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# ABSTRACT

This thesis reports research leading to a procedure for the separation and determination of zirconium and hafnium on a scale of a few micrograms. The objective was to develop methods that could be used in laboratories that are not equipped with highly expensive instrumentation.

Various considerations led to the choice of bis(2-ethylhexyl)phenylphosphonate as an extractant to be used in a reversed phase chromatographic mode. The immediate objective was a determination of distribution coefficients and separation factors for the two elements of interest.

Chapter I is devoted to a general review of the history, occurence, properties, and applications of both elements. A survey of the several analytical methods that have been used for the separation of zirconium and hafnium is the subject of Chapter II.

An overall procedure for the determination of the elements was explored in which the final step would be a classical spectrophotometric measurement. There were interferences due to the organic matter deriving from the extraction. The possible presence of phosphate from decomposition of the extractant is a potential difficulty. The

hydrolytic polymerization of Zr(IV) and Hf(IV) is a well-known phenomenon that had to be dealt with. Various approaches to these problems are described. Destruction of organic matter by wet ashing and evaporation led to polymerization. The polymers were destroyed by fusion with borax. Good recoveries of zirconium were achieved by these means from samples that had been polymerized by heating. Attempts to eliminate phosphate by the use of a cation exchange process were unsuccessful. The presence of phosphate apparently prevented the retention of zirconium by the resin. While further attempts to develop a successful separation of phosphate may be in order, it was more expedient for the present work to proceed with the extraction studies by making use of plasma emission atomic spectroscopy for the determinations.

Determination of distribution coefficients were performed in hydrochloric and nitric acid media. Results showed that an increase in nitric acid concentration and consequently in acidity, reduced the separation factor but increased the distribution coefficients of both elements. Best separation factors were obtained at 4M $HNO_3$ concentration.

The effect of doubling the concentration of the extractant in the organic phase was also studied. Distribution coefficients were almost doubled when the concentration of the organic phase was increased from 4% to 8% DE0P in pet-ether.

The aqueous phase after extraction was analyzed using DCP emission spectrophotometry.

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# Chapter I

# OCCURRENCE AND PROPERTIES OF ZIRCONIUM AND HAFNIUM.

## 1.1 Introduction.

Zirconium and hafnium are found in the titanium subgroup of group IV of the periodic table. Since their properties are very similar, they are usually discussed together.

Zirconium was first identified by Klaproth (1) while analysing the precious stone jargon, which had come from Ceylon. He had fused the specimans with sodium hydroxide, extracted the reaction product with hydrochloric acid, and found that this mineral contained an element which he could not identify and which he called zirconerde. The english equivalent is zirconia. More chemical studies were made by Thommsdorf (2).

The isolation of an impure form of the metal was achieved by Berzelius (3) in 1824, by heating a mixture of potassium metal and potassium fluorzirconate; after drying the reaction product, he found that he had obtained a black powder which consisted of impure elemental zirconium. The ductile metal was not produced until 1925, when Van Arkel and the Boer (4) developed a technique which allowed the preparation of extremely pure zirconium metal by thermal decomposition of zirconium iodide vapor on a tungsten filament.

Hafnium was isolated in 1922 and is therefore one of the most recently discovered elements. It always accompanies zirconium in minerals. There had been many false indications of the presence of at least one unrecognized element in zirconia, but none of these claims could be confirmed (5,6,7). Urbain (8) announced the discovery of element 72 while working with a soluble fraction from an ytterbium nitrate solution . He isolated a small amount of material which he claimed had distinctive properties. He concluded that the material was composed of a new member of the rare earth group and called it "celtium".

Coster and Von Hevesy (9) considered that the evidence presentd by Urbain (8) was inconclusive; using Bohr's theory of atomic structure they concluded that this new element was not one of the lanthanide elements but it was quadrivalent and an homologue of zirconium and thorium. Coster and Von Hevesy announced the discovery of element 72, naming it hafnium after the city in which the discovery was made (from Hafnia, latin for Copenhagen).

## 1.2 Ocurrence of Zirconium and Hafnium.

Zirconium is widely distributed in nature and the zirconium content of the earth's crust is estimated to be more than 0.028%. It ranks eleventh in the list of elements present in the earth's crust and actually is more plentiful in it than nickel, copper, lead, zinc, and some of the more familiar metals.

Hafnium always occurs with zirconium in minerals, hafnium being the minor constituent. The earth's crust has been estimated to contain 4.5 parts per million (0.00045%) of hafnium; this is about the same content of beryllium, germanium or uranium and more than the quantities of bismuth, cadmiun, tantalum, silver, or mercury, but less than the amount of gallium, praseodimium, or samarium.

These elements do not occur in the free state due to their vigorous chemical activity at the temperature of the enviroment during the solidification of the earth's crust. They are combined with oxygen in minerals such as zircon, baddeleyite and other complex minerals, particularly silicates.

The most abundant mineral containing zirconium is the silicate, $ZrSiO_4$, which is known as zircon. Zircon is found in igneous rocks, such as granites, pegmatites, diabase, and basalt; in sedimentary rocks, such as limestone, sandstone, conglomerate, etc.. Von Hevesy's and Wuerstlin's (10) studies of 1,175 rock specimens showed granite to contain 1 g of Zr per 3,000 g, volcanic rocks about 1 g per 4,000 g, effusive rocks 1 g per 4,500 g, and stony meteorites 1 g per 12,000 g . The mineral forms tetragonal crystals with a hardeness on Moh's scale of 7.5, is brittle and infusible, and has adamantine luster. Its color may vary but usually is some shade of brown.

Zircon usually contains less than 2% hafnia ($HfO_2$), but there are some exceptions. For example, zircon from Nigeria contains almost 5% hafnia, and altered zircon may contain up to 17%. The zirconia content of the mineral varies from 61 to 66.8%. Some varieties of zircon may contain large amount of other rare metals such as rare earths, niobium, tantalum, and uranium. The amount of thorium and uranium may be as high as 12% and 1.5% respectively.

The second most important mineral is baddeleyite, $ZrO_2$, which is the native form of the oxide of zirconium. It was first found at Jacupiranga, Brazil and was named brazilite. Later, the mineral was discovered in Ceylon and named baddeleyite, this latter name being the generally accepted one.

Baddeleyite occurs as rounded pebbles sometimes called "favas the zirconium" (favas = beans); they are associated with phonolite as the predominant rock type. This mineral contains 1.0 to 1.8% hafnia and 96.5 to 98.9% zirconia.

Some mineral waters contain dissolved zirconium carbonate complexes in a very low concentration (tenths of a part per million). Zirconium is also found in minute proportions in living organisms and in coal. By spectrographic methods, the existence of zirconium in stars has been noted. Studies by Von Hevesy and Wuerstlin led to the conclusion that hafnium occurs in the solar system in about the same proportion to zirconium, 2:100, as it occurs in the rocks in the earth (10).

Although zircon and baddeleyite are the commercial minerals of zirconium many other minerals exist which contain zirconia and hafnia. Some of them, like alvite and cyrtolite, may contain more hafnia than any of the other zirconium minerals. In Table 1, the more important hafnium-bearing zirconium minerals are tabulated.

Sources of the zircon mineral are found in several countries around the world. Beaches containing considerable proportions of zircon are known in Travancore, India; Malaya; Australia; U.S.A.; Spain; Nigeria; Brazil. The most important source of baddeleyite is in the Pocos the Caldas region of the states of Sao Paulo and Minas Gerais in Brazil, but it has been found in many other places like Kuda Padi, India; Alno, Sweden; Vesuvius, Italy. World production of zirconium concentrate is shown on Table 2.

Table 1: Minerals Containing Zirconium and Hafnium.

Source : "Zirconium, Its Production and Properties". Bureau of Mines. Bulletin 561. Washington : United States Government Printing Office, 1956.

| MINERAL | $ZrO_2$, % | $HfO_2$, % |
|---|---|---|
| Baddeleyite | 96.5-98.9 | 1.0-1.8 |
| Eudialyte | 12.2-14.3 | 0.2-0.7 |
| Thortulitite | 2.0 | 0.5-1.1 |
| Zircon | 64.2 | 0.5-2.0 |
| Var. Hyacinth | 64.8 | 1.2 |
| Zircon altered | | |
| Hagatalite | 39.5 | 2.5 |
| Oyomalite | 38.4 | 2.5 |
| Alvite | 41.9 | 3.0-15.0 |
| Cyrtolite | 52.4 | 5.5-17.0 |
| Malacon | 53.2-65.2 | 2.6-7.0 |
| Nalgite | 49.8 | 3.5-7.0 |
| Zirkelite | 51.9 | 1.0-2.7 |

Table 2: World Production of Zirconium Concentrate.

W =withheld to avoid disclosing company propietary data; excluded from TOTAL. Source : Minerals Year Book. United States of America. Bureau of Mines. 1982

(SHORT TONS)

| COUNTRY | 1980 | 1981 | 1982 |
|---|---|---|---|
| Australia | 541,837 | 468,138 | 350,000 |
| Brazil | 3,759 | 4,400 | 3,850 |
| China | 14,000 | 15,000 | 15,000 |
| India | 16,336 | 13,669 | 13,000 |
| Malaysia | 388 | 1,441 | 1,650 |
| South Africa, Rep. | 88,000 | 110,000 | 138,000 |
| Sri Lanka | 3,341 | 3,600 | 3,640 |
| Thailand | 67 | 115 | 110 |
| U.S.S.R. | 80,000 | 80,000 | 86,000 |
| United States | W | W | W |
| TOTAL | 747,728 | 696,363 | 611,250 |

## 1.3 Physical, Structural, and Chemical Properties.

Zirconium and hafnium belong to the IVA subgroup of the periodic system; they are included in the second and third transition-series elements and they exhibit electronic configurations in which d electrons play an important role. They are characteristically metallic and usually exhibit high melting and boiling points. In general, the elements belonging to the d-block are relatively unreactive with oxygen, halogens, sulfur, nitrogen, hydrogen, and water vapour under ordinary conditions; however, at elevated temperatures, reaction takes place readily.

Some important features of these two elements are the following:

### 1.3.1 Atomic and Ionic Radii.

If we consider a given series in the periodic table, we would expect a decrease in the size of atoms as the atomic number increases; however, as a consequence of the lanthanide contraction, the size of hafnium is almost identical to that of zirconium. The atomic radius of zirconium is 1.45 A while the atomic radius of hafnium is 1.44 A. The same effect is observed when the ionic radii of both elements are compared : 0.74 A ($Zr^{+4}$) and 0.75 A ($Hf^{+4}$) (11). Shannon (12) reports values of the crystal radii of both elements according to their coordination number as follow: coordination number 4, Zr 0.73 A, Hf 0.72 A; coordination number 6, Zr 0.86 A, Hf 0.85 A; coordination number 8, Zr 0.98 A, Hf

0.97 A. In all cases, the oxidation number of both elements is +4. As a consequence of these similarities in atomic and ionic size, the chemical properties of both elements are extremely similar, perhaps more than for any other pair of elements apart from the lanthanides.

### 1.3.2 Electronic Configuration, Oxidation States, and Isotopes.

The electronic configuration of zirconium is $[Kr]4d^2 5s^2$ and of hafnium is $[Xe]4f^{14} 5d^2 6s^2$. Both elements have 4 electrons outside the rare gas-like core, which in the solid state may act as conduction electrons. By loosing these 4 electrons, the two elements assume their most stable state, the tetravalent. Lower degrees of valency are known in the case of the halides and zirconium oxide (ZrO) (13).

Both elements have several natural and artificial isotopes. The application of these isotopes falls in the field of radiochemistry; they are used as radioactive indicators; e.g. the isotope $Hf^{181}$ is a ß-emitter with a half life of 70 days (14,15).

### 1.3.3 Density, Boiling and Melting Points.

The melting and boiling points, as well as the density, are strongly dependent on the purity of the metal. For example, the melting point of hafnium-free zirconium is 1815 ± 15°C while the melting point of zirconium with hafnium present has been reported to be 1830 ± 40°C (15). On the other hand the melting point for hafnium is 2222 ± 30 °C for crystal bar hafnium (with 80 ppm Zr) and 2150 °C for arc-melted crystal bar hafnium ( < 100 ppm Zr) (14).

### 1.3.4 Neutron Absorption.

An important property of both zirconium and hafnium, which has application in modern nuclear technology, is their different behavior toward thermal neutrons.

The absorption cross section of zirconium is 0.18 ± 0.02 barn for the highest purity element. This low absorption cross section is an advantage when compared with the cross section of common construction materials such as iron (2.43 barns), nickel (4.5 barns), copper (3.59 barns), aluminum (0.215 barns), and magnesium (0.059 barns). Another advantage is the relatively low radioactivity exhibited after exposure in a reactor.

For hafnium, the absorption cross section is 105 barns. Therefore, the neutron capture cross section of commercial zirconium is increased by small amounts of hafnium. As a consequence, hafnium-free zirconium must be used when constructing nuclear reactors. Reactor-grade zirconium has less than 100 ppm hafnium by weight. Hafnium, due to its high neutron capture cross section is used as control material to absorb neutrons in nuclear reactors. Some physical properties of zirconium and hafnium are shown in Table 3.

Table 3: Physical Properties of Zirconium and Hafnium.

