ZIRCONIUM AND HAFNIUM SEPARATION IN DIFFERENT INORGANIC AND NATURAL COMPOUNDS

By

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Declaration by candidate

I confirm that the dissertation submitted for the degree of Magister in Analytical Chemistry, at the University of the Free State is my own original work and has not been submitted for any other degree qualification at any other University. I further declare that all the cited that I have quoted have been indicated and acknowledged in terms of complete references.

…… ……

Roy Kankwanzi-Tuipende Date

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Roy Kankwanzi-Tuipende

TABLE OF CONTENTS

Table of Contents

LIST OF FIGURES

List of figures

List of figures

LIST OF TABLES

List of tables

LIST OF ABBREVIATIONS

ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IR	Infrared
PTFE	Polytetraflouroethylene
MIBK	Methyl Isobutyl Ketone
$Zr(Hf)SiO_4$	Zircon
PDZ	Plasma-Dissociated Zircon
ZrO_2	Zirconium dioxide
HfO_2	Hafnium dioxide
DST	Department of Science and Technology
AMI	Advanced Metal Initiative
NECSA	South Africa Nuclear Energy Corporation SOC Ltd.
ppm	Parts per million

KEY WORDS

Zirconium

Hafnium

Plasma-Dissociated Zircon

Quantitative analysis

Dissolution

Separation

Isolation

Summary

Zirconium (Zr) and hafnium (Hf) co-exist in the mineral zircon ore and its treated modified form, namely Plasma-Dissociated Zircon (PDZ), which always contain a small amount of Hf ranging between 1-3 %. The physical and chemical properties of Zr and Hf are almost identical and their separation is notoriously difficult, tedious and involves expensive processes. The purpose of this study was to initially investigate the possible separation of $(Zr/Hf)O_2$ in inorganic salts and PDZ ($(Zr/Hf)O_2.SiO_2$) and apply these optimum separation conditions to separate Zr and Hf from PDZ.

The dissolution of the inorganic salts were done using the flux fusion technique during which a mixture of 90.9 % ZrO_2 and 9.09 % HfO_2 (try to replicate the natural abundance in minerals) were fused with $NH_4F{\cdot}HF$ as flux. The successful dissolution of the metal oxides was confirmed by total and accurate recovery of 100.6(2) % for ZrO_2 while unexpectedly high HfO_2 recovery was (121.2(9) %) was obtained. Possible solution matrix effects such as high F^- concentration, were suspected as reasons for the high Hf recovery. H_2SO_4 was added to flux mixture and excess fluoride was removed by the evaporation of HF. This variation led to excellent Hf recoveries and quantitative results indicated the recovery of 100.1(2) % for Zr and 100(2) % for Hf. This method was subsequently used for the dissolution of PDZ and the analytical results indicated the presence of 66.0(4) % for Zr and 1.43(1) % for Hf. These fluoride solutions were subsequently investigated for the possible separation of Zr and Hf using, ion exchange, solvent extraction and microwave assisted dissolution.

The separation of Zr and Hf in the fluoride matrix was investigated with an ion exchange process. Three different anion resins, namely Dowex Marathon wba, Dowex 21k and Amberlite IRA-900 were investigated for elemental separation. The strong anion exchanger resin, Amberlite IRA-900 was selected and different experimental parameters such as flow rate, eluent and eluent concentrations were investigated. Quantitative results indicated the preferential elution of Zr over Hf. At 0.05 M HCl only Zr was eluted while Hf was completely retained in the column and the recovery of Zr was 86.44 % from the inorganic Zr/Hf mixture. The optimum conditions, Amberlite IRA-900 resin, 0.05 M HCl and 20 cm column length, which are

developed for the inorganic Zr/Hf mixture, were applied on the PDZ material and the recovery of Zr was 24(6) %.

The isolated of ZrO_2 from this reaction mixture, was re-dissolved using $NH_4F{\cdot}HF$ as flux. The concentration of Zr was quantitatively determined using ICP-OES. The obtained average metal recoveries were 77.8(7) and 0.11(0) % for Zr and Hf respectively which are extremely promising, pointing to the separation of the two elements and the removal of the Hf from the Zr. The drawback to this method is, the low Zr recovery (compared to the amounts initially used in the separation process).

Solvent extraction was the next technique to be investigated for separation of Zr and Hf as an alternative to ion exchange due to low Zr recoveries obtained in ion exchange separation method. The results obtained using MIBK as an extractant from H_2SO_4 solutions indicated a slight preferential extraction of Zr into the organic layer, leaving Hf in the aqueous layer with recoveries of 65(1) % Zr and 4(1) % Hf.

Microwave assisted digestion in H_2SO_4 of both $(Zr/Hf)O_2$ and PDZ were inconclusive.

Validation of the analytical results using ICP-OES was also performed. Most of the results obtained for the Zr and Hf quantification in the inorganic salt ($(Zr/Hf)O_2$), were accepted at the 95% confidence interval. However, other results indicated poor precision and accuracy of Hf hence the null hypothesis was rejected.

1 Motivation of the study

1.1 Introduction

Naturally, zirconium (Zr) and hafnium (Hf) co-exist in mineral ores but, predominantly, zirconium compounds always contain a small amount of hafnium in concentrations ranging from 1 to 3%.[1] The physical and chemical properties of these two elements are quite similar and their separation is notoriously tough. Some chemists regard this chemical procedure as one of the most difficult. The main economic source of zirconium and hafnium is zircon $(Zr(Hf)SiO_4)$[2] **(Figure 1.1)**.

Figure 1.1: Zircon sand[3]

[1] C. Skidmore, Zirconium and Hafnium, [Accessed on 10-05-2017]. Available from: https://www.scribd.com/document/81893296/Zirconium-Hafnium

[2] J.C.B.S. Amaral, L.R.T. Rocha, C. A. Morais, Study of the separation of zirconium and hafnium from nitric solutions by solvent extraction, *2013 International Nuclear Atlantic Confrence*, 2013

[3] Zircon sand, [Accessed on 10-05-2017]. Available from: https://www.exportersindia.com/amoco-general-trading-pvt-ltd/zircon-sand-2929154.htm

Worldwide, zircon is mined commercially only in a few countries. **Figure 1.2** (below) clearly shows that the leading producers of zircon are Australia, South Africa, Indonesia and the USA. Baddeleyite is another major source of zirconium but this mineral is mined commercially in Russia **(Figure 1.3)**.[4]

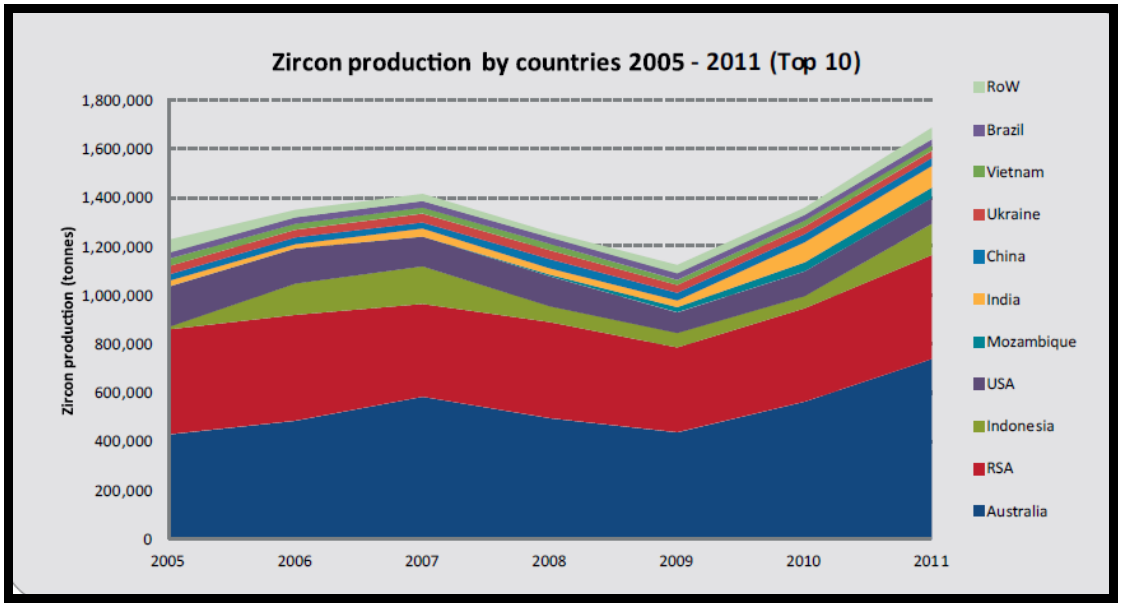


Figure 1.2: Worldwide major production of zircon from 2005-2011[4]

[4] DERA Rohstoffinformationen, [Accessed on 10-05-2017]. Available from: http://www.canadian-german-mining.com/files/March_2014_Investors_and_Procurement_Guide_South_Africa._Part_1_Heavy_Minerals_Rare_Earth_Elements_Antimony.pdf

Figure 1.3: Baddeleyite-rich ore mine in Russia [4]

Mining companies such as Iluka Resources Ltd. from Australia, Richard Bay Minerals and Exxaro Resources from South Africa are currently the three major producers of zircon in the world. In 2010, their combined zircon production totalled 794 000 tonnes[4] and in 2012, the production of zircon ore by the South African counterpart was estimated to be between 280,000 and 300,000 tonnes.[4]

The price of zircon increased from $360 to $840 per tonne during the period of 2003 – 2007, and subsequently climbed to $2,500 per tonne by mid-2012. By contrast, pure zirconium metal, with a 99% purity, clinched approximately $39,900 per tonne in 2013, which is by far higher than the price for zircon ore.[5] Currently, companies in South Africa mine and export raw zircon ore which yields very low prices on the international market, compared to the price when it has been beneficiated. This results in the loss of potentially large amounts of revenue. Accordingly, the Department of Science and Technology (DST) in South Africa recognised the need for a national mineral beneficiation initiative, especially with regard to zircon, mainly because the South Africa is rich in this mineral resource.

