepared.

Many single and multistage extractions employing immiscible organic solvents were carried out on aqueous solutions of the compounds to be separated. Analyses of the equilibrium phases allowed calculation of individual distribution coefficients and their separation factors. Single stage extractions were employed to obtain data from which the operation conditions for the multistage counter-current extractions were estimated.

A mixture composed of about 97 per cent hafnium and about three per cent zirconium as oxychlorides was dissolved in nitric acid. Extractions of this aqueous solution showed that zirconium was preferentially extracted by tributyl phosphate. The presence of nitric acid increased mass transfers to the organic phase but decreased the hafnium-zirconium separation factors. A pilot plant continuous operation employing a 17 stage countercurrent extractor yielded 90 per cent of the hafnium spectrographically free of zirconium.

* This report is based on a Ph.D. thesis by Raymond A. Foos submitted June, 1954 to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

The liquid-liquid system presented here indicated further the applicability of solvent extraction for separating inorganic compounds. Much of the information from this work is directly applicable to practical separation problems and therefore should be readily adaptable to specific laboratory and industrial scale operations.

I. INTRODUCTION*

Liquid-liquid extraction is becoming widely used for the separation of inorganic salts in industrial as well as in laboratory processes. Consequently, this technique was investigated as a method for the separation of some inorganic salts which are of current interest to the Atomic Energy Commission.

In general a number of liquid-liquid systems containing zirconium and hafnium salts were investigated. Various compositions of the aqueous phase were contacted with a variety of partially immiscible organic solvents in single stage extractions until equilibrium was obtained. Analyses of the equilibrium phases allowed calculation of the individual distribution coefficients, mass transfers from the aqueous phase to the organic phase and separation factors for each case. These equilibrium data afforded a method whereby the separation effectiveness of the various liquid-liquid systems were compared. From the single stage data the range of the optimum operating conditions was estimated for a separation by a multistage extraction. These conditions were tested in a multiple-contact counter-current extractor employing as many as 20 equilibrium stages. A few multistage extraction experiments were usually required to obtain the most effective separation conditions.

The aqueous feed was usually a mineral acid solution containing the hafnium and zirconium salts to be separated although basic media in some cases were also investigated. Such variables in the aqueous phase as pH, acid concentration, salt concentration, complexing agents and salting-out agents were investigated. For the organic phase factors such as acidity, complexing agents, diluents and type of organic were found to be important in making separations. Relative volumes of the organic and aqueous phases were also varied to obtain separation data. Since separation of these salts on a commercial scale is desired, the economics of a process was an important factor in evaluating the practicability of a liquid-liquid system.

*Editors Note: This introduction was written for a series of reports dealing with a number of liquid-liquid systems employed in separation studies. Only one of these systems is treated in this report. The other systems including tantalum from niobium and yttrium from rare earths by liquid-liquid extraction are treated in Reports ISC-694 and ISC-695.

It was found that hafnium spectrographically free of zirconium could be produced on a continuous basis by a multistage extraction. The use of liquid-liquid systems for separating these inorganic salts proved useful on a laboratory scale. In a few cases the operations were scaled up to pilot plant production where they proved equally satisfactory.

II. THE SEPARATION OF ZIRCONIUM FROM HAFNIUM

A. General History of Hafnium-Zirconium Separations

Zirconium was first isolated by Klaproth in 1789 as the carbonate salt although it was 1824 before Berzelius reduced this salt to the metal. Complete agreement on the characteristics of this new element was not possible until 1923 when Coster and von Hevesy (1) separated the hafnium from the zirconium. It has since been found that all known natural occurring zirconium ores are contaminated by a hafnium fraction which varies in composition from a few tenths of a per cent to as much as 16 per cent by weight. A great deal of work on the separation of these two chemically similar elements has been reported during the past three decades.

The similarity in chemical behavior appears to be related to the electronic configuration of the valence electrons. This configuration is $4d^2, 5s^2$ for zirconium and $5d^2, 6s^2$ for hafnium. Even though the hafnium nucleus has 32 more protons than the zirconium nucleus the difference in ionic radii for their tetravalent ions is only 0.01 of an angstrom (2). Other properties such as atomic radius, atomic volume, refractive index and solubility are quite similar for these two elements.

The use of hafnium-free zirconium has become very important in the field of atomic reactors. Zirconium metal is a useful material in the building of atomic reactors since it is highly resistant to water corrosion at elevated temperatures and has favorable neutron capture cross section values. The cross sectional areas for thermal neutron capture by zirconium and hafnium atoms are about 0.2 and 103 barns respectively (3). It is apparent that since this value for hafnium is several hundred times greater than that of zirconium, slight amounts of hafnium in zirconium would considerably increase its thermal neutron capture. Consequently, considerable research has been

carried out since 1947 in an effort to remove most of the hafnium from zirconium. There has developed also a limited interest in high purity hafnium for use in basic research. The preparation of hafnium free of zirconium was the main purpose of the work described in this section.

The first widely employed technique for separating hafnium from zirconium was fractional crystallization and precipitation. Generally, the hafnium salts are slightly less soluble and tend to concentrate in the first crystals or precipitates. Some of the systems and techniques employed for this method of separation have been the double alkali fluorides (4), sulfates (5), oxychlorides (6), fluorides (7), higher oxysalts (8), oxalates (9), ammonium citrate solutions (10), oxides (11), phosphates (12), ferricyanides (13), triethyl phosphate hydrolysis (14) and hydroxides (15). In general, fractional crystallization or precipitation is not economically feasible for large scale operation of zirconium and hafnium.

Fractional distillation of a mixture composed of the chlorides or oxychlorides of zirconium and hafnium in phosphorus pentachloride has been reported by several investigators (16-19). While employing a reflux ratio of 20 to 1 and 50 distillation plates about 40 per cent of a hafnium-zirconium mixture which originally analyzed 3.0 per cent hafnium remained in the still and analyzed less than 0.1 per cent hafnium (20).

