Zirconium and hafnium separation from chloride solutions by organophosphorous compounds

by

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Abstract

The zirconium/hafnium separation, as currently practiced, is mostly carried out by solvent extraction in which the aqueous chloride solution of metals is contacted with an immiscible organic phase containing a reagent that removes hafnium leaving zirconium in the aqueous solution. Hafnium is extracted as its thiocyanate complex using methyl isobutyl ketone (MIBK). There are environmental consequences of this system that were acceptable when the process was developed but should become a serious problem as legislation becomes more stringent. These problems are primarily the high aqueous solubility of MIBK and the potential for toxic gas generation. This work has tested four organophosphorous reagents to separate zirconium from hafnium without the need of thiocyanate, avoiding toxic gas formation. The extractants and diluent have very low aqueous solubility, removing effluents control problems. We see these features as representing a "zero waste" process. Additional advantages over MIBK process are lower vapor pressure and higher flash point (lower fire risk). This work presents the lab-scale experimental results using mainly two reagents designated by Cytec Canada Ltd as Cyanex 923 and Cyanex 925. The key feature of this work is replacement of MIBK and thiocyanate with one of a family of organophosphorous extractants that were unavailable in the 1950's at the start of the MIBK process. This work shows they can be efficiently applied to hafnium/zirconium separation in aqueous chloride solution, with minimum adjustments of the present industrial practice.

Résumé

La séparation du zirconium et du hafnium, comme elle est fréquemment réalisée aujourd'hui, est accomplie par extraction liquide-liquide avec une solution aqueuse d'acide chloridrique, qui contient les métaux, et une phase organique non miscible à l'eau, qui contient le réactif qui extrait le hafnium et laisse le zirconium dans la phase aqueuse. Le hafnium est extrait comme un complexe de thiocyanate par la méthylisobutylcétone (MIBC). L'utilisation de ce procédé apporte quelques problèmes pour l'environnement qui était considéré tolérables quand il a été developpé mais qui seront chaque fois plus sérieux et dispendieux à régler avec le durcissement progressif de la legislation sur l'environnement. Les problèmes de l'utilisation de ce procédé conventionnel sont liés fondamentalement à la grande solubilité de la MIBC et à la possibilité de génération de gaz toxiques pendant son opération. Au cours de ce travail nous avons essayé quatre réactifs organophosphorés pour séparer le zirconium du hafnium sans l'emploi du thiocyanate, et ainsi sans avoir la possibilité de génération de gaz toxiques. Les réactifs organophosphorés et le diluant ont une très basse solubilité dans l'eau, ce qui resout les problèmes de contrôle des effluents du procédé conventionnel. Nous considerons ces caractéristiques comme représentatives d'un procédé avec "emission zero". Il y a aussi deux autres avantages sur le procédé conventionel: premierement, la faible pression de vapeur de la phase organique et deuxièmement le point d'ignition plus élevé (moindre risques d'incendie et d'explosion). Ce travail présente les résultats des experiences avec deux réactifs appelés Cyanex 923 et Cyanex 925 (Cytec Canada Ltd) à l'échelle du laboratoire. Le fait plus important de ce travail est le remplacement de la MIBK et du thiocyanate par un réactif organophosphoré qui n'existait pas dans les années cinquante quand le procédé MIBC fut developpé. Ce travail démontre que ces réactifs peuvent être employés efficacement pour séparer le zirconium du hafnium en milieu aqueux chloridrique, sans beaucoup de modifications à la pratique industrielle actuelle.

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Chapter 1

Introduction

1.1 - Recent Historical Background

In the early 1950's, boosted by the American nuclear navy program several American companies began to produce zirconium and hafnium metals. These two elements coexist in nature but they have very opposite nuclear characteristics. Thus, they have to be separated prior to conversion to metals. Two different solvent extraction techniques have been used to promote Zr and Hf separation; the MIBK-thiocyanic-hydrochloric acid system and the TBP-nitric acid system. The former began to be developed at the Oak Ridge National Laboratory in 1949 and was optimized in a pilot plant at the US Bureau of Mines, Albany, Oregon. In 1954, the first commercial operation began with Carborundum Metals Corp., N.Y. The second process was developed in France in the same year by the French Nuclear Agency and subsequently improved at the Iowa State University.

For five years, the US government interfered in the market, in reality creating it, by contracting several companies to produce zirconium metal. In 1957, the US stock piled more than 7000 tons of zirconium metal. After the term of those contracts, a free market was established and several companies have abandoned this activity (Rickover, 1975).

During the 70's, Teledyne Wah Chang Albany (TCWA) was the only zirconium producer in the world using the MIBK process. In 1978, a French state company, CEZUS (Compagnie Europeene du Zirconium) began to operate, using a completely new pyrometallurgical process. These two companies now share the international market. Later Western Zirconium (WZ), a Westinghouse Group company, began to operate, using the same MIBK process, and it now has a minor participation in the zirconium market.

1.2 - Zirconium production - an integrated technology.

The zirconium industry and the need to separate hafnium from zirconium are solely based on the necessities of the nuclear industry. It is probable that, in the absence of this need, hafnium metal would be just an exotic material at the present time, perhaps zirconium too. In order to get a proper perspective of the evolution of this technology, it is important to take a look at the industrial processes used to separate zirconium from hafnium.

It is also important to observe that zirconium/hafnium separation is a bottle neck between two well established technologies. That is, the production of zirconium and silicon chlorides by carbochlorination in a fluidized bed of zircon (its more important ore) and metal's production by the Kroll process. Therefore, any innovation that causes incompatibilities with either of these processes has a low possibility of being used as an industrial process. The general flowsheet for zirconium production, according to the major producer (TWCA), is shown on the next page (Figure 1.1). Hafnium separation from zirconium is accomplished by liquid-liquid extraction (MIBK process in TWCA and WZ) or by distillation in molten salts (CEZUS process). These processes will be briefly analyzed.

The MIBK Process

In this process the thiocyanic complexes of zirconium and hafnium formed in hydrochloric acid medium are separated with a fairly high separation factor (around 5). In this case, it is the Hf, the minor component, that concentrates in the organic phase. This means that both elements (Zr and Hf) can be produced according to nuclear specifications. The organic phase is the extractant itself, which exhibits a high load capacity and excellent disengagement characteristics. Nevertheless, the waste streams contain high concentrations of ammonium, thiocyanides, cyanides and organic products. The solvent itself is highly explosive and exhibits a solubility in water around 2% (Benedict, 1980 and Voit, 1980).

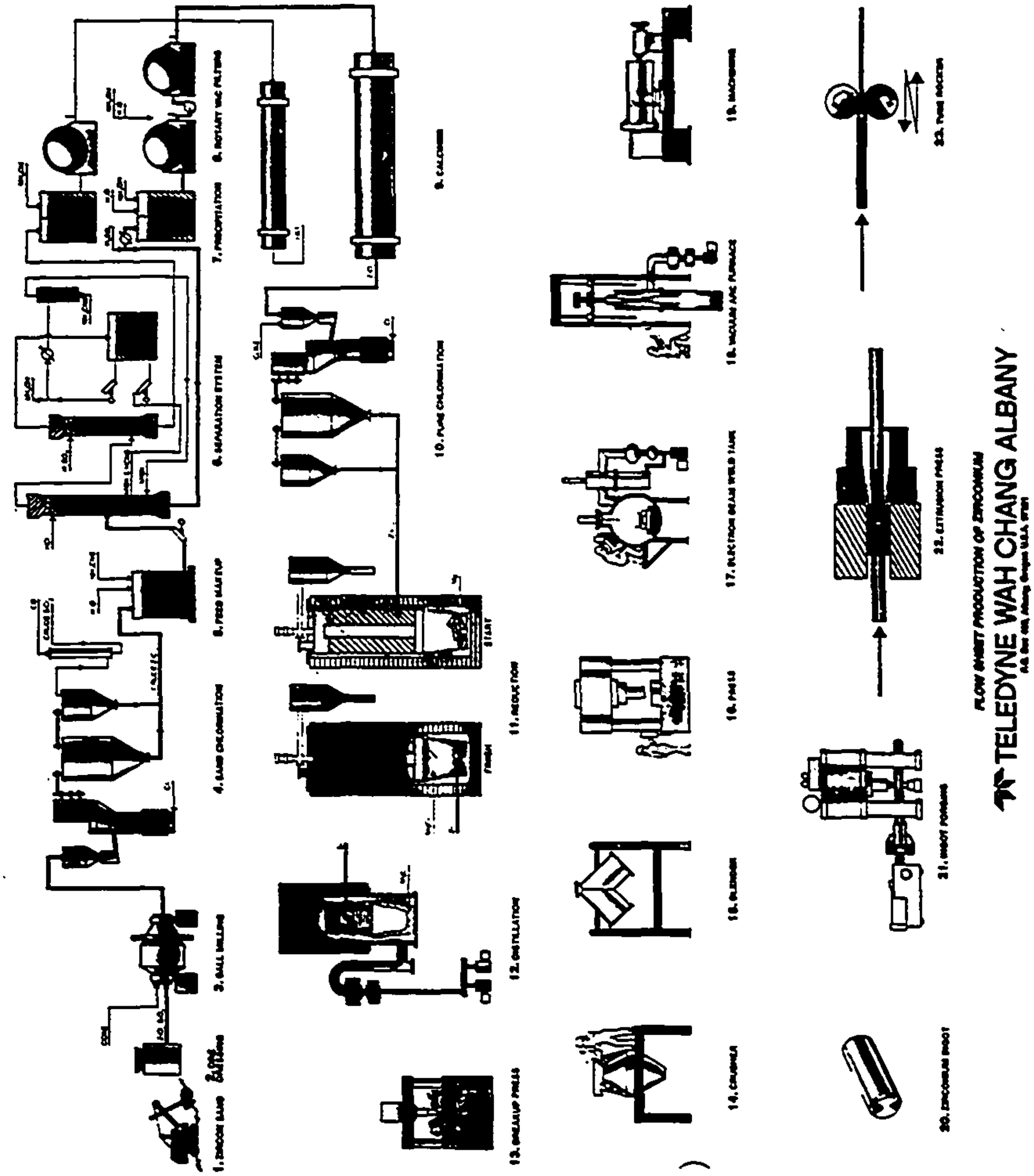


Figure 1.1 - Process Flowsheet of Zirconium Production Process

The TBP Process

In this process tributyl-phosphate is diluted in kerosene (60% of TBP v-v). The organic solution is contacted with a nitric acid solution (3N) where $NaNO_3$ (3.5N) is added as a salting out agent. The maximum metal content (Zr+Hf) of the liquor, below which third phase formation is avoided, was determined by Huré (1955) to be 30 g/l. Under these conditions, the distribution factor of zirconium is around 1.5, favoring the organic phase, and that of hafnium is around 0.15. The separation factor is thus 10. Unlike the MIBK process, the TBP process is selective to Zr, leading to the concentration of the major component (Zr) in the organic phase. Hf was not produced with high quality (usually 58% Zr/ 42% Hf), according to Huré. At Iowa University, the process was modified to use only nitric acid (6N) which was more easily recycled. A simplified flowsheet of the TBP process is shown below (Benedict, 1980).

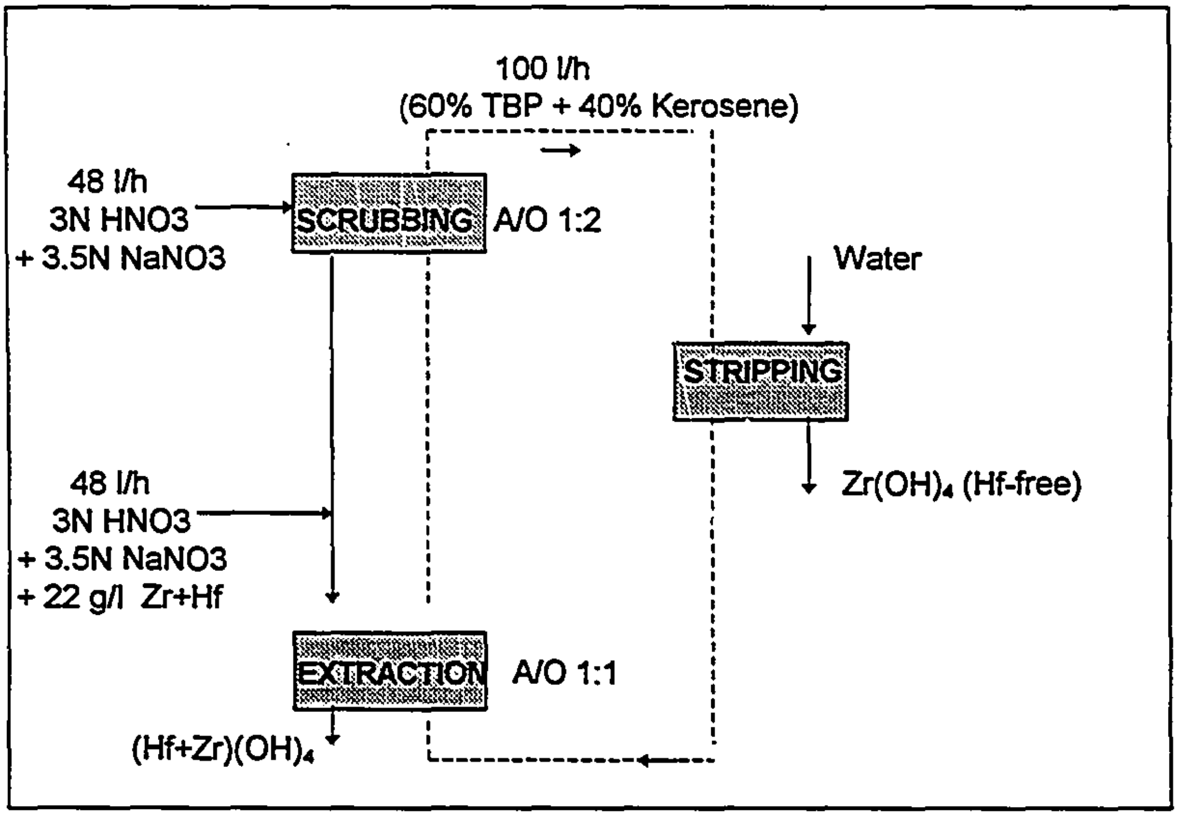


Figure 1.2 - Schematic Diagram of TBP Process (Huré, 1956)

The CEZUS Process

In 1978, the French state company, CEZUS (Compagnie Europeene du Zirconium), started a new industrial plant to produce zirconium and hafnium using the Besson's process (extractive distillation in molten salts). The success of this process is based on the elimination of several processing steps, associated with the MIBK and TBP routes. In particular, the CEZUS process avoids the transition from anhydrous to aqueous system, for hafnium separation by solvent extraction, and subsequent return to an anhydrous medium.

Skaggs (1983), from the US Bureau of Mines, evaluated more than twenty different pyrometallurgical methods to identify which among them could replace the conventional MIBK route. The Newham process (preferential reduction of zirconium tetrachloride) and extractive distillation in molten salts were considered the best possibilities.

The distillation of zirconium and hafnium chlorides in a molten salt bath is based on Besson's patent (1977). In this process, the operating pressure is one atmosphere with a temperature of around 400°C. This technology exhibits a separation factor of around 2 which means that about 90 stages are required to achieve the desired separation. Both Zr and Hf are produced according to nuclear specifications. This process represents a short cut between zirconite chlorination and the Kroll process, avoiding several steps of solubilization, liquid-liquid extraction, and precipitation and calcination to produce ZrO_2 that will be chlorinated again. This process to promote the separation of zirconium and hafnium involves distillation of their solution in molten iron and aluminum chlorides at 400°C. Highly corrosion resistant alloys are required, as well as sophisticated technologies to pump and handle the various streams, while avoiding any moisture contamination.

Sehra (1989), in a way very similar to Skaggs, has reviewed various metallurgical processes for the separation of hafnium and zirconium. His paper stressed the importance of adopting the CEZUS process in India to replace the TBP technology presently used. At the present time, around two thirds of all world zirconium production is still produced by the MIBK process. Nevertheless, the environmental bill and an eventual increase in energy demand could push the nuclear industry into adopting more environmentally attractive technology.

1.3 - Occurreace and Producers

Zirconium and hafnium are almost always found together in nature, most commonly as the mineral zircon (ZrSiO4). Commercial zircon is available only in the form of sand mined, for the most part, from ancient beach deposits. The zircon host rocks undergo a series of events that eventually liberate the zircon grains from the enclosing feldspars and quartz and ultimately end up along the marine shore. Many of the older beach sand deposits have been consolidated and the grains cemented together to form sandstone containing titanium minerals, zircon, monazite and other heavy minerals.

Australia is the major world producer and exporter of zircon sand. Presently, Australian concentrate is used to produce zirconium metal in the USA. The world's main producers are listed in Table 1.1.

Table 1.1 - Zirconium Ores World Production

Country	1988 Production (mt)‡	1994 Production (mt)†
Australia	490.000	425.000
Rep.of SouthAfrica	150.000	250.000
United States	115.000	125.000
ex-URSS	85.000	50.000
Brazil	20.000	24.000

†-Metals&Minerals, 1995;
‡- Minerals Yearbook, 1988.

Approximately 95% of zirconium is consumed in the form of zircon (0.24 - 0.35 US$/kg), zirconium dioxide (1.25 - 10 US$/kg) or other zirconium compounds. The remaining 5% is transformed into zirconium metal, which is mainly used as structural material for the nuclear fuel elements and nucleus core of light and heavy water nuclear reactors (70 -120 US$/kg). In the case of hafnium, 85% is used as control rods in nuclear reactors, the remaining amount being used as an alloying element in cutting tools and in special alloys for the aeronautical industry (200 - 350 US$/kg). Further details are given in Table 1.2.

Table 1.2 - Major World Zirconium Producers (Kennedy, 1990)

Producers	**Product**	**Location**
Allied Eneabba Pty., Ltd	Zircon sand	Australia, Eneabba, W.A.
Associated Minerals Consolidated, Inc.	Zircon sand	United States Green Cove Springs, Fl.
Associated Minerals Consolidated, Inc.	Zircon sand	Australia, Stradbroke Island, Qld.
Compagnie Europeene du Zirconium (CEZUS)	Zr metal & alloys	France, Ugine
E.I.duPont de Nemours & Co.,Inc.	Zircon sand	United States, Starke, FL.
Indian Rare Earths Ltd.	Zircon sand	India, Manavalakurichi, Tamil
Teledyne Wah Chang Albany	Zr metal & alloys	United States, Albany, OR
Terrara Ltda. (Industrias Nucleares Brasileiras - INB)	Zircon sand	Brazil, Resende, RJ
Tisand Pty, Ltd.	Zircon sand	South Africa, Richards Bay
Western Zirconium	Zr metal & alloys	United States, Ogden, UT
Zircatec	Zr products for CANDU reactors	Canada, Ontario

The US Bureau of Mines reports identified world resources of zircon to exceed 60 million tons. However, only a small fraction is economic to mine at the present time. An important future source may be Canadian tar sands. Although the amount of heavy minerals in the tar sands is less than one percent, about 41,000 short tons of zircon could be produced from the 95 million short tons of tar sands mined annually (Kennedy, 1990).

1.4 - Process Selection - Economic and Environmental Factors

The MIBK process is preferred to the TBP route for economic reasons. In addition to producing off-specification hafnium, the TBP method produces zirconium metal at around twice the cost of that for MIBK's technology. The costs of the CEZUS' process are reported as even lower than those of the MIBK technique. The reasons for the French decision to replace the TBP process for an alternative other than MIBK technology can be found in the economic reasons, as well as the obnoxious odors generated in the MIBK process due to the formation of mercaptans, the high solubility of this solvent in water (20 g/l), and the fire risk concern (low flash point) (Snyder, 1992). In contrast, the USA has had huge industrial facilities, using the MIBK process, in operation for more than 40 years. The investment has already paid-off and the fairly stable market does not invite any effort toward innovation.

According to the ideas discussed above, the ideal replacement for the present MIBK process is yet to come. The market is stable, inelastic (from the economic point of view), and highly regulated. The high cost to build a plant using the molten salt technology is a strong obstacle to its use in small scale or middle size projects. A solvent extraction process, simple in conception, with zero or low waste generation, could be a perfect solution that would change the production profile of zirconium and hafnium in the future.

1.5 - Present Work

The present work is a continuation of earlier studies carried out at McGill, involving extraction from chloride solutions containing either zirconium or hafnium individually, and using organophosphorous compounds (Suriyachat, 1992 and El-Ammouri, 1994). Based on this earlier work, separations using mixed hafnium/zirconium solutions have been investigated. The effects of major process parameters on hafnium/zirconium separation factor have been studied. These include alternative organophosphorous extractants, acidity level and organic to aqueous ratio. Additional factors explored were selective stripping, extraction kinetics, and some engineering considerations relating to high organic loading at levels relevant to commercial reality.

Chapter 2

Zirconium and Hafnium Chemistry

2.1 - Introduction

It is common, even in recent papers, to find references to the zirconyl ion (ZrO^{+2}). However several studies carried out in the earlier 1970's showed no reliable evidence for the existence of this species. One explanation of this can be found in the very complex zirconium and hafnium chemistry. The state of zirconium and hafnium in solutions has not been well explained up to the present time, and the denomination "zirconyl" and "hafnyl" appear as a suitable way to denominate more complex and not completely defined chemical species, as noted by Elison (1969).

Zirconium and hafnium compounds are characterized by their high degree of hydrolysis, and by their tendency to form various complex ions and polymer compounds (Muha and Vaughan, 1960). The complexity of this behavior is increased by the fact that in many cases the solutions take a long time to reach a state of equilibrium. Data collected up to now show very similar chemical behavior of the same compounds of zirconium and hafnium, so the differences that could be exploited to separate these elements are due to differences in equilibrium constants and the kinetics of the reactions that they take part in.

2.2 - Hydrolysis and Polymerization. Data and consequences

Due to the small zirconium and hafnium radii and their high charge, both ions exhibit a strong affinity for hydroxide anions. Thus, hydrolysis reactions characterize hafnium and zirconium chemistry. Using the concept of hard and soft acids, introduced by Pearson, it is possible to understand why zirconium has a higher affinity for water than for chloride. It was determined from precipitation studies using hydrochloric acid solutions that the general formulae for zirconium hydroxide is $Zr(OH)_{3.5}Cl_{0.5}$. With other anions, the ratio OH/anion varies depending on the coordination power of the anion in comparison to the hydroxyl group.

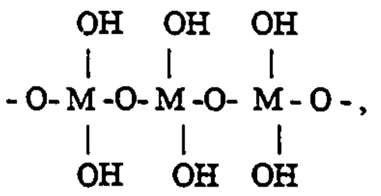
The increase in extent of hydrolysis with time, temperature and metal concentration is stated by Elison (1969) as a general rule for zirconium and hafnium aqueous chemistry. The hydrolysis of zirconium and hafnium compounds in solution is directly connected with the formation of polymeric compounds. In several works the formation of trimers and tetramers are reported and the real reaction that occurs is actually much more complex than as shown below:

$$aM^{+4} + bH_2O \rightarrow M_a(OH)_b^{4a-b} + bH^{+}$$

As suggested by the equation above, this reaction should predominate at low acidities and high metal content. Both conditions are highly desired in industrial processes.