[5] Alkane resources and its zirconium- what comes around, [accessed on 30-04-2017]. Available from: https://investorintel.com/sectors/technology-metals/technology-metals-intel/alkane-resources-and-its-zirconium-what-comes-around/

The Advanced Metals Initiative (AMI) was established in 2003 by DST to develop local beneficiation technology for manufacturing hafnium-free zirconium metal from the local zircon ore which can then be supplied to the nuclear industry. The development of effective methods for the separation of hafnium and zirconium will not only increase revenues for South Africa, but it will also create new jobs and develop downstream industries in the country.[6]

Zirconium chemicals are used for several industrial applications, such as in refractories, foundry sands, ceramics, construction of chemical plants, electronic devices, medicine and finally, in nuclear reactors.[7] Hafnium chemicals, on other hand, are used in the production of super alloys, refractory metal alloys and also in nuclear applications, but for a very different application as zirconium.[8] Presently, China and Europe are the biggest consumers of zircon and zirconium chemicals. China consumes nearly half of the world's production (about 53%) due to its large ceramics industry and high capacity.[9]

As previously indicated, both zirconium and hafnium metals **(Figure 1.4)** are often used in the nuclear energy and chemical processing industries.[8,9] In nuclear energy production, high purity metallic zirconium is used as the cladding material for the nuclear fuel assemblies due to the fact that the zirconium metal is 'transparent' to neutrons, has good high temperature performance, as well as, good anti-corrosion

[6] Decision on $2,1bn titanium, zirconium project pending, [Accessed on 8-05-2017]. Available from: http://www.miningweekly.com/article/prefeasibility-study-on-integrated-beneficiation-plant-complete-2011-03-11/rep_id:3650

[7] Applications of zirconium, [Accessed on 8-05-2017]. Available from: http://repository.up.ac.za/bitstream/handle/2263/27817/03chapter3.pdf?sequence=4

[8] Hafnium: Small Supply, Big Applications, [Accessed on 8-05-2017]. Available from: http://www.etf.com/sections/features-and-news/2572-hafnium-small-supply-big-applications?nopaging=1

[9] The industrial chain of zirconium products, [Accessed on 8-05-2017]. Available from: http://metalpedia.asianmetal.com/metal/zirconium/application.shtml

properties.[10] On other hand, hafnium metal is often used as control rods in a nuclear reactor due to its very high neutron absorption cross-section area which is 600 times greater than that of zirconium (0.18 barn).[11] The hafnium rods are inserted with guide tubes into the nuclear reactor in order to decrease the neutron flux that split further uranium atoms and control the nuclear process resulting in the energy produced.[8] On that note, the zirconium used for construction of nuclear cladding containers should have as little hafnium concentration (≤100ppm) as possible.[12]

Figure 1.4: Zirconium [13] and hafnium metal [14]

The separation of zirconium and hafnium is difficult, tedious and involves expensive processes due to their almost identical physio-chemical properties.[11] Most of the existing commercial separation processes include solvent extraction using thiocyanate or sulphuric acid[15] which are environmentally more friendly methods than

[10] Zirconium cladding is the reactor's primary safety barrier,[Accessed on 6-4-2017]. Available from: http://www.areva.com/EN/operations-2294/zirconium-cladding-is-the-reactors-primary-safety-barrier.html

[11] Separation method of zirconium and hafnium by solvent extraction process, [Accessed on 4-05-2017]. Available from: http://patents.justia.com/patent/8778288

[12] J.Amaral, L. Rocha, C. Morais*, International Nuclear Atlantic Conference - INAC 2013*, 2013

[13] Crystal bar. An example of the element zirconium, [Accessed on 20-4-2017]. Available from: http://www.periodictable.com/Items/040.17/index.html

[14] Hafnium, [Accessed on 20-4-2017]. Available from: http://www.theodoregray.com/periodictable/Elements/072.s7.html

[15] Z. Xu, L. Wang, Y. Wu, *Transaction of Nonferrous Metals Society of China,* 2012, 22(7), 1760-1765

chemicals.[16] Their separation is further compounded by the fact that many of these existing separation methods involve complicated multistage procedures that are time-consuming.[16] Efforts are continually being made to develop alternative separation methods which are more eco-friendly and cost-effective.[17]

The ability to separate zirconium and hafnium from inorganic oxides ($(Zr/Hf)O_2$) and/or Plasma-Dissociation Zircon (PDZ)[18] as feedstock is of crucial importance to the development of a zirconium beneficiation process since zircon mineral is the feedstock available for beneficiation in the country. The efficiency and effectiveness of any zirconium and hafnium separation process needs to be monitored by highly accurate, precise and robust analytical methods.

The applications of high purity zirconium and hafnium metals make the separation of the two elements extremely desirable for nuclear applications. Hydrometallurgical separation techniques, as well as, monitoring of these separation steps (analytical procedures) often require homogenous solutions. Thus, the first step in many of these processes involve the dissolution of the zircon ores, which themselves are extremely resistant to chemical manipulation.

1.2 Aim of the study

The main aim of this project is to investigate the possible separation of zirconium (Zr) and hafnium (Hf) in inorganic salts $(Zr/Hf)O_2$ mixture. This will be done by using ion exchange and solvent extraction and applying the optimum separation conditions to

[16] L. Xu, Y. Xiao, A. Sandwijk, *Energy Materials,* 2014, 451-457

[17] Y. Xiao, Y. Yang, Q. Xu, Separation of Zirconium and Hafnium: A Review [Accessed on 9-4-2017]. Available from: https://www.researchgate.net/publication/287457696_Separation_of_Zirconium_and_Hafnium_A_Review

[18] J. Havenga, J. Nel, *Journal of the Southern African Institute of Mining and Metallurgy*, 2012, 112(7), 497-500

Plasma-Dissociated Zircon (PDZ). The South African Nuclear Energy Corporation SOC Ltd (NECSA) has developed a method for the conversion of natural zircon, which is highly resistant to chemical attack, into a more reactive product referred to as Plasma-Dissociated Zircon (PDZ). These samples will be mainly used in this study. The quality of newly produced zirconium and hafnium metals or compounds must meet all the required specification in terms of purity but the challenge is to develop a separation procedure using pure $(Zr/Hf)O_2$ and PDZ as starting materials. Previous studies indicate that oxides can be used as model reagents to study and understand the chemistry of the two elements.

1.3 Objectives of the study

The following are the objectives of the study:

- To develop an energy efficient and economically viable dissolution method for zirconium (Zr) and hafnium (Hf) oxides and Plasma-Dissociated Zircon (PDZ);
- To improve analytical techniques for accurate analysis of zirconium and hafnium in the different matrices;
- To quantitatively determine zirconium and hafnium concentrations in different sample matrices;
- To develop procedures for separation of Zr and Hf in inorganic salts $(Zr/Hf)O_2$ mixtures and develop the optimum conditions to the separation of Zr and Hf in PDZ;
- To perform method validation of all the developed analytical techniques in order to assess their reliability in accordance with good laboratory practices.

2 Introduction to zirconium and hafnium

2.1 Introduction

Zirconium (Zr) and hafnium (Hf) are often found together in the earth's crust with abundances of 0.013 %[19] and 0.00033 %[20] respectively. Zirconium is the 18th most abundant element while hafnium ranks 47th. These elements result as metal oxides or silicates in nature. Zirconium and hafnium elements have molar masses of 91.224 and 178.49 g/mol; melting points of 1857 and 2150 ^{o}C and densities of 6.5 and 13.1 g/cm^3 respectively.[21] One of the most notable properties of the two elements is their very similar physical and chemical properties. These include properties such as atomic radius, ionic radius, electronegativity and corrosion resistance due to their affinity for oxygen which form passive oxide layers on the metal's surface.[22]

Zirconium was discovered in 1789 by Martin Klaproth **(Figure 2.1)**, while analysing jargon ($Zr(Hf)SiO_4$) - a form of zircon, from "Ceylon", the present day Sri Lanka.[21] Many chemists then confused the element to be another form of alumina (Al_2O_3), until Klaproth isolated zirconium dioxide from zircon, thus, confirming the discovery of a new element.[23] It took another 134 years for hafnium to be discovered in zirconium

[19] Technical data for zirconium, [Accessed on 19-06-2017]. Available from http://periodictable.com/Elements/040/data.html

[20] Technical data for hafnium, [Accessed on 19-06-2017]. Available from: http://periodictable.com/Elements/072/data.html

[21] R. Krebs, *Our Earth's Chemical Elements: A reference The History and Use of Our Earth's Chemical Elements*, 2006. 90-92

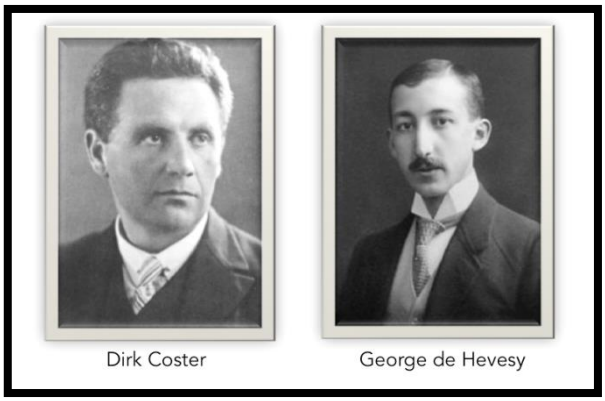
[22] N. Wiberg, M. Eagleson, W. Brewer, J. A Bernhard, *Inorganic Chemistry,*2001, 2

[23] Periodic table, zirconium,[Accessed on 17-03-2017]. Available from: http://www.rsc.org/periodic-table/element/40/zirconium

containing ore.[24] The close similarity between zirconium (Zr) and hafnium (Hf) (see **Chapter 1**, **Section 1.1**), is believed to be the reason why the latter remained undetected in zirconium ores for so long. In 1869, Mendeleev predicted that an element with atomic number of 72 would be found in titanium ore, not in zirconium ore.[24] However, in 1923, Mendeleev was disproved by Dirk Coster and George von Hevesy **(Figure 2.2)** who discovered hafnium in zirconium ore by using x-ray spectroscopy while studying the arrangement pattern of electrons in the outer shell of zirconium in zircon. The analysis and subsequent discovery took place in Copenhagen, Denmark. This led to the element being named after the Latin name for Copenhagen - "Hafnia".[21]

Martin Klaproth[25]

Figure 2.1: The scientist that discovered zirconium element



Dirk Coster George de Hevesy

Figure 2.2: The chemists that discovered hafnium element [26]

[24] Wikipedians, *Chemical Elements, the First Elements, Ordered Alphabetically*

[25] Martin Heinrich Klaproth- pioneer of analytical chemistry, [Accessed on 18-05-2017]. Available from: http://www.worldofchemicals.com/66/chemistry-articles/martin-heinrich-klaproth-pioneer-of-analytical-chemistry.html

As stated previously, the almost identical chemical and physical properties of Zr and Hf makes their separation extremely difficult.[27] The first zirconium impure metal isolation was accomplished in 1824 by Jöns Jacob Berzelius as a black powder, while its first separation from Hf was achieved by A. E. van Arkel and J .H. de Boer in 1925.[22]

2.2 The natural occurrence of zirconium and hafnium

Zirconium containing minerals are found in different natural environments of the universe which include the sun, meteorites, the earth's crust (highest natural abundance), our oceans and within the human vicinity with varying natural abundances which range between 2.6×10^{-9} and 0.013%.[28] Zirconium and hafnium are found in more than ten different minerals[29] which include zircon, baddeleyite, eudialyte, weloganite, painite and vlasovite (**Figure 2.3**).[30] However, from this list, only zircon and baddeleyite are economically important. Currently, zircon is mined in more than seven countries while baddeleyite is mined in only one country in the world (see **Section 2.4**).