Source : MUKHERJI, Anil K., Analytical Chemistry of Zirconium and Hafnium. London : Pergamon Press, 1970.

| | ZIRCONIUM | HAFNIUM |
|---|---|---|
| Atomic Number | 40 | 72 |
| Atomic Weight | 91.22 | 178.6 |
| Atomic Radius (A) | 1.452 | 1.442 |
| Ionic Radius (A) | 0.74 | 0.75 |
| Density | 6.489 g/cm3 (low Hf)<br>6.574 g/cm3 (high Hf)<br>6.046 g/cm3 at 979 °C | 13.09 g/cm3 at 20 °C |
| Melting Point | 1852 ± 2 °C | 2222 °C |
| Boiling Point | 3580 °C | 5400 °C |
| Specific Heat | 0.067 cal/g °C at room temp.<br>0.08 cal/g °C above 862 °C | 0.035 cal/g °C between 25 and 100 °C |
| Electrochemical equivalent | Valence 4, 0.2363 mg/C | Valence 4, 0.4626 mg/C |
| Thermal Neutron Cross Section | 0.18 barns | 105 barns |
| 4th. Ionization Potential | 34.33 ev | 33.3 ev |

### 1.3.5 Chemical Reactivity.

The reactivity of zirconium and hafnium towards several substances is almost the same. They are very stable at room temperature to reactions with common gases such as oxygen, nitrogen, and hydrogen. Only when the temperature reaches a few hundred degrees Celsius do they begin to react appreciably.

Hafnium oxide is slightly more basic than zirconium but less basic than thorium. In general terms, the chemistry of hafnium is more related to that of zirconium than to that of thorium, probably due to the fact that the atomic size of hafnium is nearer to that of zirconium.

Zirconium and hafnium become oxidized on being heated in air. Compact metals are oxidized much less rapidly than metallic powders. Zirconium reacts easily with oxygen at a temperature of 200 °C at 7.6 mm of oxygen pressure (16). Various workers have found that large amounts of oxygen can be dissolved in zirconium without showing any zirconium dioxide structure. Lower zirconium oxide ($Zr_2O_3$ and ZrO) can probably also be prepared (17). Hafnium reacts with oxygen in the range 350-1200 °C at 1 atm of oxygen pressure (18), forming the dioxide $HfO_2$ . The dioxides form a continuos series of solid solutions with one another.

Hafnium and zirconium dioxides are practically insoluble in water. They are somewhat soluble in concentrated sulfuric acid or by fusion with alkalis, potassium pyrosulfate, or solid alkali borate. Both dioxides can be dissolved in hydrofluoric acid as a result of the formation of complex fluorides.

The reaction between zirconium and nitrogen is very slow at 400 °C but increases rapidly at 800 °C; this reaction is independent of pressure (16). With hafnium the reaction takes place in the range 876-1034 °C (19).

Zirconium absorbs hydrogen at temperatures between 300-1000 °C. The absorption of hydrogen makes zirconium so easy to breake that it can be crushed. Hafnium absorbs hydrogen at 700 °C to give the composition $HfH_{1.86}$ (20). With the thermal recycling to 500 °C and slow cooling to room temperature, both in hydrogen at 1 atm, the composition $HfH_{2.1}$ is obtained (21).

Neither dissolved oxygen nor nitrogen can be removed from zirconium by heating; however, by prolonged heating in vacuum above 1000 °C, hydrogen is completely removed.

Reaction of zirconium with $CO_2$ occurs above 800 °C and with CO and $H_2O$ vapor above 1000 °C. The product of these reactions is $ZrO_2$ and when the temperature is sufficiently high, reaction with CO or $CO_2$ leads to zirconium carbide formation. Due to this, the use of zirconium for gas-cooled reactors is limited to 500 °C or less.

Zirconium and hafnium also react with all the halogens in the range 200-400 °C and with sulfur, carbon, phosphorous, boron, and aluminum at still more elevated temperatures.

Zirconium also reacts with all metals oxides and other refractory materials, making impossible the use of zirconium in refractory crucibles, for contamination of the metal will occur (13).

Since compounds of zirconium and hafnium have similar physical and chemical properties, separations of these elements based on properties such as boiling and melting points are impractical. In Tables 4 and 5 the melting and sublimimg temperatures as well as the free energies of formation of corresponding hafnium and zirconium compounds are compared.

Separation of zirconium from hafnium is rather based on substantial differences in solubilities of hafnium and zirconium compounds in water, organic solvents, fused salts, or liquid metals. As this question is the central issue in this thesis, we shall return to the problem of separation in Chapter II.

Table 4: Melting and Subliming Temperatures of compounds of Zr and Hf.

( ) = estimated; X = hafnium or zirconium. Source: BENEDICT, M., et al., Nuclear Chemical Engineering. New York : MacGraw-Hill, 1981.

| | MELTING T, °K | | SUBLIMING T, °K;P, 1 ATM | |
|---|---|---|---|---|
| COMPOUND | HAFNIUM | ZIRCONIUM | HAFNIUM | ZIRCONIUM |
| $XO_2$ | 3063 | 2953 | | |
| XC | 4110 | 3805 | | |
| $XF_4$ | (1200) | 1205 | (1200) | 1177 |
| $XCl_4$ | 705 | 710 | 590 | 608 |
| $XBr_4$ | 693 | 723 | 595 | 633 |
| $XI_4$ | (750) | 772 | (700) | 701 |

Table 5: Free Energies of Formation of Halides of Zr and Hf at 1000 °K.

Source: BENEDICT, M., et al., Nuclear Chemical Engineering. New York : MacGraw-Hill, 1981.

| | FREE ENERGY OF FORMATION Kcal/g mol | |
|---|---|---|
| COMPOUND | HAFNIUM | ZIRCONIUM |
| Tetrafluoride (s) | - 363 | - 378 |
| Tetrachloride (g) | - 203 | - 180 |
| Tetrabromide (g) | - 172 | - 154 |
| Tetraiodide (g) | - 118 | - 104 |

### 1.3.6 Corrosion Resistance.

The resistance of zirconium and hafnium to corrosion in different media has been investigated. Zirconium slowly dissolves in sulfuric and in concentrated hydrochloric acid, but is resistant to cold and hot 5% hydrochloric acid, organic acids, solutions of a number of salts, and a solution of iodine in potassium iodide (22). The corrosion resistance of zirconium was also studied in water, steam, a number of gases, and several organic reagents. According to Lustman and Kerze (23), zirconium has a corrosion rate less than 0.0127 mm per year in almost all the media studied, except for gaseous chlorine and the chlorinated derivatives of acetic acid.

Reactions of zirconium with molten dissolved alkalis have been investigated and different results have been reported. According to (24), zirconium reacts readily with alkalis, but Broughton (25) reports that zirconium is stable both in solutions of alkalis and in molten alkalis. Songina (13) considers this discrepancies to be due to the different degrees of purity of the metal employed. When alloying additives are introduced into metallic zirconium, its resistance to corrosion is enhanced. Additives used are tin, niobium, tantalum, molybdenum, and tungsten (23).

Hafnium is slightly less resistant to the attack of acids than is zirconium; however, with the addition of ammonium fluoride, reaction with acids becomes rapid. Hafnium is very resistant to bases, showing no attack by boiling sodium hydroxide solution even when sodium peroxide is present (26).

## 1.4 Applications.

Zirconium as well as hafnium possess certain physical, chemical, and nuclear properties which are unique. They therefore have several uses in modern industry.

### 1.4.1 Zirconium.

#### 1.4.1.1 Nuclear Power Applications.

With the development of nuclear energy and the knowledge of the nuclear properties of zirconium, it has been proved that this element is particularly suitable as a material for reactors.

The requirements for such reactors, according to Miller (15), are: (1) low neutron absorption cross section; (2) mechanical strength and stability under severe stresses resulting from high thermal gradients; (3) leakage reliability in high temperature, high pressure, corrosive, dynamic and radioactive systems; (4) resistance to mechanical damage by radiation; (5) limited formation of high activity products by nuclear reaction; and (6) adaptability to simple remote maintenance and repair.

Zirconium has not only a low thermal neutron cross section but also an exceptional corrosion resistance under certain conditions as well as relatively high strength at the elevated temperatures obtained in thermal reactors. Zirconium can therefore be used as a cladding material for nuclear fuel elements, as an alloying metal with uranium, or as the material for the structure of the reactor core.

### 1.4.1.2 Chemical Equipment Applications.

Zirconium combines extreme resistance to corrosion in both alkaline and acid exposures. It has low corrosion rates in nitric, hydrochloric, and sulfuric acids, dry chlorine, sodium and potassium hydroxide, sea water, halide salts, and sodium hypochlorite. The combination of these factors with its mechanical properties has led to the development of many applications in the chemical industry.

Some of these applications are as a component of: (1) heat exchangers and acid concentrators; (2) tubing, pipe, and pipe fittings for caustic and acid service; (3) crucibles; (4) high-speed agitators used in zirconium phatalite solution.

### 1.4.1.3 Miscellaneous uses.

Zirconium has been used in vacuum applications as a good getter. Several experiments have confirmed that zirconium will absorb or form solid solutions with oxygen and with nitrogen without X-ray evidence of an actual compound being formed (up to 40 atomic % and 20 atomic % respectively) (27).

It has been suggested that zirconium can be used in electrolyte condensers. However, high leakage results (5 to 20 times greater) when zirconium is used instead of tantalum. Oxide films of the metal such as those required in electrolitic condensers have been obtained by anodizing zirconium in various electrolites such as citric acid, ammonium borate, boric acid or sulphuric acid (28).

Zirconium has found another uses as refractories, in enamels, glass polish, pigments, heat transfer pebbles, porcelains, and abrasives. Doped zirconia serves as an oxygen senser in computerized automobile emission control systems.

### 1.4.2 Hafnium.

Hafnium had had just a few commercial uses owing to the difficulty in separating it from zirconium; nevertheless, it has become more available as a by-product of reactor grade zirconium.

Hafnium has an adequate absorption cross section for thermal neutrons, its resistance to corrosion is very high, and it has excellent mechanical properties. All these have made hafnium a very useful material in nuclear reactors where high cross section and high temperature corrosion resistance are desirable. It is used to fabricate control rods which are used in water-cooled nuclear reactors. The rods absorb thermal and epithermal neutrons. Hafnium control rods were successfully used for a full core life in the reactor of the submarine Nautilius (29).

Hafnium has advantages over substitute materials because of its resistance to water corrosion, its stability under the intense radiation within a reactor and the fact that it does not require cladding or other difficult fabrication operations. However, other elements such as boron, cadmiun samarium, europium, gadolinium, and even gold, silver, and platinum also have high cross sections and have been used for reactor control. Of these, cadmium and boron appear to be most competitive with hafnium (14).

### 1.4.2.1 Other Uses of Hafnium.

Hafnium has been used for filaments in electric light bulbs, as electrodes in X-ray tubes, rectifiers, high pressure tubes, and special glasses (30,31).

A certain number of hafnium alloy systems have been developed. For example, hafnium-titanium alloys which are free from oxygen, nitrogen, carbon, and silicon can be used as getters in evacuated or gas-filled devices such as lamps, radio and television tubes (32).

Hafnium has also been used in photographic flash powders, as a component of detonating caps and ammunition, and in bright coatings for ceramic decorations.

# Chapter II

## METHODS OF SEPARATION. GENERAL REVIEW.

### 2.1 Introduction.

Zirconium and Hafnium are invariable associated in natural sources and because of their similarity in chemical properties, they are very difficult to separate. Early research on separation of these elements was only of academic interest, for the hafnium content of zirconium did not interfere with its industrial applications. However, in recent years, the separation problem has assumed a greater importance owing to the fact that the presence of hafnium renders zirconium unfit for nuclear applications.

As stated earlier in Chapter I, zirconium has a very low neutron capture cross-section (0.18 barns) while hafnium is characterized by its high value (105 barns). If the hafnium is allowed to remain with zirconium, the absorption cross-section of the latter would be about 1.6 barns, which is unaceptable for its use in reactors. Therefore, the main problem in the production of reactor grade zirconium is the separation of the metals. Methods which have been developed include fractional crystalization and precipitation, fractional distillation, ion-exchange, chromatographic methods, and solvent extraction. Some of these methods are suitable only for refining operations, while others, like chromatography, have been adapted for use in analysis.

## 2.2 Fractional Crystallization and Precipitation.

Differences in solubilities of corresponding salts of zirconium and hafnium have led to using fractional crystallization and precipitation for the separation of both elements. Table 6 compares the solubilities of some salts of zirconium and hafnium. In general, the solubility of hafnium salts is greater and depending on the hafnium-zirconium solubility ratio, the separation will be more or less successful.

Double oxalates of ammonium and potassium have been used to separate both elements by this technique. The hafnium salt remains in the mother liquor while the zirconium compound precipitates. This separation is dependant upon the hydrochloric acid concentration (18). Potassium and ammonium sulfates of both elements behave similarly. Both the citrate (33) and acetylacetonate (34) of hafnium are more solubles than the corresponding zirconium compounds. The difference in solubilities of $ZrOBr_2$ and $HfOBr_2$ and $ZrOCl_2$ and $HfOCl_2$ has also been employed (35). Hafnium oxyhalides are less soluble than the corresponding zirconium compounds; however, the solubility of both hafnium and zirconium compounds increases as the concentration of hydrochloric acid increases.