In 2.8 M HCl solutions the main species appears to be trinuclear $[Zr_3(OH)_6Cl_3]^{3+}$, perhaps tetramers, according to Cotton (1973). In concentrations of HCl lower than 0.2 M, zirconium ions are more highly polymerized than in 1 M HCl. The polymerization of hafnium ions proceeds in a similar manner.

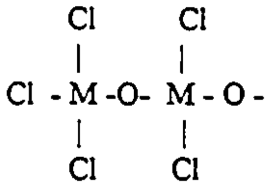
It is of considerable interest to note the observation made by Babko, and described by Elison (1969), who investigated the effect of the state of zirconium on the rate of formation of colored compounds with xylenol orange. He determined that the maximum color only developed immediately in low zirconium concentrations (10^{-4} - 10^{-3} M) in 1 - 2 M HCl. At lower acidity (0.1 M HCl), there is an appreciable decrease in the rate of color development. This could be explained by the time needed to break up the polymers and to form a complex with xylenol orange. It was assumed by Elison that the polymer ions formed at lower acidities are;



$$\begin{array}{ccccccc} & OH & & OH & & OH & \\ & | & & | & & | & \\ -O- & M & -O- & M & -O- & M & -O-, \\ & | & & | & & | & \\ & OH & & OH & & OH & \end{array}$$

M = Zr or Hf

and differ in composition from polymer ions formed in more acid media



$$\mathrm{Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{M}}-O-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{M}}-O-}$$

The bond Zr-OH is stronger than Zr-Cl, therefore the polymers formed at higher acidities are more readily decomposed when zirconium reacts with xylenol orange.

The results of Johnson et al (1956), indicated that small zirconium and hafnium polymers (trimers and tetramers) are dominant in the range 0.5 M to 2 M HCl. At high acidities the degree of polymerization decreases. The same authors also determined that zirconium shows a greater tendency to polymerize than hafnium. The table below summarizes some other literature data.

Table 2.1 - Ionic state of zirconium in hydrochloric acid

HCl Concentration, M	Dominant Zr ion	Reference (#)
0.1	$Zr(OH)_3^{+}$	Beliyavskaya, 1959
0.5 - 1.5	$Zr(OH)_2^{+2}$	Beliyavskaya, 1959
2	$Zr(OH)^{+3}$	Beliyavskaya, 1959
0.5 - 2	Cations	Lister, 1952
6	Neutral complexes	Lister, 1952
7 - 12	Anions	Kraus, 1956

(#) from Elison, 1969.

One point open to discussion is the formation of mixed complexes. The general polymers formulae, depicted above are extensively discussed in all texts, nevertheless, no reference has been found concerning the formation of mixed complexes of zirconium and hafnium and what is the role of such species in the separation of these metals. To discuss this point, some experiments have been performed in the present work and are discussed in section 5.7.

2.3 - Coordination Chemistry of Zirconium and Hafnium

In 1893, Alfred Werner, Nobel prize laureate in 1913, proposed a new theory about the nature of the metals' complexes. The most important postulates of that theory are: i) Most metals exhibit a second type of valence - in modern terminology: Coordination number or secondary valence; ii) Every element tends to satisfy also this secondary valence; and iii) The secondary valence is spatially oriented. Werner's theory explained very well the experimental evidences on chloroaminocobalt complexes, $[Co(NH_3)_6].3Cl$ (and not, $CoCl_3.6NH_3$). The primary valence of cobalt is 3 and its secondary valence is 6. The ammonia molecules attach to the metal ion satisfying the secondary valence and the chloride ions are accommodated in the secondary sphere, farther from the metal ion. Therefore, the chloride ions are not firmly bound to the cobalt and they are readily precipitated by Ag^+ as silver chloride.

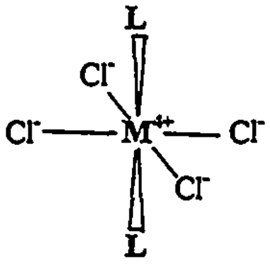
Werner's theory on metal complexes matched well ideas developed subsequently by other workers. These later developments include the Lewis concepts on acids and bases (1916), further developments of quantum mechanics (1935), e.g., the new concept of molecular orbitals and electronic structure of the atoms, as well as the Pauling valence bonding theory (1940). The electronic configurations of zirconium and hafnium are depicted below. The inversion of *d* and *s* orbital stability order (Free atom versus Ion) is a characteristic of all transition metal ions.

Free atom		**Ion**	
Zr	[Kr] $4s^2$ $3d^2$ 4p	Zr^{+4}	[Kr] 3d 4s 4p
Hf	[Xe] $5s^2$ $4d^2$ 5p	Hf^{+4}	[Xe] 4d 5s 5p

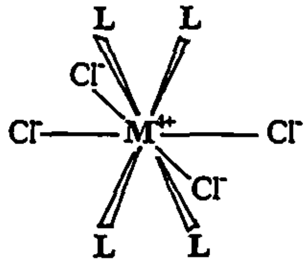
The above electronic configurations of the ionic species explains the absence of color of zirconium and hafnium solutions and allows us to conclude that zirconium and hafnium are present in solution in only one valence state, since no inner 'd' transition (gives color) is allowed in these configurations.

Next it is necessary to observe the molecular orbitals' shapes. Zirconium and hafnium have 8 and 6 as characteristic coordination numbers (CN). Very strong complexing agents form the dodecahedral complex anion (e.g., oxalic acid, $[Zr(C_2O_4)_4]^{4-}$). The dodecahedral arrangement of some zirconium complexes was proved by several authors, as reported by Butler (1989). As with other transition metals, zirconium and hafnium also exhibit a six-coordination number with an octahedral structure.

The general extraction mechanism (by solvation of neutral species) usually involves only bisolvates formation. Difficulty in incorporating more molecules of large organic ligands can be understood in terms of sterically unfavorable positions. Probably due to this, the bisolvate is the dominant form in all systems that extract zirconium by solvation, as demonstrated by Suriyachat (1992) and El Ammouri (1994).



Octahedral



Dodecahedral

M = Zr^{4+} or Hf^{4+}
L = Water or other ligand

The true spatial distribution of zirconium and hafnium complexes is not yet completely understood. The work of Morse (1989), demonstrated that some complexes formerly believed as octahedral are really distorted forms of trigonal prismatic structures. This example exemplifies the complexities of zirconium and hafnium chemistry.

A very important point that coordination chemistry can help us to clarify is the relative order of metal-ligand interactions. Basolo (1964), summarizes the general order of ligand strength as:

$$CN^- > NO_2^- > NCS^- > H_2O > F^- > OH^- > Cl^-$$

Using this information it is possible to predict the relative stability of the different complexes formed. In the context of the present work, to replace the water complexes of zirconium and hafnium requires high concentration of chloride, or very high concentration of hydroxyl ion. This explains why the extraction process is so difficult at low concentrations of hydrochloric acid.

In summary, the coordination chemistry of zirconium and hafnium governs complex formation and helps us to understand the bisolvate formation observed in all previous work on extraction of these metals by organophosphorous compounds.

Chapter 3

Zirconium and Hafnium Extraction

3.1 - Introduction

Hydrolysis and polymerization are the dominating reactions of zirconium and hafnium in aqueous solutions at low acidity levels. Under such conditions the use of acid extractants is not selective regarding these metals. Both metals are extracted in the same way by cation extractants, as showed by Witte (1985). Thus, the separation of zirconium and hafnium is usually carried out by extraction using the solvation phenomenon at medium-high acidity levels. We can see below several reactions that take place in hydrochloric medium as the acidity of the solution increases. The acidity domains exhibited in table 3.1 were furnished by Ellisson and Petrov (1969).

Table 3.1 - Hydrolysis and Chloride substitution reactions as [HCl] increases

Successive Reactions of Zr and Hf in HCl Solution		HCl level (for Zr)	
$M^{4+} + H_2O + H^+ + OH^-$	$\rightarrow [M(H_2O)_2(OH)_4]$		
$[M(H_2O)_2(OH)_4] + H^+ + Cl^-$	$\rightarrow [M(H_2O)_3(OH)_3]^+.Cl^-$	< 0.1 M	
$\downarrow$	$\rightarrow [M(H_2O)_4(OH)_2]^{2+}.2Cl^-$		
	$\rightarrow [M(H_2O)_5(OH)]^{3+}.3Cl^-$	< 2 M	
	$\rightarrow [M(H_2O)_6]^{4+}.4Cl^-$		
	$\rightarrow [M(H_2O)_5Cl]^{3+}.3Cl^-$		
	$\rightarrow [M(H_2O)_4Cl_2]^{2+}.2Cl^-$		
	$\rightarrow [M(H_2O)_3Cl_3]^+.Cl^-$		
$H^+ + Cl^- + [M(H_2O)_3Cl_3]^+.Cl^-$	$\rightarrow [M(H_2O)_2.Cl_4]^\circ + H_2O$	6 M	(eq. 3.1)
	$\rightarrow [M(H_2O).Cl_5]^-$		
	$\rightarrow [MCl_6]^{=}$	> 8 M	

The reactions' order depicted in Table 3.1, despite significant overlap, obey the relative order of metal-ligand interactions summarized by Basolo (1964), as discussed in chapter 2 (ligand strength order: $H_2O > OH^- > Cl^-$). The stability constants found in several references were not self-consistent, probably due to differences in measurement methodologies.

In the work of Ruer, described by Ellison (1969), zirconium species in chloride medium were shown to migrate towards the cathode of an electrochemical cell. This is consistent with the predominant cationic species shown in Table 3.1 at up to 6 M HCl, and also agrees with the speciation diagram developed by El-Ammouri (1994). In the latter case, the amount of neutral tetrachloride complex increases with increasing acidity, but does not become predominant until 6 M HCl is approached.

Today, there is still controversy concerning the precise nature of dissolved zirconium species in acidic solutions. According to Cotton (1973), hydrolysis occurs so that it is doubtful that simple $Zr(H_2O)_x^{+4}$ aquo ions exist even in strongly acid solutions. Ellison (1969), however, stated these species form at high acidity, while Wilkinson (1987) considered their existence possible only at trace concentrations ($<10^{-4}$ M) as $[Zr(H_2O)_8]^{+4}$. Devia and Sykes (1981) showed that at 0.5 M $HClO_4$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is the single dominant species in solution, accounting for more than 90% of total Zr(IV).

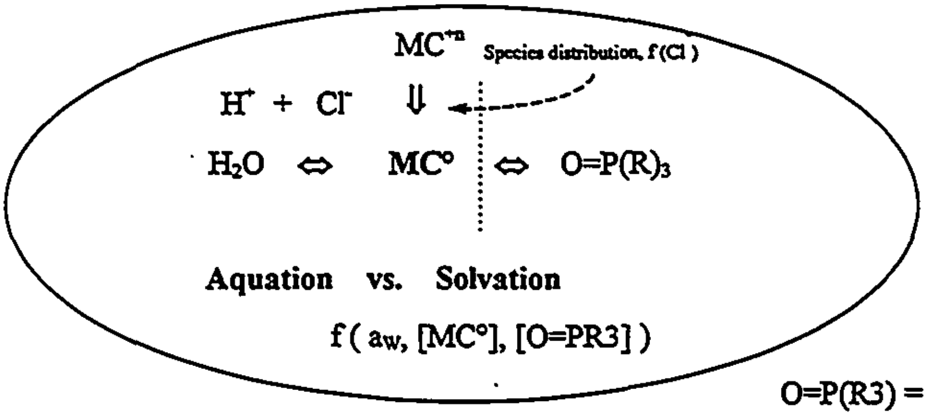
The former work of Suriyachat (1992) stated that zirconium is loaded in phosphane extractants as chloride complexes by solvation in a molecular ratio, extractant to metal ion equals two. The same conclusion was reached by El-Ammouri (1992) concerning hafnium. In both cases, the calculations referred to 2M HCl and 0.002 M Zr/Hf.

$$ZrCl_4|_{aqueous} + 2\ O{=}P(R)_3\ |_{org} \rightarrow ZrCl_4\{O{=}P(R)_3\}_2|_{org}$$

$$HfCl_4|_{aqueous} + 2\ O{=}P(R)_3\ |_{org} \rightarrow HfCl_4\{O{=}P(R)_3\}_2|_{org}$$

A similar mechanism was proposed by Levitt (1955), for comparable conditions. Levitt worked at higher acidity (6 -8 M HCl), with zirconium concentration about 0.004 M using TBP as extractant. The main difference between the conclusions of the cited works was the kind of zirconium complex proposed. In his work Levitt claimed the formation of $Zr(OH)_xCl_y$ complexes. Sato (1983) also proposed the same mechanism in his work concerning extraction of zirconium by TOPO with different acid media. The above cited authors also observed a decreasing distribution factor with increasing metal concentration. This behavior of the solutions of the individual metals was considered as evidence of polymerization. These studies were carried out in synthetic solutions of the individual elements and at low concentrations.

The extraction of zirconium and hafnium from aqueous solutions by organophosphorous compounds require neutral overall charge on extracted complexes. The metal-extractant bonds have to be stronger than the metal-water (aquated) bonds to form a hydrophobic complex, but not so strong that eventual stripping becomes difficult. So, to separate zirconium from hafnium two points have to be observed. First, the optimum chloride level of the aqueous solution has to take into account the process selectivity. The chloride level should be manipulated such that the concentration of neutral species of one element is as different as possible to that of the other. Second, the activity of water in the aqueous solution has to be set such that the strength of the water-complex interaction is weaker than that of the extractant-complex. Figure 3.1, below, depicts the relationship described above.



O=P(R3) = Extractant
MC = Zr and Hf chlorocomplexes

Figure 3.1 - Sketch of the extraction model

Choppin (1990) has assessed the role of the ionic strength in solvation processes. Increasing the acidity or salts concentration would result in less water availability for hydration of the extractable species, and solubility in the aqueous phase can be expected to decrease. This would result in greater extraction. The additional problem in zirconium-hafnium separation is that the addition of hydrochloric acid also affects the relative amount of extractable species of both metals.

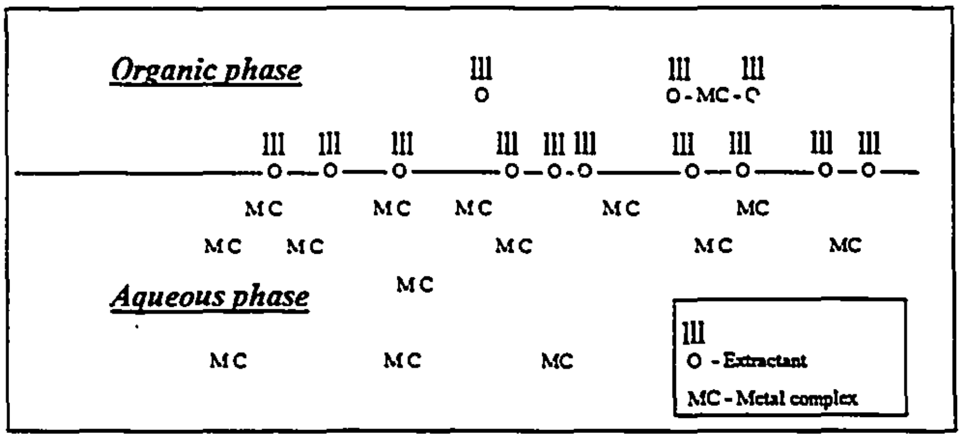
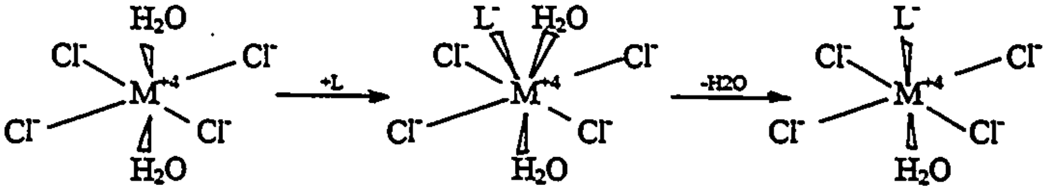


Figure 3.2 - Solvent Extraction Process

Rozen (1990) proposed a new approach to analyze the extraction process. He noted that the extremely low solubility of modern commercial extractants makes the model of complexation in the aqueous phase less realistic. He considers the phenomenon to occur at the organic/aqueous interface, as depicted above. The extractant molecules compete for the metal complex (MC) in a substitution reaction. This reaction results in the displacement of waters of hydration by the extractant with the formation of hydrophobic species. The extractant is the entering group and the water is the leaving group. (M^{+4} = Zr or Hf)



Since only neutral species (MC°) can be extracted by phosphanes, only the zirconium complex related to eq. 3.1 can be responsible for the separation of zirconium and hafnium in hydrochloric acid medium. At least two steps should occur:

$$M(H_2O)_2.Cl_4 + L \Leftrightarrow M(H_2O).Cl_4.L + H_2O \qquad \text{(eq. 3.2)}$$

$$M(H_2O).Cl_4.L + L \Leftrightarrow MCl_4.2L + H_2O \qquad \text{(eq. 3.3)}$$

The overall zirconium and hafnium extraction reaction can be represented as:

$$M(H_2O)_2.Cl_4 + 2\,L_{(org)} \Leftrightarrow MCl_4.2L_{(org)} + 2H_2O \qquad \text{(eq. 3.4)}$$

and the extraction constant can be represented as:

$$K_{ex} = \{ a_{MCl4.2L} \,.\, a_W^2 \} / \{ a_{M(H2O)2.Cl4} \,.\, a_L^2 \} \qquad \text{(eq. 3.5)}$$

Since activities depend on the ionic strength (*I*) of the solution, Kex will always refer to a particular value of *I*, at which it has been determined. At that specific condition equation eq.3.5 can be re-written in terms of distribution coefficient as follows:

$$Kex = D_M \,.\, a_W^2 \;/\; [L]^2 \qquad \text{(eq. 3.6)}$$

where $D_M = [M]_{org} / [M]_{aq}$, and,

$$\text{Log } Kex - 2 \log a_W = \log D_M - 2 \log [L] \qquad \text{(eq. 3.7)}$$

A plot of log D vs. log [L], at constant ionic strength (*I*) and [M], should be a straight line if certain requirements are fulfilled. First, the chemical reactions should be fast. It is noteworthy that equilibrium[1] is reached after less than ten minutes in the shake-out experiments. Second, the acid level should be kept constant throughout the experiments, and water and acid pick up should be small. Thus, no important variation in the activity coefficients would be expected during the experiments. Third, the acid level should be also high, so that neither polymerization nor hydrolysis are very important reactions under the experimental conditions, if the metal concentration is kept sufficiently low. A further assumption is that only monomeric neutral species exist in the aqueous phase. In reality other chlorocomplexes are also present, possibly as polymers. Despite all possible deviations from ideal behavior, the plot log D vs log [free-L] are reasonable straight line fits as shown in Figure 3.3.

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[1] maybe not the thermodynamic equilibrium

Equations 3.2 and 3.3 can also be rewritten to represent the sequential steps of water/ligand substitution followed by solvation. Also it is easy to see that the free energy of extraction of a particular species is the difference between its solvation and hydration energies, as follows:

$$[M(H_2O)_2.Cl_4] \Leftrightarrow MCl_4 + 2H_2O \qquad -\Delta G^\circ_{hydr}$$

$$MCl_4 + 2L \Leftrightarrow MCL_4.L_2 \qquad \Delta G^\circ_{solv}$$

$$\Delta G^\circ_{ex} = -\Delta G^\circ_{hydr} + \Delta G^\circ_{solv}$$

$$K_{ex} = \exp -(-\Delta G^\circ_{hydr} + \Delta G^\circ_{solv}) / RT \qquad \text{(eq. 3.8)}$$

It is interesting to observe similar arguments being applied to other systems. Table 3.2, presented by Rozen (1990), compares the extractability of HCl and HNO_3 by TBP. It shows that the low extractability of HCl by TBP, if compared to HNO_3, is mainly due to a more powerful hydration of HCl rather than to a weaker bond to TBP. We believe that hydration-solvation competition may be also an important factor controlling separation in the zirconium-hafnium-HCl system.

Table 3.2 - Comparison of HNO_3 and HCl extraction with TBP

	Extraction constant	ΔG_{ex} kcal/mol	ΔG_{hydr} kcal/mol	ΔG_{solv} kcal/mol
HNO_3	$2\ 10^{-1}$	0.95	-7.3	-6.3
HCl	$2\ 10^{-4}$	5.0	-10.7	-5.7

According to the reasoning developed up to this point, we can expect that the overall extraction constants of our system will depend mostly on two parameters. First, the chloride level, which will be responsible for the different metal species concentrations in solution. Thus, the major factor that governs the zirconium and hafnium separation should be the prevalence of neutral zirconium species over hafnium analogues in a defined acidity range. Such explanation is consistent with the MIBK separation mechanism determined by Golub (1966). Second, the acidity level, which will change the equilibrium between hydrated and solvated species. In such a context, the best extractant will be the one which has the ability to solvate the metal species inside that specific acidity range.

3.2 - Single Element Solution Trends

In previous work leading to the present thesis (Suriyachat, 1992, and El-Ammouri, 1994), hafnium and zirconium were extracted from single metal chloride solutions into Cyanex 923 or Cyanex 925. The nature of these organophosphorous reagents is described in the following Section 3.3. Tables 3.3 and 3.4 give an example of single metal extraction data obtained under comparable conditions in these earlier studies. At 3.5 M HCl, distribution coefficients are up to one order of magnitude in favor of zirconium extraction when using Cyanex 925. This information provided the entry point for the present work, which focused on developing a process for hafnium/zirconium separation without using any other complexing agent. When Cyanex 923 is used the best selectivity is found around 2.5 M HCl.

Table 3.3 - Zirconium Extraction after contacting its solution with a Solution of Cyanex 925 in kerosene (O/A =1) (Suryiachat, 1992)

	[Zr] = 0.002 M		
[Cy925] → **[HCl]**	**0.026 M**	**0.065 M**	**0.131 M**
2.5 M	36%	58%	95%
3.5 M	53%	72%	97%
4.5 M	68%	82%	98%
6.0 M	81%	95%	99%

Table 3.4 - Hafnium Extraction after contacting its solution with a Solution of Cyanex 925 in kerosene (O/A =1) (El-Ammouri, 1994)

	[Hf] = 0.002 M		
Cy925 → **[HCl]**	**0.026 M**	**0.065 M**	**0.131 M**
2.5 M	18%	40%	70%
3.5 M	33%	53%	78%
4.5 M	70%	73%	86%
6.0 M	99%	99%	99%

The data of Tables 3.3 and 3.4 can also be used to estimate solvation numbers for hafnium and zirconium extraction, which then allows the loading reaction to be defined for 2.5 to 6 M HCl, this being the range applicable to the present work. Previous calculations (Suryiachat, 1992, and El-Ammouri, 1994) were restricted to 2 M HCl, and produced a solvation number of 2. As discussed in connection with deviations from equation 3.7, the slope of log D vs Log [L] should provide an estimate of the solvation number.