Hafnium and zirconium have been separated by employing paper chromatography (21,22), by adsorption on silica gel (23-26) and by use of ion-exchange resins (27-35). Hansen and Gunnar (23) passed a methanol solution of the tetrachlorides of zirconium and hafnium through silica gel to preferentially adsorb hafnium and recover high purity zirconium. Beyer, Jacobs and Masteller (26) concentrated a mixture containing originally two per cent hafnium to 90 per cent hafnium in two passes through silica gel. In the ion-exchange method of separation, the hafnium-zirconium mixture is generally first mixed with the resin in a separate batch process. This resin-hafnium-zirconium mixture is elutriated after being placed on top of a column which contains the same resin. The order of elution for the anion-exchange resins is inverse to the cation-exchange resins. Zirconium is more difficult to elute from a cation-exchange resin. A zirconium product containing 0.1 per cent hafnium (27) and a hafnium product containing 0.04 per cent zirconium (30) have been reported from work

employing this technique. These ion-exchange column experiments were all carried out on a milligram scale. Neither ion-exchange, adsorption on high surface materials or distillation have been used for large scale separation of hafnium and zirconium.

At the present time liquid-liquid extraction is being employed industrially for the separation of hafnium from zirconium. In 1947 Fischer and co-workers (36,37) reported that when the thiocyanates of zirconium and hafnium were distributed between water and ether, hafnium concentrated in the ether phase. The original ether contained 1.0 molar thiocyanic acid while the aqueous phase was a sulfuric acid solution of hafnium, zirconium and ammonium thiocyanate almost saturated with sulfate ions. In a typical case a starting material with a hafnium content of 0.5 per cent yielded in one extraction an organic phase product containing 7 per cent hafnium with a recovery of 50 per cent of the total hafnium.

Extensive investigation of the Fischer system for separating hafnium from zirconium has been carried out at the Oak Ridge National Laboratory (38-45). Some of the extraction variables studied were flow rates, temperature, complexing agents, organic solvents and composition and concentration of the acidic aqueous phases. Fischer's original system was eventually varied since a hexone-hydrochloric acid system employing thiocyanate was found to be more practical. Hafnium also favored the organic phase in this variation of the thiocyanate extraction. Large scale extractions now in operation employ an aqueous solution containing 1.0 molar zirconium tetrachloride, a few per cent hafnium and 1.5 molar ammonium thiocyanate. The organic phase consists of hexone which is 2.0 molar in thiocyanic acid. The flow ratios are about 3.7 volumes of the organic phase to one volume of the aqueous phase. Starting with a mixture containing about 2 per cent hafnium and about 98 per cent zirconium approximately 75 per cent of the zirconium containing 75 ppm hafnium is produced on a continuous basis. Higher recovery of zirconium can be maintained although its purity in regards to hafnium is decreased. Production of some zirconium believed to contain less than 20 ppm hafnium has also been reported.

Further purification of the hafnium obtained from the above large scale liquid-liquid extraction process has been reported. The hafnium in the organic product phase was back-extracted into an aqueous phase by a series of scrubs

employing either hydrochloric or sulfuric acid. This concentrate which was recovered from the aqueous phase contained about 93 per cent hafnium with respect to zirconium. It was dissolved in concentrated hydrochloric acid and diluted to obtain a hafnium-zirconium concentration equivalent to 27 grams of oxides per liter. This aqueous phase was made 2.0 molar in ammonium thiocyanate. The organic hexone phase contained 1.9 molar of thiocyanic acid per liter. A 0.3 molar sulfuric acid solution was employed as the aqueous scrub. When using this system in a 12 stage mixer-settler extractor, 94 per cent of the input hafnium containing approximately 200 ppm zirconium was recovered from the organic product phase. This was the purest hafnium in respect to zirconium ever produced at that time on a continuous basis. It was believed that zirconium contamination in the equipment limited the purity of hafnium at about 200 ppm zirconium.

Another liquid-liquid extraction system for the separation of zirconium from hafnium was introduced by Connick and McVey (46). Several investigators (46-48) have reported hafnium-zirconium separation factors of about 20 with these systems. In general the organic phase consists of a benzene solution of such 1,3-diketones as 2-thenoyltrifluoroacetone, 2-furoyltrifluoroacetone, 2-pyrryltrifluoroacetone, or trifluoroacetylacetone. A perchloric or hydrochloric acid solution containing about 1×10^{-3} molar hafnium and zirconium constituted the organic phase. When these two phases are contacted zirconium favors the organic phase although attainment of equilibrium between phases requires approximately two hours. Because of this slow equilibrium time, high cost of most 1,3-diketones and low hafnium-zirconium concentration of the aqueous phase this system has not been employed industrially.

In 1950, Wilhelm, Walsh and Kerrigan (49-51) reported that tributyl phosphate would preferentially extract zirconium from hafnium when they were present in a mixture of nitric and hydrochloric acids. Ordinarily the oxychloride salts of zirconium and hafnium were dissolved in this mixed acid system and a salting-out agent such as calcium chloride added. When carrying out a 13 stage counter-current extraction, zirconium containing less than 100 ppm hafnium was produced on a continuous basis.

An all nitrate aqueous phase which contained hafnium and zirconium but no salting-out agent was employed in a

14 stage mixer-settler extractor by Peterson and Beyer (52, 53) for the separation of zirconium from hafnium. The initial aqueous phase which was 1.0 molar in zirconium contained about two weight per cent hafnium. Both the aqueous feed and scrub solutions were about 5.2 molar in nitric acid. The organic phase containing 0.65 molar nitric acid was composed of 60 volume per cent tributyl phosphate and 40 volume per cent heptane. At steady state the organic product phase contained zirconium with less than 100 ppm hafnium with an over-all zirconium recovery of about 97 per cent. The aqueous phase product was about 45 per cent hafnium. The chief advantage of such a process over the use of the thiocyanate system described above is that zirconium is reduced of many minor impurities when transferred to the organic phase. However, transfer of the major constituent to the organic phase is less desirable in large scale production because of the usually increased relative organic flow rates required.

In the work reported here the separation of a small amount of zirconium from a hafnium concentrate was effected by employing a modification of the Wilhelm, Walsh and Kerrigan system (49-51). A nitric acid solution of the hafnium and zirconium as oxychlorides was employed as the aqueous feed solution. The purpose of this study was to develop a procedure and to prepare a few hundred pounds of a high purity hafnium salt essentially free of zirconium. The purified hafnium salt was to be converted to hafnium metal for basic studies of the metal and its alloys.