Table 6: Solubilities of salts of Zr and Hf.

M = Hafnium or Zirconium. Source: BENEDICT, M.,T. PIGFOLD, and H.W. LEVI. Nuclear Chemical Engineering. New York: McGraw-Hill, 1981.

| | | | SOLUBILITY g mol/liter | | |
|---|---|---|---|---|---|
| SALT | SOLVENT | T °C | ZIRCONIUM | HAFNIUM | Hf/Zr RATIO |
| $(NH_4)_2MF_6$ | $H_2O$ | 0 | 0.611 | 0.890 | 1.46 |
| $(NH_4)_2MF_7$ | $H_2O$ | 0 | 0.360 | 0.425 | 1.18 |
| $K_2MF_6$ | 0.125N HF | 20 | 0.0655 | 0.1008 | 1.54 |
| $MOCl_2$ | 11.6N HCl | 20 | 0.33 | 0.15 | 0.46 |

One of the earliest separations accomplished by this method was based on the difference in solubility of $K_2ZrF_6$ and $K_2HfF_6$ . The hafnium salt is 1.5 times more soluble than the zirconium salt; therefore, during fractional crystallization, hafnium accumulates in the mother liquor. Ammonium analogs have also been employed (18) but the solubility ratio is not favourable for separation. When ammonium hexafluoro salts are used, the diammonium hexafluoro salts are preferred to triammonium heptafluoro salts, because the difference in solubility between zirconium and hafnium compounds is greater with the former salts (36).

Separations using fractional crystallization are generally faster and more efficient than crystallization methods but they are still not economical.

The phosphates of zirconium and hafnium show different solubility in sulfuric acid. Using an appropriate reagent, like triethyl phosphate, acid ethyl phosphate, and trimethylphosphate, the corresponding phosphates of zirconium and hafnium are precipitated. One disadvantage of this method is the difficulty in converting the precipitates to soluble compounds .

Schumb and Pitman (37) used the fractional precipitation of ferrocyanides of zirconium and hafnium; after four fractionations,a starting material containing 12% $HfO_2$ was enriched to a product containing 80% $HfO_2$ . One disadvantage is the partial decomposition of sodium ferrocyanide by sulfuric acid during the process, leading to the formation of hydrochloric acid. Therefore, good ventilation is needed during precipitation.

Based on the difference in pH at which the hydroxides of zirconium and hafnium precipitate, a variation in acid concentration leads to fractional precipitation. Zirconium hydroxide precipitates at a lower pH than hafnium hydroxide; therefore, during hydrolitic precipitation hafnium concentrates in the supernatant solution. According to Larsen and Gamill (38), the difference in the pH of precipitation is most marked in nitrate and chloride solutions while in sulphate solutions, the order of precipitation is reversed. This demonstrates the complexing ability of sulfate.

When hydrogen peroxide and sodium hydroxide are added to zirconium and hafnium solutions, the corresponding perzirconate and perhafnate salts are precipitated, the former being less soluble (39). Since these salts are unstable, zirconium and hafnium are precipitated by heating the mixture.

Conditions for the precipitation of zirconium and hafnium with m-nitrobenzoic acid were studied by Ramous (40). He found that by adjusting the pH properly below 2, the precipitate was enriched in zirconium; the precipitation should be done in a perchlorate medium, since he observed that the amount of precipitate increased in the order $SO_4^=$, $NO_2^-$, $Cl^-$, $ClO_4^-$. However, the amount of hafnium could not be reduced below 0.3% in the final product.

A simple and effective method of separation was developed by Purkayastha and Sinhamahapatra (41). By fractional precipitation as pyrophosphate, pure hafnium can be prepared from natural zirconium, following a process of 8 or 9 stages of fractional precipitation. By this method, reactor grade zirconium and pure hafnium can be obtained.

Fractional precipitation processes are tedious and time consuming and are not used for industrial processes.

### 2.3 Fractional Distillation.

The tetrachlorides of zirconium and hafnium form addition compounds with phosphorus oxychloride and phosphorus pentachloride. Since the boiling points for the compounds of hafnium and zirconium are in the neighborhood of 360 °C and differ by about 30 °C, separation is possible by fractional distillation, using a large number of theoretical plates in a column.

Van Arkel and the Boer (42) found that the analysis of these compounds corresponded to $2ZrCl_4.PCl_5$ and $2HfCl_4.PCl_5$ and $2ZrCl_4.POCl_3$ and $2HfCl_4.POCl_3$. Later studies by Nisel'son (43), Sheka (35) and Larson (44) reported the compositions of zirconium and hafnium complexes as $ZrCl_4.PCl_5$, $ZrCl_4.2POCl_3$, $ZrCl_4.POCl_3$, $HfCl_4.2POCl_3$, and $HfCl_4.POCl_3$. According to (45), the products of the reaction with $POCl_3$ are azeotropic mixtures in the vapour state.

Green and Katz (46) found that the phosphorus oxychloride complexes have lower boiling points and greater thermal stability than the corresponding phosphorus pentachloride compounds. In the case of the phosphorus oxychloride complexes, the hafnium addition compound has the lower boiling point; therefore, hafnium is enriched in the first distillates and is almost entirely absent from the residues (42).

Bradley and Warddan (47) examined the fractional distillation of the alkoxides. The tetraisopropoxides of zirconium and hafnium are prepared by the action of dry ammonia on a suspension of the pyridinium metal hexachloride compound in a dry mixture of isopropanol and benzene. Other alkoxides from less volatile alcohols may be obtained by refluxing this product with the appropriate alcohol. The boiling points of the tertbutoxides of zirconium and hafnium, at 5 mm-Hg are 89.2 °C and 87.6 °C, respectively. Boiling point differences increase toward higher pressures.

## 2.4 Vapor Phase Dechlorination.

This process is based on the selective decomposition of zirconium tetrachloride to the oxide whereas the conversion of hafnium tetrachloride to the corresponding oxide is not highly favoured under the same conditions. At 1200 °C the equilibrium pressure ratios for chloride and oxygen for the formation of oxide is 114 for the zirconium and $6.97 \times 10^{-5}$ for the hafnium reaction.

When mixed chlorides of hafnium and zirconium react with a gas mixture composed of chlorine and oxygen, Funaki and Uchimura (48) observed an appreciable dechlorination of hafnium tetrachloride too, which reduces the efficiency of separation. After dechlorination, 90 to 97 % of zirconia was recovered; however, the hafnia content in the condensate was 2.5 %.

## 2.5 Partial Reduction of the Tetrachlorides.

Reduction of zirconium tetrachloride to zirconium trichloride with aluminum in liquid aluminum chloride was first studied by Ruff and Wallstein (49) and the Boer and Fast (50). Since the use of aluminum as the reducing agent yielded a zirconium trichloride that was contaminated with aluminum and zirconium oxide, the Boer and Fast suggested that zirconium could probably be used to reduce its own halides. This was proved by Fast (51), who reduced zirconium tetraiodide to the triiodide by using zirconium as the reducing agent. Young (52) and Schumb and Morehouse (53) investigated this process further. All these studies were done in order to compare the chemical behaviour of the halides of both zirconium and hafnium. Larsen (54), who studied the separation and reduction of the tetrahalides of both elements, concluded that the difference in the ease of reduction of the tetrahalides of zirconium and hafnium did not appear to be great enough to be utilized in a separation process. However, Newnham (55) developed a method of separation based on the work of Young (52) and Schumb and Morehouse (53). Young concluded that the reduction by aluminum of zirconium tetrabromide to the tribromide occurred at or above 450 °C while Schumb and Morehouse observed the reduction of the hafnium compound to the corresponding tribromide took place at 600 °C. Newnham showed that this difference in temperature of reduction can provide a method of separation.

Newnham's method uses zirconium metal to reduce zirconium tetrachloride to the di- or trichloride with subsequent separation of unreduced hafnium tetrachloride. It was observed that in the temperature range of 330-550 °C, the hafnium content of the reduced chloride was always less than 0.1% and if hydrolysis of the zirconium tetrachloride was eliminated, the hafnium content of the lower chloride of zirconium could be reduced to 0.01%. One disadvantage of the zirconium reduction is that zirconium trichloride begins to disproportionate even at 300 °C; at 450 °C, the trichloride disproportionates completely but the disproportionation of the dichloride is more difficult. The presence of this unreduced zirconium tetrachloride causes the dilution of hafnium tetrachloride in the vapor state; this can be eliminated by carrying out a reduction with aluminum powder at 300 °C. A great advantage of this method is that zirconium can be introduced as the chloride and recovered as chloride; in this way, the hafnium impurity is removed without the use of aqueous solution chemistry, which is involved in other processes of separation. After separation in an aqueous process, zirconium has to be recovered by precipitation and rechlorinated.

Two recent patents (56) describe a process in which a mixture of $Na_2ZrF_6$ and $Na_2HfF_6$ is reduced by aluminum dissolved in liquid zinc; a very high separation factor between hafnium and zirconium is obtained, with almost no contamination of the zirconium by aluminum. Reactor grade zirconium containing less than 0.01% hafnium content is produced.

### 2.6 Chromatographic Methods.

This simple and very effective procedure has been used for the separation of zirconium and hafnium; the separations have been achieved by adsorption, reversed-phase and ion-exchange chromatography.

#### 2.6.1 Adsorption Separations.

Various compounds of zirconium and hafnium show different adsorption on silica gel and cellulose. In both cases, hafnium is preferentially held by the column. Based on this, several methods have been developed for separation of these elements.

Hansen et al. (57) worked with the tetrachlorides of zirconium and hafnium dissolved in methanol and they observed that silica gel adsorbs hafnium preferentially from the solution and good separations were obtained. Yaturajam and

Gupta (58) and Giffen (59) improved the efficiency of the process and obtained zirconium dioxide containing 0.01% or less of hafnium oxide from starting materials containing several percent of $HfO_2$. Olsina et al. (60) successfully used a thin layer chromatohraphy technique on silica gel G. An $HCl:H_3PO_4:H_2O$ (10:1:9) mixture was used to develop the plates.

A column of cellulose was used by Kember and Wells (61). The column was packed with ashless filter paper pulp in ether; a saturated solution of zirconium nitrate was passed through the column and a solution of nitric acid and dichlorotriethylenglycol (3:7) was used as the eluent. From two hundred grams of zirconium nitrate, fifty grams of pure zirconium metal containing less than 0.01% hafnium was obtained. This method is not commercially atractive because of the large number of individual operations involved, the risks of fire and explosion, and also because the yields are poor.

### 2.6.2 Reversed Phase Chromatography.

While adsorption chromatography may be especially suitable for refining operations, the reversed phase mode may be appropriate for analytical work owing to the fact that it can accept aqueous samples. This thesis is essentially concerned with the analytical separation of zirconium and hafnium.

Fritz and Frazer (62) used Teflon-6 as the solid support and methylisobutylketone equilibrated with HSCN as the stationary phase. Zirconium and hafnium in the ratios 5:1-500:1 were separated; the separated zirconium contained less than 0.01% hafnium. See fig. 1.

Yagodin and Chekmarev (63) used a 2N sulfuric acid solution as the eluant and a column packed with paper treated with tri-n-octylamine bisulfate solution in benzene. The separation coefficients is about 10 when the concentration of tri-n-octylamine in the solution is 12%.

Other organic solvents have been used as the stationary phase. Choe and Han (64) used a column packed with polyethylene with cyclohexane and a mixture of ammonium thiocyanate and sulfuric acid as the eluant for zirconium; Choe (65) also worked with cyclohexanone and acetophenone as the stationary phase and sulfuric acid at different concentrations as the eluent. Although capable of achieving good separations, these methods possess the disadvantage that the eluates contain a considerable quantity of $SCN^-$ and/or $SO_4^=$ salts which prevent the analyst from evaporating to a small volume in an attempt to achieve high sensitivities for small amounts of analyte. The present author has been interested in developing a procedure that employs a volatile acid as the eluent.