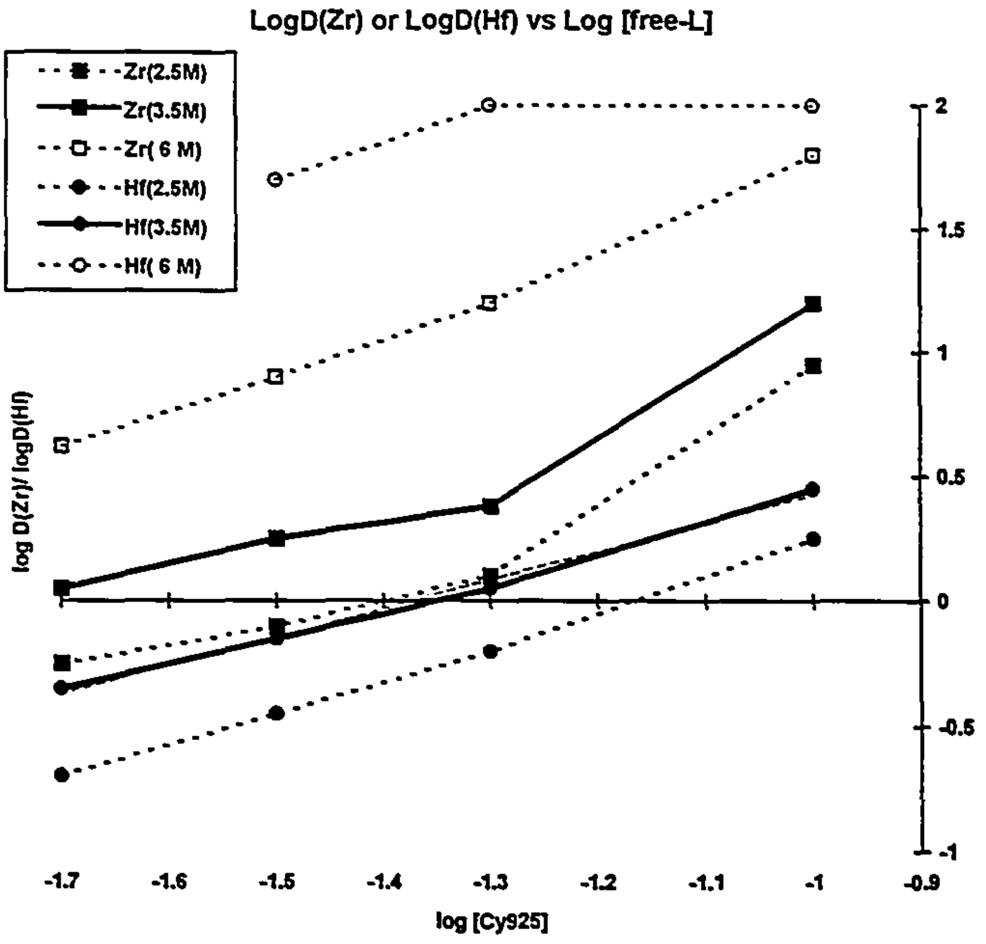

Figure 3.3 - log of distribution factor of Zr and Hf versus log of free extractant (molarity) for individual solutions of each element (0.05M) at different acidities (Suryiachat, 1992 and El-Ammouri, 1994)

This is showed in Figure 3.3, which suggests a first or second power dependency on extractant concentration, indicating the formation of mono or di-solvates. Such a result seems to be agreed upon by all researchers working with zirconium in hydrochloric acid medium, regardless of neutral organophosphorous extractant used. White and Ross (1958) found a solvation number of 2 when extracting zirconium with TOPO from hydrochloric or nitric medium. Sato (1970) found a solvation number between 1.55 and 1.6 for zirconium being extracted by TOPO at 3 and 8 M HCl and 0.02 M Zr, and Levitt (1955) found 1.97 using TBP at around 7 M HCl aqueous phase and 0.004 M Zr.

It is important to note that fundamental work designed to determine reaction stoichiometry uses low metal concentrations. Nevertheless, industrial processes must run at high metals contents to be commercially competitive. Table 3.5 and Figure 3.4 show the concentration effects in single metal solutions of zirconium and hafnium.

Table 3.5 - Metals extraction after contacting with a solution of Cyanex 925 (0.13 M) in kerosene (O/A =1). (Suryiachat, 1992 and El-Ammouri, 1994)

[HCl]	[Zr] (pure solution)			[Hf] (pure solution)		
	0.002 M	0.02 M	0.05 M	0.002 M	0.01 M	0.05 M
2.5 M	95 %	53 %	29 %	70 %	32 %	11 %
3.5 M	97 %	77 %	64 %	78 %	53 %	30 %
4.5 M	98 %	92 %	90 %	86 %	78 %	56 %
6.0 M	99 %	97 %	98 %	99 %	98 %	89 %

The observed decrease in extraction is attributed to polymerization. Connick and Reas (1951) studied the polymerization of zirconium as a function of the zirconium concentration in 1 and 2 M $HClO_4$ solution by extracting with thenoyltrifluoroacetone. They concluded that above a certain definite concentration of zirconium, the distribution coefficient is dependent on the metal concentration, owing to polymerization in solution.

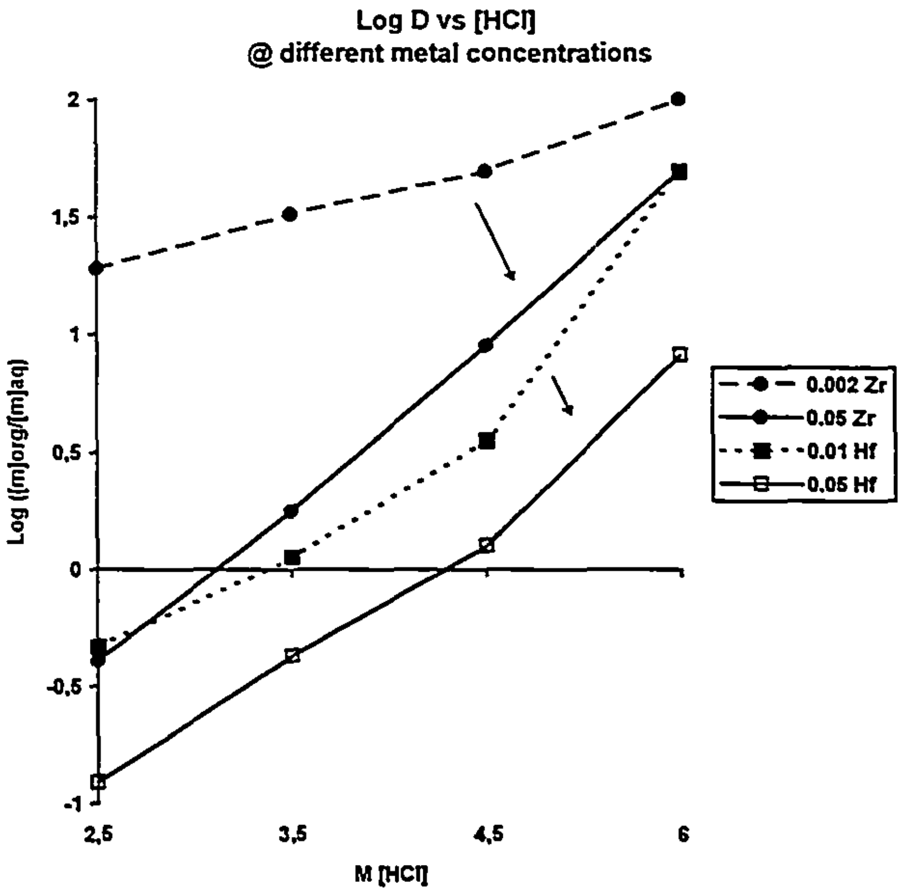

Figure 3.4 - Distribution factor of Zr and Hf versus initial acidity as function of the metals concentration for individual metal solutions (O/A=1)

In their studies on the extraction of zirconium by phosphanes, Suryiachat (1992), Tribalat (1974), and several other investigators observed a decrease in the distribution coefficient of zirconium at higher concentrations. In Figure 3.4 we compare the distribution coefficient behavior found by Suryiachat and El-Ammouri. Later on, in Chapter 5 we will compare the behavior of these single metal solutions with mixed solutions of zirconium and hafnium.

3.3 - The Role of Neutral Organophosphorous Extractants

The introduction of neutral organophosphorous compounds in the solvent extraction field arose from the need for nuclear reprocessing initiated at Oak Ridge National Laboratory, USA, at the end of the 40's. Tri-butyl phosphate (TBP) is by far the most used extractant of this type. Other organophosphorous reagents, such as trioctylphosphine oxide (TOPO), were developed and their importance can be seen by the almost complete replacement of ethers and ketones in many solvent extraction processes.

Over the last two decades a new family of tailor-made organophosphorous compounds has been extensively used in a large number of applications: uranium purification and reprocessing, rare earths fractionating, niobium and tantalum separation, nickel purification and several others (Rickelton, 1988). These reagents present an interesting opportunity to examine the effects on zirconium and hafnium separation of the progressive replacement of R-O-P=O bonds by R-P=O bonds and the influence of changing the identity of the alkyl substituent (R) group (Figure 3.5). The phosphoryl radical is highly polarized, giving a basic character to the molecule, and different compounds can be developed to achieve the ideal strength in the covalent bond between the phosphoryl oxygen and the target metal complex. Depending on the other radicals bonded to phosphorous, the basic character of the molecule can be enhanced or decreased. In other words each O-P bond replaced by a C-P bond via an alkyl group increases the coordination ability of the molecule and its extracting power.

In the present work, we compared extractants with different basicities, as in Figure 3.5. In terms of the extraction process itself, Preston (1986) showed that for iron, indium and zinc, the distribution equilibrium correlated much more closely with the electron donating nature of the extractant molecule than with the composition of the alkyl groups. The role of the alkyl group in the organophosphorous molecule is also important in that aqueous solubility decreases with increasing chain length. In addition, selectivity may be as important as extracting power. Branched alkyl chains give a more selective reagent than linear chains, this being a major reason for comparing Cyanex 923 and Cyanex 925 (Fig. 3.5) in the present work.

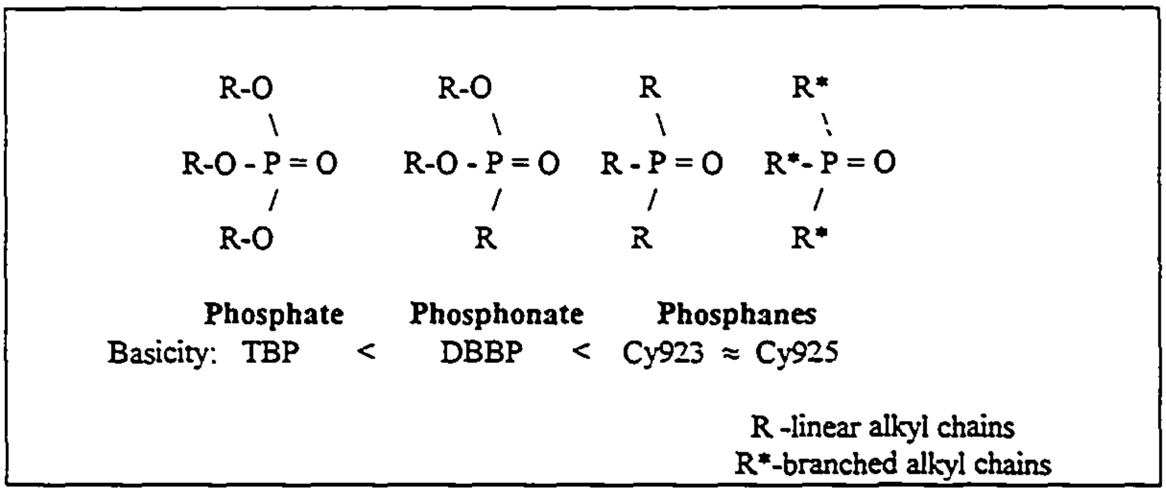

Figure 3.5 -Chemical structures (generic) of the extractants used in this work

The extraction efficiency of the various extractants results from how effectively they compete against water and other anions for the available coordinating positions around the metal ion. The stronger the extractant basicity, the more able it is to replace water and other anions around the metal ion, so promoting its extraction. On this point it is noteworthy to observe that when most studies on zirconium and hafnium were developed, the only phosphane available was TOPO.

Oxygen-containing organic extractants have been used for more than forty years to solvate inorganic complexes. Ketones, alkyl-phosphates, ethers and, recently, crown-ethers (Deorkar, 1992) and phosphanes have been used to promote selective separation of metals. Although phosphine was discovered more than two hundred years ago, it was only in 1955, when Cyanamid began a systematic research on the production of synthetic organophosphorous compounds, that other phosphine derivatives appeared on the commercial market. In the mid 70's the first important phosphine oxide, tri-octylphosphine oxide (TOPO) became commercially available. Some years later Cyanex 923 appeared, which retained the outstanding characteristics of TOPO without some of its drawbacks. More recently, a new member of this family of solvents was developed in order to increase extraction selectivity: Cyanex 925. An interesting description of this development is depicted in the work of Rickelton and Boyle (1988).

Table 3.6 summarizes information about organophosphorous compounds commonly used as metal extractants by a solvation mechanism. The work of Preston (1986) is a good example of the role of basicity in the extraction of neutral species. Their results are summarized in Figure 3.6 and are useful to illustrate our discussion. Different extractants exhibit different extraction behavior and selectivity for rare-earth elements depending on the substituent groups attached to the phosphoryl group.

Table 3.6 - Summary of some organophosphorous compounds commonly used as metal extractants by solvation mechanism (see Appendix 1 and 2)

TRADE NAME	CHEMICAL FORMULA	GENERAL INFORMATION
TOPO (Cyanex921[2])	$(n\text{-}CH_3(CH2)_7)_3P{=}O$	Advantage - High extraction capacity due to its high coordination power Disadvantage - Solid at room temperature. Some difficulty with solution stability Major use - Uranium industry and recovery of carboxyl acids and phenols from effluent streams.
Cyanex923[2]	$(n\text{-}CH_3(CH_2)_5)_3P{=}O$ $(n\text{-}CH_3(CH_2)_7)_3P{=}O$	Similar to TOPO but liquid and completely miscible with all common diluents.
Cyanex925[2]	$[(CH_3)_3C(CH_2)_3(CH_3)]_2$ $(n\text{-}CH_3(CH_2)_7)P{=}O$	Same characteristics as Cyanex 923. A small decrease in extraction and an increase in selectivity due to the use of branched alkyl groups.
Cyanex471[2]	$[(CH_3)_2CH\text{-}CH_2]_3P{=}S$	Experimental. Possibility of higher selectivity to certain species
DBBP	$(n\text{-}CH_3(CH_2)_3O)2$ $(n\text{-}CH_3(CH_2)_3)P{=}O$	Medium basic extractant (Between TBP and TOPO). Can exhibit best selectivity to certain elements
TBP	$(n\text{-}CH_3(CH_2)_3O)_3P{=}O$	Best known extractant. Extensively used in the nuclear industry. Usually demands aqueous solutions of high ionic strength.

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[2] Trade names of Cytec Canada Inc.

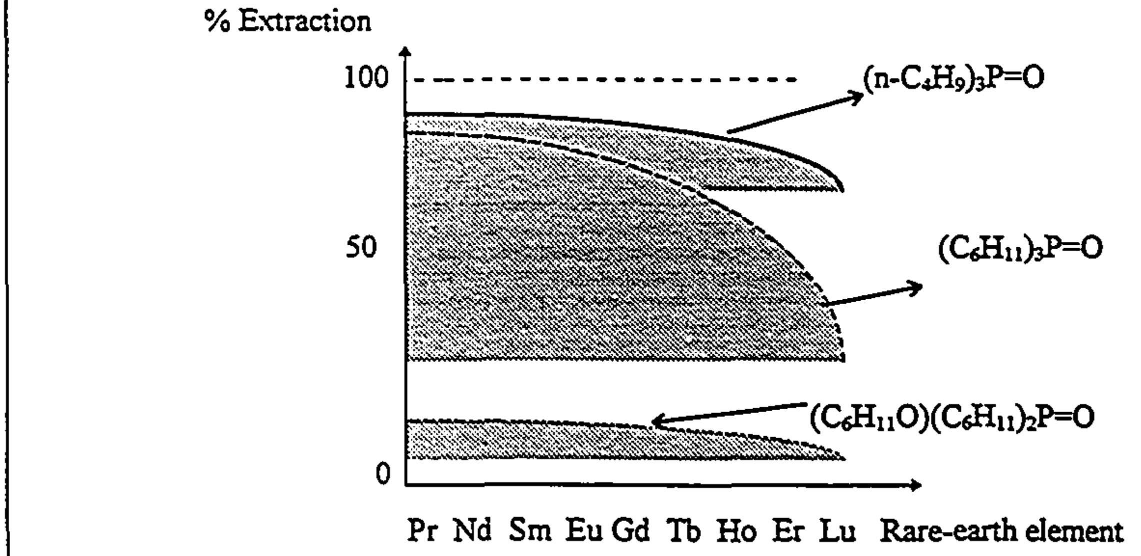


Figure 3.6 - Extraction (approximate curves) of rare-earth metals by toluene solutions of organophosphorous compounds (Preston, 1986).

During the last decade, Yuan (1990) developed a systematic method to evaluate the efficiency of organophosphorous extractants. His model takes into account several characteristics of the extractant: its polarity; and the number of carbons in the substituent group. A steric parameter is also introduced, which takes into account the configuration of the extractant molecule. This model has been applied to extraction of rare earth-elements by organophosphorous compounds, and gives a useful way to assess quantitatively the role of extractants in the solvent extraction process.

3.4 - Criteria for a new process

Several criteria must be met for a new zirconium/hafnium separation process to be successful. It must be at least comparable to the MIBK process and perform better than the TBP process. Some essential features to be considered are:

- The separation coefficient should be larger than 10 (better than TBP);
- The load capacity should be higher than 0.5 M of metal to allow high Zr concentration in feed (0.3 M in TBP and 1.1 M in MIBK);
- The process should work at minimal acidity (lower than 4 M);
- The system should possess good phase stability. It should not suffer from emulsion or third phase formation; and
- The use of thiocyanic acid should be avoided.

The overall concept is to develop a process that minimizes the losses or decomposition of the solvent and extractant so that minimal waste is generated and other environmental problems are avoided.

One troublesome aspect of working at high acidity is the increase in mutual solubility that usually occurs. Processes that use TBP are good examples of such a problem in nitrate systems. Similar behavior occurs in extraction processes using hydrochloric acid solutions, which show a sharp increase in organic solubility at about 7 M acid. At this acidity level, the aqueous HCl solution becomes water deficient. At this very same acidity, the extractibility of the acid increases sharply. Marcus (1969), explains this fact on the basis that extractant molecules are transferred to the aqueous phase where they provide solvating molecules for the hydronium ion, which thus becomes organic soluble. Nitric acid solutions exhibit the additional phenomenon of extraction of undissociated acid. However, in the case of hydrochloric acid solutions, this does not occur since HCl is completely dissociated.

In the specific case of the present work, another problem that arises when the acidity is increased is the decrease in zirconium solubility in water. This fact could also limit in a very important way the economics of the process.

3.5 - Impurities Behavior

This work is about the fundamentals of a new process. Thus, at this point, the main goal is to identify possible conditions for separating zirconium from hafnium in a clean and economical way. A logical further step would be continuous running and scale-up, with optimization of parameters. In this context the role of impurities becomes an important issue. Although no measurements concerning impurities behavior have been made, the probable extractibility of various metals may be predicted from literature information.

The results presented in Table 3.7 come from the compilation made by White and Ross (1961) of the extraction of several elements by TOPO. It is reasonable to assume that, qualitatively, these elements might show the same relative behavior with the extractants used in the present work. On the other hand, since a separation process is a competition for extractants, some surprises could show up. A remarkable example is in fact the separation of zirconium/hafnium itself. This will be analyzed in more depth in Chapter 5.

Table 3.7 - Extractability of some elements by TOPO in 3-4M HCl (White and Ross, 1961)

Element	*Extraction*
Sn, Zr, Hf, Au(III), Zn, Sb(III), Cr(VI), U, Mn(VII)[1],Nb[2]	**High**
Ga(III), In(III), Sb(V), Ta[2], Fe(III), Th	**Medium**
Cu(II), Cd, Hg(II), Ti, V, As, Bi, Pt	**Low**
Li, Na, K, Be, Mg, Ca, Sc, Ba, Mn(II), Fe(II), Co(II), Ni(II), Cr(III), Ag(I), Y, Lanthanides and Al[3]	**Very reduced**

[1] Not stable, easily oxidized

[2] In presence of complexing agent

[3] Enhances zirconium extraction (White and Ross, 1958)

From the overall process perspective, the most important elements to be controlled in the separation step are aluminum, phosphorus, and iron, which commonly are present in high concentrations in the ore. Uranium, thorium, indium and cadmium must be also monitored since the end product specifications ask for extremely low levels (ppb range).

3.6 - Hollow fiber membrane contactors

The conventional methods used in hydrometallurgical processes are based on the dispersion of one phase, as droplets or bubbles, into the other. Due to the small dimensions and large interfacial area presented by the dispersed phase in the continuous phase, the solute mass transfer is maximized. The phases are then separated, usually due to density differences.

However, the time required to separate the phases is such that it is not possible to get reliable data about mass transfer in small periods of time (seconds to few minutes range). Another problem with the conventional system is the lack of control and inability to measure the effective transferring area. Thus, research in the solvent extraction field is more usually based on equilibrium rather than kinetics studies. The minimum time required to establish equilibrium is determined and the contacting time is kept above the former value.

In this work, in addition to separatory funnels, we also used a membrane contactor. The physical and operational description of the system is as shown in Section 4.3.2. This system, a new type of contactor, consists of microporous hydrophobic hollow fiber membranes assembled in a way very similar to the conventional tube and shell heat exchanger. This kind of equipment allows the solute to be transferred from one phase to another through the membrane without dispersion of the phases.

Dispersion-free solvent extraction has recently been demonstrated for several systems, as reported by Prasad (1990). Preliminary studies have shown several advantages of this system:

(1) No dependence on density in the parameter adjustments;

(2) Independent variation of phases flow without hydrodynamic limitations;

(3) Easier control of organic losses through the membrane by controlling the overpressure of the aqueous phase;

(4) Ability to provide several extraction stages in a single equipment unit;

(5) Ability to handle systems which form emulsions; and

(6) Absence of moving parts.

The use of a membrane contactor allowed us to observe the extraction kinetics and take advantage of them to design the separating process. The separator funnels, currently used in the lab-tests, have an intrinsic "dead" time for phase disengagement of around a few minutes. When the process is scaled-up, this dead time could reach tens of minutes. In a membrane system, the residence time could be as small as tens of seconds. This factor could open a new range of possibilities in the solvent extraction field.

Chapter 4

Experimental and Analytical Methods

4.1 - Materials

All chemicals used in this work were of reagent grade. The extractants were commercial samples kindly furnished by Albright and Wilson of America (TBP and DBBP) and Cytec Canada Inc.(Cyanex 923 and 925). They were used as delivered. The extractants' physical properties are exhibited in Table 4.1.