B. Experimental Details

Since tributyl phosphate was reported to extract zirconium in preference to hafnium from an aqueous nitric acid solution medium, this system was ideal for separating small amounts of zirconium from hafnium. Consequently, a series of single and multistage extractions was carried out in which the composition of the organic phase and content of nitric acid in the system were varied. A saturated or nearly saturated solution of the hafnium-zirconium mixture was used in each extraction.

The zirconium-hafnium mixture used in this investigation was obtained from the Bureau of Mines Separation Plant operated for the United States Atomic Energy Commission at

Albany, Oregon. It was essentially the mixture delivered by the organic product phase in the hexone-thiocyanate extraction of hafnium from zirconium. The hexone phase was scrubbed with dilute mineral acid to back-extract hafnium and zirconium. These elements were precipitated by the addition of ammonium hydroxide and were subsequently converted to oxides and then to the tetrachlorides. This resulting tetrachloride mixture was the starting material for the investigation described here. It contained from 2.0 to 4.0 per cent zirconium with respect to hafnium. The metal content analysis of one of the shipments as received appears in Table 1.

Addition of water to the solid tetrachloride mixture as received caused the formation of the oxychloride salts according to the following over-all reaction:

Since the resulting aqueous solution was usually quite cloudy a small amount of carbon was added and the solution filtered. The filtrate was then evaporated until the hydrochloric acid concentration in the hot solution reached a value of about 6.0 to 8.0 molar. At this concentration range the solubility of hafnium and zirconium oxychlorides has a minimum value. When this solution was cooled about 95 per cent of the hafnium and zirconium crystallized as their oxychloride octahydrates. This white crystalline mixture was filtered, washed with acetone and air dried. Its solubility in water is approximately 800 grams of the oxychloride salt per liter. The aqueous phases employed for the extraction studies were prepared by dissolving the oxychlorides in the water or acid and adjusting to the desired concentrations.

In these single and multistage extractions the organic phase consisted of either pure tributyl phosphate or its solution with dibutyl ether. Since equilibrium conditions were rapidly approached, a mixing time of about 30 seconds was employed. After the liquids had separated some or all of the following analyses were performed on the equilibrium phases: zirconium and hafnium oxide weights and percentages, chloride ion concentration, hydrogen ion concentration and nitrate ion concentration.

Hafnium and zirconium are completely precipitated as the hydroxides (or oxyhydroxides) by addition of excess ammonium hydroxide. The aqueous phase product was

Table 1

Analysis of the Initial Hafnium-Zirconium Mixture
(Received as Tetrachlorides)

Element	ppm	Element	ppm	Element	ppm
Al	50	Fe	73000	B	0.5
Sn	<5	Cr	100	Co	<10
Cu	200	Mn	20	V	<20
Pb	30	Ni	200	Cd	<1
Mg	>500	Si	50	Zr	2.5%
				Hf + Zr	
Zn	<50	Ti	500	Hf	97.5%
				Hf + Zr	
Fe	3300 (chem.)	Mo	<10		

precipitated directly while acetone was first added to the organic phase to maintain only one liquid phase. This addition of acetone also aided in the filtering operation. It is possible to back-extract all the hafnium and zirconium from the organic phase product by three consecutive separate equal volume extractions with water. After filtering, the precipitates were calcined at 600 degrees Centigrade for two hours to yield the zirconium and hafnium oxides.

All qualitative and quantitative analyses of these highly refractory oxides were done spectrographically. The hafnium and zirconium percentages are given relative to the total amount of only these elements with all impurities disregarded. The method of Fassel and Anderson (54) was employed for analyzing mixtures containing up to 98 per cent hafnium while the procedure of Fassel and Gray (55) was used for assaying mixtures containing more than 98 per cent hafnium. In the former method the standard deviation was given as ± 2 per cent

of the entire zirconium content while for the latter case the accuracy was believed to be within ± 10 per cent of the true value for this minor constituent. The lower limit of detection is about 20 ppm of zirconium in hafnium.

An anion and cation balance on the aqueous and organic phases required determination of hydrogen, zirconium, hafnium, chloride and nitrate ion concentrations. The concentrations and percentages of hafnium and zirconium were readily determined by the ammonium hydroxide precipitation combined with the spectrographic analyses described above. A sodium hydroxide titration using phenolphthalein as the indicator was employed to determine the total acidity of the solution. This was done by adding excess standard base to the aqueous phase until all the zirconium and hafnium was precipitated and the hydrogen ions neutralized. The precipitate was filtered and washed well with water to remove all the residual basic liquid. After combining the filtrate and washing, the excess base was back-titrated with standard acid. It was observed that the end point of this titration was much more precise and reproducible if the precipitates of zirconium and hafnium were first removed. When assaying the organic phase for total acidity, the only difference in the procedure was the addition of acetone to the organic phase to insure only one liquid phase.

From the data on total acidity the free hydrogen ion concentration can be calculated. Although the knowledge of zirconium and hafnium solution chemistry is limited, it is generally believed that in an acid solution the zirconyl ions, ZrO^{++} , and hafnium ions, HfO^{++} , exist primarily. Since these are divalent, two equivalents of hydroxide ions are required per equivalent of hafnium or zirconium according to following equations:

As the concentrations of both hafnium and zirconium were known in each phase, the moles of base reacting with them can be calculated. Consequently, the remaining base was assumed to react with the free hydrogen ions.

For the chloride analysis of the aqueous and organic phases the method of Volhard was employed. In the aqueous phase excess silver nitrate was added to precipitate all the chloride ions. About two milliliters of nitrobenzene was used to produce a thin film on the silver chloride in order

to prevent its reaction with other reagents (56). This eliminates the need for filtering the silver chloride. Approximately a milliliter of a saturated aqueous solution of ferric alum constituted the indicator. The excess silver nitrate was titrated with standard potassium thiocyanate until a yellow-orange color appeared indicating the end point. The chloride analysis of the organic phase was carried out in a similar manner except that sufficient acetone was added to maintain a one liquid phase system. Determination of the concentration of chloride ion was calculated from the amount of silver nitrate consumed.