[26] Hafnium, [Accessed on 18-05-2017]. Available from: http://72hafnium.weebly.com/

[27] E. Felipe, H. Palhares, A. Ladeira, *International nuclear Atlantic Conference-INAC*, 2013, 1-8

[28] Zirconium resources, reserves and production, [Accessed on 03-02-2017]. Available from: http://metalpedia.asianmetal.com/metal/zirconium/resources&production.shtml

[29] C.Murty, R. Upadhyay, S. Asokan, *Recovery of zircon from Sattankulam deposit in India*, 2007, 69-74

[30] G. Malefo, *Quantification of Hafnium in Selected Inorganic and Organometallic Compounds*, MSc, Thesis, Bloemfontein; University of Free State, 2016

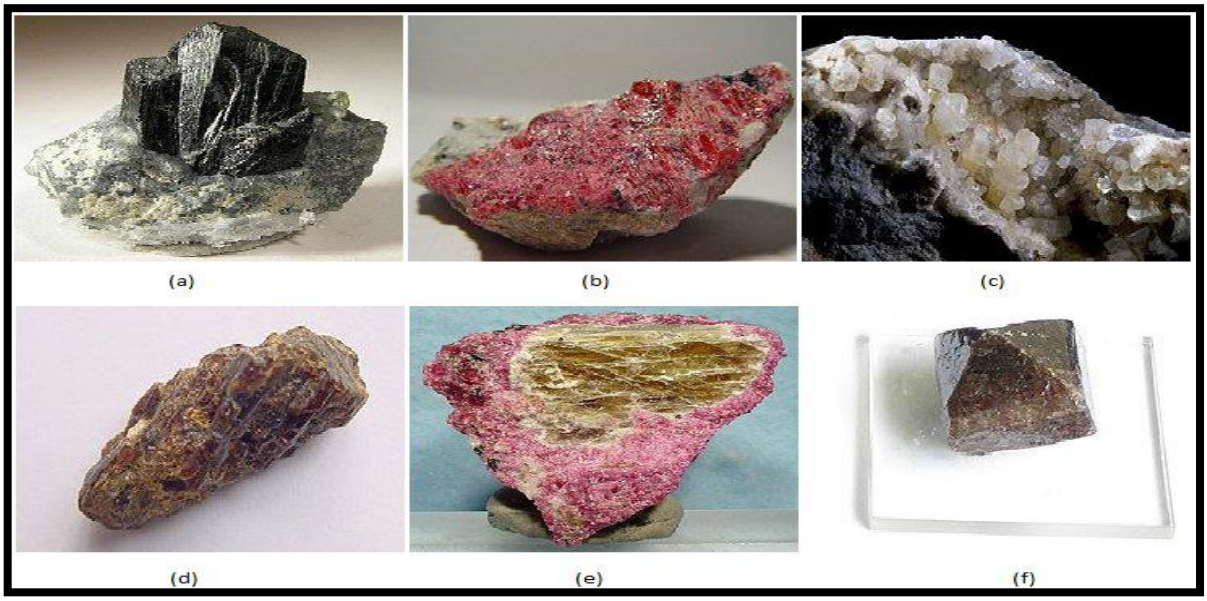


Figure 2.3: Mineral ores: (a) baddeleyite, (b) eudialyte, (c) weloganite, (d) painite, (e) vlasovite, (f) zircon [30]

2.3 The worldwide production of zircon mineral

Worldwide, zircon is mined in a number of countries that include Australia, South Africa, Indonesia, Brazil, China, Kazakhstan, Madagascar, Malaysia, Mozambique, Nigeria, Pakistan, Russia, Sri Lanka, Thailand, Ukraine, USA and Vietnam.[31] Zircon is usually mined as a heavy mineral sand along with titanium deposits, such as, rutile, ilmenite and leucoxene.[32] In Russia and Brazil, for instance, zirconium is mined as baddeleyite and caldasite.[31] Australia is the largest producer of zircon followed by South Africa. In 2015, the two countries produced 500,000 and 380,000 tonnes per annum respectively.[31] The other zircon producing countries mentioned above produce less than 10,000 tonnes of zircon or baddeleyite annually. The global production of zircon for the period of 2005 - 2011 are reported in **Table 2.1**.[29]

[31] DERA Rohstoffinformationen, [Accessed on 26-04-2017]. Available from: http://www.zircon-association.org/Websites/zircon/images/rohstoffinformationen-14.pdf

[32] C. Skidmore, Zirconium and hafnium, [Accessed on 18-05-2017]. Available from: https://www.scribd.com/document/81893296/Zirconium-Hafnium

Table 2.1: The production of zircon by countries from 2005 - 2011 [31]

Country	2005	2006	2007	2008	2009	2010	2011
Australia	428,602	485,040	583,606	495,529	437,478	563,396	738,902
RSA	430,600	434,400	380,800	394,000	348,000	382,987	427,000
Indonesia	10,100	128,350	153,960	65,000	60,000	50,000	127,500
USA	163,957	142,954	120,967	121,967	82,800	100,200	104,935
India	27,133	20,535	35,977	29,158	31,499	85,309	89,796
Mozambique	0	0	0	6,654	21,100	37,122	43,500
China	26,000	28,000	25,000	38,000	31,500	33,500	33,500
Ukraine	33,000	30,000	35,000	35,000	31,000	30,000	27,000
Vietnam	29,100	23,900	24,300	25,303	19,368	23,730	24,020
Brazil	25,440	26,319	26,656	27,258	28,043	23,365	23,765
Russia	10,025	11,311	10,737	12,193	12,354	12,770	12,778
Madagascar	0	0	0	0	4,755	7,490	13,075
Pakistan	0	0	0	0	25	0	6,150
Nigeria	8,980	4,280	1,095	3,240	1,210	1,685	5,630
Sierra Leone	0	0	0	0	3,340	4,260	5,100
Malaysia	4,954	1,690	7,393	984	1,145	1,267	1,685
Sri Lanka	23,587	8,321	381	1,447	10,267	796	641
Kazakhstan	4,990	3,690	8,680	2,280	0	0	600
Thailand	100	100	100	100	100	100	100
Gambia	0	410	355	0	0	0	0
Total	1,226,568	1,349,300	1,415,007	1,258,111	1,123,984	1,357,977	1,685,677

Seven major companies in Australia produce zircon and they include Iluka Resources Ltd as the country's leading zircon producer, Tronox Management Pty Ltd and Cristal Mining Australia Ltd in collaboration with Iluka Resources Ltd. There are also several other new companies waiting to be commissioned in the near future and these include Alkane Resources Ltd, Astro Resources NL, Astron Ltd, and Australian zircon NL. **Figure 2.4** shows a mining site of the Iluka Resources Ltd based in Perth, Australia.[31]

Figure 2.4: Jacinth mine pit – lluka, South Australia [29]

South Africa, which produces 45% of the world's zircon sands,[33] has two major companies, namely Richards Bay Mining Pty Ltd, as the biggest zircon producer in the country and Tronox Resources Ltd. These companies are involved in the mining of heavy mineral sands that contain zirconium and titanium.[29] There are plans to commission another heavy mineral mining company, Mineral Commodities Pty Ltd, in the near future. Richards Bay Mining Pty Ltd mining activities are conducted at Richards Bay in KwaZulu Natal at the following sites - Tisand, Zulti North and Zulti South **(Figure 2.5)**. Tronox Resources Ltd, however, mines zircon at the Namakwa Sands on the coast of the Western Cape and also at KwaZulu-Natal sands.[31]

[33] S. Lubbe, R. Munsami*, D. Fourie*, Benefication of zircon sand in South Africa, [Accessed on 10-02-2017]. Available from: https://www.scribd.com/document/216108228/Beneficiation-of-Zircon

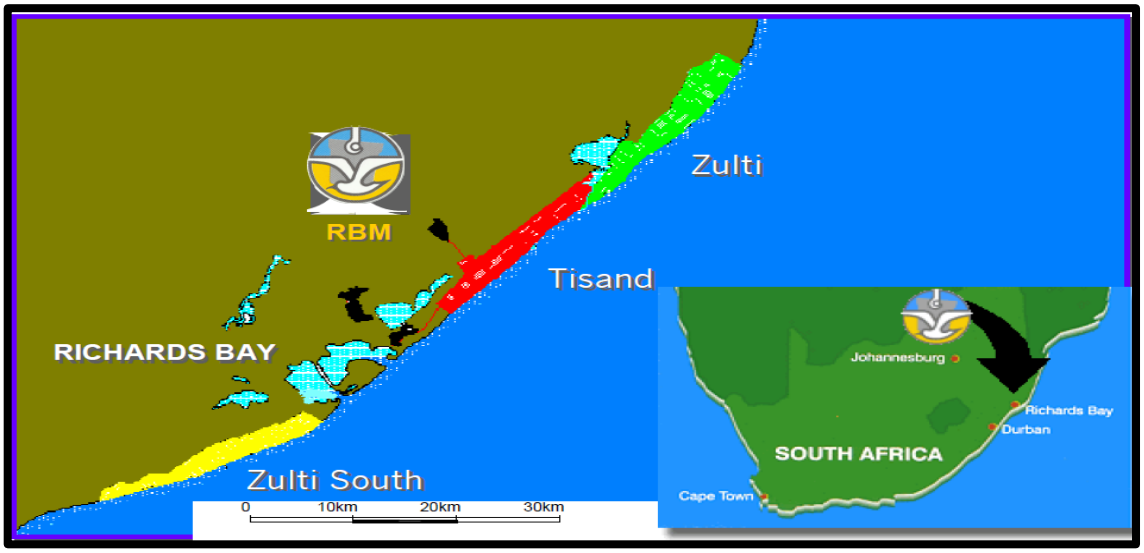


Figure 2.5: Richards Bay's mining sites [34]

The heavy mineral sands, which are mined for its zircon (ZrSiO4), ilmenite ($FeTiO_3$) and rutile (TiO_2) content, are separated from the lighter quartz and clay impurities by spiral separators to produce a heavy mineral concentrate.[35] The different heavy minerals (zircon, ilmenite and rutile) are separated from each other using electrostatic, magnetic and density separation techniques. Zircon, which has the lowest magnetic susceptibility, electrical conductivity and specific gravity (4.70), is easily separated from the highly magnetic ilmenite and rutile.[36] The raw zircon concentrate is then exported to China, one of the few countries with the skills and technology to beneficiate it.[34] The world reserves of zircon are estimated to be approximately 124 million tonnes with Australia being the country with the largest reserves of zircon.[29]

[34] G. E. Wiliams, J. D. Steenkamp, Heavy mineral processing at Richards Bay minerals, *South African Pyrometallurgy 2006,* 2006, March, pp. 5-8

[35] Zircon sand, [Accessed on 18-05-2017]. Available from: http://www.zircon-association.org/zircon-sand.html

[36] G. Jones, Iluka (unpublished), 2009, (4), 38-41

2.4 The market of zircon, zirconium and hafnium

The price of zircon increased steadily from $360 to $850 per tonne between 2003 and 2009.[37] Nevertheless, a sharp price increase to $2,500 per tonne of zircon was observed between 2010 and mid-2012 due to the excessive demand of the mineral in the ceramic industry. However, after mid-2012, the price of zircon began to drop and by mid-2014 it was $1,000 per tonne.[37] This was attributed to an increased zircon supply which exceeded the demand. In addition, the demand for zircon in some European and Asian countries has been declining (**Figure 2.6**) due to the use of aluminosilicate minerals as substitute for zircon in traditional ceramics and foundries manufacturing. The aluminosilicate minerals are relatively cheaper, readily available and perform almost the same function as zircon in ceramics and foundries. It is anticipated that the demand for zirconium chemicals in future will result in an upward trend in the selling price and that the growth in demand for zircon will increase to approximately 5% per annum.[37]