Zirconium and hafnium solutions were prepared by dissolving zirconyl chloride octahydrate powder ($ZrOCl_2.8H_2O$), 98%, and hafnium tetrachloride ($HfCl_4$), 98%, both from Aldrich, in a suitable solution of hydrochloric acid and distilled water. The zirconium salt contained 0.5 % of hafnium and the hafnium chloride contained 1.5% of zirconium. Since the mutual contamination was lower than analysis precision it was not taken into account in our calculations. The typical precision of the zirconium and hafnium analysis by atomic absorption was around 1 - 3% (confidence limit of 95%).

The major chloride source in this work was hydrochloric acid (typically 3.5 M), while a relatively small amount was introduced from zirconium/hafnium salt addition. Typically 0.1 M Zr and 0.01 M Hf were added as zirconyl oxychloride and hafnium tetrachloride, respectively. This permitted quotation of acidity values as initial hydrochloric acid concentrations, which decreased the number of acid analyses required, without introducing significant errors to the results. Conversely, if zirconium tetrachloride had been used as starting material, the amount of chloride introduced and hydronium ion generated by hydrolysis would have to be taken into account. For example: when a 0.55 M zirconium solution is prepared by the addition of zirconium tetrachloride into 3.5 M HCl, the final total acidity equals 5 M, as measured by titration with NaOH. Part of the HCl generated by chloride hydrolysis is lost as gas during the reaction. Due to these problems, and following the procedures of several other researchers, the zirconyl oxychloride was used as starting material and initial acidity values were quoted in this work. In the case of hafnium, the amount used was always very small, so that it was acceptable to prepare solutions from tetrachloride salt.

Each batch of hydrochloric acid was titrated against a sodium hydroxide solution, prepared from an analytical standard.

The diluents tested were kerosene, containing less than 1% aromatics, and hexane from Fisher Scientific, A.C.S. Grade, both used as delivered.

Zirconium and hafnium standard solutions were supplied by Johnson Matthey (for AAS, with 1000 ppm of metal in 5% HCl) and used in developing analytical procedures.

Table 4.1 - Physical Properties of the Extractants

Typical Properties	MIBK	TBP	DBBP	Cyanex923	Cyanex925
Molecular Weight	100.2	266	250	348	386
Specific Gravity (25 °C)	0.80	0.98	0.95	0.88	0.88
Solubility in Water (%)	1.9	0.04	n.a.	0.001	0.0003
Water Solub.inExtractant	1.9%	0.1%	n.a.	7%	3%
Viscosity at 25 °C	0.60 cp†	3.4 cp	n.a.	40 cp	117 cp
Viscosity at 40 °C	-	2.7 cp	3.1 cp	14 cp	24 cp
Flashpoint	13°C	160°C	257°C	182 °C	126°C

† - Yaws(1995)

4.2 - Solvent Extraction Procedure (Shake-out tests)

The extraction and stripping experiments were carried out in 125 ml polypropylene separatory funnels and mechanically shaken, using wrist action movement, with a BURREL shaker, model 75. Preliminary experiments showed that equilibrium was reached rapidly for both zirconium and hafnium. Nevertheless the shaking time was set at 20 minutes in order to be consistent with the previous work on single metal solutions

(Suriyachat, 1992 and El-Ammouri, 1994). The standard procedure was to place 20 ml of organic and aqueous phases in a tightly stoppered polypropylene separatory funnel. The funnels were shaken at room temperature (21°C) for 20 minutes, then left to rest for about a further 10 minutes. If necessary, the raffinate was centrifuged to avoid entrained organic. The results were based on the raffinate, while concentrations in the organic were calculated by difference. No variation in phase volumes was identified, no matter how the experimental parameters were changed.

4.3 - Kinetic Studies

The conventional shake-out experiments, described in section 4.2, do not give much information about kinetics of metals transfer. The observed effect is the result of a combination of transport phenomena with chemical reaction (solvation) occurring at the organic/aqueous interface, and gives results for equilibrium conditions. The evaluation of mixing efficiency of solutions, and interfacial area in shake-out tests is very difficult to do. We used two additional procedures to study the effects of kinetic phenomena in this work.

The term "kinetics studies" should be understood in the present context as being a simple study of mass transfer against time. It was not the objective of this work to carry out a fundamental kinetic study to evaluate intrinsic mass transfer rates or any other kinetic parameter. The purpose was only to infer if kinetics could be exploited to enhance zirconium/hafnium separation, and thus to determine the need, if any, for further research in this area. The methods described in the next pages also eliminate the phase disengagement period associated with shake-out tests.

4.3.1 - Transfer across a direct aqueous/organic interface

The first technique used for kinetic studies was characterized by possessing a single, direct aqueous/organic interface of constant known area in a similar manner to that created by the conventional, rotating disk procedure proposed by Albery (1976) for diffusion studies. When the latter was attempted, there were problems such as acid attack of the membrane at high acid level, and very slow transfer rates at the small disc areas possible with this method. Figure 4.1 shows the experimental set-up actually adopted, which is equivalent to the rotating disc approach, but without the membrane.

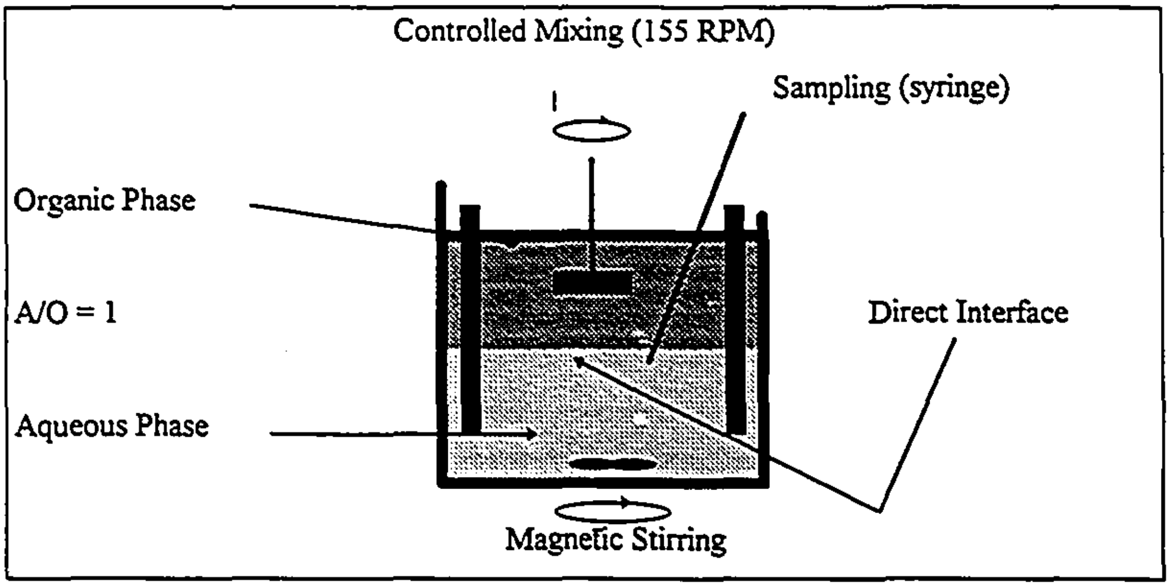


Figure 4.1 - Scheme for direct interface experiments

The operational conditions were optimized as shown above. Here, a jacketed 600 ml beaker was used into which 200 ml of each phase were carefully poured to avoid mixing. Four baffles were introduced and the maximum stirring rates in each phase were determined such that an essentially flat, stable interface was maintained. The phases were stirred in different directions to avoid vortex formation and mixing of the phases.

Experiments performed initially demonstrated that mass transfer without stirring was negligible. Stirring was initiated and small samples were taken from the aqueous phase periodically. The samples were diluted with adequate HCl solution and analyzed by AAS. The first results obtained showed very significant differences in extraction rates of zirconium and hafnium, and justified the purchase of a more expensive apparatus to evaluate these initial observations. It was also seen from measurements at 40°C that zirconium extraction rate increased more rapidly with temperature than hafnium.

4.3.2 - Transfer across membrane interface

Initial results, using the method described above, motivated us to conduct experiments using new technology phase contactors, specifically the Hoechst-Celanese Liqui-Cel Laboratory LLE System. This is a small laboratory-scale contactor that makes possible liquid-liquid separation under easily controlled conditions using a constant interfacial area. The system consists of a microporous hollow fiber (MHF) contactor which provides a defined contacting area in an arrangement very similar to a shell-and-tube heat exchanger (Figure 4.3). The tubes are formed by microporous hollow fibers. Two independent circuits confine the organic and aqueous streams separately to either the tubes or shell. The control is very stable and provides independent adjustment of pressure and flow rate in each circuit. Figure 4.2 illustrates the experimental arrangement. Table 4.2 provides additional information about the system.

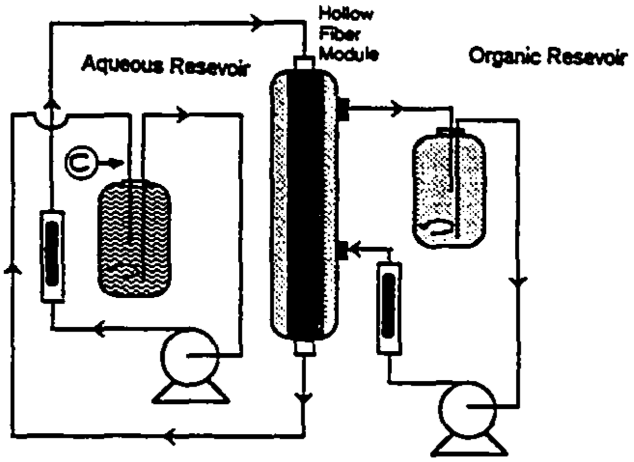


Figure 4.2 - Experimental set-up using the Hoechst-Celanese Microporous Hollow Fiber Contactor

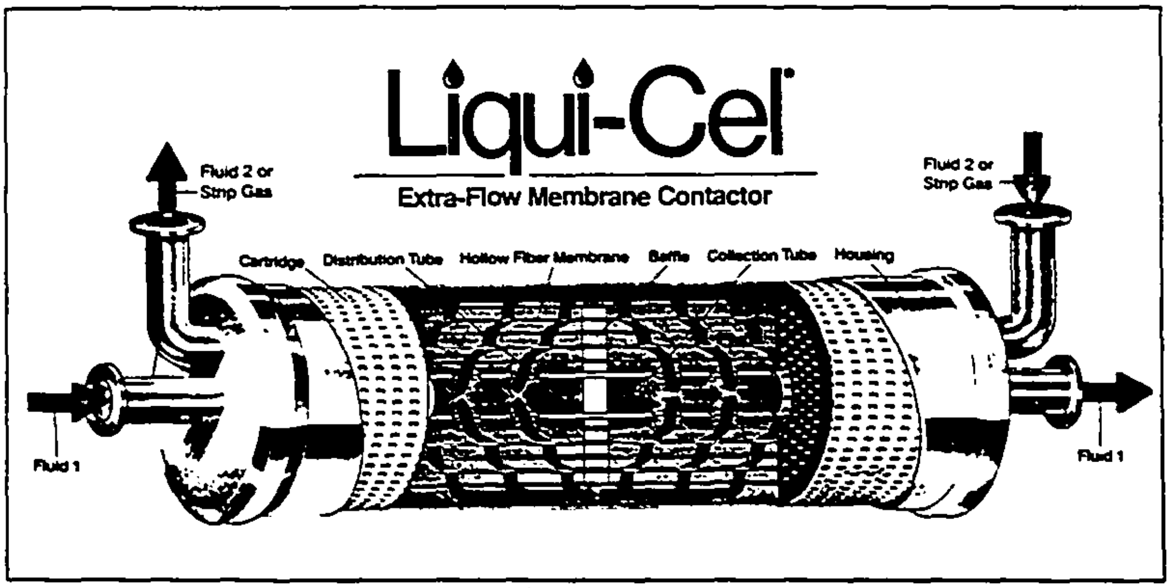


Figure 4.3 - Hoechst-Celanese Hollow Fiber Contactor

Table 4.2 - Characteristics of Hoechst-Celanese Hollow Fiber Contactor

DESCRIPTION		
Hollow fiber membrane contactor		
	Fiber type	Celgard X-30
	Material	Polypropylene (hydrophobic)
	Effective surface area	1.4 m^2
	Effective pore size	0.03 μm
Dimensions	Tubeside Volume	145 ml
	Shellside Volume	195 ml
	Length	20.3 cm
Pumping System	maximum pressure	4.1 bar (60 psig)
	Flowrate range	100-800 ml/min

Using the experimental setup depicted in Figure 4.2, 1.5 l of each solution (extractant in kerosene and metals in hydrochloric acid) are stored in a different container.

The aqueous solution is pumped and the flowrate and circuit pressure are adjusted. The aqueous side pressure is always kept at least 10 psig higher than the organic side pressure. Since the membrane is hydrophobic this procedure proved to be efficient to avoid organic leakage toward the aqueous side. The samples are taken at point "C" marked in Figure 4.2, diluted, and analyzed by AAS.

4.4 - Analytical procedures

The former work of Suriyachat (1992) and El-Ammouri (1994) used a titrimetric method to determine the concentration of zirconium or hafnium in hydrochloric acid solution. The method consisted of the back-titration of EDTA excess, added to a given solution, with bismuth nitrate and xylenol orange as indicator. This method was developed by Cheng in 1954, and is described by El-Ammouri(1994). In the present study, however, such a procedure is not suitable. The titration process cannot discriminate zirconium from hafnium. For this reason, atomic absorption spectrometry (AAS) was selected. This method was used for several years in the zirconium industry to analyze Zr and Hf, until it was replaced by inductively coupled plasma atomic emission (ICP-AE) spectrometry. This more modern technique was not available for the present work.

AAS, however, has its' limitations, particularly in the case of refractory elements for which a vast range of variables must be carefully controlled. Refractory metals are very reactive and react vigorously with the combustion gases inside the flame. Chemical interference and reaction with flame products are the most common source of problems.

4.4.1 - Determination of Zr and Hf by Atomic Absorption Spectrometry

Two types of interference are encountered in atomic absorption methods. *Spectral interference* occurs when the absorption of one or more elements overlap or lie close to the analyte, while *Chemical interference* occurs when some chemical process occurring during the atomization alters the absorption characteristics of the analyte. One example of the first phenomenon is iron interference over hafnium at 286.6 nm, if a wide slit width is used. The second phenomenon can be exemplified by reaction between the analyte and other species that can make the atomization easier or more difficult, consequently increasing or decreasing the analyte signal.

In addition to the interferences described above, there are several factors that must be controlled to keep the operational conditions stable during the analysis. Samples and standards must have the same viscosity and density to keep the same flowrate into the flame. The beam from the hollow cathode lamp must be aligned and adjusted to reach the flame at an optimum height which represents the analytes' highest absorbance. This latter is usually low for refractory metals. Successful analysis of refractory metals requires reductive conditions in the flame. They oxidize very easily, and only at high temperatures and in the absence of oxygen can their spectra be collected.

Initially, several experiments were run using standard solutions to determine the optimum conditions to operate the equipment for analysis of each element. The detection limits were determined, as well as the best wavelength, slit width, flame height, fuel-oxidant ratio and integration time. Although, at the present time, only synthetic solutions of zirconium and hafnium are being used, the role of some impurities was also assessed.

The fuel-oxidant ratio was the most important single parameter of all operational variables studied. Before each analysis, the nitrous oxide-acetylene mix was optimized to give a slightly fuel rich flame, and the observation height was taken around 10 mm above the burner top.

Dean and Rains (1975) reported a moderate signal enhancement in Zr analysis when Hf is present as a result of the formation of compounds which are more easily decomposed by the flame than zirconium oxide. This was not observed in our analysis. Such behavior is reported as very important with aluminum and iron. Niobium, titanium, molybdenum, chromium and tungsten are indicated as being responsible for large signal suppression. These phenomena demonstrate the special care that must be taken to get meaningful analytical results. The features of the equipment used in the present work are summarized in Table 4.3.

Table 4.3 - Basic specification of the AAS Perkin-Elmer 3110

Parameter		Typical Value
Wavelength	Zirconium	360.1 nm
	Hafnium	286.6 nm
Slit width		0.2 nm
HCL current	Zirconium	18 mA
	Hafnium	28 mA
Flame		Acetylene + Nitrous oxide (fuel rich, 5 cm red feather)
Distance light beam-flame base		10 mm
Sample volume		~ 4 ml
Integration time		5 s (at least 3 replications)
Detection limit (Typical)	Zr	30 ppm
	Hf	40 ppm

Some results from our operational variables study are shown below:

Ratio Oxidant/Fuel - Zirconium and hafnium are very reactive, so the amount of oxygen in the flame has to be carefully controlled to avoid formation of ZrO_2/ HfO_2 and other oxidized species. A reducing atmosphere with approximately 5 cm of 'red feather' over the burner slit was used. The fine tune was achieved by maximization of the absorbance signal, via the continuous mode (absorbance versus time) on the equipment monitor screen.

Slit width - The equipment does not allow many options (0.7 or 0.2 nm). The narrowest showed better signal-to-noise ratio. In addition there is spectral interference of iron on hafnium near 286.6 nm, the most sensitive wavelength for hafnium analysis.

Height of burner head - Due to the stability of zirconium oxide formed in the flame, the region closest to the burner tip showed the highest absorbance, approximately 10 mm above the burner surface.

HCl concentration - When acidities are increased above 3.5 M, there were no differences (less than 2%) in absorbance of solutions with same concentration of Zr. When lower acidity solution was used the Zr signal decreased with decreasing acidity.

Handling errors - Several solutions of 200 ppm Zr were prepared with different micropipets and solutions. The relative error among all absorbance values was around 3%, very close to the reciprocal of the standard deviation for the same sample repeated several times.

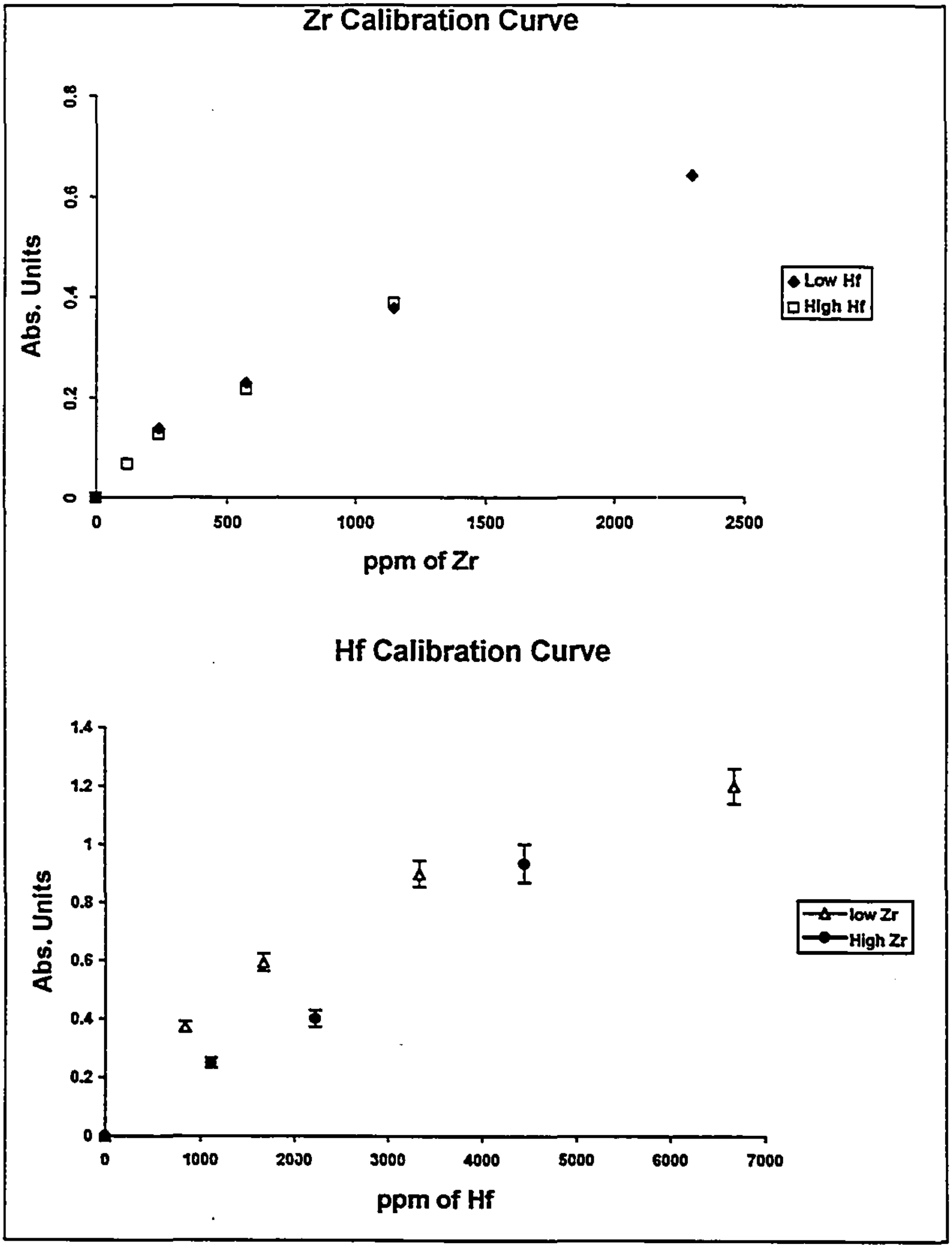
Sensitivity - A calibration curve for the range 10 - 500 ppm Zr was obtained with 14 ppm Zr/1% Abs, this being close to the literature value (10 ppm/1%Abs).

Detection Limit - During initial method setup, the detection limits within a confidence limit of 95% were evaluated as 28 ppm for Zr and 40 ppm for Hf. These figures are well below the usual concentrations for samples from all our experiments. The lamp used in this work for zirconium analysis (Hamamatsu mod# LI788-40NB) always exhibited a 'noisier' behavior than that for hafnium (Perkin-Elmer mod# 303-6032).

Poor sensitivity for zirconium and hafnium analysis is mainly due to the inefficient formation of free metal atoms. Hydrofluoric acid and iron are reported to increase the Hf signal significantly. This enhancement is attributed to a decrease in formation of hafnium oxide with a resultant increase in the concentration of free hafnium atoms. However, no element was added to increase sensitivity in the present work.

CALIBRATION CURVES AND ANALYSIS PROCEDURE

Calibration curves were built using the identical 'background acidity' solution used for the extraction experiments. This solution had been diluted for different concentrations, as needed, using a HCl solution with the same acidity as the starting metal solution. This procedure, however, introduces an additional error in the hafnium analysis due to the influence of large amounts of zirconium on the hafnium signal (see Figure 4.4). Thus, when the relative amount of zirconium in the raffinate is very far from the starting Zr/Hf ratio, the amount of hafnium is over estimated. The absolute value of this error was estimated as being lower than 10% in the extreme case of only hafnium being present in the raffinate. This error would be responsible for evaluation of smaller separation factors than the reality.