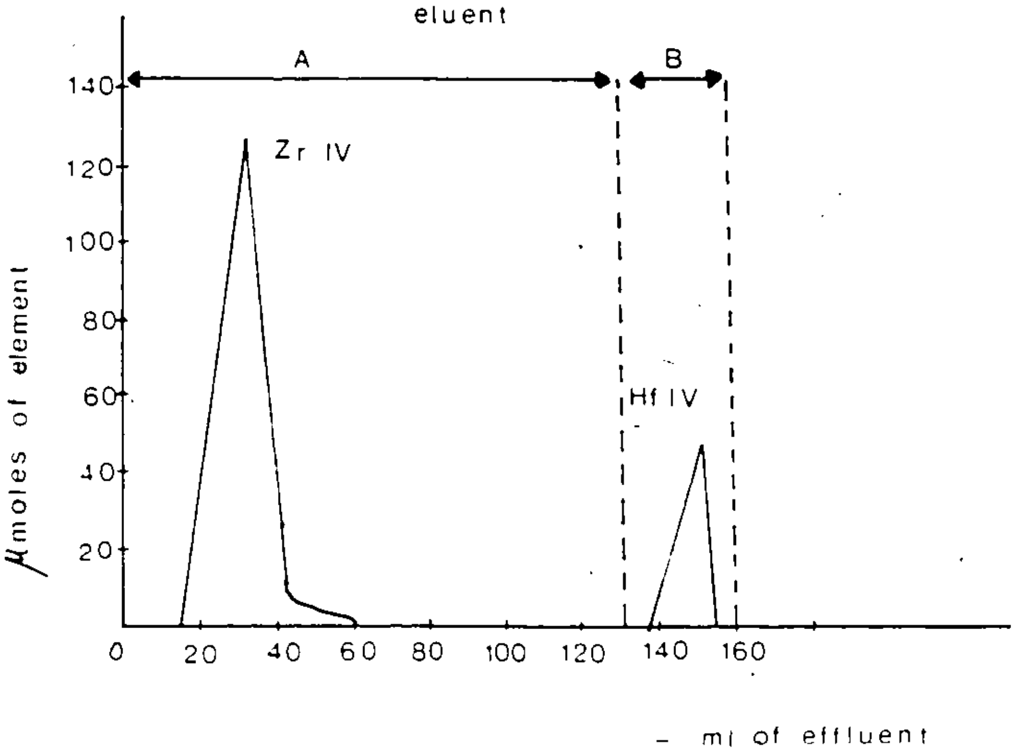

Figure 1: Reversed Phase Chromatography of Zirconium-Hafnium Mixture. Separation of zirconium and hafnium according to Fritz and Frazer (62). Eluent A contains 4M $NH_4SCN$ and 0.2M $(NH_4)_2 SO_4$. Eluent B is aqueous 1.2M $(NH_4)_2SO_4$. Source :MUKHERJI, ANIL K., Analytical Chemistry of Zirconium and Hafnium. London : Pergamon Press, 1970.

### 2.6.3 Ion-Exchange Separations.

The methods that have been described achieved a relative amount of success, but the aplication of them to large scale economical operations for the production of hafnium-free zirconium did not seem to be possible; the use of ion-exchange resins as a feasible way of separating these elements showed better industrial possibilities. In Table 7, a review of the different types of ion-exchange resins that have been used is showed.

Street and Seaborg (66) performed a separation at miligram levels using the resin Dowex-50 and observed that after elution with 6M hydrochloric acid, hafnium was eluted from the resin before zirconium. The initial mixture has a ratio of 2:1 zirconium to hafnium; 60% of the starting hafnium oxide was recovered containing about 0.1% zirconium oxide. See Fig. 2. Newnham (67) extended the method to gram samples of the initial mixture (2 grs oxide mixture containing 20% hafnium oxide). He reported a total hafnium recovery of 42%.

Lister (68) proposed that, based on economical grounds zirconium should be eluted first and the smaller quantity of hafnium should be retained on the column. He worked with mixtures of zirconium and hafnium (as the oxychlorides or nitrates) containing 2% hafnium. Dowex-50 was used as the resin and several acids (hydrochloric, oxalic, nitric, perchloric, sulfuric) were tested as eluents. Sulfuric acid

Table 7: Separation of Zirconium and Hafnium Using Ion-Exchange.

| ION-EXCHANGER | TYPE | ELUENT | REF. |
|---|---|---|---|
| Dowex-50 | Sulfonated Polystyrene | 6M HCl | 66.67 |
| | | 0,5M $H_2SO_4$ | 73 |
| | | 0.09 citric acid + 0.045M $HNO_3$ | 70 |
| | | 1M formic acid and 4M $HNO_3$ | 71 |
| Zeo-Karb 225 | Sulfonated Phenolic | 0.5M $H_2SO_4$ | 68 |
| Dowex-1 | Quaternary Ammonium Chloride | 0.05M HF + 1M HCl | 69 |
| | | 3% $H_2SO_4$ | 123 |
| Amberlite Ira-400 | Quaternary Ammonium | 0.01M HF + 02M HCl | 74 |
| Dowex-2 | Quaternary Ammonium | 9M HCl | 76 |
| Dowex-3 | $HSO_4^-$ form | 1.4-10N $H_2SO_4$ | 124 |
| AN-2F,EDE-10 | Amines | 1N $H_2SO_4$ | 77 |
| AV-16,AV-17 | Amines | 1N $H_2SO_4$ | 77 |
| KU-2 | Sulfonated Polystyrene | $H_2SO_4$ | 78,119 |
| | | 0.025M citric ac. + 1M $HClO_4$ or $HNO_3$ | 78 |
| | | HCl with organic solvents. | 120 |
| KU-2 & RF | Sulfonated Polystyrene | 0.65 M $H_2SO_4$ and ammonium oxalate | 72 |
| EDE-10P | Amines | 0.5M $H_2SO_4$ | 121 |
| Zerolit FF-200 | $Cl^-$ type | 1.25N $H_2SO_4$ + 0.1% $H_2O_2$ | 122 |

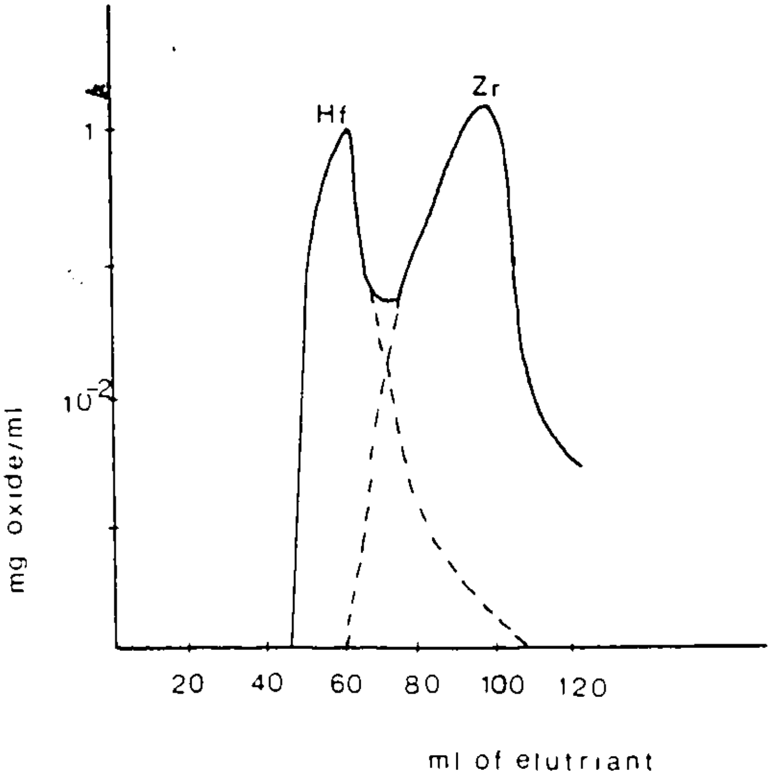

Figure 2: Separation of Hafnium and Zirconium by Ion-Exchange.. Elution of Zirconium and Hafnium with 6M HCl, according to Street and Seaborg (66). Source : MUKHERJI, ANIL K., Analytical Chemistry of Zirconium and Hafnium. London : Pergamon Press, 1970.

seemmed to achieve the simplest and more satisfactory separation. Gramme quantities were separated by one passage through the column. Zirconium was eluted first and 95 to 98% of it was recovered containing less than 0.1% hafnium. Lister and MacDonald (69) scaled up the process to kilogram quantities using the cation exchanger resin Zeo-Karb 225 which is similar to Dowex-50.

The above methods are probably not suited to analytical work as recoveries close to 100% are not observed. However, Benedict et al. (70) developed a procedure that is probably applicable in analytical work. They observed that a good separation is achieved when a mixture of nitric and citric acid is used as the eluent, due to the big differences in the distribution ratio of the elements' complexes in Dowex-50 when using that mixture of acids. Zirconium is eluted first. See Fig. 3.

Quereshi and Husain (71) used Dowex-50 WX-8 resin in hydrogen form to separate zirconium and hafnium solutions of 1M formic acid with great success. Zirconium is eluted with 1M formic acid, the column is washed with water, and the hafnium is eluted with 4M nitric acid. Under these conditions, the separation factor is 40. See Fig. 4. The use of formic acid rather than citric acid is most attractive owing to the ease with which it can be destroyed by wet oxidation.

Larkorin et al. (72) based their investigation on the differences between the fluoro-sulfate complexes of hafnium

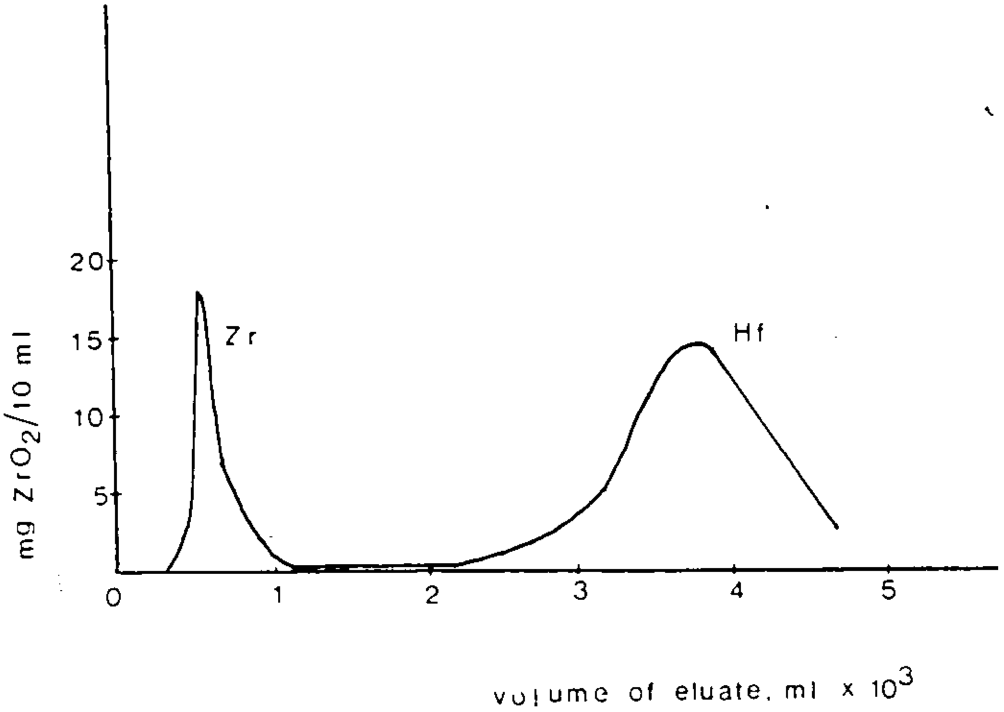

Figure 3: Separation of Zirconium and Hafnium by Ion-Exchange. Elution of zirconium and hafnium with 0.045M $HNO_3$ + 0.09M citric acid, according to Benedict et al. (**70**). Source :MUKHERJI, ANIL K., Analytical Chemistry of Zirconium and Hafnium. London: Pergamon Press, 1970.

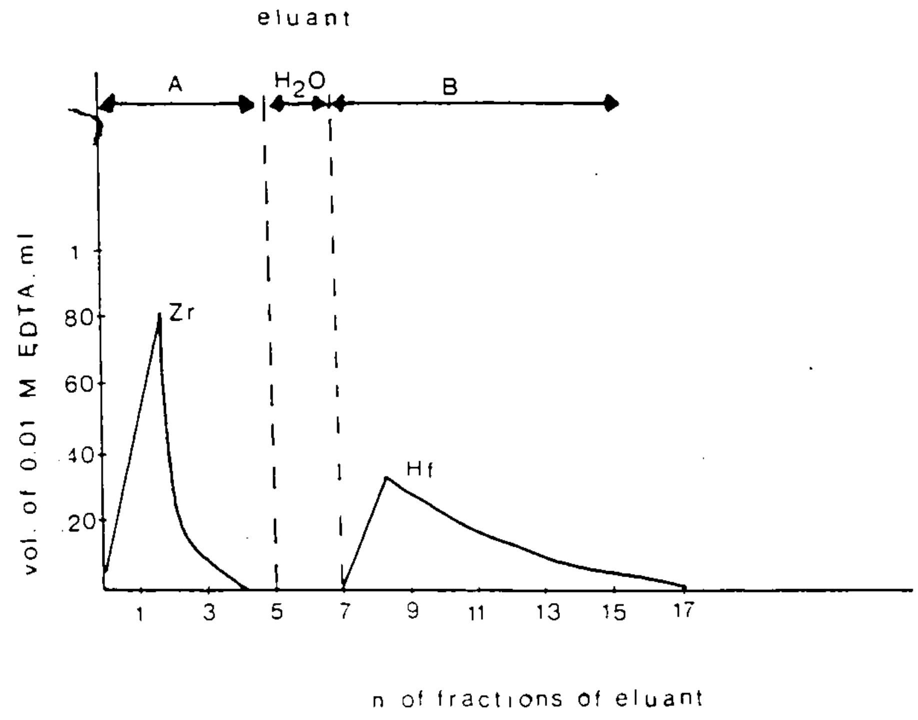

Figure 4: Separation of Zirconium and Hafnium by Ion-Exchange.. According to Quereshi and Husain ( 71 ). Eluent A is 1M formic acid. Eluent B is 4M nitric acid. Source : QUERESHI,M. AND HUSAIN, K., Anal. Chem., 43, 447 (1971).

and zirconium. Using KU-2 resin, they observed that the hafnium complexes are retained more strongly by the column. After elution with 0.65M $H_2SO_4$, the first fraction of the eluate contained less than 0.01 to 0.08% hafnium in relation to zirconium; the intermediate fraction which contained some zirconium contaminated with hafnium was recovered and added to the starting solution; the third fraction containing mainly hafnium is passed through a column of RF resin. Hafnium is retained by the column and eluted from it with ammonium oxalate solution. 99% pure hafnium oxide was obtained.