Since the concentration of all the ions in each phase except the nitrate ion is known, the molarity of this ion could then be calculated. As in the case of the chloride ion, it is not possible to assign any one definite cation to balance the nitrate ion. However, the nitrate molarity could probably be expressed quite accurately in terms of nitric acid.

Single stage extractions were carried out in ordinary glass separatory funnels while for the multistage extractions the extractors shown in Figure 1 and Figure 2 were employed. This latter multistage extractor, consisting of 17 stages, will be discussed in detail in another publication (57). However, during one cycle of operation (or 360 degrees rotation about its axis) two separate mixing and settling steps are performed although only one portion of each of the aqueous and the organic product phases was delivered.

C. Results and Discussion

1. Composition of the initial hafnium-zirconium mixture

The purpose of this work was to prepare very pure hafnium with respect to zirconium when starting with the hafnium concentrate obtained from the thiocyanate-hexone system. The tetrachloride mixture of hafnium and zirconium was first converted to the oxychloride and then employed for the preparation of aqueous feed solutions. Although there were slight variations in the relative zirconium and hafnium compositions, the mixtures contained between two and four per cent zirconium. As stated above, all the hafnium and zirconium percentages are relative values which are based only on the total hafnium and zirconium content of the sample. Table 1 contains quantitative data on this mixture as reported by the Bureau of Mines. All values except one for iron were determined spectrographically.

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Figure 1. Twenty Stage Countercurrent
Liquid-Liquid Extractor.

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Figure 2. Seventeen Stage Countercurrent
Liquid-Liquid Extractor.

2. Single stage extractions

Several single stage extractions were carried out at room temperature in order to determine favorable conditions to employ in the multistage extractor for effective separation of the hafnium-zirconium mixture. The effect of dibutyl ether as an organic diluent and of the nitric acid concentration in the initial aqueous phase was studied. Equal volumes of the organic and aqueous phases were employed in all single stage extractions. Figures 3 to 8 inclusive illustrate the data that were obtained from these experiments.

The initial aqueous phase, or feed solution, employed for these single stage extractions was a saturated hafnium-zirconium salt solution. The zirconium content of these aqueous solutions was almost negligible since it composed only a small part of the mixture. The nitric acid concentrations of the feed solutions determined the solubility of this hafnium-zirconium mixture. Figure 3 shows the variation in solubility of the zirconium-hafnium oxychloride mixture expressed as oxides with variable nitric acid concentrations. It is apparent from this figure that an increase in the nitric acid concentration generally decreased the solubility of the hafnium-zirconium mixture.

The effect of nitric acid concentration in the initial aqueous phase on mass transfer from the aqueous to the organic phase for both pure and diluted tributyl phosphate is shown in Figure 4. It is apparent from this figure that an increase in nitric acid concentration results in an increase in the per cent of the total zirconium and hafnium extracted by the organic phase. This relationship appears to be linear over the complete range that was studied. The use of the diluent, dibutyl ether, resulted in a decrease in the mass transfer for any given nitric acid concentration. The difference between the per cent mass transfer values for extractions with diluted and undiluted tributyl phosphate decreased as the nitric acid concentration decreased. When both curves were extrapolated to zero per cent transfer they converged at about 3.6 molar nitric acid.

The hafnium oxide analyses of the aqueous product phases that were obtained from these single stage extractions are given in Figure 5. The zirconium oxide content in the product phases can be obtained by subtracting the hafnium oxide percentage from 100. It is apparent from this figure that the hafnium oxide percentage in the aqueous product phase

Figure 3 - Solubility of the Hafnium-Zirconium Mixture Expressed as Oxide Equivalent for Various Nitric Acid Solutions.

Figure 4 - Mass Distribution of the Hafnium-Zirconium Mixture at Various Nitric Acid Concentrations in Pure and Diluted Tributyl Phosphate.

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Figure 5 - Per Cent Hafnium Oxide in the Equilibrium Aqueous Phase at Various Nitric Acid Concentrations.

Figure 6 - Zirconium Distribution Coefficient as a Function of Nitric Acid Content.

Figure 7 - Hafnium Distribution Coefficient as a Function of Nitric Acid Content.

Figure 8 - Hafnium-Zirconium Separation Factors at Various Nitric Acid Concentrations.

increased with increasing nitric acid concentration in the initial aqueous phase. It can also be noted that the aqueous product phase contained the greatest percentage of hafnium oxide when the initial aqueous solution was extracted with pure tributyl phosphate. On a weight basis less hafnium would be recovered by extracting the aqueous solution with pure tributyl phosphate because of the large mass transfer to the organic phase (see Figure 4). However, as shown by Figure 5, the hafnium oxide purity in the aqueous phase product was as great as 99.3 per cent in a one stage extraction. As stated above, the composition of the aqueous phase product depends not only on the nitric acid concentration but also on the amount of diluent added to the tributyl phosphate.

The zirconium and hafnium distribution coefficients are shown in Figures 6 and 7, respectively, as functions of the nitric acid concentration in the initial aqueous phase. In practically all of the extractions the distribution coefficient for zirconium was considerably greater than unity while the value for the hafnium distribution coefficient was always less than unity. Figures 6 and 7 indicate that the distribution coefficients are greatest when the aqueous solutions of hafnium and zirconium were extracted with undiluted tributyl phosphate. As the mass distribution data presented in Figure 4 would indicate, the distribution coefficients increased with the nitric acid content of the system.

The effect of the nitric acid concentration in the initial aqueous phase on the Hafnium-zirconium separation factor is indicated in Figure 8. It is apparent from this figure that an increase in the nitric acid concentration resulted in a decrease in the value of the separation factor. Beyer and Peterson (58) when extracting an aqueous nitric acid solution containing a mixture of 98 per cent zirconium and 2.0 per cent hafnium with diluted tributyl phosphate reported a similar trend. A hafnium-zirconium separation factor of 57 was obtained when the 4.0 molar nitric acid solution of hafnium and zirconium was extracted with undiluted tributyl phosphate. For given concentrations of nitric acid and hafnium and zirconium in the aqueous phase the use of pure tributyl phosphate as the organic phase gave a higher separation factor than extraction with tributyl phosphate which had been diluted with dibutyl ether. The separation factor was higher even though more material was extracted by pure tributyl phosphate. These data indicate that the lower concentrations of nitric acid are most effective for separating zirconium from hafnium.