Zr Calibration Curve

Hf Calibration Curve

Figure 4.4 - Typical calibration curves for zirconium and hafnium

Table 4.4 - Typical Absorbance Readings used for Zr & Hf Calibration Curves.

ppm of Zr	Abs.Unit (low Hf)	Abs.Unit (High Hf)	ppm of Hf	Abs.Unit (low Zr)	Abs.Unit (High Zr)
			6675	1.199	0
			4450		0.934
2300	0.642		3338	0.898	
1150	0.379	0.388	2225		0.401
575	0.230	0.217	1669	0.594	
238	0.139	0.127	1112		0.250
119		0.068	835	0.373	
0	0.000	0.000	0	0.000	0.000

(high Zr/low Hf = 0.05M Zr + 0.05M Hf; low Zr/high Hf = 0.025M Zr + 0.075M Hf)

4.5 - Supplemental analytical methods for zirconium and hafnium solutions

Research on solvent extraction of refractory metals such as Zr and Hf, as well as lanthanides and actinides is usually limited by analytical capability. A major feature of these metal groups is their chemical similarity which makes it difficult to distinguish between members of a given group. In this situation, analytical methods that look for structural differences become especially important. These methods include Mossbauer, Raman, infrared (IR) and far-infrared (Far-IR) spectroscopies. Mossbauer spectroscopy is perhaps the most powerful of these alternatives, but in the case of hafnium, an expensive cryogenic system is required to host the radiation source, this being unavailable for the present study (Zr is not Mossbauer active).

RAMAN SPECTROSCOPY - Raman spectrometry is usually better than IR for investigating inorganic systems because aqueous solutions can be employed (water is not a Raman active molecule). Raman studies are potentially useful to determine composition and structure of coordination compounds. The only trial done during this study revealed differences between zirconium spectra depending on the medium (water or 11 M HCl). Such an observation is potentially useful for developing the speciation diagram for zirconium. Hafnium solutions, however, fluoresced extensively causing difficulties to get meaningful spectra.

INFRARED SPECTROSCOPY - Traditional Mid-IR spectra were used to compare differences in extractant spectra (new and old batches) and to assess the general nature of the organic phase. The O-P stretch peak disappears when zirconium or hafnium is added to the extractant (Figure 4.5). By subtracting the ligand spectrum from that of the metal-ligand (Figure 4.6) it is possible to see a small increase in the water content (1650 cm^{-1}), the complete disappearance of the pure O-P band (1152 cm^{-1}), and a fairly complex Hf spectrum, when compared with that for zirconium. The Zr-ligand and Hf-ligand solutions represent pure organophosphorous compound saturated after contact with 5 M HCl solutions, and loaded with the respective metal.

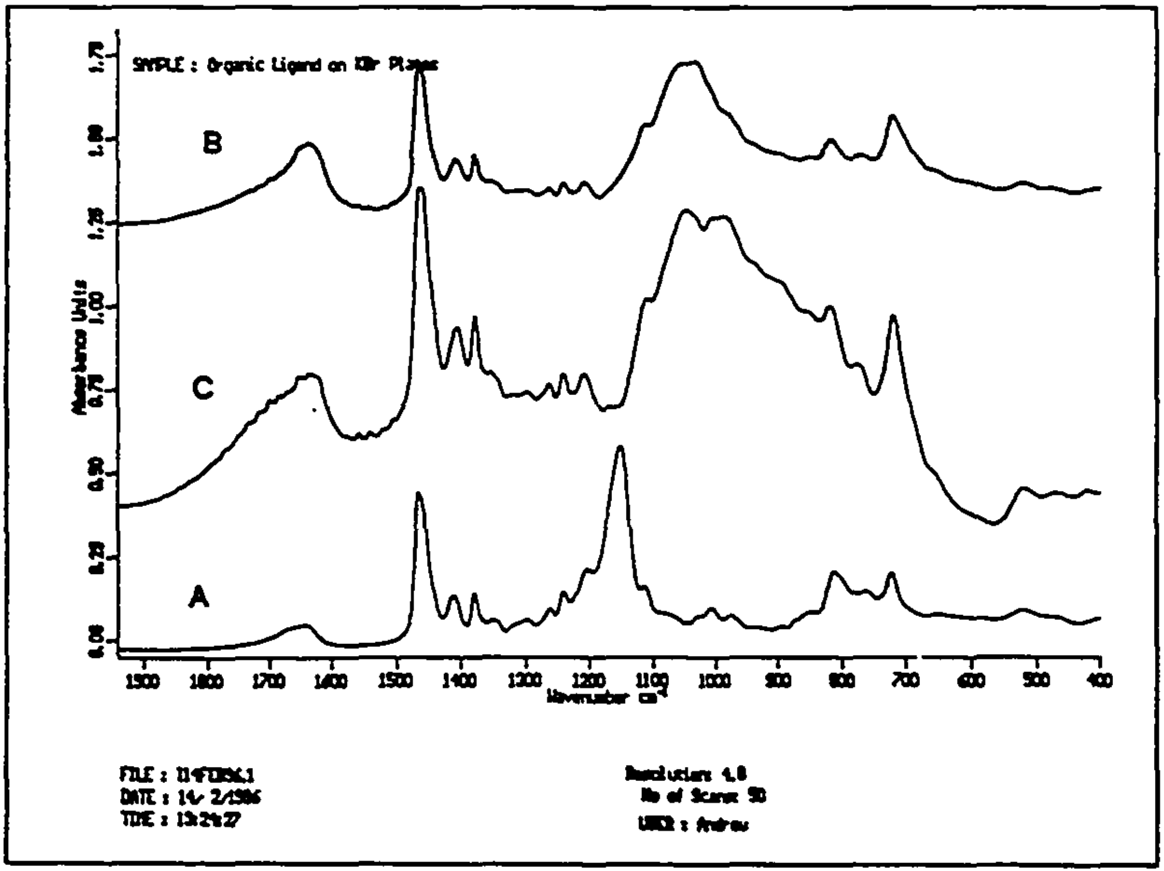


Figure 4.5 - IR spectra of organic phase (Cyanex 923 only). (A) metal-free extractant, (B) Zr-loaded extractant, and (C) Hf-loaded extractant

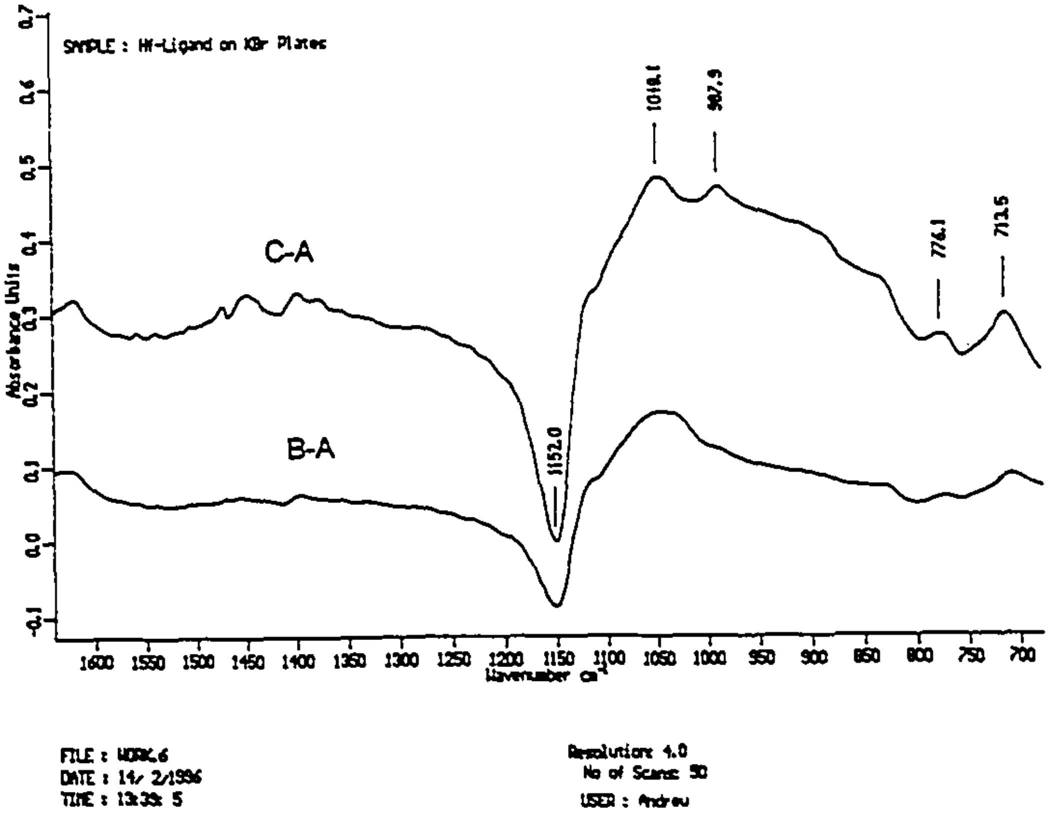


Figure 4.6 - IR spectra of organic phase subtracted from pure ligand spectrum. (B-A) Zr-loaded extractant, and (C-A) Hf-loaded extractant

FAR-INFRARED SPECTROSCOPY - Bonds between metals and both inorganic and organic ligands generally occur at frequencies lower than 650 cm^{-1}. For this reason, we found it useful to analyze our samples using FAR-IR. Since absorption by water in this region is troublesome, only the organic phase could be analyzed. This technique has only recently been implemented. Conventional spectroscopes that use dispersive systems are complicated to operate in this region due to interference, low energy throughput and the overlapping of different orders of the diffracted radiation. It was only after the development of Fourier transform spectrometers, with interferometric systems that improvement in spectral quality became possible.

Figure 4.7 shows the FAR-IR spectra of pure Cyanex 923, unloaded and loaded with Zr or Hf. It is possible to see an important shift of the 371.8 cm^{-1} peak. In the case of Zr-loaded material. the peak appears at 312.5 cm^{-1} and at 287.3 cm^{-1} when loaded with Hf. This observation represents a good opportunity to differentiate the metals in the organic phase. The intensities, however, were weak and use of this technique was not pursued in detail.

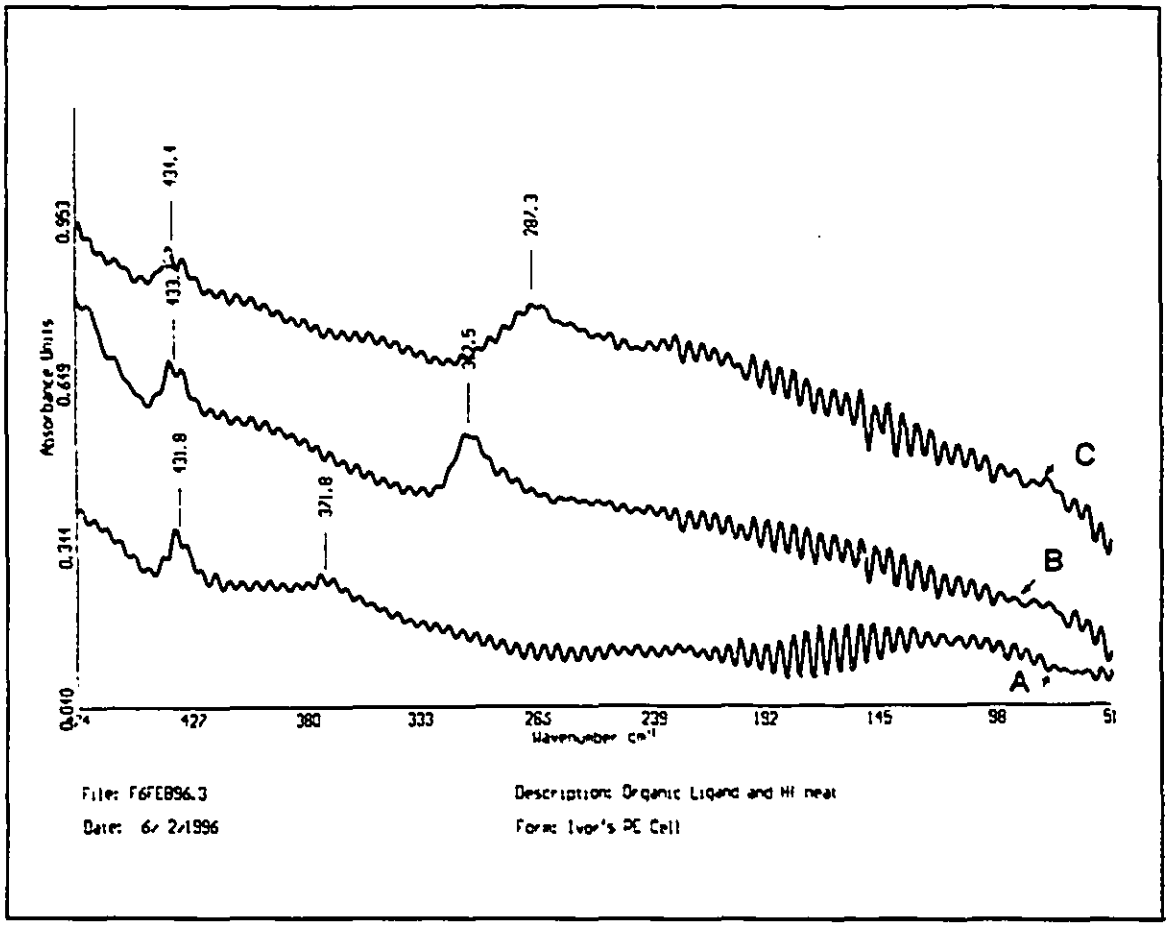


Figure 4.7 - Far-IR spectra of organic phase. (A) metal-free extractant, (B) Zr-loaded extractant, and (C) Hf-loaded extractant

Chapter 5

Results and Discussion

5.1 - Process development pathway

Few extractants have been tested for zirconium and hafnium separation. Tributylphosphate (TBP), methyl-isobutyl-ketone (MIBK), dibutyl-butyl-phosphonate (DBBP), and trioctylphosphine oxide (TOPO) are the most important that have been studied for this application. Initially, TOPO (White and Ross, 1958) seemed to be a good alternative for MIBK to separate zirconium from hafnium, but third phase formation, i.e., the segregation of the loaded extractant inside the organic phase, even at moderate metal concentration, decreased interest in TOPO.

At the beginning of our study, four extractants were tested: TBP, DBBP, and two phosphanes (Cyanex 923 and Cyanex 925). The excellent results achieved by Cytec's (formally Cyanamid) phosphanes encouraged us to perform a more complete study using only these latter reagents.

Earlier work using zirconium and hafnium in pure solutions (Suriyachat, 1992, and El-Ammouri, 1994) identified large metal extractions at high concentration of hydrochloric acid. However, an important difference was later observed in the extraction profile of Zr and Hf around 3 to 4 M HCl, as can be seen in Figure 5.1. At high acidities, although metals extraction is large, the separation factor between Zr and Hf was fairly low. Following these observations, we decided to approach the separation problem in such a way as to avoid the use of any complexing agent, and at the lowest possible acid level. Initially, we began taking advantage of differences in metals' speciation at equilibrium against the acidity of the aqueous phase. Eventually, differences in loading kinetics began to be assessed.

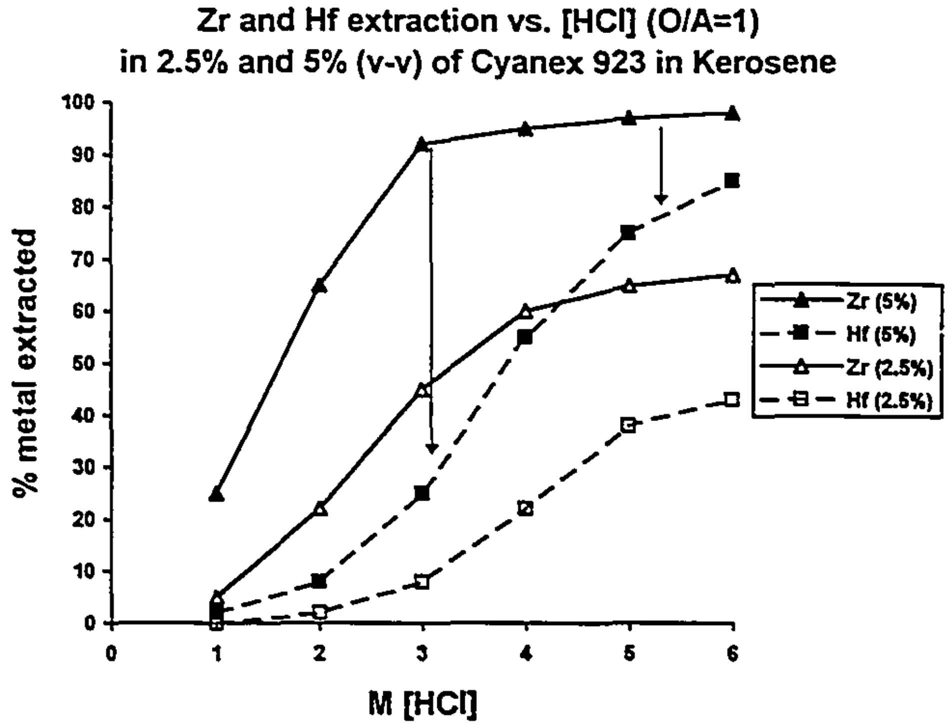


Figure 5.1 - Extraction behavior of single element solution (0.05 M Zr and 0.05 M Hf) against acidity level (Suriyachat, 1992, and El-Ammouri, 1994)

The aqueous medium was selected to avoid incompatibilities with the commercial raw material supply - zirconium (hafnium) tetrachloride, from zircon carbochlorination. The acidity range was studied to achieve the maximum separation factor. Fortunately, it was possible to attain remarkable separation factors in a commercially suitable range, between 3 and 4 M HCl. It is important to note that zirconium solubility decreases sharply with acidity, but at the 3 to 4 M HCl level it is possible to reach around 1 M of metal in the aqueous feed. Another important point favoring working at low acidities is the extractant stability, and low water and acid pick-up.

Several experiments were done to assess the significance of kinetics on the extraction process. It was determined that zirconium is transferred to the organic phase faster than is hafnium. Such an observation led to some ideas to maximize the extraction efficiency in a continuous circuit. Preliminary studies on stripping of the loaded organic were also done. It was observed that zirconium and hafnium are easily stripped from the extractant. Nevertheless, it is possible to strip hafnium selectively and later zirconium. Such a fact is important in improving the quality of the end products.

An initial comparison of the phosphanes raised several questions. The process using Cyanex 923 has an optimum acidity at 2.5 M HCl. When Cyanex 925 is used this level has to be increased to 3.5 M. This was one factor favoring use of the former extractant. On the other hand, Cyanex 923, similarly to TOPO, shows third phase formation when the metal concentration in the loaded organic increases. To avoid this phenomenon, we tested n-decanol as modifier, and the problem was solved. It was determined that 4% was the optimum modifier concentration. However, at this level, the alcohol competes with the metal compounds for the phosphoryl groups, so decreasing the metal extraction. On the other hand, Cyanex 925 did not show any problem of third phase formation, even when 0.5 M metal concentration was tested.

5.2 - Establishment of Equilibrium

Some experiments of Suriyachat and El-Ammouri were repeated and the fairly fast approach to equilibrium and the equilibrium conditions were confirmed. The Zr 'plateau' was achieved in less than 5 minutes, and for Hf, this equilibrium was achieved in less than 10 minutes. In the present work, the shaking time of the "shake-out" experiments was set at 20 minutes to be conservative, this also being the conditions chosen by the above cited workers.

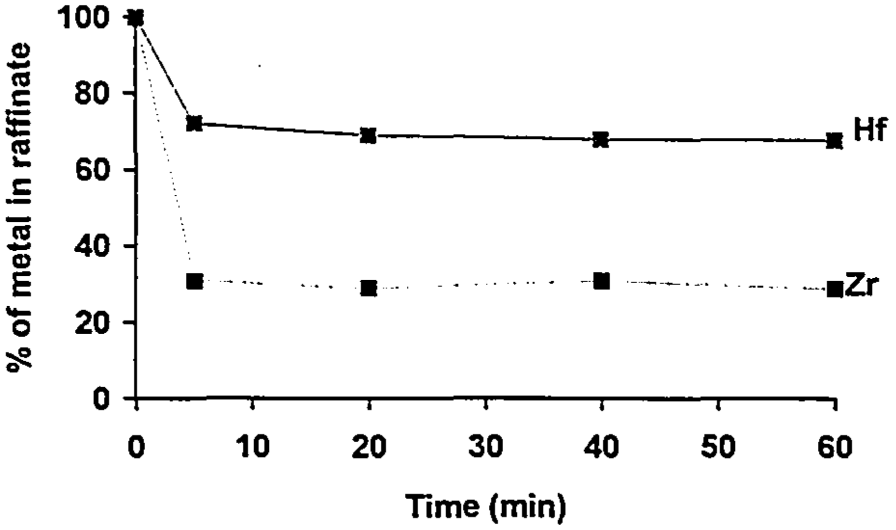


Figure 5.2 - Kinetics of zirconium and hafnium extraction from 0.1 M Zr and 0.01 M Hf in 2.5 M HCl into 0.23 M Cyanex 923 in kerosene

5.3 - Behavior of different extractants

Extractant selectivity is an important issue in the solvent extraction field. Several studies in analytical chemistry (Deorkar, 1992) and in engineering fields (Nandi, 1983, and Rickleton, 1988) deal exclusively with it. Commercial constraints, however, reduce dramatically the number of options available for industrial use. As discussed in Chapter 3, the search for an ideal strength of the metal-extractant bond is an important issue in the selectivity of any process, and is the basis of the development of tailor-made solvents that has been pursued by Cytec Canada Inc. and other companies all over the world.

We chose to test four different commercially available extractants. The idea was to identify the level of basicity which gave the highest selectivity and metals extraction consistent with zirconium and hafnium separation, and under reasonable operational conditions.

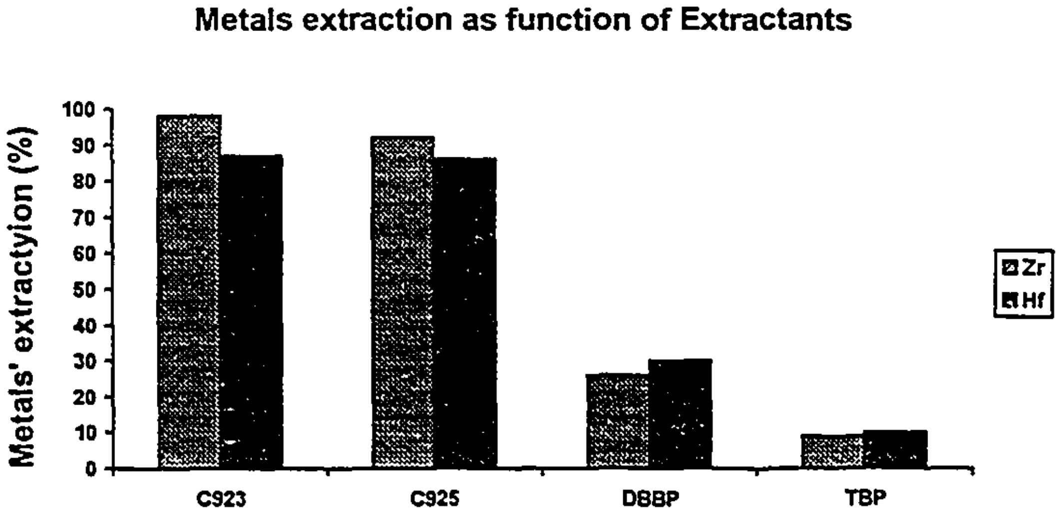


Figure 5.3 - Extraction of Zr & Hf against different extractants at maximum realistic acidity (O/A=1, 10% v-v of extractant in kerosene,[Zr]=[Hf]=0.05 M and [HCl] = 4.6 M)

The results achieved by Cytec's phosphanes were better than the results attained by the less basic extractants (DBBP and TBP) which showed poor extraction data, as we can see in Figure 5.3, above. These comparative tests were done under conditions considered at the time, as limiting. The acidity was set at the highest desired level and the zirconium to hafnium ratio corresponded to 95% of zirconium recovery (i.e., representing a solution with 50% of Zr and 50% of Hf, molar basis)[1]. The results achieved by both phosphanes were better than the commercial TBP process, running at high concentration of nitric acid (6N). No further work was done with DBBP and TBP.