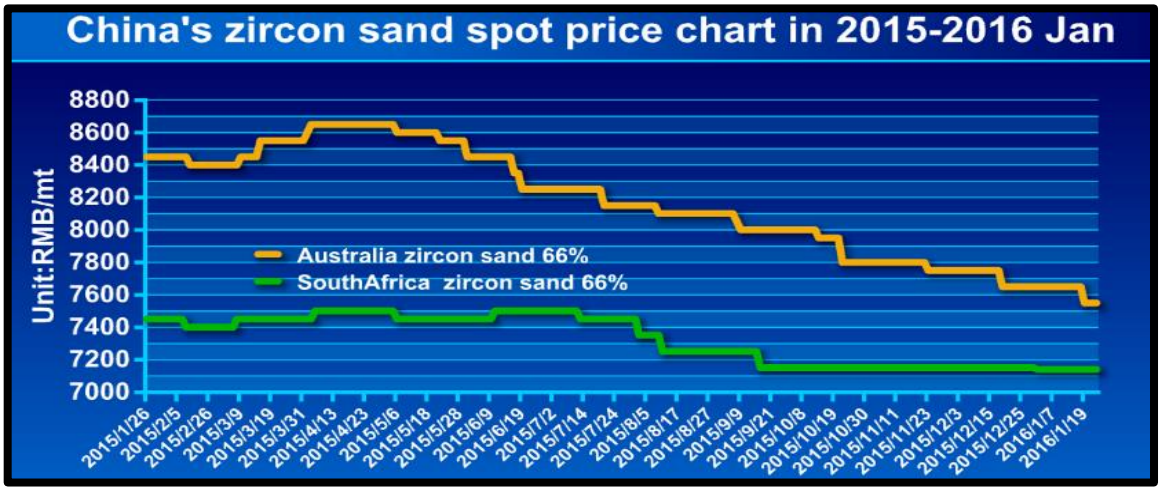


Figure 2.6: Recent decreases in zircon demand [37]

Prices of the pure zirconium metal are not readily available, but unwrought zirconium metal prices (contain hafnium as impurity) are available. From 2003 to 2007, the price of unwrought zirconium metal decreased from $39,900 to $ 22,700 per tonne

[37] Alkane resources and its zirconium- what comes around, [Accessed on 18-05-2017]. Available from: https://investorintel.com/sectors/technology-metals/technology-metals-intel/alkane-resources-and-its-zirconium-what-comes-around/

because there was a lesser demand from the nuclear industry.[38] Hafnium prices, on the other hand, showed little volatility for period between 1970 and 2000. From 2003 to 2009 the price of hafnium continued to increase (**Figure 2.7**), mainly due to the discovery of its use in specialized applications, especially in the aerospace industry.[39] The price of the hafnium metal varied significantly based on the purity of hafnium - the lower the percentage of zirconium in hafnium, the higher the price of hafnium. For example, hafnium containing 0.2-0.5 % zirconium sold for $1200-1300 per kilogram and 0.5-1.0 % zirconium in hafnium sold for $800-900 per kilogram while 1-3 % zirconum in hafnium sold for $500-700 per kilogram.[38]

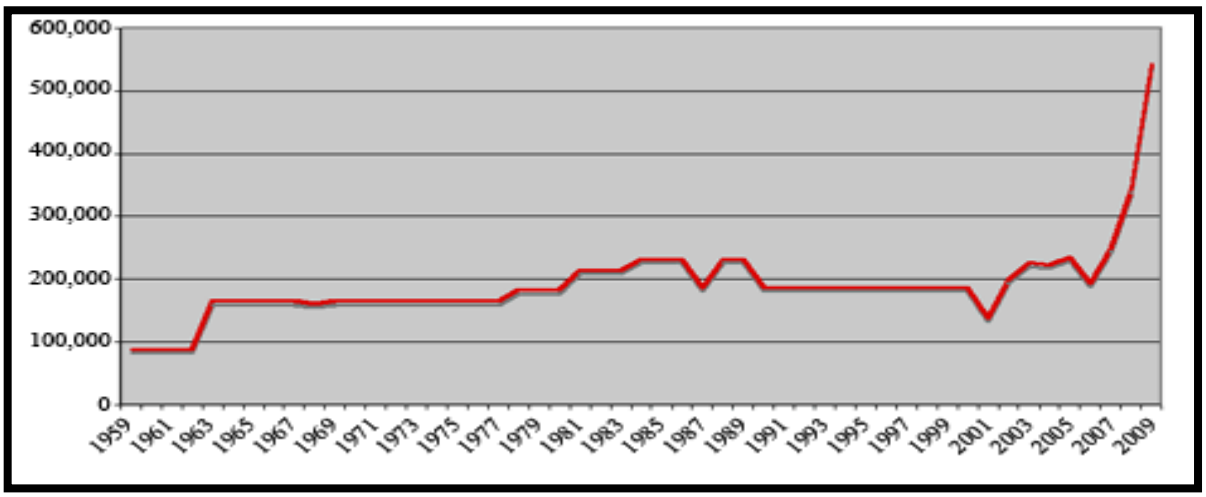


Figure 2.7 Hafnium prices USD/tonne [39]

2.5 The application and uses of zirconium and hafnium chemicals

Zirconium chemicals are well known as very useful compounds in different multi-industrial and scientific applications because they are regarded as high-technology materials due to their mechanical, thermal, electrical, chemical and optical

[38] Global zirconium market, [Accessed on 19-06-2017]. Available from: https://www.mordorintelligence.com/industry-reports/global-zirconium-market-industry?gclid=CKWApN2BytQCFUu-7QodHSMPHQ

[39] Hafnium, *the 6th annual cleantech & technology metals summit*, alkane resources LTD

properties.[40] Zirconium chemicals such as zirconium dioxide and zirconium hydroxide play an important role in the glass indus because of their ability to increase the refractive index of optical glasses and glass toughening.[41] In glass-melting furnaces, zirconium oxide and zirconium silicate are used as zirconium-containing refractories to increase the thermal shock resistance of the final products. In the electro and other ceramics industries, zirconium hydroxide, zirconium acetate and zirconium propionate are used as dielectrics in capacitors, sensors and piezoelectrics.[40]

Inorganic zirconium salts such as the metal hydroxide, propionate, oxychloride, hydroxychloride, nitrate, phosphate and orthosulphate play an important role as support and controllers' catalysts in autocatalysis, stationary, refinery and chemical catalysis.[40] Zirconium phosphate, hydroxide, acetate, propionate and ammonium chemicals are used as pigments in the production of ink and paint. Zirconium oxychloride, hydroxychloride and nitrate chemicals are also added as decorative products to provide waterproof and flameproof properties to wall surfaces in the textile industries. Finally, zirconium diboride-containing materials are used in jewellery manufacturing, (see **Figure 2.8**) because of their high-wear oxidation and corrosion resistance, as well as, their non-biological reactivity with the body tissues.[39]

[40] Z. Metal, *Zirconium chemicals in the ceramic industry*, 17-20

[41] Picture of sample of zirconium, [Accessed on 18-06-2017]. Available from: http://www.chemistry.pomona.edu/chemistry/periodic_table/elements/zirconium/zirconium.htm

Figure 2.8 Rings made from zirconium [42]

Hafnium, on the other hand, has fewer uses compared to zirconium due its scarcity and difficulty to produce pure hafnium metal. Hafnium carbide is used in super alloy production for the hot parts in jet engines, as well as, in the production of refractory binary materials which improve their hardness and corrosion resistance.[39] Hafnium chloride and hafnium oxide are used in microprocessors as silicon replacement due to their better performance to temperature.[43]

In nuclear energy production, high purity metallic zirconium is used as the cladding material for nuclear fuel assemblies because zirconium metal is 'transparent' to neutrons, has good high temperature performance and has good anti-corrosion properties.[44] Hafnium metal, conversely, is often used as the control rods in a nuclear

[42] Zirconium uses in everyday life, [Accessed on 24-06-2017]. Available from: https://alfa-img.com/show/what-are-the-uses-of-zirconium.html

[43] Hafnium: Small Supply, Big Applications, [Accessed on 12-05-2017]. Available from: http://www.etf.com/sections/features-and-news/2572-hafnium-small-supply-big-applications?nopaging=1

[44] Zirconium cladding is the reactor's primary safety barrier, [Accessed on 6-4-2017]. Available from: http://www.areva.com/EN/operations-2294/zirconium-cladding-is-the-reactors-primary-safety-barrier.html

reactor due to its high neutron cross-section area which is 600 times greater than that of zirconium (0.18 barn).[45] The hafnium rods are inserted with guide tubes into the nuclear reactor in order to decrease the neutron flux that split further uranium atoms and thus control the nuclear process.[37] The zirconium used for the construction of the nuclear cladding containers should be ultra-pure and contain as little hafnium (≤100ppm) as possible (see **Table 2.2**).[46]

Table 2.2 Chemical specification of zirconium sponge, reactor grade R60001[47]

Element	Thermal neutron capture (barns)	Permissible impurities (ppm_{max})
Aluminium	0.232	75
Boron	767	0.5
Cadmium	2450	0.5
Carbon	0.0035	250
Chlorine	35.5	1300
Chromium	3.1	200
Cobalt	37.2	20
Copper	3.78	30
Hafnium	104	100
Iron	2.56	1500
Manganese	13.3	50
Molybdenum	2.6	50
Nickel	4.49	70
Nitrogen	1.91	50
Oxygen	0.00019	1400
Silicon	0.171	120
Titanium	6.09	50
Tungsten	18.3	50
Uranium (total)	7.57	3.0

[45] Separation method of zirconium and hafnium by solvent extraction process, [Accessed on 4-05-2017]. Available from: http://patents.justia.com/patent/8778288

[46] J. Amaral, L. Rocha, C. Morais, *International Nuclear Atlantic Conference - INAC 2013*, 2013

[47] Standard specification for zirconium sponge and other forms of virgin metal for nuclear application, *Designation:B349/B349M-03*

The demand for pure zirconium and hafnium metals is currently increasing due to their role in nuclear energy. This places a lot of emphasis on finding cost-effective and eco-friendly methods of separating zirconium and hafnium from zircon ore since the two elements always occur together in nature.[37] **Figure 2.9** highlights the use of zirconium chemicals in the different industries.