Several important trends resulted from these single stage extractions of the saturated solutions of the hafnium-zirconium mixtures. In general, the addition of nitric acid to the system increased mass transfer to the organic phase while decreasing the hafnium-zirconium separation factors.

The use of pure tributyl phosphate as the organic phase resulted in greater mass transfers and hafnium-zirconium separation factors than the use of tributyl phosphate which was diluted with dibutyl ether. These single stage extraction data were used to determine approximate extraction conditions for operating the multistage extractors in order to efficiently separate zirconium from hafnium on a continuing basis.

3. Multistage extractions

Since the primary goal of this work was to produce high purity hafnium on a pilot plant scale a nearly saturated solution of hafnium and zirconium was employed as the feed solution. Extractor 2 (shown in Figure 2) which consisted of only 15 stages (at that time) was to be employed for these production experiments. Consequently in the small scale extractions which were carried out in Extractor 1 (shown in Figure 1) only 15 of its 20 stages were used. The first three multistage extractions were carried out in Extractor 1 while two large scale extractions required the use of Extractor 2.

The single stage data indicated that favorable hafnium-zirconium separation factors as well as mass transfers could be obtained when preferentially extracting zirconium with tributyl phosphate from a saturated solution of a hafnium-zirconium oxychloride mixture dissolved in nitric acid. Pure tributyl phosphate gave the most favorable separation and mass distribution data. Unfortunately this pure organic solvent tended to form an emulsion and consequently at least five minutes were required for complete phase separation. When 40 or more volume per cent of dibutyl ether was added to tributyl phosphate, this phase separation time was reduced to about 20 to 50 seconds depending on the acid concentration of the system. Consequently the organic phase used in all phase multistage extractions was a mixture composed of 40 volume per cent dibutyl ether and 60 volume per cent tributyl phosphate.

In addition to the organic phase composition other similarities existed in each of these five multistage extractions. In each extraction the organic phase was introduced and the aqueous product phase delivered at stage 1. Similarly the aqueous scrub phase was introduced and the organic product phase delivered at stage 15 for all the multistage extractions except the last one. Since 17 stages were employed in this extraction the 17th stage was used to add the aqueous scrub and deliver the organic product phase. The aqueous feed was introduced at stage 9 for all of these multistage extractions except for the last one where stage 11 was used. The relative volumes of the organic phase, aqueous scrub phase and aqueous feed phase were the same in all of these multistage extractions. Their relative volumes were 4, 1 and 4 respectively. The actual volumes in the first three extractions were 20, 5 and 20 milliliters respectively while a scale up factor of 10 was used in the last two multistage extractions. All multistage

extractions were carried out at room temperature. The solutions employed for these five multistage extractions differed essentially in nitric acid content. The results of these extractions appear in Table 2 and a short discussion of each is given below. The feed material for these extractions contained in the neighborhood of two to four per cent zirconium oxide in hafnium oxide.

Table 2

Hafnium-Zirconium Multistage Extractions

Ext. No.	Aqueous phase product		Organic phase product		
	Grams of oxide/liter	ZrO ₂ (ppm) ²	Grams of oxide/liter	ZrO ₂ (%) ²	% ZrO ₂ + HfO ₂ delivered in org. prod.
1	310	9,500	11.6	99.93	3.0
2	284	50	19.0	50.	7.5
3	310	75	28.5	45.	7.0
4	250	20	37.0	35.	12.0
5	225	< 20	33.0	25.	14.0

(a) Extraction 1. The single stage data obtained by extracting the nitric acid aqueous solutions of hafnium and zirconium indicated that at low acid concentrations the hafnium-zirconium separation factors were high while the mass transfer to the organic phase was low. Consequently an intermediate acid concentration of about 6.0 molar nitric acid appeared to be practical since the hafnium-zirconium separation factor would be about 35 with 17 per cent of the material transferred to the organic phase. The aqueous feed contained the equivalent of 380 grams of the combined hafnium-zirconium oxide mixture per liter of solution. In order to maintain a nearly constant nitric acid condition in all stages of the extractor the organic phase was made 2.68 molar in nitric acid while the aqueous feed and scrub solutions were 3.15 molar in nitric acid. These nitric acid concentrations represent nearly equilibrium values.

Analyses of the products from every tenth cycle showed that essentially steady state conditions were reached at about the 40th cycle. The extraction was discontinued after 100 complete cycles and the phases from the odd numbered stages were analyzed. These stagewise data appear in Table 3 while Figure 9 indicates the variation of these analyses with stage numbers.

Table 3

Stagewise Data for the First Zirconium and Hafnium Extraction

Stage No.	Organic phase		Aqueous phase		K_{Zr}	K_{Hf}	Hf-Zr sep. factor
	Grams of oxide/liter	Zr (%)	Grams of oxide/liter	Zr (%)			
1	18.1	31.3	321	0.95	1.79	0.0375	47.5
3	22.5	37.1	337	1.57	1.48	0.0405	36.7
5	28.5	51.8	340	2.53	1.60	0.0387	41.4
7	30.4	50.0	336	2.44	1.74	0.0432	40.1
9	34.1	51.5	340	2.82	1.71	0.0465	36.8
11	25.1	92.9	52.5	47.5	0.878	0.0606	14.5
13	21.4	99.6	37.0	93.5	0.611	0.0337	18.2
15	10.8	99.93	22.2	98.9	0.491	0.0321	15.3

It is apparent from Table 2 and Figure 9 that for multistage extraction 1 the aqueous phase product was about 99.1 per cent hafnium oxide while the organic phase product analyzed 99.93 per cent zirconium oxide. Approximately 70 per cent by weight of the zirconium was recovered from the organic phase product while the loss of hafnium in this phase was less than 0.002 per cent of its total weight. Recovering most of the zirconium remaining in the aqueous phase product as well as obtaining a higher purity hafnium could be effected by a subsequent multistage extraction employing similar conditions. However by properly varying the operating conditions a more nearly quantitative separation could likely be effected in only one multistage extraction.