5.4 - Effect of hydrochloric acid concentration

Although the best extraction of zirconium and hafnium occurs at higher acidities, a comparison of single element extraction curves shows, an important difference in the behavior of Zr and Hf between 2 and 4 M HCl, as seen in Figure 5.1 for Cyanex 923. As observed by El-Ammouri, at high acidities the separation factor between Zr and Hf should

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[1] A typical industrial starting solution has 98% of Zr and 2% of Hf (molar basis)

be fairly low. This reason led him to propose the use of thiocyanic compounds at high acidity to perform the separation of the two elements. The approach of the present work, however, was to avoid the use of any complexing agent and try to take advantage of the previously mentioned differences within the 2 M to 4 M HCl range.

In Chapter 3, we showed results relevant to single element solutions. Those extraction data will now be compared with mixed solutions of zirconium and hafnium. Tables 5.1 and 5.2 exhibit the results of shake-out tests using Cyanex 923 and Cyanex 925. In these tests, zirconium and hafnium were added to hydrochloric acid solutions at different initial acidity, and contacted under mechanical agitation for 20 minutes with an organic phase at different organic to aqueous ratios. The variation in the O/A corresponded to molar ratio extractant/metal between 1 and 6. Assuming the extraction of di-solvates, these ratios correspond to 50%, stoichiometric, 100% and 200% of the extractant amount required to extract the metal present in the aqueous phase.

Table 5.1 - Metal Extraction (%) from mixed solutions (0.1 M Zr + 0.01 M Hf) into Cyanex 923 in kerosene (0.26 M).

HCl	*Zr extraction (%)*				*Hf extraction (%)*			
[Cy923]/[Metal] ⇒	**1**	**2**	**4**	**6**	**1**	**2**	**4**	**6**
1.1 M		33				12		
2.3 M	35	85	97	99	22	42	93	99
4.2 M		88				63		

Table 5.2 - Metal Extraction (%) from mixed solutions (0.1 M Zr + 0.01 M Hf) into Cyanex 925 in kerosene (0.23 M).

HCl	*Zr extraction (%)*				*Hf extraction (%)*			
[Cy925]/ [Metal]	**1**	**2**	**4**	**6**	**1**	**2**	**4**	**6**
2.5 M	11	26	46	60	0.5	3	12	18
3.5 M	43	61	79	89	1.5	4	18	31
4.5 M	54	90	98	99	7.4	44	86	95

A more detailed comparison of the above results are shown in Tables 5.3 and 5.4, where the distribution coefficient, D_{metal} is given (i.e., the ratio of the metal concentration in the organic over aqueous phases for given conditions at equilibrium). The separation factor ($\alpha_{Zr/Hf}$) between zirconium and hafnium, also exhibited, corresponds to the ratio of distribution coefficients of each element for the same conditions.

Table 5.3 - Distribution Coefficients and Separation factors for mixed solutions (0.1 M Zr + 0.01 M Hf) using Cyanex 923 in kerosene.

HCl	D_{Zr} / D_{Hf}				$\alpha \equiv D_{Zr}/D_{Hf}$			
[Cy923]/[Metal] ⇒	1	2	4	6	1	2	4	6
1.1 M		0.493 0.136				3.6		
2.3 M	0.538 0.282	5.667 0.724	32.33 13.29	99.00 99.00	1.9	8	2.4	~1
4.2 M		7.333 1.702				4.3		

Table 5.4 - Distribution Coefficients and Separation factors for mixed solutions (0.1 M Zr + 0.01 M Hf) using Cyanex 925 in kerosene.

HCl	D_{Zr} / D_{Hf}				$\alpha \equiv D_{Zr}/D_{Hf}$			
[Cy925]/[Metal] ⇒	1	2	4	6	1	2	4	6
2.5 M	0.120 0.005	0.351 0.031	0.852 0.136	1.500 0.220	24	11	6.5	6.5
3.5 M	0.754 0.015	1.564 0.042	3.762 0.220	8.091 0.449	50	37	17	18
4.5 M	1.174 0.080	9.000 0.786	49.00 6.142	99.00 19.00	15	11	8.0	5.2

The extraction of zirconium and hafnium is governed by the chloride and acid level. However, since hydrochloric acid is the only source of chloride in our study, increasing acidity also represents increasing extraction. In addition to promoting formation of the neutral chloride complex, a very important purpose of the solutions' acid level is to avoid hydrolysis and polymerization reactions. The chloride content that governs the metals' speciation in solution could also be increased by chloride salts addition. In a commercial process, this practice would be restricted due to the need to control as much as possible contamination in the subsequent precipitation step, so improving the quality of the final products. The other factor governed by the acid level is the equilibrium between aquation and solvation, i.e., the extraction itself. In the case of our study it seems possible to reach fairly high separations factors by adjusting only the acidity level. One possibility, described by White and Ross (1958), but not explored in our work, is the use of aluminum chloride (more hydrophilic) or magnesium chloride (less hydrophilic) as salting-out agent to enhance or inhibit the extraction independently of the acid level. However, from the operational point of view, the ability to optimize the process by setting only the acidity level is the ideal situation.

Single element versus mixed solution comparison

In this section, the behavior of each single element solution is compared with mixed solutions containing zirconium and hafnium. In Figure 5.4 we plot the mixed solutions results from Table 5.3 (marked as #) together with the data presented in Chapter 3 for extraction of zirconium and hafnium from single element solutions (Figure 3.4). It is possible to observe that the results for zirconium are essentially identical. The same does not occur for hafnium. In a mixed solution containing 0.1M Zr, the extraction of 0.01 M Hf is suppressed by extractant unavailability and the faster zirconium loading kinetics, as will be discussed in Section 5.5. The extractant availability at the organic/aqueous interface is also an important variable affecting selectivity.

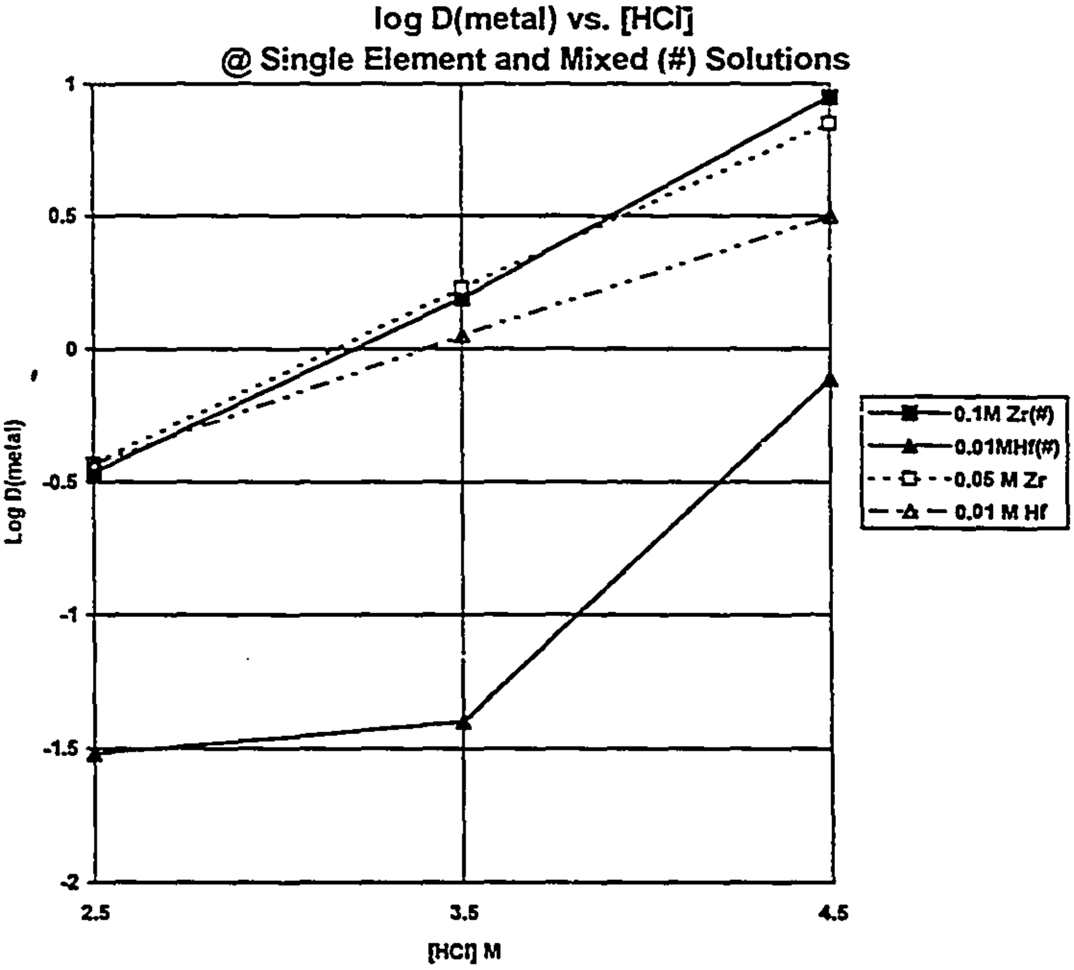


Figure 5.4 - Distribution coefficient of Zr & Hf versus initial acidity for single element and mixed metal solutions using 0.26M Cyanex 923 in kerosene (stoichiometric requirement)

Figure 5.5, on the next page, summarizes the general extraction behavior of Cyanex 925/HCl system, when both zirconium and hafnium co-exist in solution. The point of this Figure is that it shows 3.5 M HCl as optimum conditions for Cyanex 925 to separate zirconium from hafnium while maintaining a reasonable Zr extraction.

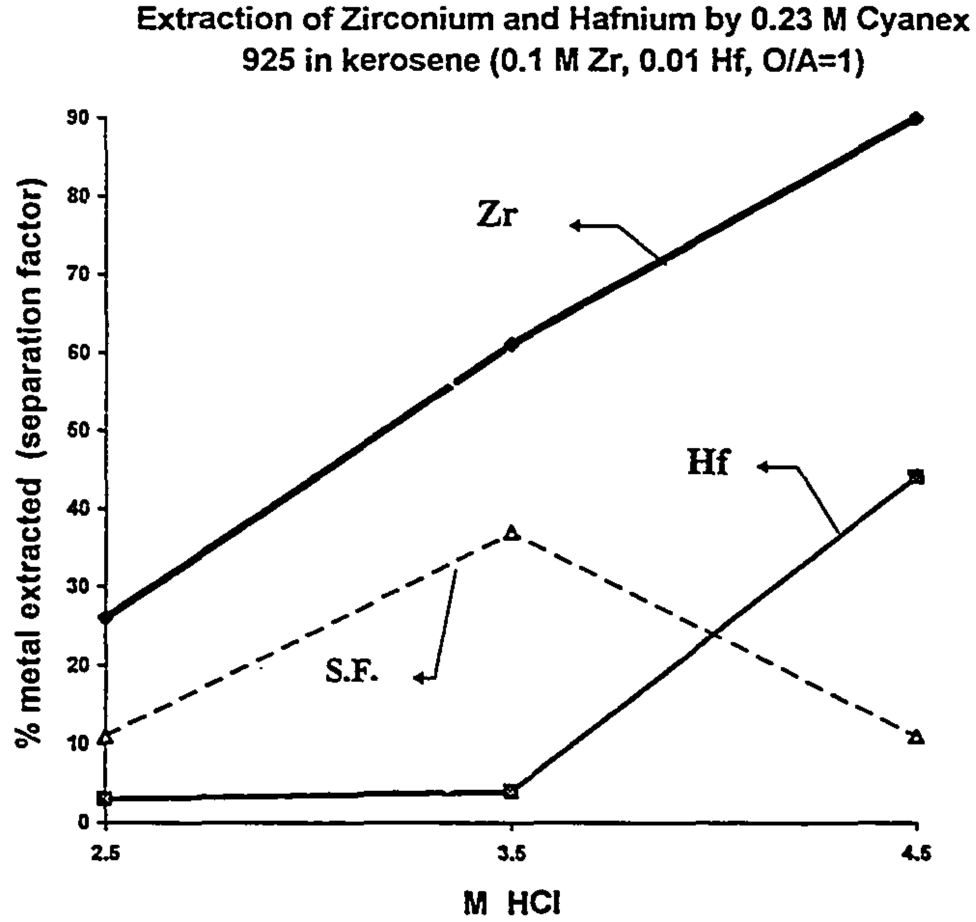


Figure 5.5 - Metals extraction and separation factor versus acidity level

To further understand hafnium behavior, we plot only hafnium data in Figure 5.6. in which all curves represent a Hf concentration of 0.01 M, either in pure solutions or in mixed solutions with 0.1 M Zr (marked as "#"). The '#' curves correspond to two different amounts of extractant which is increased from the stoichiometric amount (counting both metals) to 100% of excess.

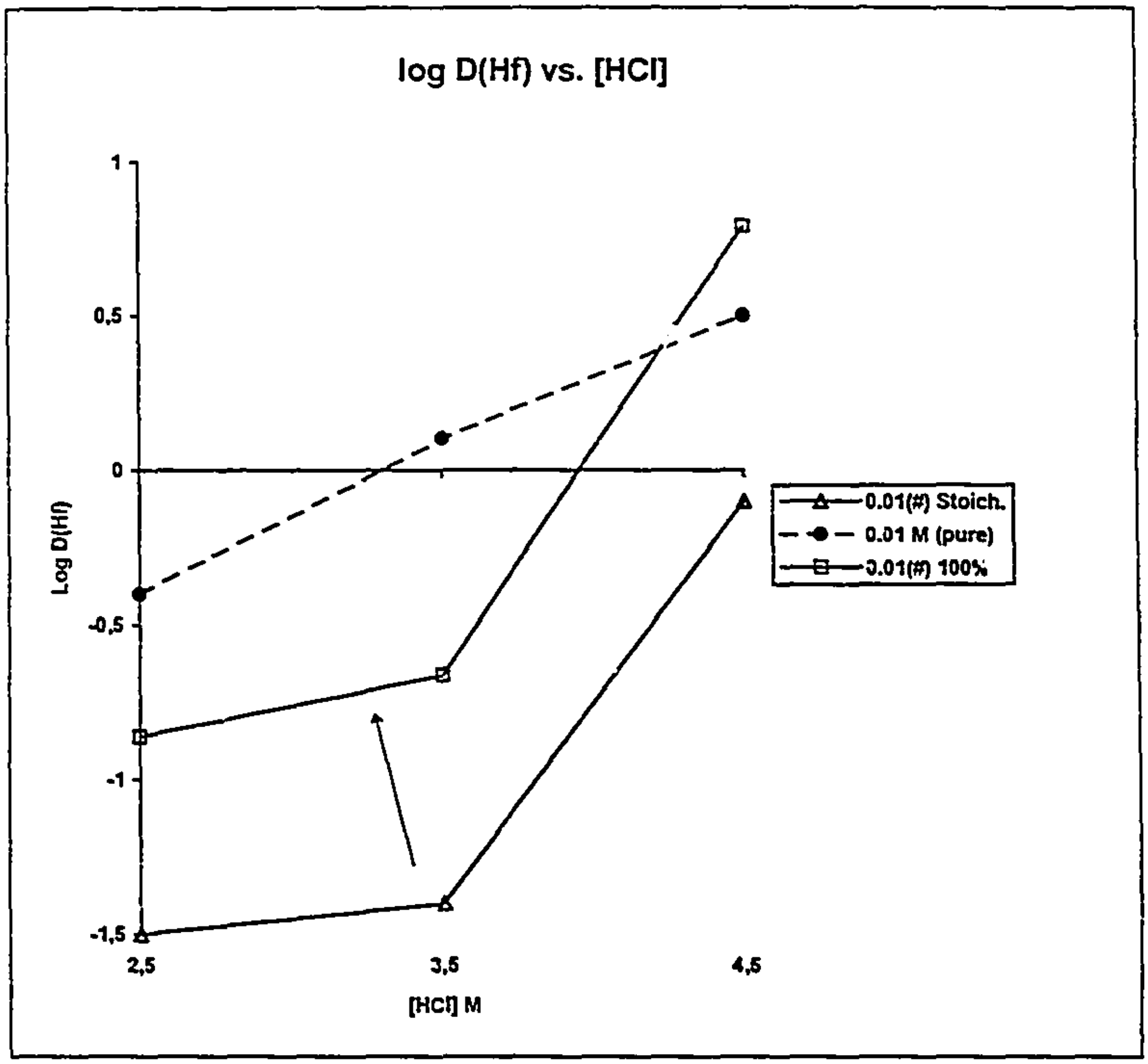


Figure 5.6 - Log of distribution coefficient of Hf versus initial acidity as function of the extractant concentration (Cyanex 923) for mixed (#) metal solutions (100% excess and stoichiometric) and single element (pure) solution (stoichiometric) at same Hf content

The main goal in studying high metal concentrations is to evaluate industrial conditions for which the assumption of constant extractant level is invalid. In such a condition, polymerization reactions influence extraction, while at the acidity levels industrially used, several different chemical species co-exist representing a long chain of equilibria being established during the extraction process, as we saw on Table 3.1. The most important conclusion of Figures 5.4 and 5.6 is the availability of the extractant at the organic-aqueous interface, this being especially important in explaining the extraction process.

5.5 - Effect of temperature

Since the separation process envisioned is based both on equilibrium considerations and on the velocity to reach this equilibrium, temperature should be an important variable. Some experiments were performed to evaluate this point. The first trial was done with Cyanex 923 and the direct interface set-up (Figure 4.1). Two experiments were run at 21°C and at 40°C for 8 hours. The results showed the amount of zirconium transferred to the organic phase increased by 20% (17% to 21%), while the amount of hafnium transferred was decreased by 35% (9% to 5%). Sato (1970), working on the extraction of 0.01 M Zr from 4 M HCl by TOPO showed that by increasing the temperature, the distribution coefficient increases (20°C, 3.1; 30°C, 6.81; 40°C, 8.31 and 50°C, 14.1). Another important feature of running the system at higher temperature is a decreased organic viscosity and a decreased probability of third phase formation. Thus, the indications are that a better separation could be obtained using warm solutions.

5.6 - Kinetic effects during extraction

It has already been shown that both Zr and Hf achieve loading equilibrium very rapidly, so that kinetic studies require a different methodology that the "shake-out" test can not provide. The first trial to assess extraction kinetics used the direct interface scheme, described in Section 4.3. Figure 5.7 represents mass transfer to the organic phase from a 0.1 M Zr, 0.01 M Hf mixed solution.

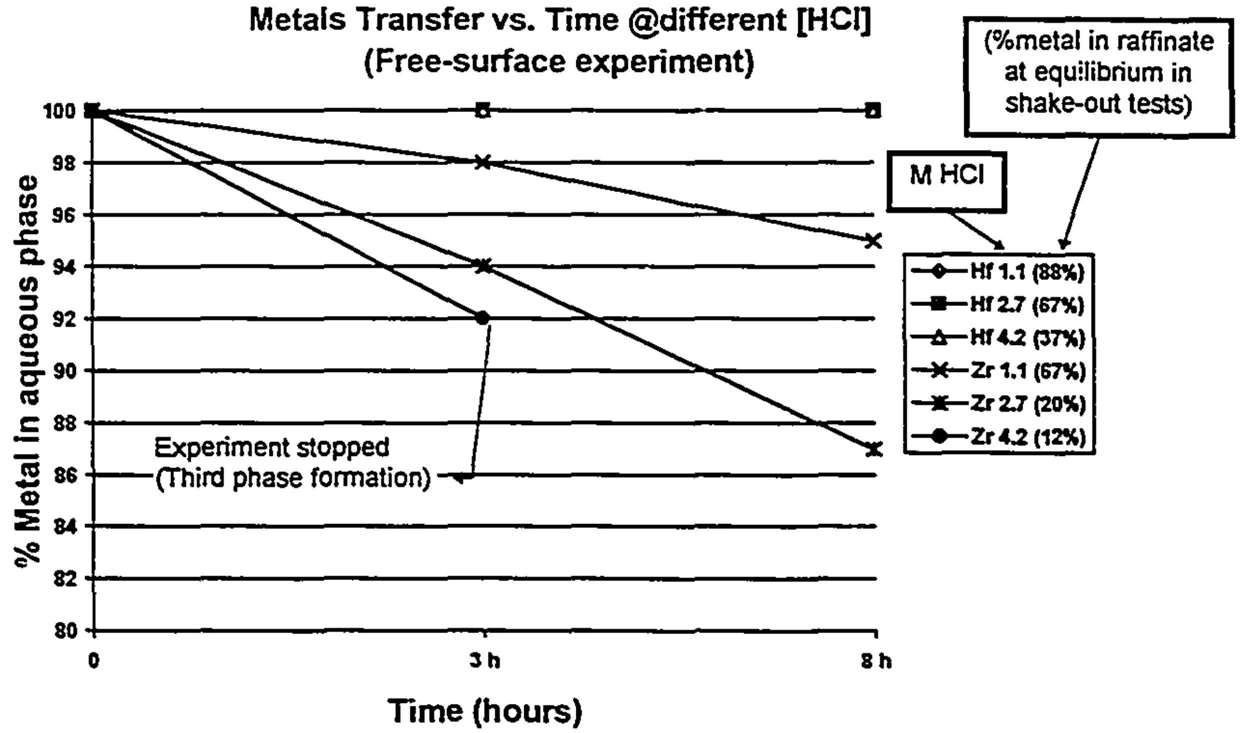


Figure 5.7 - Comparison between zirconium and hafnium loading kinetics using the direct-interface scheme (0.26 M Cyanex 923).

Figure 5.7 shows that while up to 12% zirconium is transferred to the organic phase (0.26 M Cyanex 923 in kerosene), no detectable amount of hafnium is transferred under any of the conditions shown.

A similar experiment was carried out using the membrane contactor system described in section 4.3. The data below represent the variation in concentrations of 0.1 M (9200 ppm) Zr, 0.01 M (1780 ppm) Hf, 2.5 M HCl, against time. The organic phase was 0.26 M Cyanex 923 in kerosene. The organic phase was pumped through the shell side (350 ml/min) and the aqueous phase through the tubes (205 ml/min). Both solutions (1.5 l) were circulated for 5 hours.