Both zirconium and hafnium form negatively charged complexes with fluoride ions and the differences between these anionic complexes have been used to separate the elements using anion exchange resins. Krauss and Moore (73) used the resin Dowex-1, tracer concentrations of zirconium and 0.2 mg of hafnium ($Zr^{95}$ and $Hf^{181}$ as tracers), and a mixture of HCl and HF as eluent. Zirconium is eluted first and an estimated purity of the last fractions better than 95% in hafnium is reported. Huffman and Lilly (74) and Rajan and Gupta (75) also worked with the fluorocomplexes. When a mixture of HCl and HF is used as eluent, zirconium is eluted first (74), but when sulfuric acid is used, hafnium is the one eluted first (75).

Huffman, Iddings, and Lilly (76) used the chlorocomplexes and Dowex-2 as the resin. 9M hydrochloric acid was used as the eluent. They also observed that in the absence of fluoride ions, hafnium was eluted first. See Fig. 5. However, Vinarov and Shulgina (77) reported that they dissolved the metal ions in hydrofluoric acids and the elution was performed with sulfuric acid. Under these conditions, hafnium is eluted first, in contrast to the observation of Huffman et al. (76) and Lister (68).

Differences in stability between zirconium and hafnium sulfate complexes (the former being three times more soluble than the latter) have been used by Marov et al. (78) to develop a method of separation for both elements.

Gupta et al. (79) obtained purified zirconium oxide containing less than 0.01% hafnium oxide by combining chromatography on silica gel and anion exchange on IRA-400.

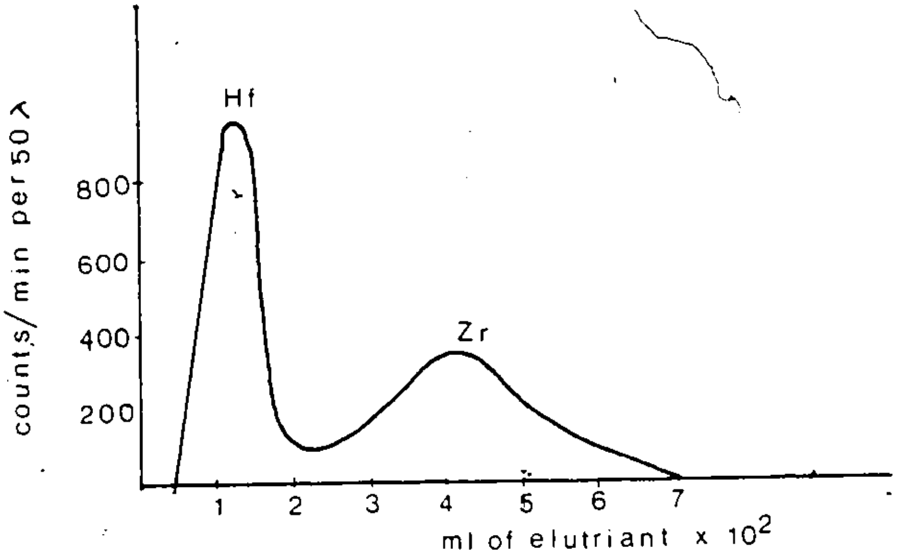

Figure 5: Ion-Exchange separation of Zirconium and Hafnium. Elution of chlorozirconate and chlorohafnate according to Huffman et al. (76). Eluent is 9.M hydrochloric acid solution. Source: MUKHERJI, ANIL K., Analytical Chemistry of Zirconium and Hafnium. London: Pergamon Press, 1970.

### 2.6.4 Liquid-Liquid Extraction.

Many studies on the separation of zirconium and hafnium by liquid-liquid extraction have been done in the last 30 years and many organic solvents have been recommended for achieving the separation. Several reviews have been published dealing with the description of these processes (80,81,82).

Two principal solvent-extraction methods are used at the industrial level in order to prepare reactor grade zirconium. One is based upon the solvent methylisobutylketone (hexone) and the other on tributylphosphate (TBP). These methods, as well as others not as important at the industrial level, are described below.

#### 2.6.4.1 Methylisobutylketone.

Fisher and coworkers (83) separated a zirconium-hafnium mixture from an aqueous solution of sulfates containing ammonium thiocyanate. As the extractant, they used an ether solution of thiocyanic acid, into which hafnium is preferentially extracted. When a starting material containing 0.5% hafnium oxide was submitted to 6 to 8 fractionations, a product containing 70-90% hafnium oxide is obtained. However, due to the volatility and hazards of working with ether, other solvents were studied. Overholser et al. (84) and Fischer et al. (85) showed that methylisobutylketone (hexone), which is less volatile and cheaper than ether, was a good substitute.

This hexone-thiocyanate separation process was first used on an industrial scale by the Oak Ridge Laboratories in USA, because it was considered as the best suited of the methods for separating hafnium from zirconium. After extraction in nine stages, 90% of zirconium remains in the aqueous phase with a hafnium to zirconium ratio of 0.01% or less (86).

Hoshino and Takuii (87,88) studied the distribution constants of zirconium and hafnium from aqueous phase containing $NH_4CNS$, $(NH_4)_2SO_4$ , and HCl by eighty different ketones, alcohols, esters, and ethers. When cyclohexanone was used as the extractant, the separation factor is about 100 if the hydrochloric acid concentration is 1-1.5M. The separation factor can be increased to 250 if the HCl concentration is lowered, but a decrease in the distribution ratio of both elements is also observed. According to these authors, cyclohexanone seems to be a better extractant for zirconium and hafnium than methylisobutylketone.

As successful as this approach has been in refining operations, the necessity of separating the elements from large amounts of thiocyanate is a decided drawback in analysis.

### 2.6.4.2 Thenoyltrifluoroacetone (TTA).

Huffman and Beaufait (89) studied the distribution ratio for zirconium and hafnium between a 2M perchlorate acid solution and various concentrations of TTA. From an initial solution containing hafnium and zirconium in the ratio 20:1, they reported that after 3 extractions with 0.02M TTA, a recovery of 50% of the hafnium with a zirconium content of 0.4% is obtained.

Schultz and Larsen (90) used a benzene solution of TTA as the organic phase and 0.2N hydrochloric acid solution as the feed solution. Zirconium was preferentially dissolved in the benzene phase as the chelate. After six extractions, the hafnium content in a mixture was increased from 7.5 to 99.8 mol percent with a 37.6% yield of the original hafnium. A drawback of these methods is the alleged severe carcinogenicity of TTA.

### 2.6.4.3 Tributylphosphate (TBP).

Tributylphosphate forms addition compounds with zirconium and hafnium nitrates; this feature has been used to develop a method of separation of these two elements.

TBP is diluted with an organic solvent to lower the density and viscosity of the organic phase; an aqueous solution acidified with nitric acid enters into contact with the organic phase and the zirconium is extracted into it. By stripping the organic phase, the zirconium nitrate is recovered. In Fig. 6 a schematic diagram of the process is shown as developed by Cox and coworkers (91). They separated hafnium and zirconium nitrates from a feed solution containing 2.4% hafnium, by extracting with TBP diluted with 40 vol% of n-heptane. They reported a separation factor of 3 to 30 and a reduction of the initial hafnium content to less than 0.01% hafnium.

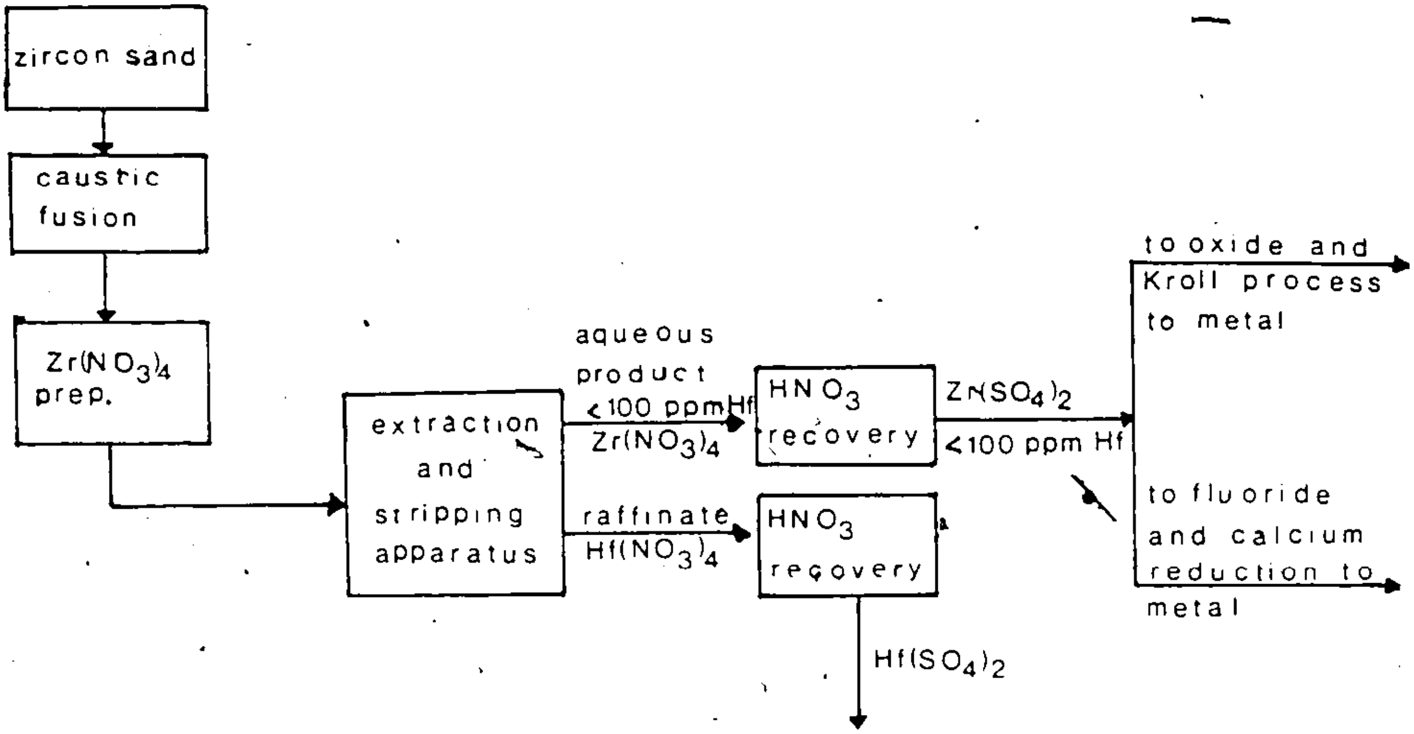

Figure 6: Schematic Diagram of TBP Extraction..Source :COX,P.P., PETERSON, H.C., and BEYER, G.H., Ind. Eng. Chem.,50., 141 (1958).

Hudswell and Hutcheon (92) found that at high acidities, the extraction is more efficient but the separation factor decreases. They also found that the formation of another phase, due to the limited solubility of the zirconium nitrate-TBP complex in kerosene, can only be avoided by increasing the TBP concentration or by changing the solvent for another. They chose a 50% TBP/xylene solution.

Hure and Saint-James (93) studied the effect of salting out agents on the extraction and found that sodium nitrates favour extraction of zirconium, ammonium nitrate is less effective as salting out agent, and calcium nitrates lead to the formation of viscous solutions. They also observed that the extraction of zirconium decreases as its concentration increases. They found that using a 60 v/o (volume percent) of TBP and 40% refined kerosene solution and an aqueous phase 3N in nitric acid and 3.5N in sodium nitrate, the distribution coefficients are 1.5 for zirconium and 0.15 for hafnium, giving a separation factor of 10.

### 2.6.4.4 Tri-n-octylamine (TNOA).

Cerrai and Testa (94) worked with a solution prepared by dissolving 36 mg of an impure zirconium sample, containing 97.8% Zr and 2.2% Hf, in a 8M HCl-0.4M $HNO_3$ solution. This aqueous solution was contacted with 0.2M TNOA in cyclohexane. After one contact, 75% of zirconium and 0.12% of hafnium are extracted into the organic phase. If $HNO_3$ concentration is increased, the extraction of zirconium is lowered.

Otsuka and Miyazaki (95) worked with a kerosene solution containing 5-20 vol percent of TNOA. They found a zirconium purity in the organic phase of 99.93% while the hafnium remaining in the aqueous phase had a purity of 98.6%. This gives a good method of separation.

De Oliveira et al. (96) used a solution of 0.3M Alamine 336 (tri-n-octylamine + N-decylalkylamine) in a mixture of 94% n-heptane-6% $CHCl_3$ as the organic phase. Experimental results showed that good separation factors (250-260) are obtained when the aqueous phase is 6.5M HCl and 0.5M $HNO_3$ ; if the total acidity of the system is increased, the separation factors decrease.

This seemingly excellent method suffers from an unexpected disadvantage for analytical work. It is extremely difficult to strip metals from the TNOA extract.