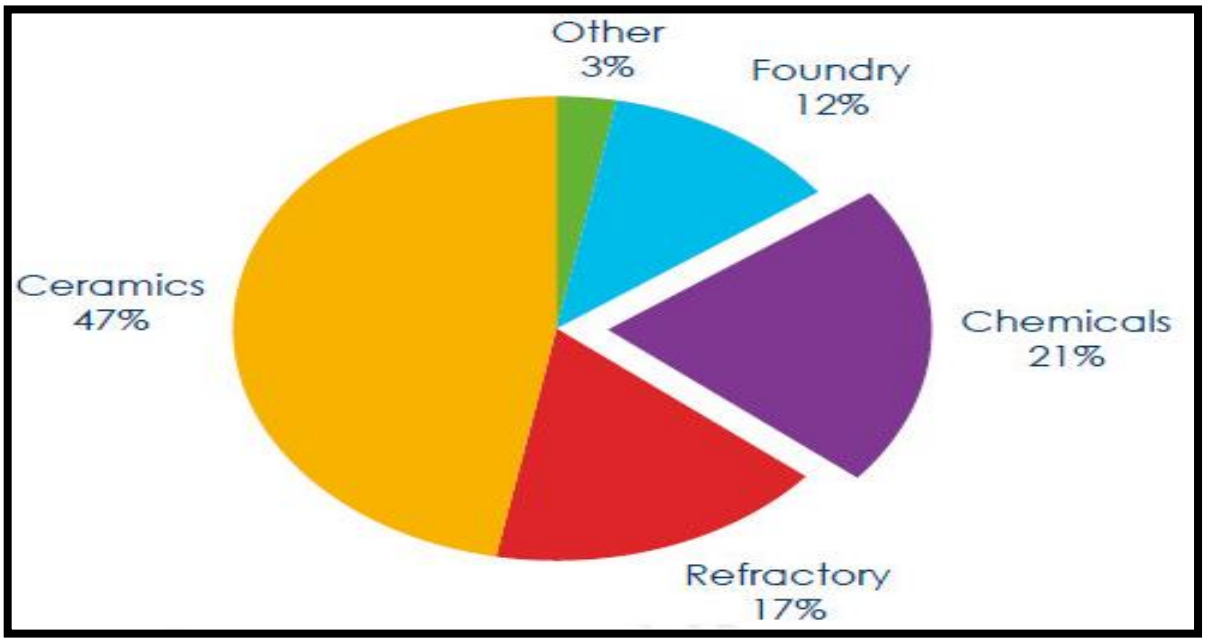


Figure 2.9 Zircon distribution in 2013-2015 [37]

2.6 Zirconium and hafnium chemistry and separation

2.6.1 The physical and chemical properties of zirconium and hafnium

2.6.1.1 Physical properties

Both the zirconium and hafnium metals are relatively soft, flexible and malleable with a silvery sheen that conducts electrical current.[48] Under normal conditions, both the metals crystallize in hexagonal close-packed lattices (α-Zr, α-Hf), and at higher temperatures, are converted into crystals with cubic body-centered packing (β -Zr, β-Hf). The most important difference in their properties is with reference to the nuclear industry with hafnium's ability to absorb neutrons which is 600 times greater than that

[48] J.H. Schemel, *Astm manual on zirconium and hafnium*, 1977

of zirconium whose applications do not require their separation due to their very similar chemical properties. The metals also have very similar atomic, ionic radii, ionisation energies (see **Table 2.3**).[49]

Table 2.3: Physical properties of zirconium and hafnium elements [48]

Physical property	Zirconium	Hafnium
Atomic number	40	72
Atomic weight	91.22	178.49
Melting point ^{o}C	1857	2150
Density g/cm^3	6.5	13.1
Boiling point ^{o}C	3577	5400
Transition temperature ^{o}C	862	1670
Atomic radius ^{0}A	1.452	1.442
Ionic radius ^{0}A	0.74	0.75
Body-centered packing(β ^{o}C)	>867	1775
Ionisation potential ($kJmol^{-1}$)		
1^{st}	674.1	530
2^{nd}	1268	1425.5
3^{rd}	2217	2244.3
4^{th}	3313	3207.5

2.6.1.2 Chemical properties

Zirconium and hafnium form many compounds with the elements in their most stable tetravalent (+4) oxidation state with electron configuration of $[Kr]4d^2 5s^2$ and $[Xe]4f^{14}5d^2 6s^2$ respectively. Zirconium (IV) and hafnium (IV) react readily with fluorine and oxygen. During their reactions with oxygen, basic metal oxides are formed. The elements also form many different complexes with coordination numbers of seven and eight (see **Table 2.4**).[50]

[49] A. F. Holleman, E. Wiberg, *Inorganic chemistry,2001, 1st ed*

[50] F. A. Cotton, G. Wilkinson, P. L. Gaus, *Basic inorganic chemistry*, 1976, 3rd ed

Table 2.4: Oxidation state and stereochemistry of zirconium and hafnium [50]

Zirconium(IV), hafnium (IV), d^o		
Coordination number	**Geometry**	**Example**
6	Octahedral	Li_2ZrF_6, $CuZrF_6{\cdot}4H_2O$
	Trigonal prismatic	$[Zr(S_2C_6H_4)_3]^{2-}$)
7	Pentagonal bipyramidal,	$(NH_4)_3[ZrF_7]$, Na_3ZrF_7
	Capped trigonal prismatic	$Ba_2Zr_2F_{12}$
8	Dodecahedral	K_2ZrF_6, $[Hf(SO_4)_4(H_2O)_2]^{4-}$, $[M(ox)_4]^{4-}$
	Square antiprismatic	$Zr(acac)_4$, $[Cu(H_2O)_6]_2[ZrF_8]$

Again, both metals react readily with aerial oxygen to form a very thin metal dioxide layer (**Equation 2.3**) which is extremely useful in protecting the metals from further oxidation and making them highly resistant to acids and alkalis.

$$M\,(s) + O_2\,(g) \longrightarrow MO_2\,(s) \qquad 2.3$$

Hafnium (IV) oxide is a colourless solid and the most stable of the Hf compounds. It is commonly used as an electrical insulator due to its band gap of around 6 eV. Hafnium oxide is also usually used as a starting material in the production of Hf metal and other hafnium chemicals.[51] Zirconium oxide, contrarily, is a white crystalline oxide

[51] Hafnium Oxide Powder HfO_2, [Accessed on 12-04-2017]. Available from: http://www.reade.com/products/hafnium-oxide-powder-hfo2

that can be synthesized into different colours for use as gemstone and/or diamond simulant (see **Figure 2.10**).[52]

Figure 2.10: Different colours made from zirconium compounds

Both Zr and Hf are extremely inert in hot or cold water, but they react with halogens to form metal (IV) halides (see **Equations 2.4 and 4.5**).[21] The different Zr and Hf halides sublime at temperatures between 180 and 330 ^{o}C respectively. [55]

$$Hf^{4+} + 4Cl^{-} \longrightarrow HfCl_4 \qquad 2.4$$

$$Hf^{4+} + 4F^{-} \longrightarrow HfF_4 \qquad 2.5$$

Zirconium, in contrast to hafnium, can also react with chloride to form stable chloride compounds with the metal in +2, +3, and +4 oxidation states (**Equations 2.6, 2.7 and 2.8)**.[21]

[52] Zirconium dioxide, [Accessed on 12-04-2017]. Available from: https://en.wikipedia.org/wiki/Zirconium_dioxide

[53] Gemstone, [Accessed on 21-08-2017]. Available from: https://en.wikipedia.org/wiki/Gemstone#/media/File:Cardinal_gems.png

[54] Diamond simulant, [Accessed on 21-08-2017]. Available from: https://en.wikipedia.org/wiki/Diamond_simulant#/media/File:CZ_brilliant.jpg

[55] N. Balwyn, *United States Patent O" potent into tetrahalides, followed by the reduction of the 70*, 1957, 2-3

$Zr^{2+} + 2Cl^- \longrightarrow ZrCl_2$ 2.6

$Zr^{3+} + 3Cl^- \longrightarrow ZrCl_3$ 2.7

$Zr^{4+} + 4Cl^- \longrightarrow ZrCl_4$ 2.8

2.6.2 Beneficiation of zircon

The low neutron cross-section area for thermal absorption, its high mechanical strength and corrosion resistance at high temperature makes zirconium alloys the mostly preferred material for cladding in nuclear power reactors. Other impurities such as B, Cd, U and Hf have to be separated from Zr prior to their application in the nuclear industry as they negatively affect the Zr properties, for example, its transparency to neutrons.[56] Different processes have been developed for the extraction of either Zr or Hf from the zircon mineral. The separation process includes decomposition and dissolution of the mineral, subsequent separation of the constituents therein and finally, production of pure metals. The decomposition procedures include caustic fusion, carbochlorination, fluorosilicate fusion and plasma dissociation processes. During the decomposition of zircon, zirconium and hafnium always remain together in the solution due to their similar physical and chemical properties.[57]

2.6.2.1 Caustic fusion

Zircon ($Zr(Hf)SiO_4$) is mixed with sodium hydroxide (NaOH) and heated at 650^oC to produce sodium zirconate ($Na_2Zr(Hf)O_3$) and/or sodium metasilicate (Na_2SiO_3), depending on the molar ratio of sodium hydroxide to zircon (see **Equations 2.9 and 2.10**). These fusion products are washed with water to dissolve sodium metasilicate while sodium zirconate is hydrolysed to an insoluble hydrous zirconia (see **Equation 2.11**).[58] This process is good for the production of zirconium oxide but it is

[56] L. Xu, Y. Xiao, A. Sandwijk, Q. Xu, Y. Yang, Production of nuclear grade zirconium, *Journal of nuclear materials*, 2015, 466, 21-28

[57] C. Silicone, *Recovery of zirconia from zircon sands*, 34-52

[58] S. Lotter, *Analysis of zirconium-containing materials using multiple digestion and spectrometric techniques*, 2014

environmentally unfriendly because of high treatment cost and large amount of chemical waste that may cause damage to the environment.[59]

$$Zr(Hf)SiO_4 + 4NaOH \longrightarrow Na_2Zr(Hf)O_3 + Na_2SiO_3 + 2H_2O \quad 2.9$$

$$Zr(Hf)SiO_4 + 6NaOH \longrightarrow Na_2Zr(Hf)O_3 + Na_4SiO_4 + 3H_2O \quad 2.10$$

$$Na_2Zr(Hf)O_3 + xH_2O \longrightarrow NaOH + Zr(Hf)O_2.xH_2O \quad 2.11$$

2.6.2.2 Carbochlorination

This process entails the carbochlorination of zircon at a temperature of 1100^oC, where chlorine is used as fluidising gas (see **Equation 2.12**). The gaseous products, $Zr(Hf)Cl_4$, $SiCl_4$ and CO are cooled down to 200^oC upon which $Zr(Hf)Cl_4$ solidifies, leaving the other products in gaseous state. The solid $Zr(Hf)Cl_4$, is then hydrolysed to form zirconium oxychloride ($Zr(Hf)OCl_2$).[57] $Zr(Hf)OCl_2$ is further cooled to 20^oC to obtain a crystalline compound ($Zr(Hf)OCl_2.8H_2O$), thereby enabling separation of impurities from the product and subsequent formation of zirconia by calcination of the crystals.

$$Zr(Hf)SiO_4 + 4Cl_2 + 4C \longrightarrow Zr(Hf)Cl_4 + SiCl_4 + 4CO \quad 2.12$$