Table 5.5 - Zr and Hf transfer from 0.1 M Zr, 0.01 M Hf, 2.5 M HCl to 0.26 M Cyanex 923 in kerosene versus time in a Liqui-Cel Membrane Contactor

	Time (min)							
ppm in aqueous	**0**	**20**	**40**	**60**	**120**	**180**	**240**	**300**
[Zr]	9200	7800	7300	6800	5400	4200	3600	3000
[Hf]	1780	1760	1740	1720	1700	1600	1550	1500

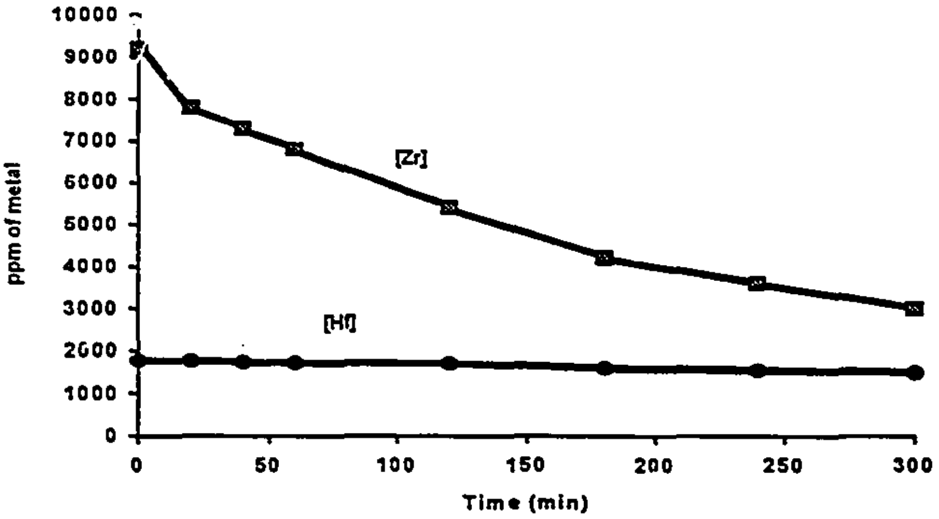


Figure 5.8 - Extraction of 0.1M Zr and 0.01 M Hf and 2.5 M HCl solution contacted with 0.26 M Cyanex 923 in a membrane Contactor

It was possible to see an important difference in extraction behavior. Zirconium extraction started rapidly, then showed a declining transfer rate, while hafnium transfer was slow. After five hours, around 67% of zirconium was extracted and only 12% of hafnium was co-extracted. Such behavior corresponds to a separation factor of 15, this being two-fold the separation factor obtained by the 'shake-out' tests (see Table 5.3). Clearly this difference is attributable to faster zirconium transfer kinetics.

5.7 - Effect of Solution Age

Since polymerization is always considered to be an important effect in zirconium and hafnium chemistry, it is logical to inquire why the polymer formed would not be a mixed (Zr and Hf) entity. In such a situation, the separation of zirconium and hafnium would be fundamentally impossible. The experiment below tries to answer this question. Mixed polymer formation, as relevant for us, would have to occur within about one week for this effect to be significant. This is because it is uncommon for a commercial solution to stay more than one week in the tanks of an industrial process.

The aging experiments were done through comparison of extraction results from solutions freshly prepared and after 7 days kept at 50°C. Four solutions of zirconium and hafnium in 2.3 M HCl were contacted with a solution of 0.26 M Cyanex 923 (10% v/v) in kerosene and an organic-aqueous ratio of one.

For purposes of comparing extraction response of 'new' and 'old' solutions, it was found sufficient to compare absorbencies only without incurring the uncertainties involved in calculating extractions. This is because we are comparing the raffinate absorbence figures for the same starting solution with the only difference being the storage time before extraction. Table 5.6 shows no significant differences in raffinate absorbance values following extractions after storage for up to one week, at 50°C. It seems that mixed complex formation is unlikely to reduce selectivity in a commercial process, at least inside a one week period.

Table 5.6 - Aging experiment. Absorbences of raffinate solutions.
New (fresh) and Old (after 7 days at 50°C)

	[Zr]	**[Hf]**	**Abs(Hf)$_{new}$**	**Abs(Hf)$_{old}$**	**Abs(Zr)$_{new}$**	**Abs(Zr)$_{old}$**
A	0.1 M	0	-	-	0.497(2)	0.476(1)
Ab	0.1 M	0.01 M	0.239(2)	0.222(15)	0.520(2)	0.515(4)
AB	0.05 M	0.05 M	0.501(7)	0.494(8)	0.185(5)	0.183(2)
B	0	0.1 M	0.732(12)	0.750(6)	-	-

Note: Standard deviation inside parenthesis

5.8 - Studies on stripping loaded organic

In a solvent extraction process, metal stripping can be as important as extraction efficiency. Very stable solvates sometimes make an otherwise attractive extractant unsuitable for practical use. Several chelates lie in this category. In this section we will discuss briefly the stripping of our loaded organic and speculate about the possibilities of a selective stripping (scrubbing).

The zirconium extracted by phosphanes will probably contain more hafnium than desirable (i.e., 100 ppm, metal basis). Re-washing the organic phase with hydrochloric acid might logically be expected to produce re-extraction (scrubbing) of a portion of zirconium, hafnium and impurities by the aqueous phase. The extraction coefficients during scrubbing should be similar to those in the extraction operation itself. Scrubbing could be an important step to further purification of zirconium.

A series of experiments was run to evaluate scrubbing and stripping operations. A loaded Cyanex 923 was contacted with different aqueous hydrochloric acid solutions (0.4, 1, 1.8 and 3 M). Table 5.8, below, shows the results of the stripping experiments.

Table 5.7 - Stripping of 0.26 M Cyanex 923 loaded with 0.055 M Zr and 0.0015 M Hf by hydrochloric acid solution at O/A = 1

HCl ⇒	**0.4 M**	**1 M**	**1.8 M**	**3 M**
Zr stripped	90%	80%	50%	10%
Hf stripped	90%	90%	80%	15%

Despite accumulated errors, which increase to 10% the relative errors of Table 5.7 data, it is possible to anticipate an easy stripping (at 0.4 M HCl, to avoid hydrolysis) and a fairly efficient scrubbing (around 1.8 M HCl). However, further studies should be made to evaluate the scrubbing/stripping steps in continuous operation. Zirconium, hafnium and impurities could build-up in the organic phase, and this accumulation could prevent their complete recovery (Huré, 1955).

5.9 - Effect of Relative Ratio of Metals

The majority of this work was done using the same concentrations ratio of zirconium/hafnium ([Zr]/[Hf]=10). This figure was chosen to represent an intermediate value between the feed ratio (50) and a reasonable raffinate ratio (one, as in TBP process). Table 5.8 shows the behavior of the separation factor that would be expected towards the final loading stage where the relative amount of hafnium begins to exceed that of zirconium. To perform these experiments, we used the same ionic strength of solutions, same acidity and same organic/aqueous ratio. The extractant was Cyanex 925, for which optimum separation is at 3.5 M HCl (Figure 5.5).

Table 5.8 - Typical extraction figures for Zr/Hf extraction by 0.23 M Cyanex 925 in kerosene (10% v-v) at 3.5 M HCl at same total metal concentration (O/A =1)

M Zr	M [Hf]	%Extraction of Zr	%Extraction of Hf	Separation Factor
0.1	0.01	61	4	37
0.05	0.05	91	25	30
0.25	0.75	93	40	20

Such observations make it possible to anticipate that a process based on Cyanex 925 will perform better than a TBP process, where equal molar raffinate ([Zr]/[Hf]=1) was the best result achieved (Huré, 1955 and Benedict, 1980).

5.10 - Effect of other parameters

The development of a viable process is more complex than just creating an efficient separation. More than thirty other processes were already developed to separate Zr from Hf, but only three have been used commercially. Economics plays a fundamental role, and several other parameters not discussed so far must be evaluated in an integrated way. In the next sections we will analyze some of these parameters that have to be taken into account during the long scale up process from bench scale studies to an eventual industrial application.

Role of the Diluent

The effect of diluent on extraction by organophosphorous compounds is considered unimportant by Markus (1969). He argued that this is due to the fact that the acid bonding of the phosphoryl oxygen is of considerable strength. Thus, the interaction between the extractant and the diluent is apparently too weak to interfere with the high affinity of the extractant toward acids (the metals). However, in the case of aliphatic hydrocarbons, Markus reports that at a given HCl level, the concentration of TBP at which third phase formation occurs, decreases as the molecular weight of the diluent increases.

It was reported by Sato (1970) that the extraction of zirconium using TBP varies according to the diluent used. The distribution coefficient, according to him, increases by 30% with TBP/6 M HCl when hexane is used instead of kerosene. In order to evaluate the importance of the diluent in the present system, hexane was also chosen as a possible substitute for kerosene. However, the behavior described by Sato was not verified for Cyanex 925/4.5 M HCl, as we can see in Table 5.9. Most experiments showed essentially the same results for a given dilution level, except in the case of 5% v-v Cyanex 925 in kerosene, where Hf extraction seems anomalously high. This latter behavior was observed more than once, and could be related to a better distribution of the extractant at the organic-aqueous interface. The subject, however, was not investigated in more detail.

Table 5.9 - Effect of the diluent and the extractant dilution on extraction (A/O=1)

Extractant dilution	Zr extracted	Hf extracted
5% in Hexane	95%	52%
10% in Hexane	95%	55%
5% in Kerosene	99%	63%
10% in Kerosene	93%	53%
20% in Kerosene	95%	47%

Aqueous solution: 0.1M Zr and 0.01 M Hf in 4.5M HCl;

Effect of modifier addition on Cyanex 923 performance

Before finalizing the choice of Cyanex 925, we tried to solve the third phase formation problem with Cyanex 923 by using n-decanol, as modifier. However, not only could this additive avoid third phase problems, it might also affect the selectivity of Zr extraction over that of Hf. In addition, the design of a process to replace that with MIBK has to take into account any reduction in loading capacity that may result from modifier addition.

First, we determined the minimum amount of modifier required to eliminate third phase formation in fully loaded organic. An amount between 4 and 6% of n-decanol by volume was enough for this purpose. Second, the effect of such an addition was determined as not being deleterious to the selectivity. In reality, it seems that the selectivity increased by 20%. Nevertheless, under these conditions using 4% n-decanol, the loading capacity of Cyanex 923 decreased by about 50%. Only 30% of zirconium was extracted against 65% without modifier. At this time, we decided to select Cyanex 925, and optimize its use.

Water and Acid pick-up

Acid pick-up depends, usually, on acid concentration in the aqueous phase. Strong acids such as hydrochloric acid, are extracted as the hydronium ion (H_3O^+), usually retaining a primary hydration shell containing three water molecules, similar to the structure prevailing in water. The phosphoryl oxygen coordinates to the water molecules and usually (e.g. in TBP systems) is not directly coordinated to the proton. Diamond and coworkers cited by Markus (1969) provide a plausible explanation for this phenomenon. In HCl systems, the bond between the chloride ion and protons is weak, so that the bonding between protonated water and the phosphoryl oxygen governs acid extraction.

The solubility of water in the extractant, when no acid is present, is reported in Table 4.1, as being 7% for Cyanex 923 and 3% for Cyanex 925. Further tests were run with both extractants to determine water and acid pick-up when HCl is present. Cyanex

923 was chosen initially since it exhibits a higher water content (7%) as delivered than Cyanex 925. The procedure followed was to contact 40 ml of the organic solution (approximately 10 mMoles of extractant) and 10 ml of aqueous phase in a closed graduated cylinder. The graduated cylinder was agitated vigorously for two minutes and the new volume and acidity level of the aqueous phase were measured. The results are recorded in Table 5.10.

Table 5.10 - Water and Acid Pick-up in 10% Cyanex 923 (0.23 M) and 10% Cyanex 925 (0.26M) in Kerosene

Initial Acidity (M HCl)	**Volume Variation in Aqueous phase**	**Final Acidity (M HCl)**	**Acid Extracted mol HCl/ mol Cyanex 923**	**Acid Extracted mol HCl/ mol Cyanex 925**	**Acid Extracted mol HCl/ mol TOPO (#)**
0	not detected	0	-	-	-
1.2	not detected	1.1	~10	-	2
2.7	not detected	2.4	~30	-	10
3.5	not detected	3.3	-	~20	15
4.8	not detected	4.4	-	~40	20

(#) White and Ross (1961)

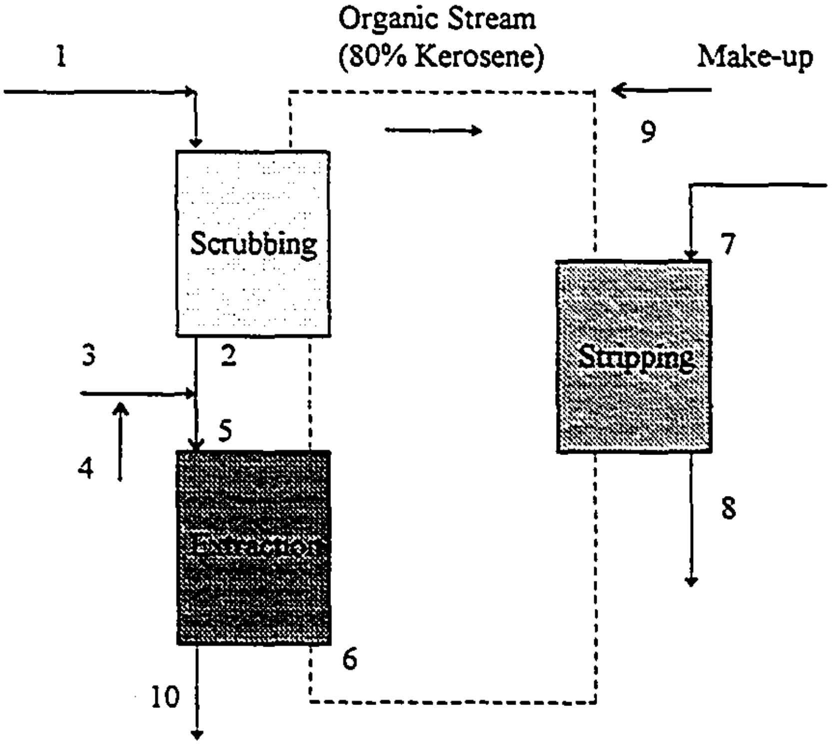
Since the solvent is delivered already saturated with water no additional water pick-up was observed (It should also be noted that similar experiments with TBP did not show any measurable variation in the acidity of the aqueous phase at the acidity levels used in this study).

In the present work, some additional experiments were carried out to compare different extractants after solvent equilibration with a hydrochloric acid solution identical to that used to prepare the feed solution for extraction. After the experiments, however, this care was perceived as excessive. The performance of the different extractants differed too much to be influenced by minor variations in acidity.

5.11 - New process proposal

The initial proposal for a new process is summarized in this section, and shown in Figure 5.9. The advantages of the proposed process when compared with previous processes are cited.

Zr and Hf Separation by Cyanex 925 - Process Sketch



1 - Scrub solution (1.0 - 2.5 M HCl)
2 - Raffinate Hf-rich
3 - High acidity Zr/Hf Feed(~ 3.5 M HCl)
4 - HCl adjustment
5 - Adjusted Feed (3 - 4.5 M HCl)
6 - Unloaded Organic
7 - Stripping Solution (~0.4M HCl)
8 - Zr to be precipitated
9 - Organic make-up (?)
10- Hf to be precipitated or recycled

Figure 5.9 - Cyanex Process General Process Flowsheet

From the processing standpoint it is possible to highlight at least three points. First, the possibility exists to run the separation without use of thiocyanates. This gives both a direct advantage by reducing costs, and an indirect advantage by the avoidance of environmental problems. Secondly, the near elimination of organic solubility in the water stream is achieved. Finally, the chemical stability and handling safety of the organic phase are both higher, if compared with MIBK. These points are achieved without important changes in the input or output of the system (i.e., full compatibility with the other process steps). The apparent price to pay is the lower loading capacity of the organic, due to its three times greater molecular weight than that of MIBK. The possibility of producing off-grade hafnium must be also weighed.

From the engineering point of view, some observations can also be made. No problems with materials selection are expected. The overall operating conditions can be considered mild. The solvents used in the Cyanex Process are less volatile, harmful, and aggressive than MIBK. Thus, polypropylene could be used without swelling problems. However, attention should be paid to select, even for the organic streams, materials compatible with hydrochloric acid. The instrumentation in this process is conventional. The flowrates and the acidity level are the most important process variables. Chemical analyses are also considerably less problematic than in conventional processes.

Chapter 6

Conclusions and Recommendations

Encouraging data have been obtained supporting the initial proposal of replacing MIBK in the traditional process with organophosphorous compounds. However, the feasibility of a mere replacement must consider the lower loading capacity of the phosphanes.

Although Cyanex 923 exhibits fairly high selectivity at only about 2.5 M HCl, third phase formation at above 8 g/l in the organic phase decreases interest in use of this extractant for zirconium/hafnium separation. However, if acidity is increased to 3.5 M HCl, Cyanex 925 performs better than Cyanex 923 without the problems of organic phase stability.

The qualitative model proposed in this work help us to understand the role of the ionic strength of the solution on the metal's extraction and separation. Here, the most important variable is the acidity, which governs both: the speciation of zirconium and hafnium in the aqueous phase, and the equilibrium between solvation and hydration - i.e., extraction. Another important point is the competition between Zr and Hf species toward the extractant at the interface between organic and aqueous phases. It can be readily seen (Table 5.4) that the separation factor is a strong function of HCl, this being the only chloride source in the system. At low levels the extraction of both elements is fairly poor. At high level, the extraction is very high but without selectivity between Zr and Hf. Between 3.0 and 4.5 M HCl, the separation factor is remarkably high. This indicates the possibility to separate Zr from Hf using Cyanex 925 without use of any other salting out element or complexing agent.

Other conclusions are firstly that increases in metal concentration decrease the metal extraction. This behavior can be attributed to polymerization in the aqueous phase that hinders the solvation reaction at the interface with the organic phase. Also, there was no evidence of mixed polymerization in our solutions up to an aging period of one week. Any possible decrease in the separation factor was too small to detect by the analytical method used. Finally, when zirconium is present at a given concentration, the coexistence of hafnium does not alter the extraction profile of the former in comparison with the behavior of single element solutions. The same behavior is not observed in the case of hafnium. Such a fact was attributed to differences in loading kinetics of each element.

In summary, use of an organophosphorous/HCl system instead of MIBK is a new idea that replaces current separation concepts such as the selective extraction of hafnium as its' thiocyanate complex. Cyanex 925 in kerosene should be competitive in terms of zirconium/hafnium separation itself when run at 3.5 M HCl. This fact along with the outstanding advantage of low aqueous solubility of phosphanes could be important reasons for further study of this process, especially taking into account continually increasing water remediation costs.

Probable advantages of the new process

In addition to the elimination of organic losses and consequent environmental impact, the process proposed in this work also avoids the use of thiocyanates and the consequent production of sulfur derivatives.

Organic losses are avoided due to three factors; the non volatility of the extractant and solvent; the immiscibility of the organic phase in water; the higher chemical stability of phosphanes relative to MIBK. These factors result in reducing costs in three areas; wastewater treatment; direct reduction in chemicals expenses; elimination of solvent make-up and recycling costs.

It should also be noted that our system has higher selectivity for zirconium than the TBP/NO_3^- process (the only industrial example using an organophosphorous extractant) and operates at a much lower acidity (3.5 M HCl vs. 6 M HNO_3) and in the same medium as the raw materials feeding the industrial process.

Probable disadvantages of the new process

The use of Cyanex 925 represents a lower zirconium throughput per volume of solutions processed than with MIBK technology. This is inevitable and derives from the four times greater molecular weight and the necessity of dilution to decrease the viscosity of the organic phase. This represents an investment increase in that bigger equipment and higher solution volumes are required for the same metal production.

While in our process, high separation factors result from selectivity for zirconium, the MIBK process is selective to hafnium. However, it is not possible in our case to assure the production of hafnium within nuclear specifications. If it will not be possible to produce hafnium with less than 2% of zirconium, this means that our system probably could not replace the MIBK process completely, but could complement it by supplying a Hf-rich raffinate for treatment using MIBK technology.

Suggestions for future work

The evident rôle of extraction kinetics, briefly investigated in this work, suggests that a study of this aspect is an important issue. An improved knowledge of extraction kinetics is essential for full advantage to be taken of them. Initial indications are that the relatively rapid zirconium extraction could help separation. One possibility for practical utilization of this concept is the utilization of a new generation of contactors, the Hollow Fibers Membrane Contactors, that permit very good control of the residence time and interfacial area.

The next step to this work is the optimization of the proposed process in a continuous circuit and its scale-up. The process should be initially optimized in sections (extraction, stripping and scrubbing) and subsequently in an integrated form. Finally, the behavior of some major impurities must be investigated. Iron, aluminum and phosphorous are the most important. Additionally, uranium and thorium may be significant depending on the raw material used in the process.

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Appendix 1

Excerpt from Cyanex 923 Data Sheet (Cyanamid)

INTRODUCTION

CYANEX 923 extractant is a liquid phosphine oxide which has potential applications in the solvent extraction recovery of both organic and inorganic solutes from aqueous solution, e.g. carboxylic acids from effluent streams and the removal of arsenic impurities from copper electrolytes.

The major advantage of CYANEX 923 extractant over similar extraction reagents, e.g. TOPO (trioctylphosphine oxide), is that it is completely miscible with all common hydrocarbon diluents even at low ambient temperatures. The major benefit of high solubility lies in the ability to prepare concentrated, stable solvents which can recover solutes (e.g. acetic acid) that are normally only weakly extracted by this type of reagent.

Composition

CYANEX 923 extractant is a mixture of four trialkylphosphine oxides as follows:

$R_3P(0)$ $R_2R'P(0)$ $RR'_2P(0)$ $R'_3P(0)$

Where $R = [CH_3(CH_2)_7]$ - normal octyl
$R' = [CH_3(CH_2)_5]$ - normal hexyl

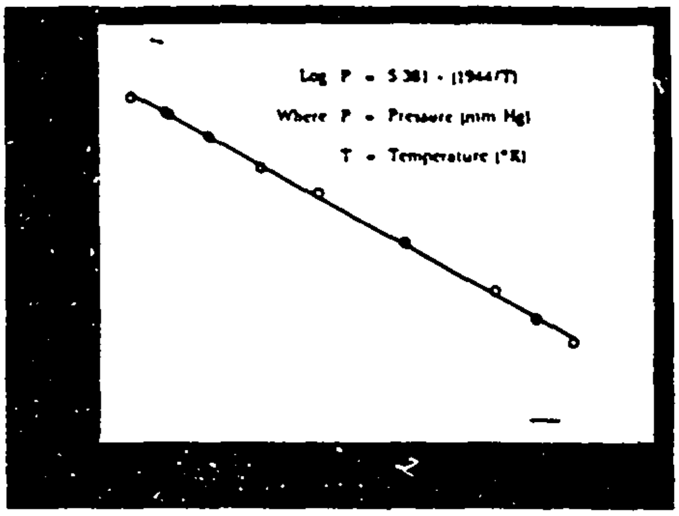
Average Molecular Weight = 348 (approximately)

Typical Properties

Trialkylphosphine oxides	:	93%
Appearance	:	Colorless mobile liquid
Specific Gravity	:	0.88 at 25°C
Freezing Point	:	−5 to 0°C
Viscosity	:	40.0 centipoise at 25°C 13.7 centipoise at 50°C
Flashpoint (Closed Cup Setaflash)	:	182°C
Autoignition Temperature	:	218°C
Vapor Pressure*	:	0.09 mm Hg at 31°C
Boiling Point	:	310°C at 50 mm Hg
Solubility in Water	:	10 mg/l
Solubility of Water in CYANEX 923 extractant	:	8 w/o

(*Shown as function of temperature in Figure 1)

FIG. 1 — EFFECT OF TEMPERATURE ON VAPOR PRESSURE



Compatible Materials

Samples of the following plastics and rubbers (in the form of tubing) were immersed for 200 hours at 50°C in glass vessels containing CYANEX 923 extractant.