### 2.6.4.5 Other Organic Solvents.

Other solvents that have been tested are: acid esters of orthophosphoric acid in xylene (97,98); Hyamine 1622 (99); Primene JMT in kerosene (100); Amberlite LA-2 in Xylene (101,102); Mesityloxide (103); diantypyrylmethane group (104); n-nonyl alcohol or n-hexanol mixtures with n-heptane (105); o-(2-hydroxy-5-dodecylphenylazo) benzoic and phenyl arsonic acids in petroleum naphta or in $CHCl_3$ (106); diheptyl sulfoxide (107); $Ph_3N$ in a petroleum fraction solvent (108); diethyl ether, diisoamyl methyl phosphate, diethylketone, methylpropylketone, isobutylmethylketone (109).

## Chapter III

# DETERMINATION OF DISTRIBUTION COEFFICIENTS. PROCEDURES AND RESULTS.

### 3.1 Introduction.

Determination of distribution coefficients for zirconium and hafnium between an aqueous phase and bis(2-ethylhexyl)phenylphosphonate (DEØP) was the main concern of the research. This extractant was chosen because it is similar chemically to tributylphosphate (TBP) but it is less soluble in acid and it is therefore suitable as the stationary phase in a chromatographic system. Moreover, Kantipuly (110) encountered large separation factors with a related monoester, (2-ethylhexyl)hydrogenphenylphosphonic acid (HEHØP), in his work with lanthanides. It was hoped that DEØP would be especially suitable for zirconium and hafnium.

It was initially intended to analyse the aqueous phase after the extraction process by means of a spectrophotometric method, using Alizarin Red S as the reagent. Some interferences were encountered and so various procedures were examined in order to deal with them. Attempts to remove phosphate were not successful, so analysis of the aqueous phase was finally performed by DCP emission spectrophotometry in which phosphate does not interfere.

Distribution coefficients for zirconium and hafnium were determined in hydrochloric and nitric acid media. The effect on the distribution coefficients of acidity, nitric acid concentration, presence of sodium nitrate, and the concentration of DEØP in the organic phase were studied.

## 3.2 Spectrophotometric Determination of Zirconium and Hafnium.

Unfortunately, owing to very poor sensitivity, atomic absorption is not suitable for the determination of zirconium and hafnium. Therefore, Alizarin Red S (sodium alizarin sulfonate) was chosen to determine both zirconium and hafnium. The reaction between these elements and the Alizarin Red S in acidic medium produces an intensily red-colored complex. The technique shows great sensitivity although interferences occur with ions that inhibit the formation of the complex Zr(Hf)-alizarin.

According to Smith and West (111) bisulfate, phosphate, and sulfate anions all interfere by complexing both elements. Fluoride interferes quantitatively up to a concentration of 0.01 mg per 100 ml; cations such as aluminum, copper, iron, lead, rare earths, manganese, and nickel also interfere (112).

The standard curve was prepared following the technique outlined by Wengert (112). Beer's law is obeyed in the range of concentrations studied for both elements.

### 3.2.1 Experimental.

Standard Zirconium Stock Solution : 1.2724 g of sublimed zirconium tetrachloride ($ZrCl_4$) were dissolved in 30 ml of concentrated hydrochloric acid. This solution was transfered quantitatively to a 500 ml volumetric flask, 50 ml of concentrated hydrochloric acid were added and the volume made up to 500 ml with de-ionized water. This solution contained 0.995 mg of Zr per ml.

Standard Hafnium Stock Solution : 5.7601 g of sublimed hafnium tetrachloride ($HfCl_4$) were dissolved in approximately 250 ml of concentrated hydrochloric acid. This solution was transfered quantitatively to a 2 liter volumetric flask and 70 ml of concentrated hydrochloric acid added. The volume was made up to 2 liters with de-ionized water. This solution contained 1.603 mg of Hf per ml.

Zirconium Standard Solution : a 5 ml aliquot of the zirconium standard stock solution was transfered to a 250 ml volumetric flask and 58.3 ml of dilute hydrochloric acid (16:100) was added. This was diluted to 250 ml with de-ionized water. This solution contained 19.9 µg of Zr per ml.

Hafnium Standard Solution : a 5 ml aliquot of the hafnium standard stock solution was transfered to a 250 ml volumetric flask and 58.3 ml of dilute hydrochloric acid (16:100) was added. This was diluted to 250 ml with de-ionized water. This solution contained 32 µg of Hf per ml.

Alizarin Red S : a 0.05% aqueous solution was prepared.

Procedure : aliquots of the standard solution of Zr(Hf) were transfered into 50 ml volumetric flasks so that they contained 0.4, 0.79, 1.19, 1.99, and 2.39 $\mu$g of zirconium, respectively (0.64, 1.28, 1.93, 3.21, and 3.85 $\mu$g of hafnium). Enough HCl (16:100) was added to each flask in order to give approximately a 0.1N solution; while swirling the flask, 3 ml of 0.05% Alizarin Red S were added and volume made up. A blank was prepared containing all the reagents used except for the standard solution of zirconium (hafnium). The flasks were shaken and allowed to stand for 40 minutes. The absorbance was measured at 515 nm in a 5 cm cell in a Varian spectrophotometer.

### 3.2.2 Results.

Absorbances were plotted against concentration for both elements. The standard curves obtained are shown on Fig. 7.

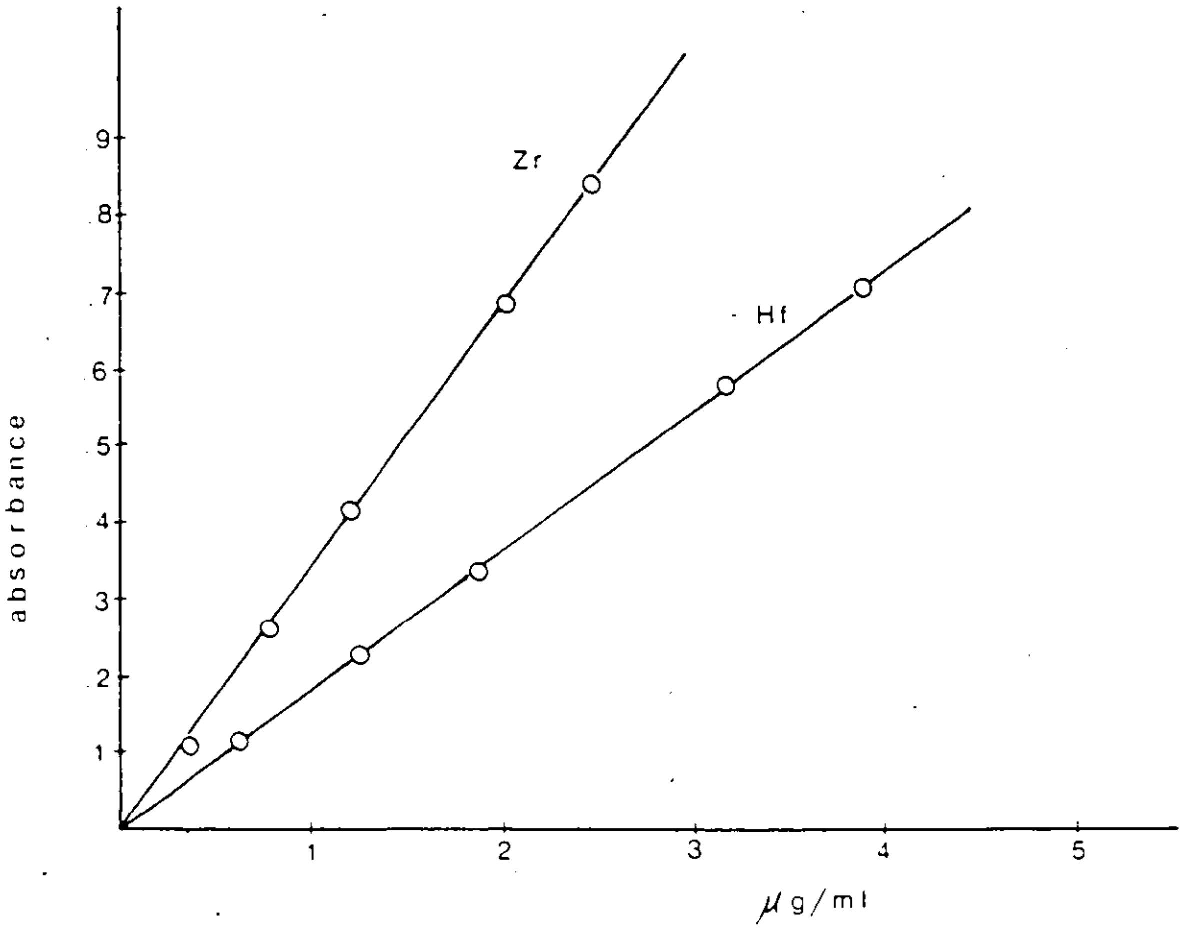

Figure 7: Determination of Zirconium and Hafnium with Alizarin Red S. Standard Curve. Absorbance measured at 515 nm, cell=5cm, 40 minutes color development. The blank absorbance has been substracted.

## 3.3 Study of Interferences in the Spectrophotometric Determination.

When an aqueous solution is brought into contact with an organic phase during the solvent extraction process, some disolution of the organic substance into the aqueous phase can be expected. The presence of this material could arise interferences in the measurement of the absorbance.

Absorbances for two set of solutions, one of them containing a small amount of diester-ether solution, were compared in order to look for interferences.

### 3.3.1 Procedure.

Synthesis of Bis(2-Ethylhexyl)Phenyl Phosphonate (DEφP) : The extractant bis(2-ethylhexyl)phenyl phosphonate was synthesized following the method employed by Kantipuly (110). Phenylphosphonic dichloride (Aldrich) and 2-ethyl-1-hexanol (Aldrich) were mixed in a 1:2 molar ratio in benzene; this reaction mixture was stirred in a bottle for 72 hours at room temperature. After completion of reaction, the mixture was washed with two-20 ml portions of water. The organic phase was taken up with ether and shaken with three-20 ml portions of a 15% sodium hydroxide solution. The diester was then dried with anhydrous magnesium sulfate and filtered. The solvent and any other volatile material were removed under reduced pressure.

Preequilibrated Acid Diester Solution : an adequate volume of a 16:100 hydrochloric acid solution was shaken with an equivalent volume of a solution of diester in petroleum ether (3:100). After equilibration, the phases were separated and the aqueous portion used for preparing the sample solution.

Zirconium Control Solution : an appropriate aliquot of the zirconium standard solution was transfered into a 50 ml volumetric flask so that it contained 1.13 μg of Zr per ml; the acid concentration was adjusted to 0.1N by the addition of a 16:100 HCl solution. While swirling the flask, 3 ml of 0.05% aqueous solution of Alizarin Red S were added and volume made up to 50 ml with de-ionized water. A blank was prepared using the same reagents.

Zirconium Sample Solution : the sample solution was prepared in the same manner as the control solution was but the acid concentration was adjusted to 0.1N by the addition of preequilibrated acid-diester solution. A blank was prepared using the same reagents.

Both the control and the sample solutions were let stand for 40 minutes and the absorbance measured at 515 nm in a 5 cm cell.

### 3.3.2 Results.

Measurements of absorbance for the sample showed a very low degree of reproducibility and the average absorbance was higher than that of the control. See Table 8. It was then concluded that the presence of even such small amount of organic substance would interfere with the colorimetric determination of both zirconium and hafnium. Before analysing the aqueous phase, it is necessary to eliminate any organic substance present.

Table 8: Effect of Organic Material on Absorbance of Zr Solutions.

| EXPERIMENT No. | ABSORBANCE CONTROL | ABSORBANCE SAMPLE |
|---|---|---|
| 1 | 0.085 | 0.087 |
| 2 | 0.083 | 0.094 |
| 3 | 0.084 | 0.101 |
| 4 | 0.084 | 0.098 |
| AVERAGE | 0.084 | 0.094 |
| RELATIVE DEVIATION | 0.3% | 5.3% |

## 3.4 Elimination of Interferences.

Evaporati[illegible] to dryness was chosen as the procedure to eliminate interferences due to the presence of organic substances in the aqueous phase. Control solutions were evaporated to dryness to test if heating of solutions would have any effect on the spectrophotometric determination. A hafnium solution was used for the testing. Being zirconium and hafnium so similar in chemical behaviour, it was assumed that any result obtained for the latter will be applicable to the former.

Two sets of solutions were prepared containing the same amount of hafnium. One set was evaporated to dryness and the absorbance measured. The absorbance of the control solution was measured without prior heating.

### 3.4.1 Procedure.

Hafnium Control Solution : an aliquot of hafnium standard solution containing 32 $\mu$g of Hf per ml was transfered to a 50 ml volumetric flask; the acid concentration was adjusted to 0.1N by the addition of a 16:100 HCl solution; while swirling the flask, 3 ml of 0.05% Alizarin Red S were added and volume made up to 50 ml. A control blank was prepared using the same reagents. Absorbance was measured after 40 minutes color developing at 515 nm in a 5 cm cell.

Hafnium Sample Solution : a similar aliquot of hafnium standard solution was transfered to a beaker and the concentration of hydrochloric acid adjusted ~~to~~ 0.2N with a 16:100 HCl solution. The beaker was covered and the solution was evaporated to 10 ml on a hot ~~plate~~ at a very low temperature. Then, using a steam bath, the remainder solution was evaporated to dryness. After evaporation, the beaker's walls were washed with distilled water and a 16:100 HCl solution added to adjust the concentration of acid to 0.1N. This solution was transfered with water rinsings to a 50 ml volumetric flask, 3 ml of 0.05% Alizarin Red S solution added and the volume made up to 50 ml. A blank was prepared using the same reagents and technique. The absorbance was measured after 40 minutes color developing at 515 nm in a 5 cm cell.