In the organic scrubbing section of the extractor, or stages one to nine inclusive, the relative flow rates were approximately five volumes of the aqueous phase to four volumes of the organic phase. The relative flow rates in the aqueous scrubbing section, stages 15 to 10 inclusive, were about four volumes of the organic phase to one volume of the aqueous phase. Figure 9 indicates that the greatest over-all change in zirconium (and hafnium) percentage in either phase occurred in the aqueous scrubbing section of the extractor. According to the data in Table 3 the organic phase extracted considerable hafnium as well as zirconium in the feed stage. Although most of this hafnium was back-extracted by the aqueous scrub solution in stages 13 to 10, minor amounts of it remained in the organic product phase delivered from stage 15. A larger relative volume of aqueous scrub would have decreased the amounts of both hafnium and zirconium reaching stage 15 although the purity of the zirconium delivered would have been greater. Similarly a relatively larger volume of the organic phase would have increased the recovery of zirconium while decreasing its purity. Furthermore, changes in the number of stages employed, in the position of the feed stage and in the composition of the solutions would also effectively alter the extraction data.

It can be seen from Table 3 that the hafnium-zirconium separation factors have considerably different values in the organic and aqueous scrubbing sections of the extractor. The separation factor in the organic scrubbing section, where the percentage of hafnium in the aqueous phase resembles the feed mixture, remained fairly near to the value of 35 to 40 predicted from the single stage data for this system. The zirconium distribution coefficients apparently were influenced by the presence of the large amounts of hafnium in the organic scrubbing section of the extractor. The distribution coefficient for zirconium in stage 15 probably represents its true value for a system essentially free of hafnium. The variation of the hafnium distribution values with stage number was small throughout the entire extractor. Since the nitric acid variation in the column should be small, this large change in separation factors was probably caused by the presence of large amounts of hafnium in the organic scrubbing section. This effect of hafnium on the zirconium distribution factor has been reported in detail from single stage extraction of varying hafnium-zirconium composition with a mixture of tributyl phosphate and heptane by Peterson and Beyer (59). They indicated a considerable variation in the zirconium

Figure 9. Zirconium Percentage in the Equilibrium Liquids as a Function of Stage Number.

distribution coefficients when a large amount of hafnium was added to form a highly concentrated hafnium-zirconium system.

Although this extraction was not successful in preparing very pure hafnium in relation to zirconium, it indicates how very small amounts of zirconium in hafnium could be separated relatively free from hafnium. As stated above, several changes could be made to improve the effectiveness of this 15 stage extraction. The hafnium-zirconium extractions presented below indicate primarily the effect of varying the nitric acid concentration.

(b) Multistage extraction 2. In the first multistage extraction delivery of insufficient amounts of material by the organic product phase made it impossible for high purity hafnium to reach the aqueous product outlet. According to the single stage data an increase in the nitric acid content of the system should increase the delivery of material by the organic product phase. The system employed in multistage extraction 2 contained about 1.5 molar more of nitric acid than the system used in multistage extraction one. The nitric acid concentration employed for both the aqueous feed and aqueous scrub solutions in this second multistage extraction was about 5.0 molar while in the organic phase it was 2.92 molar. No other changes from the conditions employed for the first multistage extraction of zirconium from hafnium were made.

Cycle analyses indicated that essentially steady state was reached after 70 cycles of operation although the extraction was continued for 100 complete cycles. The aqueous phase product at steady state contained approximately 50 ppm zirconium relative to hafnium while the organic phase product contained about equal weights of zirconium and hafnium as oxides. The stagewise analyses were not significant because the organic phase employed for the last few cycles of operation was contaminated with zirconium from some unknown source.

The extraction showed that in 15 stages about 95 per cent of the hafnium containing only 50 ppm zirconium was recovered in the aqueous product phase when starting with a mixture containing from two to four per cent zirconium. A comparison of these results with those from the first multistage extraction indicates that the addition of 1.5 moles of nitric acid per liter of solution increased the mass transfer to the organic phase about 2.5 times while decreasing the zirconium content of the high purity hafnium product about 600 times.

(c) Multistage extraction 3. For the third hafnium-zirconium multistage extraction, conditions somewhat similar to multistage extraction one were employed. Although the amount of nitric acid introduced into the extractor per cycle of operation was nearly equal in both these experiments, the organic phase used for multistage extraction 3 did not contain nitric acid. While the organic phase contained no nitric acid, the aqueous feed and aqueous scrub solution were about 5.5 and 6.0 molar in nitric acid, respectively. This low nitric acid concentration in the organic scrubbing section of the extractor was expected to result in the extraction of less material by the organic phase. In the aqueous scrubbing section the high nitric acid concentration should result in considerable transfer to the organic phase. The over-all effect should be a greater mass transfer to the organic product phase than was obtained in the first zirconium-hafnium multistage extraction. The aqueous feed solution contained the equivalent of 380 grams of oxide per liter.

Cycle analyses, although incomplete, indicated that essentially steady state was reached after about 50 cycles of operation. As can be seen from Table 2 the aqueous phase product contained about 75 ppm zirconium relative to hafnium while the organic product phase was composed of about 55 per cent hafnium oxide. It is also apparent that approximately 7.0 per cent of the total hafnium and zirconium content as oxides were delivered by the organic product phase.

Stagewise analyses after 100 complete cycles indicated that the aqueous phase of stage two contained only 43 ppm zirconium relative to hafnium. This minimum in the zirconium percentage was also noted for the organic phase to stage two. A similar effect might have resulted in multistage extraction 2 although the large contamination in the last few cycles prevented its detection by the stagewise analyses. It appeared that the organic phase used in this extraction was contaminated by a small amount of zirconium. Before carrying out this experiment all the glassware employed for preparing the organic phase was washed with concentrated nitric acid. The organic phase mixture was also contacted four times with an equal volume of distilled water before it was added to the extractor. However, the room in which this extraction was carried out, as well as the extractor itself, was highly contaminated with zirconium because of previous experimental work on the preparation of pure zirconium. Consequently, the environment, equipment or impure chemicals could have been the source or sources of this zirconium contamination. Whenever very pure products are

desired, extreme care must be taken throughout the entire procedure.