2.6.2.3 Fluorosilicate fusion

Potassium hexafluorosilicate (K_2SiF_6) is reacted with zircon to form hexafluorozirconate ($K_2Zr(Hf)F_6$) in a rotary furnace at a temperature of 700 ^oC (see **Equation 2.13**). K_2CO_3 or KCl is added as a catalyst to ensure the completion of the reaction and to prevent the dissociation of K_2SiF_6 into silicon tetrafluoride ($SiCl_4$), where $SiCl_4$ is lost by sublimation.[55] The solid product is filtered and washed with 1% HCl solution to separate the insoluble silica from the solution. $K_2Zr(Hf)F_6$ crystals are

[59] S. Yugeswaran[a], P.V.Ananthapadmanabhan[b],* T.K.Thiyagarajan[b], K.Ramachandran[c], Plasma dissociation of zircon with concurrent in-flight removal of silica, *Ceramics international* 2015, 41, 8, 9585-9592

obtained during the cooling of the hot solution. A solid product that is formed is then washed with water.

$$Zr(Hf)SiO_4 + K_2SiF_6 \longrightarrow K_2Zr(Hf)F_6 + 2SiO_2 \quad 2.13$$

2.6.2.4 Plasma process

The plasma process involves transferring zircon sand through a plasma flame at a very high temperatures (>2500^oC). In this process, the zircon crystal dissociates into the monoclinic zirconia and silica crystal structure (see **Equation 2.14**). The molten zircon is cooled rapidly to prevent the re-association of the zirconia and silica species. The resultant monoclinic zirconia (Plasma Dissociated Zircon – (PDZ)) is embedded in an amorphous silica matrix and can easily be leached using mineral acids such as H_2SO_4 (in excess), HF and NH_4HF_2 (see **Equations 2.15 to 2.20**).[60]

$$Zr(Hf)SiO_4 \longrightarrow Zr(Hf)O_2.SiO_2 \quad 2.14$$

By leaching the PDZ with excess H_2SO_4, the zirconia is dissolved in H_2SO_4 at 337^oC, while the silica precipitate is separated from the zirconium sulphate solution by filtration.[60]

$$Zr(Hf)O_2.SiO_2 + 3H_2SO_4 \xrightarrow{\Delta} Zr(Hf)(SO_4)_2 + SiO_2 + SO_3\uparrow + 3H_2O\uparrow \quad 2.15$$

Hydrofluoric acid (HF) is another mineral acid that can dissolve PDZ into $H_2Zr(Hf)F_6$ and H_2SiF_6 solution (see **Equation 2.16**) and are separated by evaporative crystallization. Steam pyrolysis (600-800 ^oC) of the product ($H_2Zr(Hf)F_6$), produce pure ZrO_2. $K_2Zr(Hf)F_6$ can also be produced by reacting $H_2Zr(Hf)F_6$ with KF. $K_2Zr(Hf)F_6$ can also be used in the separation of Zr and Hf by fractional

[60] S. Lubbe, R. Munsami, D. Fourie, Beneficiation of zircon sand in South Africa, *Journal of the Southern African Institute of Mining and Metallurgy*,2012, 112(7), 583-588

crystallization. $H_2Zr(Hf)F_6$ can also be used as starting material for the separation of Zr and Hf by ion exchange.[61]

$$Zr(Hf)O_2.SiO_2 + 12HF \longrightarrow H_2Zr(Hf)F_6 + H_2SiF_6 + 4H_2O \quad 2.16$$

Ammonium bifluoride (NH_4HF_2) is also a reagent used to decompose PDZ to obtain $Zr(Hf)F_4$ (see **Equations 2.17 – 2.20**). These **Equations** are based on different temperatures at 180 ^oC, 300 ^oC, 350 ^oC, and 400 ^oC respectively.[62]

$$Zr(Hf)O_2{\cdot}SiO_2 + 8NH_4HF_2 \longrightarrow (NH_4)_3Zr(Hf)F_7+(NH_4)_2SiF_7+3NH_4F +4H_2O \quad 2.17$$

$$(NH_4)_3Zr(Hf)F_7 \longrightarrow (NH_4)_2Zr(Hf)F_6+NH_4F \quad 2.18$$

$$(NH_4)_2Zr(Hf)F_6 \longrightarrow (NH_4)Zr(Hf)F_5+NH_4F \quad 2.19$$

$$(NH_4)Zr(Hf)F_5 \longrightarrow Zr(Hf)F_4+NH_4F \quad 2.20$$

2.6.3 Zirconium and hafnium separation

The strong similarity between Zr and Hf (see **Section 2.6.1**) makes the separation of these elements extremely challenging. However, this separation is inevitable for Zr applications in the nuclear industry where only a maximum of 100 ppm Hf concentration may be tolerated in the Zr metal.[46] Different separation techniques have been developed (see **Chapter 3, Section 3.3)** and some have even been applied on the industrial scale. The most commonly used processes will be discussed in the following sections and these include fractional crystallization, ion exchange and solvent extraction.[63]

[61] T. N Nhlabathi, J. T. Nel, G. J. Puts, P. L. Crouse, Microwave digestion of zircon with ammonium acid fluoride: derivation of kinetic parameters from non-isothermal reaction data, 2012

[62] M. M. Makhofane, J. L. Havenga, J. T. Nel, W. du Plessis, C. J. Pretorius, Manufacturing of anhydrous zirconium tetrafluoride in a batch reactor from plasma-dissociation zircon and ammonium bifluoride, *The Journal of the Southern Africa Institute of Mining and Metallurgy*, 2012, Vol.7A , 559

[63] L. Xu, Y. Xiao, A. Sandwijk et al., *Energy materials*, 2014, 451-457

2.6.3.1 Fractional crystallization

Fractional crystallization is one of the oldest methods for the separation of Zr and Hf. Beaver, in 1950,[64] reported on the separation of Zr and Hf using the mixture of $(NH_4)_2Zr(Hf)F_6$ (with solubilities of 0.611 for Zr and 0.891 mol/L for Hf). These are more soluble in water than the potassium salts of Zr and Hf (with solubilities of 3.304 x 10^{-5} for Zr and 6.079 x 10^{-5} mol/L for Hf).[65] This method was limited by the unstable nature of ammonium salt and the corrosive conditions which resulted from the use of highly acidic solutions to decompose the sample. The fractional crystallization of $K_2Zr(Hf)F_6$ was created to overcome the problems of using ammonium salt. This method gave a higher separation factor and a larger change in solubility between room temperature and 100 ^oC. This process involves a multi-step recrystallization process. K_2ZrF_6 crystallizes upon cooling the solution while K_2HfF_6 remains soluble. This is facilitated by their different solubilities, whereby, Hf salts have a higher solubility than Zr salts.[66] This process is tedious and expensive as it involves 18 stages of separation to obtain nuclear quality products and has a low process efficiency.[67,68]

2.6.3.2 Ion exchange

Ion exchange is another method used for the separation of similar ions in aqueous solution. The selection of this separation method usually depends on the type of ion exchange resin used, as well as, the composition of the aqueous solution.[69] K. Prakashan[70], used an anion exchange resin Amberlite IRA-400 as a stationary phase to separate the mixture of $(NH_4)ZrF_6$ and $(NH_4)_2HfF_6$ which was eluted with H_2SO_4 as a mobile phase. Zr and Hf hexaflouroanions were then absorbed into the resin with

[64] W. W. Beaver, BB54, 1950

[65] H. J. Emeleus, A. G. Sharpe, Advances in inorganic chemistry and radiochemistry, 1970, Vol.13

[66] M. Shamsuddin, Physical chemistry of metallurgical processes, 2016

[67] D. J. Branken, Separation of Zr and Hf via fractional crystallization of $K_2Zr(Hf)F_6$, 2009

[68] D. Royston, P. G. Alfredson, Review of processes for the production of hafnium-free zirconium, 1970

[69] X. J. Yang, C. Pin, A. G. Fane, Separation of hafnium from zirconium by extraction chromatography with liquid anionic exchangers, *Journal of chromatographic science*, 1999, 37

[70] B. K. Sharma, Chromatography, GOEL Publishing House, Meerut, 2007

different capacities and Hf was eluted in the first fraction.[70] The downside to this method is that the ion exchange resin is also very expensive when it comes to its use on a commercial scale.[57]

2.6.3.3 Solvent extraction

Solvent extraction is extensively used to separate zirconium and hafnium on a commercial scale. The conventional extractants that are mostly used in their separation include thiocyanate, Methyl Isobutyl Ketone (MIBK) and Tributyl Phosphate (TBP). Union Carbide in the USA developed this method.[67] The procedure involves the mixing of zirconium and hafnium oxychloride ($Zr(Hf)OCl_2$) (as starting material) with NH_4SCN in NH_4OH. The resultant zirconyl and hafnyl thiocyanate complexes ($Zr(Hf)O(SCN)_2$) form the feed solution which are then extracted with MIBK. The Hf thiocyanate complex ($HfO(SCN)_2$) is selectively extracted into the organic solvent, leaving the zirconium complex in the aqueous phase.[67,71] The Zr-enriched aqueous solution is further mixed with H_2SO_4 acid, where pentazirconyl sulphate is precipitated, filtered, washed and then calcinated to obtain zirconia.[71]

The use of MIBK offers some advantages that can enable the production of Zr and Hf on the nuclear industry level because MIBK as an extractant is characterised by such a high load capacity. However, the use of MIBK as an extracting solvent also has several challenges which include a large consumption of the organic solvent, high MIBK volatility and its solubility in water (0.019 g/ml).

The TBP extraction procedure, on the other hand, involves the dissolution of hafnium and zirconium oxide in nitric acid and subsequent extraction of the Zr and/or Hf into a kerosene solution containing TBP as ligand. The high formation constant (K_f) of neutral zirconium complex caused by nitric acid enhances Zr to be selectively extracted into the organic layer while hafnium remains in the aqueous layer.[56]

[71] R. H. Nielsen, J. H. Schlewitz, H. Nielsen, *Zirconium and zirconium compounds. In Kirk-Othmer encyclopaedia of chemical technology*, 2001, 5th ed. John Wiley & Sons. 26, 621 - 664.

Distillation is used to recycle the nitric acid from both metal streams and the solutions are then neutralized with NH_4OH to precipitate. The Zr and Hf hydroxides are then calcined to obtain the relatively pure zirconia or hafnia products.

Nielsen *et al.*,[71] indicated that the TBP extraction process has a higher extraction efficiency for zirconium than hafnium. However, this extractant produced relatively low elemental concentrations in both phases, consumed a lot of chemicals and was found to seriously corrode the equipment.[63] This is the major reason why the technique has been abandoned by countries such as France, Britain and USA.[59,67]

2.7 Conclusion

The almost identical physical and chemical properties of Zr and Hf have always made their separation extremely challenging. However, separation is inevitable for the two metals in a very specialized application such as in the nuclear industry. Currently, the techniques used for the separation of these two elements are either tedious, involve multi-stage processes, very costly, or require the use of corrosive and environmentally unfriendly chemicals such as HF. Therefore, research has to constantly seek to try and find better cost-effective and environmentally-friendly alternative processes. In addition, South Africa as the second leading zircon producer only benefits from the sales of zircon ore. The ability to process the zircon mineral to a more value-added product in South Africa will not only improve the economy through increased revenue collection, but will also assist in job creation. The main aim of this project is to investigate the possible separation of Zr and Hf in inorganic salts $(Zr/Hf)O_2$ using ion exchange and solvent extraction, and further apply the optimum separation conditions to separate the two elements of interest in Plasma-Dissociated Zircon (PDZ).