### 3.4.2 Results.

The sample solutions gave a lower absorbance than the controls. Results are shown on Table 9.

Table 9: Effect of Evaporation to Dryness on Absorbance of Hf Solutions.

| EXPERIMENT No. | CONTROL ABSORBANCE | $\mu g/ml$ | SAMPLE ABSORBANCE | $\mu g/ml$ | RELATIVE ACCURACY |
|---|---|---|---|---|---|
| 1 | 0.590 | 3.21 | 0.453 | 2.47 | 76.94% |
| 2 | 0.591 | 3.21 | 0.412 | 2.50 | 77.88% |
| 3 | 0.588 | 3.18 | 0.410 | 2.50 | 78.61% |
| 4 | 0.589 | 3.18 | 0.363 | 2.00 | 62.89% |
| AVERAGE | 0.589 | 3.19 | 0.409 | 2.24 | 74.08% |

According to these values, there seem to be a "loss" of hafnium during the process. It is unlikely that mechanical losses were large enough to account for the discrepancy. The "loss" of hafnium is doubtless due to a loss of reactivity.

Searching for an explanation in the literature for this apparent loss of hafnium, the author found that Ruer (113) reported marked changes in chemical behaviour of $ZrOCl_2$ solutions when they were heated even for short periods. Ruer considered these differences were due to polymerization of species in solution. Johnson and Kraus (114) attribute these differences to structural changes of polymers during aging or heating of solutions. Taking these facts into consideration we can explain the lower absorbance of the sample solution as due to the incomplete formation of the hafnium-alizarin complex because of polymerization of the element during heating.

### 3.5 Fusion with Borax Glass.

Fusion with borax glass was employed to decompose polymers formed during evaporation to dryness. This procedure is based on the one used for the decomposition of the mineral zircon by Lundell and Knowles(115). A posible interference due to the presence of borax in the colorimetric determination with Alizarin Red S was studied first and no interference was observed when 0.3 g of borax glass was present in samples containing 3.21 $\mu$g of Hf per ml. See Table 10.

Table 10: Effect of Borax Glass on Absorbance of Hf Solutions.

Amount of Borax Glass = 0.3 g

| EXPERIMENT No. | ABSORBANCE | | RELATIVE ACCURACY |
|---|---|---|---|
| | CONTROL | SAMPLE | |
| 1 | 0.588 | 0.588 | 100.0% |
| 2 | 0.588 | 0.585 | 99.5% |
| 3 | 0.588 | 0.584 | 99.3% |
| AVERAGE | 0.588 | 0.586 | 99.6% |

#### 3.5.1 Procedure.

An aliquot of the zirconium (hafnium) standard solution containing the appropriate amount of the element was transfered to a platinum crucible and evaporated to dryness. After evaporation, 0.1 g of borax glass were added and the mixture fused at bright red heat for about 3 minutes. Enough 16:100 HCl solution was added to adjust the acid concentration to 0.1N. This solution was let stand overnight to completely dissolve the melted mixture. The sample was then transfered quantitatively to a 50 ml volumetric flask, 3 ml of 0.05% Alizarin Red S added and the volume made up to 50 ml. Absorbance was measured after 40 minutes color developing at 515 nm in a 5 cm cell. A control solution was prepared containing the same amount of zirconium (hafnium) as the sample solution, but it was not evaporated. Absorbance was measured under the same conditions.

### 3.5.2 Results.

Values obtained for the control and sample solutions are shown on Tables 11 and 12.

Table 11: Effect of Fusion with Borax Glass on the Absorbance of Zr solutions.

| CONTROL AVER. ABSORBANCE | µg/ml | SAMPLE AVER. ABSORBANCE | µg/ml | RELATIVE ACCURACY |
|---|---|---|---|---|
| 0.275 | 0.79 | 0.249 | 0.74 | 93.67% |
| 0.413 | 1.19 | 0.384 | 1.12 | 94.12% |
| 0.688 | 1.99 | 0.633 | 1.84 | 92.46% |

Absorbances of the samples are still lower than absorbances of the controls, but now the relative accuracy is higher and the differences in concentration of the solutions with and without evaporation are smaller. We think that the

Table 12: Effect of Fusion with Borax Glass on the Absorbance of Hf solutions.

| CONTROL AVER. ABSORBANCE | $\mu$g/ml | SAMPLE AVER. ABSORBANCE | $\mu$g/ml | RELATIVE ACCURACY |
|---|---|---|---|---|
| 0.234 | 1.28 | 0.221 | 1.20 | 93.75% |
| 0.354 | 1.93 | 0.315 | 1.72 | 89.12% |
| 0.589 | 3.21 | 0.527 | 2.87 | 89.41% |

fusion with borax effectively destroys the polymers formed during heating of the solutions. It was thought that increasing the amount of borax glass would increase the amount of zirconium (hafnium) recovered after fusion. Therefore, some fusions were done with 0.4 g of borax. The crucible was tipped in various directions during the fusion in order to ensure good contact of the melt with the bottom area of the crucible. 9.0 ml of 1M HCl were used to dissolve the melt overnight. Results are shown on Table 13.

Table 13: Standardizations with 0.4 g of borax glass. Amount of Zr taken = 57.8$\mu$g. Blank absorbance has been substracted.

| EXPERIMENT No. | CONDITIONS OF EXPERIMENT | ABSORBANCE | $\mu$g/ml |
|---|---|---|---|
| 1 | no fusion | 0.329 | 0.96 |
| 2 | no fusion | 0.343 | 1.00 |
| 3 | fusion | 0.350 | 1.02 |
| 4 | fusion | 0.333 | 0.98 |

Results showed that the decomposition of polymers formed during evaporation was complete when enough borax glass (0.4

g) was used for the fusion. Recovery of zirconium is about 100%.

### 3.6 Interference from Phosphate.

When the interferences due to the presence of organic materials are eliminated by wet or dry ashing, the extractant bis(2-ethylhehyl)phenyl phosphonate is decomposed and produces phosphoric acid. As discussed previously, phosphate interferes with the Alizarin Red S determination of the elements. However, the amount of phosphate present after decomposition of the extractant was suspected to be very small. A test using micrograms of phosphate was performed and the effect of these microamounts on the absorbance of the sample determined.

### 3.6.1 Procedure.

An aliquot of hafnium standard solution containing 64.1 μg of the element was placed in a platinum crucible and 50 μl of a sodium phosphate solution containing 12 μg of phosphate were added. The solution was evaporated to dryness and fused with borax glass as explained before. A blank was prepared by following the same procedure.

A control solution was prepared containing the same amount of hafnium as the sample solution, but it was neither evaporated nor fused. No phosphate was present. A blank was also prepared following the same procedure.

Absorbances of both the control and the samples solutions were measured at 515 nm after 40 minutes color developing in a 5 cm cell.

### 3.6.2 Results.

Values for the absorbance of the control and sample solutions are given on Table 14.

Table 14: Fusion of a Hafnium+Phosphate solution with Borax Glass.

| CONTROL AVER. ABSORBANCE | μg/ml | SAMPLE AVER. ABSORBANCE | μg/ml | RELATIVE ACCURACY |
|---|---|---|---|---|
| 0.234 | 1.28 | 0.173 | 0.95 | 74.22% |

The relative accuracy of the determination if phosphate is present is very low compared to the same determination done in absence of phosphate (see Table 11). The interference due to the presence of such a small amount of phosphate can not be ignored. The elimination of any phosphate present in the solution is necessary before analysing the aqueous phase after extraction.

### 3.7 Elimination of Phosphate Interference Using Ion-Exchange.

The determination of zirconium and hafnium in phosphate containing samples is difficult owing to the strong complexing and precipitate formation that occurs. The classical procedure for macro and semi-micro quantities consists in precipitating the metal phosphate. The precipitate is treated with molten alkali carbonate which produces the metal oxide and alkali phosphate. The oxide is separated and fused with potassium pyrophosphate to render it soluble. It is conceivable that microgram quantities of zirconium and hafnium might be handled by co-precipitation with a few miligrams of bismuth and treating the precipitate as above.

It was felt that a new promising approach would be to use cation-exchange in moderately concentrated acid in order to collect Zr and Hf. This succeeded in the separation of thorium from phosphate (110).

### 3.7.1 Procedure.

Aliquots of zirconium in 1M $HNO_3$ were passed onto strong cation exchange resin (Biorad AGW 50-X8, 200-400 mesh) in columns of dimensions 0.8x5 cm. The zirconium was eluted with either nitric or formic acid. The latter eluent was suggested by Quereshi and Husain (71). The eluates were evaporated to dryness in platinum crucibles and the residues fused with 0.4 g. of borax glass. Alizarin Red S was used for the determination. The results are shown in Table 15.

Despite the reported success with formic acid, our results are very unsatisfactory. We suspect that samples made up in formic acid and added to the ion exchanger in that form were relatively simple, i.e. unhydrolyzed. Our

Table 15: Recoveries of Zr from Strong Cation Exchange Resin.

Amount of Zirconium taken = 57.8 μg.

| EXPERIMENT No. | ELUATE | VOL. OF ELUATE ml | % Zr RECOVERED |
|---|---|---|---|
| 1 | 1M formic acid | 80 | 29 |
| 2 | 1M formic acid | 80 | 26.5 |
| 3 | 4M nitric acid | 100 | 102.8 |
| 4 | 4M nitric acid | 100 | 96.0 |
| 5 | 4M nitric acid | 100 | 34.0 |
| 6 | 4M nitric acid | 100 | 41.0 |
| 7 | 7.5M nitric acid | 180 | 100.3 |
| 8 | 7.5M nitric acid | 180 | 97.5 |

samples, which were made up in 1M nitric acid were doubtless more complex. A polycation would presumably be held more firmly to the resin than would a mononuclear ion.

Samples 3 and 4 were recovered satisfactorily, but this result could not be repeated. Samples 5 and 6 are typical. Large volumes of 7.5M $HNO_3$ were generally required for quantitative recoveries.

The separation of zirconium from phosphate was attempted by essentially the same procedure.

### 3.7.2 Procedure.

Samples were prepared by adding 20 mg of $H_3PO_4$ to aliquots containing 57.8 μg of Zr. The solution were made up to 30 ml volume and were ca. 1M in $HNO_3$ . The subsequent procedure was the same as in the preceeding experiment except that after adding the samples to the columns, the resin was washed with 100 ml of 1M $HNO_3$ . The results are shown in Table 16.

Table 16: Attempted separation of Zr and Hf from phosphate. Amount of Zr taken = 57.8 μg. Amount of $H_3PO_4$ mg = 20

| No. | % Zr RECOVERED |
|---|---|
| 1 | 73.5 |
| 2 | 50.2 |

These recoveries are so far from quantitative that it was felt that further attempts to develop the procedure would be fruitless. It is assumed that the zirconium was incompletely retained by the resin. Freiling and coworkers reported evidence of anionic complexes in the Zr(IV)-$H_3PO_4$ system (116). These may be of the form $ZrO(H_2PO_4)_3^-$ as the precipitate $ZrO(H_2PO_4)_2$ is known with a solubility product of $2.4\times10^{-18}$ (117).

## 3.8 Determination of Distribution Coefficients of Zr and Hf.

The atomic emission system utilized was the Beckman Spectro Span V combined with a high energy dc plasma excitation source with a high resolution Echelle grating. The liquid samples are converted into aerosol form and introduced into the excitation region. The intensity of the emitted light at predeterminated characteristic wave lengths is proportional to the concentration of the element. The signal was integrated for five seconds and the integration repeated twice under computer control. The calibration was done by measuring a low and high standard of the element to be determined everytime before the test was performed for the samples.

The analytical wave lengths used were 339.20 nm for zirconium and 277.34 nm for hafnium. The operating parameters were: Argon flow rate, 7 liters per minute; sample uptake, 2 ml per min; temperature in the excitation region, 6000-7000 K.

A study of the distribution ratios of zirconium and hafnium in bis(2-ethylhexyl)phenyl phosphonate was carried out. The distribution ratio is defined as: D = [M]org./[M]aq.; [M]org. is the concentration of the element in the organic phase and [M]aq. is the concentration in the aqueous phase.

For our purposes, the concentration of the elements in the aqueous phase was determined by DCP spectrophotometry, while the concentration in the organic phase was not determined analytically but assumed to be the difference between the initial concentration of the solution and the aqueous phase concentration after extraction.

### 3.8.1 Procedure.

4:100 Extractant Solution : 4 ml of DEØP was diluted to 100 ml with petroleum ether.

8:100 Extractant Solution : 8 ml of DEØP was diluted to 100 ml with petroleum ether.

Preequilibrated Extractant Solution : an appropriate volume of the extractant solution was shaken in a separatory funnel with an equivalent volume of acidic solution. After equilibration of the phases, the organic phase was separated and used for the extractions.

Extraction Procedure : a 25 ml aliquot of the zirconium (hafnium) solution containing a known amount of the element and a specific acidity was transfered to a separatory funnel and 20 ml of a preequilibrated extractant solution with the desired concentration were added. The system was shaken for about 1 minute and the layers allowed to settle for 20 minutes. After equilibration, the aqueous phase was separated, the acid concentration adjusted and the volume made up to 50 ml. The resultant solution was analyzed by DCP.