The results are summarized below:

Material	Remarks
Butyl Rubber	Unsuitable. Rapid swelling and softening.
Teflon Fluorocarbon Film*	Suitable. No detectable effect.
Polypropylene	Suitable. No detectable effect.
Natural ~~& Black~~ Latex Rubber	Unsuitable. Complete dissolution in less than 192 hours.
PVC (Laboratory Grade)	Short-term suitability. Loss of plasticity in less than 192 hours.
PVC (Solvent Grade)	Suitable. Only a slight increase in dimension observed.
Red Gum Rubber	Unsuitable: Rapid swelling and softening.
Viton Fluoroelastometer*	Suitable. No detectable effect.
Silicone	Unsuitable. Disintegrated after 56 hours.

Samples of the following metals in the form of coupons (approximate dimensions 50 mm x 20 mm x 3 mm) were immersed for 1000 hours at 50°C in glass vessels containing CYANEX 923 extractant. The following observations were made.

Metal	Remarks
Mild Steel	No detectable corrosion.
Stainless Steel (316)	No detectable corrosion.
Stainless Steel (304)	No detectable corrosion.
Aluminum	No detectable corrosion.

Product of E.I. DuPont de Nemours & Co.

ANALYSIS IN ORGANIC SOLVENTS

As described, the gas chromatographic procedure is suitable for analyzing solvents containing approximately 120 g/l CYANEX 923 extractant. Other concentrations may be determined by diluting the solvent appropriately or adjusting the composition of the standard solution.

CYANEX 923 extractant is a mixture containing four major components, as follows: Trihexylphosphine oxide (1), dihexylmonooctylphosphine oxide (2), dioctylmonohexylphosphine oxide (3) and trioctylphosphine oxide (4).

The method is based upon the fact that, within the limits of experimental error, the response factors for components 1, 2 and 3 are the same as for 4 and that 4 (TOPO) is readily available and may be easily purified to AR grade.

Reagents

1. Didecylphthalate (AR grade - internal standard)
2. TOPO (purified - see note 1)
3. Process diluent (e.g. Escaid* 110 diluent)

Calibration

1. Accurately weigh 1g (±1 mg) of pure TOPO and 2g (±0.1 g) of didecylphthalate into a 50 ml volumetric flask. Dissolve and make up to volume with the process diluent.
2. Analyze the above standard solution as described under "Gas Chromatographic Conditions" to determine the relative response factor of TOPO vs. didecylphthalate.

Procedure

1. Centrifuge the solvent to be analyzed or filter through PS paper** to remove entrained aqueous or suspended solids.
2. Accurately weigh 2g (±0.1g) of didecylphthalate into a 50 ml volumetric flask and pipette 25 ml of the clarified solvent into the same flask. Make up to volume with the process diluent.
3. Determine the relative response factor of each component of CYANEX 923 extractant vs. that of the internal standard as described under "Gas Chromatographic Conditions".

Calculations

Total Concentration of Trialkylphosphine Oxides (g/l)

$$\sum \left[\frac{R_{st}}{R_{n}} \right] \times 2 \times C_{st}$$

Where R_{st} = Relative response factor for TOPO in the standard solution
R_{n} = Relative response factor for the n^{th} component in the analyte solution.
C_{st} = Concentration of TOPO in the standard solution (g/l)

Gas Chromatographic Conditions

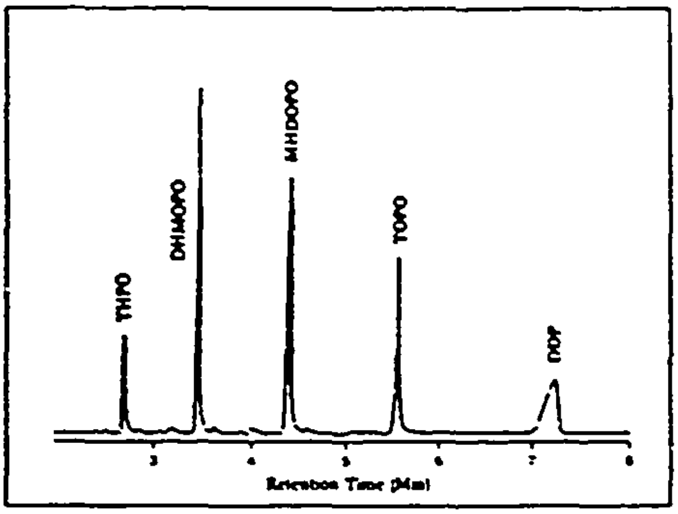
Instrument	:	Perkin Elmer Sigma 115 or equivalent
Column	:	30 m x 0.32 mm fused silica capillary column coated with 0.25 μm of DB1
Detector	:	FID
Carrier Gas	:	Helium at 18 psig
Vent Flow	:	100 ml/min
Column Flow	:	4.3 ml/min
Split Ratio	:	23/1
Temperatures °C		
Detector	:	340
Injection Port	:	340
Column	:	220 to 330 at 10°C/min
Sample Injection Volume	:	0.1 μl
Peak Areas	:	Determined by electronic integration

Notes

1. A chromatogram of commercial CYANEX 923 extractant is shown in Figure 1A.
2. Pure TOPO (>99.5%) can be obtained by recrystallizing commercial grade TOPO from hexane (three recrystallizations are necessary).
3. Megabore columns may be used as an alternative to capillary columns. A thermal conductivity detector may also be used in place of an FID.
4. The method is based upon a single point determination. If required, a calibration curve can be constructed by varying the concentration of TOPO in the standard solution while maintaining a constant concentration of the internal standard.
5. This method has not been validated.

** Product of Exxon Co. U.S.A.*
*** Phase separation paper available from Whatman, Inc., Clifton, NJ*

i. 2A — CHROMATOGRAM OF CYANEX 923 EXTRACTANT CONTAINING DIDECYLPHTHALATE (DDP) AS AN INTERNAL STANDARD



ANALYSIS IN AQUEOUS SOLUTION

e aqueous solubility of each component of CYANEX 923 extractant will normally be <2 mg/l. The method s based on analysis of the aqueous sample by gas omatography. The response factors of the four active components are equal within the limits of experimental error.

Reagents

1. Tetrahydrofuran (THF). "Baker Analyzed Reagent, 100%."
2. TOPO (purified - see note 1.)

Calibration

1. Prepare a stock solution by accurately weighing (± 1 mg) approximately 0.5 g of TOPO into a 50 ml volumetric flask. Dilute to 50 ml with THF and dissolve the TOPO.
2. Dilute aliquots of the stock solution with distilled water to prepare standard solutions containing 2, 5, 10 and 30 mg/l of TOPO.
3. Analyze the solutions as described under "Gas Chromatographic Conditions."

Procedure

1. Filter the aqueous solution to remove entrained organic
2. Inject 3 μl of the analyte solution and analyze as described under "Gas Chromatographic Conditions."

Calculation

1. *Response Factor for TOPO (R) =

$$\frac{\text{Conc. of TOPO in Standard (mg/l)}}{\text{Area of TOPO Standard Peak}}$$

2. Concentration of Component in Aqueous (mg/l) = Area of Component Peak (analyte) × R

*Response factor for the standard closest in concentration to the sample.

Gas Chromatographic Conditions

Instrument : Hewlett Packard 5730A or equivalent
Column : 2 ft × 1/4 inch × 2 mm ID glass Column packed with 9% OV-17 and 12% SP2401 on 80/100 mesh Supelcoport
Detector : FID
Carrier Gas : Helium at 57 psi (Flowrate 40 ml/minute)
Temperatures °C
FID : 300
Injection Port : 250
Column : 230 (Isothermal)
Sample Injection Volume : 3 μl

Notes

1. Pure TOPO can be obtained by recrystallizing commercial grade TOPO from hexane. (Three recrystallizations are necessary).
2. Retention time for TOPO is approximately 12 minutes.
3. Detection limit approximately 2 mg/l.
4. This method has not been validated.

DETERMINATION OF WATER

The method is based on distilling water from CYANEX 923 extractant in the form of an azeotrope with toluene. On contacting a condenser, the water and toluene separate and fall into a graduated trap. The volume of the distillate is then measured.

Apparatus

1. 500 ml round-bottomed, short-necked glass flask with a 40/50 ground glass fitting.
2. Water-cooled condenser. Cold-finger type.
3. Dean and Stark type trap. 10 ml capacity graduated in 0.1 ml divisions with a 40/50 ground glass fitting.
4. Heating mantle controlled by a rheostat.

Reagents

1. AR grade toluene (water-free)

Procedure

1. Weigh 50 g of the sample (± 0.5 g) into the 500 ml flask.
2. Add approximately 200 ml of toluene to the flask and assemble the apparatus.
3. Heat the contents of the flask to boiling and allow to reflux for 30 to 60 minutes or until the volume of water in the trap is constant.
4. Read the volume of water in the trap at room temperature.

Calculation

$$\% \text{ Water} = \frac{\text{Volume of Water in Trap (ml)} \times 100}{\text{Sample weight (g)}}$$

Notes

1. This method has not been validated.
2. Karl-Fisher titration is not recommended.

HEALTH AND SAFETY

The oral and dermal toxicity of CYANEX 923 extractant is low. CYANEX 923 extractant produces mild eye irritation and severe skin irritation upon contact. Repeated dermal exposure for 28 consecutive days produced severe skin irritation, but no systemic toxicity. CYANEX 923 extractant did not produce dermal sensitization in guinea pigs after repeated dermal exposure. This product did not produce mutations in bacteria nor did it produce chromosomal effects in the mouse micronucleus test. CYANEX 923 extractant is toxic to fish and invertebrates and great care should be exercised to avoid environmental exposure.

IMPORTANT NOTICE

The information and statements herein are believed to be reliable but are not to be construed as a warranty or representation for which we assume legal responsibility. Users should undertake sufficient verification and testing to determine the suitability for their own particular purpose of any information or products referred to herein. NO WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE IS MADE. Nothing herein is to be taken as permission, inducement or recommendation to practice any patented invention without a license.

Appendix 2

Excerpt from Cyanex 925 Data Sheet (Cyanamid)

INTRODUCTION

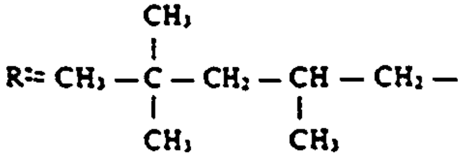
CYANEX 925 extractant is a unique trialkylphosphine oxide in that it is the only commercially available reagent of this type in which the alkyl groups are branched. Chain branching has a significant effect on the properties of the extractant in comparison to conventional straight chain phosphine oxides e.g. TOPO* (trioctylphosphine oxide).

Chemical Structure

CYANEX 925 is a mixture of two compounds which have the following structure.

$R_3P(O)$ (I) $R_2R'P(O)$ (II)

Where



$$R = CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_2-$$

$R' = CH_3(CH_2)_7-$

The molecular weight of both components is 386. Component II predominates; representing approximately 85% of the mixture.

Typical Properties

Trialkylphosphine Oxides	:	93%
Appearance	:	Colorless to light amber liquid
Pour Point	:	-30°C
Specific Gravity	:	0.88 at 21°C 0.86 at 50°C
Viscosity (Brookfield Viscometer)	:	117 centipoise at 21°C 24 centipoise at 50°C (Viscosity is shown as a function of temperature in Figure 1).
Vapor Pressure	:	1 Torr at 24°C (Vapor pressure is shown as a function of temperature in Figure 2).
Solubility in Water	:	2 mg/L
Solubility of Water in	:	3.6%

**TOPO is available commercially from American Cyanamid Company as CYANEX 921 extractant.*

FIG. 1—EFFECT OF TEMPERATURE ON VISCOSITY

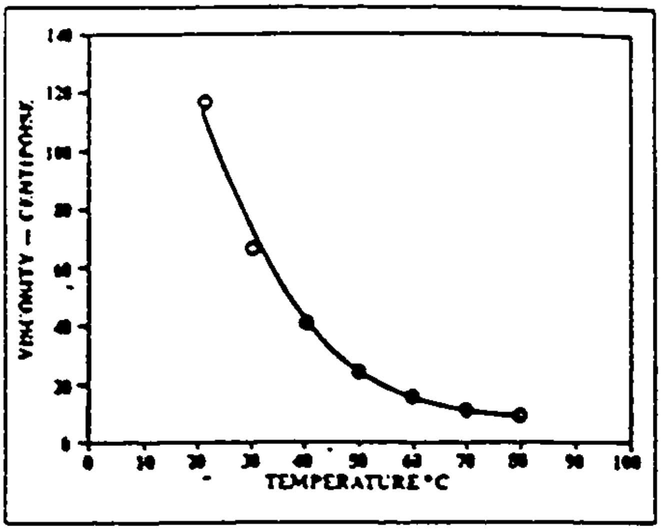
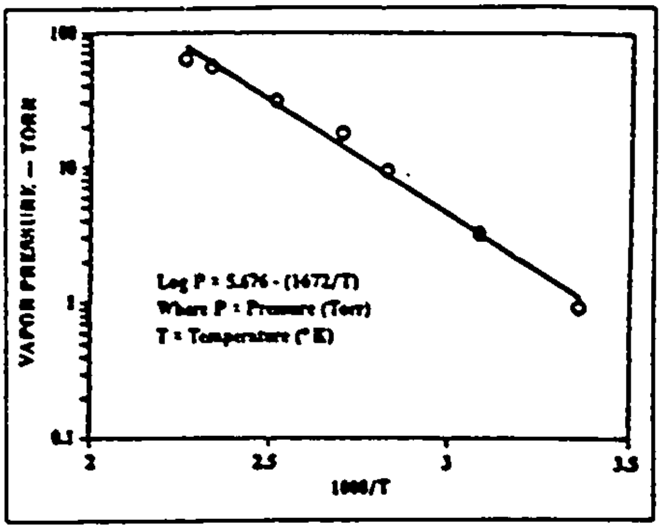


FIG. 2—EFFECT OF TEMPERATURE ON VAPOR PRESSURE



Compatible Materials

Samples of the following plastics and rubbers (in the form of tubing) were immersed for 2500 hours at 50°C in glass vessels containing CYANEX 925 extractant.

The results are summarized below.

Material	Remarks
Polypropylene	Suitable; minor changes in dimensions and weight. No change in appearance.
TEFLON* Fluorocarbon Film	Suitable; no change in dimensions, weight or appearance.
Silicone	Not recommended; significant increase in dimensions and softening.
Latex Rubber (Yellow and Black)	Unsuitable; large increase in dimensions followed by complete disintegration.
Red Gum Rubber	Unsuitable; large increase in dimensions and noticeable softening.
VITON* Fluoroelastomer	Unsuitable; increase in dimensions, loss of integrity and softening.
Butyl Rubber	Unsuitable; large increase in dimensions, softening.
PVC (Laboratory and Solvent Grade)	Unsuitable; swelling followed by disintegration.

Samples of the following metals in the form of coupons (approximate dimensions 50 mm x 20 mm x 3 mm) were immersed for 1500 hours at 50°C in glass vessels containing CYANEX 925 extractant.

The following results were obtained.

Metal	Remarks
Mild Steel	No detectable corrosion
Stainless Steel (316)	No detectable corrosion
Stainless Steel (304)	No detectable corrosion
Aluminum	Corrosion rate 0.2 mils/year

Product of E.I. Dupont de Nemours & Co.

Health and Safety

CYANEX 925 extractant has a low degree of oral and dermal toxicity. It is severely irritating to rabbit skin, but is only mildly irritating to the rabbit eye. CYANE 925 was not mutagenic in the Ames test.

ANALYTICAL METHODS

ANALYSIS IN ORGANIC SOLVENTS

CYANEX 925 extractant is a mixture containing two major components, bis(2,4,4-trimethylpentyl) octylphosphine oxide (I) and tris(2,4,4-trimethylpentyl)phosphine oxide (II). I is the major component and represents approximately 85% of the mixture. For all practical purposes, the relative response factors of I and II are equal.

As described, the gas chromatographic procedure is suitable for analyzing solvents containing 30–450 g/L extractant. Other concentrations may be determined by diluting the solvents appropriately or adjusting the composition of the standard solution. Trioctylphosphine oxide (TOPO) is used as an internal standard.

Reagents

1. TOPO (internal standard—see note 1)
2. Standard solution containing 100 g/L CYANEX 925 extractant in the process diluent.

Calibration

1. Dissolve approximately 100 mg of TOPO in an accurately measured 1 mL aliquot of the standard solution.
2. Analyze as described under "Gas Chromatographic Conditions" to determine the relative response factor of CYANEX 925 vs TOPO.

Procedure

1. Centrifuge the solvent to be analyzed or filter through PS paper to remove entrained aqueous or suspended solids.
2. Pipette accurately a 1 or 2 mL aliquot of the clarified solvent into a vial. Add 100 mg of TOPO and dissolve.
3. Analyze as described under "Gas Chromatographic Conditions".

Calculation

Weight of CYANEX 925 extractant $= \frac{A_c}{A_i}$ x RRF x W(g)
in the analyte solution (g)

Where RRF = Relative response factor

A_c = Total peak area of both components of CYANEX 925 extractant in the analyte solution

A_i = Peak area of TOPO internal standard in the analyte solution

W = Weight of TOPO internal standard in the

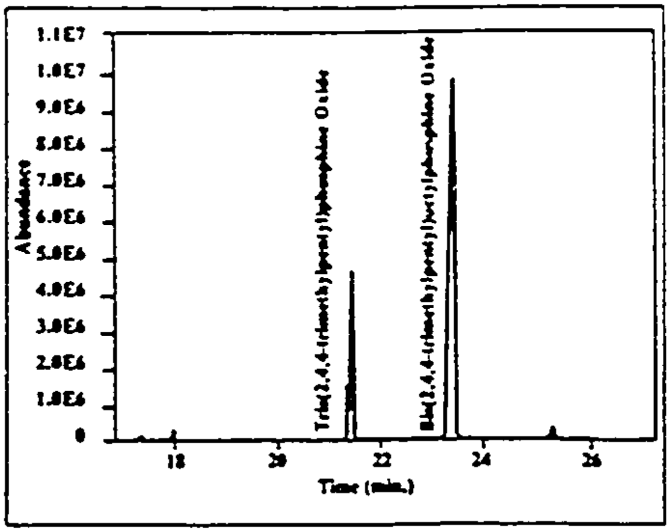
Gas Chromatographic Conditions

Gas Chromatograph	:	Perkin-Elmer Sigma 115 or equivalent
Detector	:	FID
Column	:	Supelco SPB-5 capillary column, 30 m, 0.32 mm I.D., 0.25 µ film thickness
Initial Oven Temperature	:	220°C
Initial Time	:	0 min.
Temperature Rate	:	10°C/min.
Final Oven Temperature	:	300°C
Final Time	:	7 min.
Injection Port Temperature	:	290°C
Detector Temperature	:	290°C
Carrier Gas (Helium) Flow	:	1.0 mL/min.
Injection	:	Split, 0.1 µL
Split Ratio	:	40:1
Area Sensitivity	:	300
Baseline Sensitivity	:	20
Chart Speed	:	20 mm/min.
Attenuation	:	2
Peak Areas	:	Determined by electronic integration

Notes

1. Pure TOPO (>99.5%) can be obtained by recrystallizing technical grade TOPO from hexane. Three recrystallisations may be necessary.
2. PS (Phase Separation) paper is available from Whatman Inc.
3. The relative response factor was found to be constant for solvents containing 30 to 450 g/L CYANEX 925 extractant.
4. A typical chromatogram is shown in Figure 1A.
5. This method has not been validated.

FIG. 1A — TYPICAL GAS CHROMATOGRAM OF CYANEX 925 EXTRACTANT



ANALYSIS IN AQUEOUS SOLUTION

The aqueous solubility (total of both components) will normally be in the range 0-3 mg/L. The method is based on extracting CYANEX 925 extractant from the aqueous solution with methylene chloride followed by concentration and analysis of the extract.

Reagents

1. TOPO (internal standard—see note 1).
2. Methylene chloride (AR grade).

Calibration

1. Prepare a standard solution in methylene chloride containing 2 mg/L TOPO and 2 mg/L CYANEX 925 extractant.
2. Analyze as described under "Gas Chromatographic Conditions" to determine the relative response factor of CYANEX 925 vs TOPO.

Procedure

1. Filter the aqueous solution to remove entrained organic.
2. Contact 100 mL of the filtered solution with 35 mL methylene chloride for 5 minutes. Repeat the contact twice using fresh aliquots of methylene chloride and the same aqueous solution.
3. Combine the aliquots of methylene chloride and evaporate to dryness. Add 0.5 mL of methylene chloride containing 2 mg/L internal standard and warm to dissolve.
4. Analyze as described under " Gas Chromatographic Conditions".

Calculation

Weight of CYANEX 925 extractant = $\frac{A_s}{A_i}$ x RRF x W x C (mg) in the aqueous solution (mg)

Where RRF = Relative response factor

A_s = Total peak area of both components of CYANEX 925 extractant

A_i = Peak area of TOPO internal standard in the analyte solution

W = Weight of TOPO internal standard in the analyte solution

C = Correction factor for incomplete extraction (1.3).

Gas Chromatographic Conditions

Gas Chromatograph : Perkin-Elmer Sigma 115 or equivalent

Detector : FID

Column : Supelco SPB-1 (100% methyl silicone) column, 30 m, 0.32 mm I.D., 0.25 μ film thickness

Initial Oven Temperature : 40°C

Initial Time : 0 min.

Temperature Rate : 20°C/min.

Final Oven Temperature : 300°C

Final Time : 3 min.

Injection Port Temperature : 290°C

Detector Temperature : 290°C

Carrier Gas (Helium) Flow : 1.0 mL/min.

Injection : Splitless, with purge after 30 sec.

Area Sensitivity : 300

Baseline Sensitivity : 20

Chart Speed : 20 mm. min.

Attenuation : 3

Peak Areas : Determined by electronic integration

Notes

1. Pure TOPO (>99.5%) can be obtained by recrystallizing technical grade TOPO from hexane. Three recrystallizations may be necessary.
2. Detection limit of the method is approximately 0.5 mg/L.
3. This method has not been validated

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