3 Dissolution and separation of zirconium and hafnium: literature survey

3.1 Introduction

The separation of zirconium (Zr) and hafnium (Hf) from each other is often complicated by the low Hf concentrations (2-3%) present in the different Zr minerals, as well as, the similar chemical and physical properties of these elements. In addition, the chemical resistance of Zr minerals to dissolve, even using aggressive experimental conditions such as high temperatures and acidity, limits the number and types of analytical and separation techniques which can be investigated. The most successful dissolution procedures include HF leaching [72] and flux fusion at high temperatures,[73] while the most commonly used and highly successful separation techniques include solvent extraction[74] and fractional distillation of some metal halogen salts.[75] This chapter will review some of the research work that has been done to date concerning the dissolution, separation, recovery of the zirconium and hafnium from zirconium-bearing materials and analytical techniques used.

[72] G. J. Neuerburg, a method of mineral separation using hydrofluoric acid, *The American Mineralogist*, 1961, Vol.46

[73] S. J. Lötter, W. Purcell, J. T. Nel, E. Snyders, Alternative dissolution of zircon samples and simultaneous analysis of major and trace components, *The Journal of the Southern African Institute of Mining and metallurgy*, 2012, Vol.112

[74] J. C. B. S. Amaral, L. R. T. Rocha, C. A. Morais, Study of the separation of zirconium and hafnium from nitric solutions by solvent extraction, *2013 International Nuclear Atlantic Conference*, 2013

[75] L. Q. Minh, N. V. D. Long, P. L. T. Doung, Y. Jung, A. Bahadori, M. Lee, Design of an extraction distillation column for the environmentally benign separation of zirconium and hafnium tetrachloride for nuclear power reactor applications, *Energies*, 2015 (8)

3.2 The dissolution and analysis of zirconium-bearing materials

The proper choice of decomposition and dissolution techniques of analytical samples are critical to successfully separate the minerals' elements within the mixture. Additionally, this choice of sample preparation should be aligned appropriately with the available analytical techniques. Most analytical measurements are often performed on homogeneous solutions and the dissolution of the samples are often achieved by dissolving them in water, acids, or bases, as well as, flux fusions at elevated temperatures.[76]

Chieko *et al.*,[77] used caustic soda as flux in the decomposition of zircon (see **Chapter 2**, **Section 2.6.2.1)**. The procedure involved the mixture of 50% NaOH solution with zircon and the subsequent heating to 600 ^{o}C for two hours. The resultant slurry was filtered, washed in water, dried and calcined. The solid product was then analysed by XRF and recoveries of up to 98.5 % ZrO_2 and 99.5 % SiO_2 were obtained. This method proved to be effective for the dissolution and separation of Zr from most of the other mineral constituents, but not necessarily from Hf.

Carbochlorination was found to be good for the production of $ZrCl_4$ from a zircon concentrate or zirconium oxide as the starting materials (see **Equation 2.12, Chapter 2**). Chiba *et al.*,[78] carried out a study on the synthesis of $ZrCl_4$ from ZrO_2, by mixing ZrO_2 (77.7 % in weight), graphite (9.8% in weight) and sugar (12.5 % in weight). The mixture was dried in an oven and pelletized. The isolated pellets were transported into an alumina reactor located inside the chlorination furnace, where it

[76] Decomposing and dissolving the sample, [Accessed on 31-05-2017]. Available from: http://www.cengage.com/resource_uploads/downloads/0495558281_371363.pdf

[77] Y. Chieko, J. B. Andrade, V. Ussui, N. B. Lima, J. O. A. Paschoal, High purity zirconia and silica powders via wet process: Alkali fusion of zircon sand, *Material Science Forum*, 2008, Vols. 591-593, 771-776

[78] R. Chiba, E. G. R. Menezes, M. Andreoli, E. S. M. Seo, Obtaining of the nuclear grade zirconium tetrachloride by the chlorination process, *IPEN- Nuclear and Energy Research Institute*

reacted with chlorine gas at 600 ^{o}C and then condensed to form $ZrCl_4$. The isolated product ($ZrCl_4$) was characterized by ICP-OES and a yield of 95 % for $ZrCl_4$ was obtained. The study concluded that the nuclear grade $ZrCl_4$ produced by this procedure should be used as raw material for the production of nuclear grade metallic zirconium sponge (see **Table 3.1**).

Table 3.1: The nuclear grade $ZrCl_4$ produced by ATI Metals[78]

Chemical Elements	Concentration (ppm)
Aluminium	50-100
Iron	500-1000
Hafnium	50-100
Silicon	<25-100
Titanium	<50-200

Jamrack,[79] isolated a high purity Zr compound from zircon using fractional crystallization. A mixture of $ZrSiO_4$ and K_2SiF_6 was decomposed in a rotary furnace at 650 – 700 ^{o}C for four hours (see **Chapter 2, Equation 2.13**). The conversion of zircon to fluorozirconate was found to be very successful with almost total conversion (97 – 99 %). The isolated product was ground to a 100 mesh powder and leached with 1 % HCl solution at 85 ^{o}C. Potassium fluorozirconate crystals formed upon cooling, while the resultant mother solution contained 0.044 % Fe, 0.041, 0.06 and 0.007 % Ti, Si and Cl respectively, as impurities.[80]

Havenga and Nel[81] investigated the conversion of zircon into a more soluble form PDZ (plasma-dissociated zircon), thereby looking into different experimental

[79] W. D. Jamrack, Rare metal extraction, *Chemical Engineering Techniques*, 1963

[80] M. Shamsuddin, Physical chemistry of metallurgical processes

[81] J. L. Havenga, J. T. Nel, The manufacture of plasma-dissociation zircon (PDZ) via a non-transferred arc process utilizing three 150kW DC plasma torches, The Journal of the Southern Africa Institute of Mining and Metallurg, 2012, Vol.7A

parameters such as particle size, the feed rate and different plasma gases. They reported the conversion percentages ranging between 94 – 96 %. Currently, hydrometallurgists also use PDZ as the starting material as opposed to the highly dissolution resistant zircon mineral.

Cremer and Schlocker[82] digested zircon using lithium metaborate as a fluxing agent. The digestion was performed at 950 ^{o}C for 15 minutes and the resultant melt was dissolved in diluted HNO_3. This method was found to produce either incomplete sample digestions or incomplete melt dissolutions, thereby, giving unsatisfactory results. Lötter *et al.*,[83] used lithium tetraborate as a fluxing reagent for the digestion of SARM 62, a certified reference material of zirconium compound as well as PDZ. The digestion was carried out at 1100 ^{o}C for four hours and the resultant melt dissolved in dilute HNO_3. This flux fusion procedure was found to suffer from sample contamination by reagents such as lithium and boron. The resultant solution was analysed using a standard addition technique with ICP-OES (see **Table 3.2)**.

Table 3.2: Flux fusion analysis of SARM 62 and PDZ results[83]

Component	SARM 62 certified value (mass %)	SARM 62 result (mass %)	PDZ results (mass %)
ZrO_2	64.2	66(6)	65(6)
SiO_2	32.8	44(12)	27(1)
HfO_2	1.31	1.7(1)	1.61(5)
TiO_2	0.13	0.15(1)	0.41(2)
Al_2O_3	0.88	1.4(1)	0.60(4)
Fe_2O_3	0.07	0.14(5)	0.6(1)

[82] M. Cremer, J. Schlocker, Mineralogical notes Lithium Borate Decomposition of Rocks, Minerals and Ores, *American Mineralogist*, 1976, 61, 318-321

[83] S. Lötter, W. Purcell, J. Nel, *Alternative Dissolution of Zircon Samples and Simultaneous Analysis of Major and Trace Components*, 2012, (1), 69-76

Ayranci[84] reported a rapid decomposition procedure of zirconia using a combination of 2.500 g $(NH_4)F$ and 5.0 g $(NH_4)_2SO_4$ as a fluxing reagent at a fusion temperature of 350 ^oC for 45 - 60 minutes. The molten sample was dissolved in dilute HCl. Despite all indications of complete sample dissolution, Ayranci reported highly inaccurate elemental recoveries.

Ma and Li[85] dissolved high-purity zirconium dioxide (ZrO_2) with a mixture of $(NH_4)_2SO_4$ and 10mL concentrated H_2SO_4 using microwave-assisted acid digestion applying the procedures below in **Table 3.3**. Experimental results indicated the complete sample digestion within 30 minutes. They reported recoveries in the range of 87 – 112 % using ICP-OES.

Table 3.3: The microwave-assisted digestion programmes used[85]

Programme	Stage 1		Stage 2		Total time (min)
	Time (min)	Power (W)	Time (min)	Power (W)	
1	10	315	20	630	30
2	20	315	10	630	30
3	10	315	20	473	30
4	10	315	35	473	45

Nhlabathi *et al.*,[86] also investigated the dissolution of zircon with using microwave-assisted acid digestion in the presence of ammonium bifluoride ($NH_4F.1.5HF$). A 5 g zircon sample was mixed with 5 g of $NH_4F.1.5HF$ and the mixture was reacted in a

[84] B. Ayranci*, Arapid decomposition method for analysing zirconia,1989,109, 75-79,

[85] X. Ma, Y. Li, Determination of trace impurities in high-purity zirconium dioxide by inductively coupled plasma atomic emission spectrometry using microwave-assisted digestion and wavelet transform-based correction procedure, *Analytica Chimica Acta*, 2006, 579(1), 47-52

[86] T. N. Nhlabathi, An investigation into the fluorination capabilities of ammonium acid fluoride under microwave radiation with respect to zircon, MSc Thesis, Pretoria; University of Pretoria, 2012

microwave at 189 ^{o}C, 1600 W and 5.5 MPa. The results showed a maximum conversion of 70 % of zircon to $(NH_4)_3Zr(Hf)F_7$ and $(NH_4)_2SiF_6$ (see **Equation 3.1)** with standard deviations of 0.05 and 0.16 respectively. The excess fluoride was complexed or neutralised by the addition of 3 % boric acid to form NH_4BF_4 (see **Equation 3.2**).

$$3Zr(Hf)SiO_4+16NH_4F\cdot1.5HF\rightarrow3(NH_4)_3Zr(Hf)F_7+3(NH_4)_2SiF_6+12H_2O+NH_4F \quad 3.1$$

$$H_3BO_3 + 2NH_4F\cdot1.5HF \rightarrow NH_4F + NH_4BF_4 + 3H_2O \quad 3.2$$

Furthermore, Lötter *et al.*,[83] carried out a study on the dissolution of certified reference material (SARM62) and Plasma-Dissociated Zircon (PDZ) using microwave-assisted digestion. Different acids/salt and base - H_2SO_4, $(NH_4)_2SO_4$, HNO_3 and NaOH were investigated as possible dissolution agents under different power and time settings. H_2SO_4 was reported to have given the highest recoveries of 44.3(1) %, 49.75(7) %, 78.3(3) % and 90.0(7) % for Zr, Hf, Al, and Fe respectively, compared to the rest of the other acids/salts investigated.[83]

Malefo *et al.*,[87] also conducted a study on the dissolution of hafnium oxide (HfO_2) using microwave-assisted digestion. Different acids and salt mixtures - HCl, HNO_3, aqua regia, H_2SO_4, a mixture of $(NH_4)_2SO_4$ in H_2SO_4 and a mixture of NH_4F in H_2SO_4, were investigated as possible dissolution agents under different time and pressure settings. They found out that H_2SO_4, on its own or mixed with $(NH_4)_2SO_4$ or NH_4F, dissolved the HfO_2 completely with recoveries ranging between 97 and 100 % (see **Table 3.4)**.