Comparison of the data from the first, second and third zirconium-hafnium extractions indicate that the nitric acid concentration of each phase introduced into the extractor, as well as the total acid content, influences the results. It is apparent that for these extractions that the use of an organic phase which contained no nitric acid gave the most favorable results assuming the total nitric acid content of the system was about constant. The use of the unacidified organic phase permitted approximately the same recovery of hafnium with about the same purity relative to zirconium although requiring about 1.5 mole less acid per liter. Consequently, the two extractions presented below employed an organic phase containing no nitric acid.

(d) Multistage extraction 4. The liquid-liquid extractor shown in Figure 2 was used for this multistage extraction of the hafnium-zirconium mixture. Since the only previous use of this extractor was a multistage extraction of a high purity hafnium mixture, it had not been contaminated by high purity zirconium. The extraction was also carried out in a different room which recently had been thoroughly scrubbed. The organic phase, as well as the extractor, prior to use in this experiment, were treated in a manner similar to that described for multistage extraction 3.

With the exception of hafnium and zirconium concentration the conditions employed for multistage extraction 4 were essentially the same as used for multistage extraction 3. A flow rate scale up factor of ten was employed in extraction 4. The nitric acid concentration in the aqueous scrub and feed was 5.8 and 6.2 molar, respectively. This aqueous feed also contained the equivalent of 310 grams of oxides per liter. The relative amount of nitric acid introduced per cycle of operation was about the same as in extraction 3.

Cycle analyses of the product phases indicated that about 30 cycles were required to reach essentially steady state. After 65 complete cycles the extraction was discontinued, and the phases from each stage analyzed for hafnium and zirconium content, chloride concentration and total acidity. The nitrate concentration was determined by difference. These data appear in Tables 2 and 4.

From Table 2 it is apparent that the aqueous phase product was primarily hafnium which analyzed only about 20 ppm zirconium. A qualitative spectrographic analysis

Stagewise Data for Hafnium-Zirconium Multistage Extraction 4

Stage no.	Aqueous phase								Organic phase							
	Vol.	Oxide conc.	% ZrO ₂	Total acid conc.	Zr + Hf conc.	Chlo-ride ion conc.	Nit-rate ion conc.	Chlo-ride conc./Hf+Zr conc.	Vol.	Oxide conc.	% ZrO ₂	Total acid-ity	Zr+Hf conc.	Chlo-ride ion conc.	Nit-rate ion conc.	Chlo-ride conc./Hf+Zr conc.
	(ml.)	(g/l.)		(M.)	(M.)	(M.)	(M.)		(ml.)	(g/l.)		(M.)	(M.)	(M.)	(M.)	
1	207	250	0.0021	6.09	1.19	2.93	3.71	2.47	221	5.20	0.043	2.23	0.025	0.067	2.18	2.68
3	232	247	0.010	7.93	1.17	2.71	5.55	2.32	230	52.7	0.11	3.64	0.25	0.16	3.14	0.64
5	234	272	0.020	8.52	1.29	2.70	5.94	2.09	206	77.5	0.98	3.86	0.37	0.22	3.12	0.60
7	234	287	0.065	8.85	1.36	2.73	6.13	2.00	243	86.8	0.92	4.08	0.41	0.26	3.26	0.63
9	250	283	0.51	8.68	1.34	2.61	6.00	1.94	224	86.6	19.1	4.88	0.47	0.30	3.94	0.64
11	59	201	3.00	8.13	0.97	0.49	6.19	0.51	230	73.6	20.5	4.83	0.40	0.10	4.03	0.25
13	57	159	2.92	7.41	0.74	0.12	5.93	0.17	244	66.2	21.0	4.13	0.36	0.059	3.41	0.16
15	54	78.2	4.54	7.22	0.38	0.036	6.46	0.092	213	41.3	34.2	3.54	0.24	0.043	3.06	0.18
Feed		310	3.0	9.18	1.50	3.05	6.18	2.04								
Aq. Scrub		0	0	5.80	0	0	5.80	0								
Org. Phase		0	0	0	0	0	0	0								

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indicated that only trace amounts of aluminum, beryllium, magnesium, calcium, tin and copper were present. A pound of the high purity oxide recovered from this aqueous product phase from the last 20 cycles of the extraction has been submitted for analysis by other Atomic Energy Commission Laboratories to determine its purity and to compare various methods of analyzing high purity hafnium. This sample was reported to contain between 20 and 30 ppm zirconium by analysts at the Ames Laboratory. The only report which has been received from another laboratory indicated zirconium was not present in the sample, although the method of analysis was reported to have a lower limit of detection of 50 ppm zirconium in hafnium (60).

The oxide mixture recovered from the organic product phase which contained about 12 per cent of the initial hafnium and zirconium oxide weight was about one-third zirconium oxide. This increase in mass transfer from that reported for multistage extraction 3 was probably caused by the higher ratio of nitric acid concentration to hafnium and zirconium concentration. Approximately 92 per cent of the total hafnium was delivered by the aqueous product phase as the highly purified salt.

The stagewise data obtainable only in the odd numbered stages of the extractor employed indicate that the zirconium percentage did not have a minimum value at an intermediate stage as reported in multistage extraction 3 (see Table 4). Evidently the location of and the extractor change effectively reduced the zirconium contamination at the organic inlet end of the extractor. The zirconium oxide percentage (and hafnium oxide percentage) in each phase generally showed a gradual change throughout the extractor. Operative errors and sample contamination probably explain the three deviations from this trend.

The anion and cation analysis indicated that for the organic and aqueous phases the total acidity, total molarity of hafnium plus zirconium, chloride ion concentration and nitrate ion concentration were usually a maximum in the feed stage, stage number 9. These values gradually decreased as the liquids progressed toward the ends of the extractor. The organic scrubbing section in the extractor contained greater concentrations of these ions than the aqueous scrubbing section. The aqueous phase was always more concentrated in these ions than its equilibrium organic phase.

Since no other source of chloride ion was present in this system, all the chloride ions resulted from the zirconyl and hafnyl chlorides. It is apparent from the data that relatively few chloride ions were transferred to any organic phase. Since all the material in the aqueous scrubbing section of the extractor must be introduced through the organic phase of stage 9, very few chloride ions would be expected in this aqueous scrubbing section. The ratio of the chloride concentration to the total hafnium plus zirconium concentration in the organic phase was less than 0.65 in every stage except in stage one and had a minimum value of 0.16. Consequently, it is concluded that the hafnium and zirconium species extracted by the organic phase probably does not contain a chlorine atom.