### 3.8.2 Results.

#### 3.8.2.1 Effect of HCl concentration.

Extractions for both elements were performed adjusting the hydrochloric acid concentration in the aqueous phase to 0.05N, 0.5N, 1.5N, and 3N. Concentration of the extractant was 4:100 DE0P-petether. Results are shown in Table 17.

The extraction of zirconium and hafnium into the organic phase decreased as the concentration of the hydrochloric acid increased. At 1.5M HCl hafnium did not seem to be extracted into the organic phase, but zirconium was although the amount extracted was not very large. At 3M HCl, hafnium

Table 17: Effect of HCl Concentration on Extraction of Zr and Hf.

Extraction performed with 4:100 DE0P-pet ether. Phase ratio 25:20.

| HCL MOLARITY | % Zr EXTRACTED | % Hf EXTRACTED | D Zr | D Hf | SEPARATION FACTOR |
|---|---|---|---|---|---|
| 0.05 | 35.34 | 68.22 | 0.54 | 1.64 | 0.33 |
| 0.5 | 10.84 | 12.59 | 0.12 | 0.14 | 0.85 |
| 1.5 | 1.21 | 0 | 0.012 | 0 | very large |
| 3.0 | 3.82 | 0.24 | 0.039 | 0.003 | 13 |

was extracted into the organic phase in a small proportion. A separation factor of 13 was obtained under these conditions, a good value eventhough the amount of zirconium extracted was very small.

### 3.8.2.2 Effect of $HNO_3$ Concentration.

Keeping the concentration of hydrochloric acid at 0.05M, the concentration of nitric acid was varied from 1M to 4M. The concentration of the extractant was 4:100. Results are shown in Table 18.

Table 18: Effect of $HNO_3$ Concentration on Extraction of Zr and Hf

Extraction performed with 4:100 DE0P-pet ether. Phase ratio 25:20. Aqueous phase 0.05M HCl.

| $HNO_3$ MOLARITY | % Zr EXTRACTED | % Hf EXTRACTED | D Zr | D Hf | SEPARATION FACTOR |
|---|---|---|---|---|---|
| 1 | 42.97 | 23.69 | 0.75 | 0.31 | 2.4 |
| 2 | 30.42 | 15.7 | 0.44 | 0.19 | 2.3 |
| 3 | 31.02 | 12.84 | 0.45 | 0.15 | 3.0 |

When nitric acid was added, distribution ratios were higher for zirconium than for hafnium. As the concentration of nitric acid increased, distribution ratios decreased but the separation factor increased. At 3M $HNO_3$ , a separation factor of 3 was obtained which was not as good as the one obtained at 3M HCl, but the amount of zirconium and hafnium extracted was larger. It was thought that increasing the concentration of nitric acid would increase the separation factor and some extractions were done varying the nitric acid concentration between 4M and 9M. Results are shown in Table 19.

Table 19: Effect of Increasing Concentration of $HNO_3$ on Extraction.

Extraction performed with 4:100 DEØP-pet ether. Phase ratio 25:20. Aqueous phase 0.05M HCl.

| $HNO_3$ MOLARITY | % Zr EXTRACTED | % Hf EXTRACTED | D Zr | D Hf | SEPARATION FACTOR |
|---|---|---|---|---|---|
| 4 | 16.59 | 0 | 0.20 | 0 | very large |
| 7 | 23.40 | 8.05 | 0.31 | 0.09 | 3.4 |
| 9 | 26.17 | 17.77 | 0.35 | 0.22 | 1.59 |

Distribution factors decreased to a minimun when the nitric acid concentration reached 4M. At this $HNO_3$ concentration, the separation was very large. As the concentration of nitric acid increased, the separation factor decreased.

### 3.8.2.3 Effect of Nitrate Concentration.

The concentration of nitrate was increased to 5M and 7M by the addition of a sodium nitrate solution. The concentration of nitric and hydrochloric acids was kept constant. Results are shown on Table 20.

Table 20: Effect of Nitrate Concentration on Extraction of Zr and Hf.

Extraction performed with 4:100 DE0P-pet ether. Phase ratio 25:20. Aqueous phase 3M $HNO_3$ and 0.05M HCl.

| $NaNO_3$ MOLARITY | % Zr EXTRACTED | % Hf EXTRACTED | D Zr | D Hf | SEPARATION FACTOR |
|---|---|---|---|---|---|
| 2.0 | 8.03 | 0 | 0.09 | 0 | very large |
| 4.0 | 9.60 | 3.7 | 0.11 | 0.04 | 2.75 |

Increasing the concentration of nitrate decreased the amount of both elements extracted into the organic phase. Experimental results showed a very large separation factor when the solution is 0.05M HCl, 3M $HNO_3$, and 2M $NaNO_3$.

### 3.8.2.4 Effect of Extractant Concentration.

Extractions were done with a 8:100 DE0P-pet ether solution. In the aqueous phase, the concentration of hydrochloric acid was kept at 0.05M and the concentration of nitric acid was varied from 4M to 9M. Results are shown in Table 21.

When the concentration of the extractant was doubled, the distribution coefficients were almost doubled if we compare them with values in table 17. At 4M $HNO_3$, a good separation

Table 21: Effect of Extractant Concentration on the Extraction of Zr and Hf.

Extraction performed with 8:100 DE0P-pet ether. Phase ratio 25:20. Aqueous phase 0.05M HCl.

| $HNO_3$ MOLARITY | % Zr EXTRACTED | % Hf EXTRACTED | D Zr | D Hf | SEPARATION FACTOR |
|---|---|---|---|---|---|
| 4 | 28.04 | 0.55 | 0.39 | 0.006 | 65 |
| 7 | 38.26 | 15.27 | 0.62 | 0.180 | 3.4 |
| 9 | 48.04 | 35.00 | 0.92 | 0.54 | 1.7 |

factor was obtained, with a better extraction of zirconium than using a 4:100 extractant solution. As the concentration of nitric acid increased, the distribution ratios also increased, but the separation factors became similar to those obtained under the same conditions with a 4:100 extractant solution.

## 3.9 General Discussion and Conclusions.

Alizarin Red S is a good spectrophotometric reagent for zirconium and hafnium because of its sensitivity in detecting microamounts of the elements. However, interferences due to the presence of common anions such as phosphate, sulfate, and fluoride limit its direct application to samples containing even microquantities of those anions and pretreatment of the samples is necessary.

Interferences were found in the Alizarin Red S determination of the elements due to the presence of organic substances after extraction. Evaporation to dryness followed by fusion with borax glass allowed us to overcome part of these interferences. The organic substances were eliminated by evaporation; however, heating of solutions caused polymerization of the elements which interfered with the analysis; polymerization of zirconium and hafnium was eliminated by fusing the residues after evaporation with borax glass. This substance proved to be very effective in decomposing the polymers formed.

Another interference that had to be eliminated was the phosphate left as residue after decomposition of DEØP. An ion-exchange procedure using Dowex 50 cation exchanger was selected to eliminate any phosphate present , but the recovery of zirconium turned out to be difficult; zirconium was incompletely retained by the resin apparently because it was in the form of phosphate anions. Analysis of the aqueous phase after extraction was performed using DCP emission spectrophotometry.

The distribution coefficients as well as the separation factors showed dependance on the acidic concentration of the system. Extractions were performed in hydrochloric acid and in a mixture of hydrochloric and nitric acid media. In both cases, an increase in acid concentration produced a decrease in the distribution ratios.

In hydrochloric acid medium, values obtained for the separation factors when the HCl concentration were varied from 0.05M to 3M were fairly low compared to those obtained in nitric acid medium.

Extractions performed in a 0.05M HCl-XM $HNO_3$ (where X was varied from 1 to 9) mixture were relatively successful. Eventhough the distribution ratios decreased as the nitric acid concentration increased, at 4M $HNO_3$ those values reached a minimum and a very high separation factor was obtained; from 5M to 9M $HNO_3$, the distribution ratios increased again but the separation factors decreased. From the experimental results, a solution which is 4M in $HNO_3$ and 0.05M in HCl gives good conditions for obtaining a high separation factor. However, the extraction of zirconium at this point is not very large. This can be overcome by making the extractant solution more concentrated. When the concentration was changed from 4:100 DE0P-pet ether to 8:100 DE0P-pet ether, the amount of zirconium extracted was almost doubled while the amount of hafnium extracted remained about the same, keeping the separation factor high. Extractions performed in the presence of $HNO_3$ seemed to be more effective than those performed in the presence of hydrochloric acid alone.

A razionalization of the difference in the behaviour of zirconium and hafnium was the primary objective of the present work. Two factors are considered most important in determining that behaviour: electrostatic Coulombic effects and polarization.

Coulombic factors should favour bond formation by the smaller atom or ion. Hafnium being slightly smaller[1] should

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[1] The reported difference in radii is only 0.01 A so the

form slightly stronger bonds with fluoride and oxy anions. Hafnium (IV) should carry a stronger effective nuclear charge and it therefore should also form stronger bonds with more polarizable entities like $Cl^-$ and $Br^-$ (118). It has long been felt in our laboratory that efficient separation of zirconium and hafnium should exploit polarization by hafnium. However, on the other hand, the best separation described in the literature employ oxy anions as complexing agents, e.g. citrate and formate.

In the present work, also, coulombic factors have appeared to be more important. The best separation factors observed in the present study occurred in the presence of nitrate ion while hydrochloric media were quite unsatisfactory. The following inferences are suggested.

In dilute hydrochloric acid, relatively large distribution coefficients were observed. It is certain that the solutions are extensively hydrolyzed in 0.05M acid to form oxy-hydroxy species, e.g. $ZrO_x(OH)_y^{z-}$ as well as polycondensed forms. Being anionic, these are readily extracted by protonated ester. As the HCl concentration is increased, the metal species are progresively de-hydrolyzed to form $ZrO^{2+}$, $ZrO(OH)^+$, etc. These are not extracted. This occurs more readily with hafnium (38). As a consequence of the preferential de-hydrolysis, the separation factor changes from being less than unity to greater. The formation of chlorohafnate, if it occurs, is not beneficial for separation.

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matter is debatable.

The addition of nitric acid has a two-fold effect. The de-hydrolysis occurs as just described, but the nitrate ion has the ability to chelate the metal ions so as to retain anionic forms, e.g. $ZrO(NO_3)_3^-$ . Zirconium should show a more pronounced tendency to be so complexed, so the extraction of zirconium is favoured over that of hafnium. The effect of acidity and of chelation, respectively, have opposing effects on the extraction. Only the chelation favours the extraction, therefore the addition of nitrate salt rather than nitric acid appeared to be desirable. The use of ammonium nitrate would allow the subsequent removal of all the reagents by volatilization, if desired. This would be useful in trace analytical work.

There is a necessity for compromise in the choice of conditions for extraction. Acidity is required in order to protonate the ester but high acidity possibly favours cationic forms of zirconium. It is therefore understandable that nitrate ion is a particularly favourable choice as a chelating ligand. Nitrate has an extremely feeble basicity, therefore the chelated group is not much susceptible to removal by protonation in strong acid. Carbonate ion, with a double charge would clearly be more strongly held in neutral or basic solutions, but it is certainly more easily lost from the complex in fairly acid media.

The comparative readiness of zirconium and hafnium to form complexes with $NO_3^-$ , $SO_4^=$ , citrate, etc. is in contrast to the behaviour of elements such as $Fe^{3+}$, $Ni^{2+}$, $Cu^{2+}$, etc., i.e. those ions for which a wealth of information about complexing is available. It seems that the difference lies in the relatively weak hydration of the larger zirconium and hafnium ions. The coulombic ion-dipole interaction energy is given by $U = -e\mu/r$ where e and $\mu$ are the ion charge and the dipole moment of the water molecule respectively. Because the energy falls off as the square of the separation, r , it is seen that large ions are solvated much less strongly than smaller ones. Ion-ion energy, i.e. the energy of attraction between a cation and a charged ligand, varies as the first power of r . Consequently, complexes with charged ligands are stronger with larger cations. Thus carbonate complexes with thorium are very stable even in moderately strong acid.

The equilibria are complicated by the readiness with which Zr(IV) is hydrolyzed. The principles outlined above fail to account for this. However, the hydrolysis behaviour is paralled by that of niobium which hydrolyzes more readily than tantalum while these two elements are reported to have exactly the same ionic radii. The cause of this may be a difference in the component in oxygen bridges: $Nb \overset{\cdots}{-} O \overset{\cdots}{-} Nb$ . It may be that the greatest distinguishing feature of zirconium and niobium lies in this phenomenon. It is certainly the basis of the Marignac method for the separation of niobium and tantalum.

The best condition found for differentiating between the two metallic elements were 0.05M HCl and 4M $HNO_3$. As the tables show, the extraction is not satisfactory with dilute extractant. By extrapolation from the data given, it appears that if the extractant is concentrated to 50% or more, it would be quite effective toward zirconium. The most promising conditions for the separation of the two elements would be a reversed phase chromatographic system with essentially pure ester on a solid support. Zirconium should exhibit a long retention time while hafnium should pass relatively quickly through the column. A change of eluting solution to moderately strong hydrochloric acid should remove the zirconium fairly rapidly.

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