The high concentration of the nitrate ion in the equilibrium organic phases relative to the total hafnium plus zirconium content indicate that the nitrate radical might possibly constitute part or all of the extracted zirconium and hafnium anion. An ion balance indicated that about 45 per cent of the total nitrate ion introduced into the extractor were delivered by the organic product phase. These ionic data indicate the importance of nitrate ions in the transfer and separation of zirconium from hafnium.

(e) Multistage extraction 5. Since the hafnium product from the multistage extraction 4 was very pure, it was requested that sufficient high purity hafnium salt equivalent to 100 pounds of elemental hafnium be produced. The conditions employed for this production extraction, or multistage extraction 5, were quite similar to those used in extraction 4. The aqueous scrub and aqueous feed solutions were each 5.8 molar in nitric acid with the latter containing 280 grams of oxide per liter. Two more stages were added to the extractor to insure a high purity hafnium product. These additional stages were used in the organic scrubbing section of the extractor.

The production of the required amount of purified hafnium salt required 1300 cycles of operation. Average analysis of every 100 to 200 cycles indicated that most of the aqueous product phase contained hafnium with less than 20 ppm zirconium. The stagewise data at the completion of the extraction also substantiated this value. Since the spectrographic method of determining zirconium in high purity hafnium has appreciable error at zirconium contents below 20 ppm, the exact composition is unknown. The oxide recovered from the organic product phase was about 25 per cent zirconium oxide. A material balance indicated that about 90 per cent

of the total hafnium was delivered by the aqueous phase product. It is believed that the aqueous phase product from this extraction contained the purest hafnium salt relative to zirconium that has ever been produced in quantity. Most of this high purity hafnium salt has been reduced to the metal in this Laboratory.

D. Conclusions

1. Single stage extractions

a. A mixture composed of about 96 to 98 per cent hafnium and 2 to 4 per cent zirconium was dissolved in nitric acid. This aqueous solution was extracted with either pure tributyl phosphate or its dilutions with dibutyl ether. In all cases zirconium was preferentially extracted by the organic phase.

b. The addition of nitric acid to the aqueous solution up to a concentration of 8.0 molar acid decreased and solubility of hafnium and zirconium oxychlorides.

c. An increase in the amount of nitric acid in the system increased the mass transfer of hafnium and zirconium from the aqueous phase to the organic phase.

d. The dilution of tributyl phosphate with dibutyl ether decreased mass transfer to the organic phase.

e. Hafnium-zirconium separation factors as large as 57 were obtained by variations of this liquid-liquid system.

f. The addition of nitric acid decreased the hafnium-zirconium separation factors.

2. Multistage extractions

a. A series of countercurrent multistage extractions was carried out to prepare hafnium free of zirconium. Variables such as nitric acid concentration, hafnium plus zirconium concentration, flow rates and number of stages were considered. The conditions selected were based on the single stage extraction data.

b. A nearly saturated solution of the hafnium-zirconium mixture dissolved in about 6 molar nitric was employed as the feed solution for operating a 17 stage extractor. A hafnium salt equivalent to about 100 pounds of hafnium metal containing less than 20 ppm zirconium was produced. The organic phase employed was a mixture of tributyl phosphate and dibutyl ether. About 90 per cent of the total hafnium was recovered in the pure form.

c. A 15 stage extraction of a low nitric acid solution which was saturated with the hafnium-zirconium oxychloride mixture gave an aqueous phase product containing 99.1 per cent hafnium and an organic phase product containing 99.93 per cent zirconium.

d. The stagewise chloride analysis indicated that a very small amount of chloride ion was extracted by the organic phase. It was concluded that the extracted species probably does not possess a chlorine atom.

III. SUMMARY

The separation of hafnium and zirconium was accomplished by liquid-liquid extraction. Portions of a salt mixture which analyzed about 3 per cent zirconium and 97 per cent hafnium relative to their total were dissolved in varying concentrations of nitric acid. These aqueous solutions were extracted with either pure or diluted tributyl phosphate. The organic diluent employed was dibutyl ether.

In all the single stage extractions zirconium was preferentially extracted by the organic phase. Hafnium-zirconium separation factors and mass transfers as large as 57 and 51.2 per cent, respectively, were obtained when employing equal volumes of the aqueous and organic phases in single stage extractions. The use of an organic diluent decreased the mass transfer from the aqueous to the organic phase as well as the hafnium-zirconium separation factor. The presence of nitric acid increased the mass transfers to the organic phase and decreased the hafnium-zirconium separation factors.

The apparent optimum conditions for hafnium-zirconium separation obtained from these single stage extractions were employed for estimating the operating conditions for multistage countercurrent extractions. In one 15 stage extraction the hafnium and zirconium were separated into

a fraction containing 99.93 per cent zirconium and a fraction containing 99.1 per cent hafnium relative to their sum. In another 15 stage extraction the product from the organic phase contained 35 per cent zirconium oxide and 65 per cent hafnium oxide while the hafnium from the aqueous phase contained only 20 ppm zirconium.

A small scale production extraction was carried out in which the equivalent of about 100 pounds of pure hafnium spectrographically free of zirconium was recovered. The aqueous feed solution for this 17 stage extraction was 5.8 molar nitric acid which contained the equivalent of 280 grams of the combined zirconium and hafnium oxides per liter. A 40 volume per cent solution of dibutyl ether in tributyl phosphate constituted the organic phase while a 5.8 molar nitric acid solution was the aqueous scrub. The organic product phase from this extraction contained 25 per cent zirconium oxide relative to hafnium oxide while the hafnium in the organic product phase contained less than 20 ppm zirconium. Since this amount of zirconium was below the limit of accurate detection by the spectrographic method employed, the hafnium product was considered to be spectrographically free of zirconium. A material balance indicated that 90 per cent of the total hafnium was delivered by the aqueous product phase. As stated above, the starting material on a hafnium plus zirconium basis analyzed about three per cent zirconium and 97 per cent hafnium. It is believed that the aqueous product phase from this production extraction contained the purest hafnium relative to zirconium that has ever been produced in quantity.

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