[87] G. Malefo, Quantification of hafnium in Selected Inorganic and Organometallic Compounds, MSc, Thesis, Bloemfontein; University of Free State, 2016

Table 3.4: The recoveries of hafnium from hafnium oxide after microwave digestion with different reagents[87]

Reagents used	Average Hf in HfO_2 (ppm)		% Hf recoveries (S.D)
	Expected	Found	
HCl	1.622	0.351	21(1)
HNO_3 (65%)	1.475	0.09	6.5(6)
Aqua regia	1.487	0.016	10.8(1)
H_2SO_4 (98%)	16.87	16.26	97(2)
$H_2SO_4 + (NH_4)_2SO_4$	17.48	17.53	100(3)
$H_2SO_4 + NH_4F$	15.29	14.361	98(2)

3.3 Separation of zirconium and hafnium

Both zirconium and hafnium play important roles in nuclear applications (see **Chapter 2, Section 2.6.1**). It is vital that the nuclear industry find new cost-effective and eco-friendly methods to separate the two elements from mineral ores. Due to their similar physical and chemical properties, it has been a great research challenge to find applicable right methods to produce pure zirconium and hafnium metals.[88] The current separation processes used for the separation of zirconium and hafnium involve multi-stage processes that are extremely time-consuming.[89] The three hydrometallurgical methods that are used for separation of zirconium and hafnium are ion exchange, solvent extraction and fractional crystallization. These methods are discussed in more detail in the following paragraphs.

[88] A. L. Machlan, J. L. Hague, Separation of Hafnium from Zirconium and their determination: Separation by anion-exchange, *Journal of Research of the National Bureau of Standard- A Physical and Chemistry*, 1962, Vol.66

[89] Chapman, Hall, *Hydrometallurgy 94*, a review, [Internet. [Cited 1994 July 11 to 15], 222, available from: https://books.google.co.za/books?isbn=9401112142

3.3.1 The ion exchange method

The separation of zirconium and hafnium using different anion and cation ion exchange resins has been investigated by different researchers.[90,91] Felipe *et al.*,[91] reported the separation of zirconium and hafnium in a mixture of $Zr(OH)_4$ and $Hf(OH)_4$ dissolved in 1 M HNO_2 using strong cation exchange resins. Different cationic resins, Dowex 50WX4, Dowex 50WX8 100, Dowex 50WX8 50, Amberlite IR-120 and Marathon C were investigated under similar experimental conditions of constant temperature of 28 ^oC and acidity. They reported separation factors (see **Chapter 4**, **Section 4.4.2**) (β or α=Zr/Hf) which indicated unsuccessful separations between the two elements on all the investigated resins (see **Table 3.5**).

Table 3.5: The separation factors for each resin[91]

Resins	α = Zr/Hf
Dowex 50WX4	0.93
Dowex 50WX8 100	0.98
Dowex 50WX8 50	0.98
Ambarlite IR-120	0.98
Marathon C	0.84

Smolik *et al.*[92] also studied the separation of Zr and Hf sulphates on diphonix and monophos resins. Different mineral acid solutions (H_2SO_4, HNO_3 and HCl) of various concentrations were investigated as mobile solvents. The study found that the 0.5 M H_2SO_4 was the best eluent for the optimum separation of Zr and Hf on cation resin at 22 ^oC with linear flow rate <7.5 BV/h (bed volumes per hour) (see **Figure 3.1**).

[90] X. J. Yang, C. Pin, A. G. Fane, Separation of hafnium from zirconium by extraction chromatography with liquid anionic exchangers, Journal of Chromatographic Science, 1999, Vol.37

[91] E. C. B. Felipe, H. G. Palhares and A. C. Q. Ladeira, Separation of Zirconium from hafnium by Ion Exchange, *2013 International Nuclear Atlantic Conference-INAC*, 2013

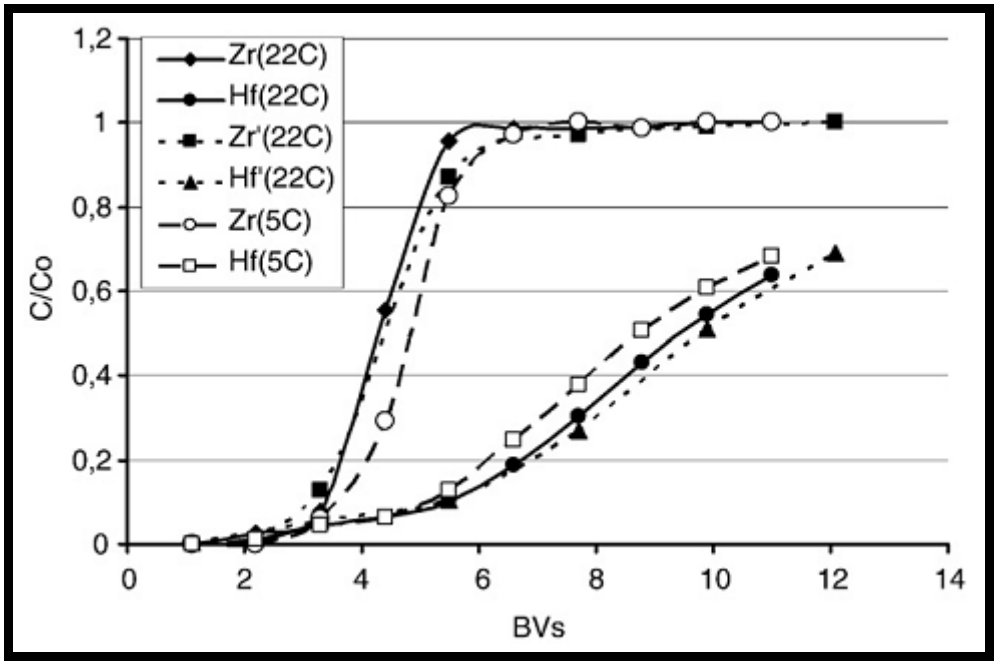


Figure 3.1: Elution curves of zirconium and hafnium separation on diphonix resin at T= 5 and 22^{o}C [92]

Another investigation on the separation of Zr and Hf was conducted by Yang *et al.*,[90] using tri-n-ocytyl amine (TNOA) and Aliquat 336 as anion exchanger resins and HCl as the mobile phase. They investigated the effect of the HCl concentration, extractant loading, particle size and column dimensions. The study found that Aliquat 336 offered better separation compared to TNOA and Zr was eluted with 2 M while Hf was eluted with 8 M HCl (see **Figure 3.2**). Separation factors ranged between 36 and 164.

[92] M. Smolik, A. Jokóbik-Kolon, M. Porański, Separation of zirconium and hafnium using Diphonix chelating ion-exchange resin, *Hydrometallurgy*, 2009, 95, 350-353

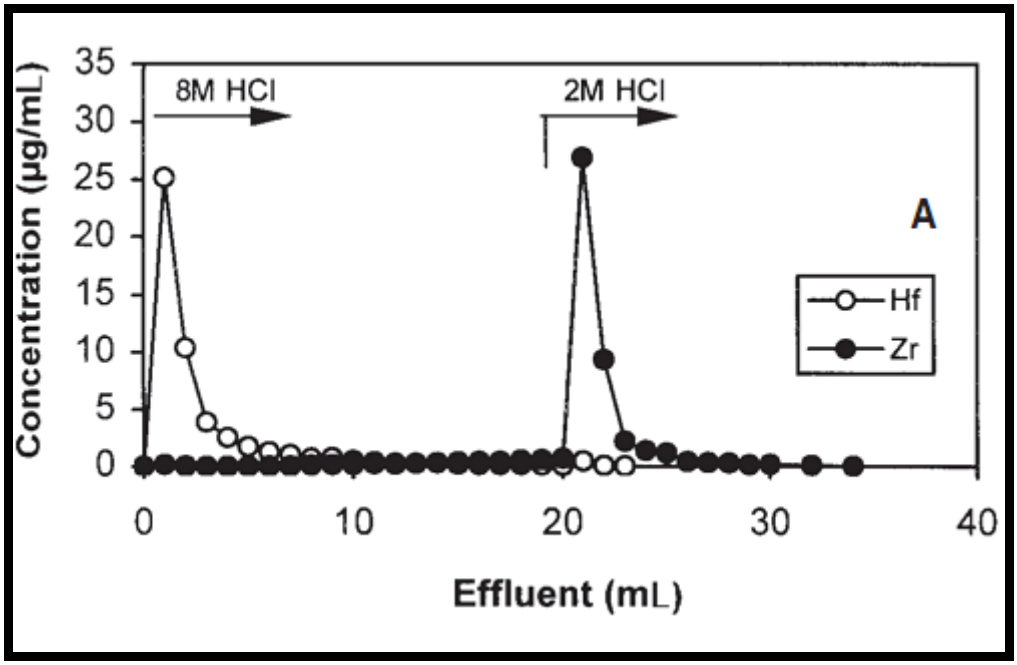


Figure 3.2: Separation of Zr and Hf using Aliquat 336 resin[90]

3.3.2 The solvent extraction method

Solvent extraction is one of the most successful techniques for the separation of zirconium and hafnium on an industrial scale.[93] Zhi-gao *et al.*,[94] investigated the separation of zirconium and hafnium from a thiocyanic acid medium using a mixture of diisobutyl ketone (DIBK) and tributyl phosphate (TBP) as an organic extractant. The study reported a successful extraction of hafnium into the organic phase while zirconium remained in aqueous phase. The separation factor was 3.9 (see **Figure 3.3**).

[93] D. Royston, P. G. Alfredson, Review of processes for the production of hafnium-free zirconium, *National Library of Australia card number and ISBN 0643993947*,1970

[94] X. Zhi-gao, W. Li-jun, W. Yan-ke, C. Ru-an, Z. Li, W. Ming, Solvent extraction of hafnium from thiocyanic acid medium in DIBK-TBP mixed system, *Trans. Nonferrous Met. Soc. China*, 2012, 22, 1760-1765

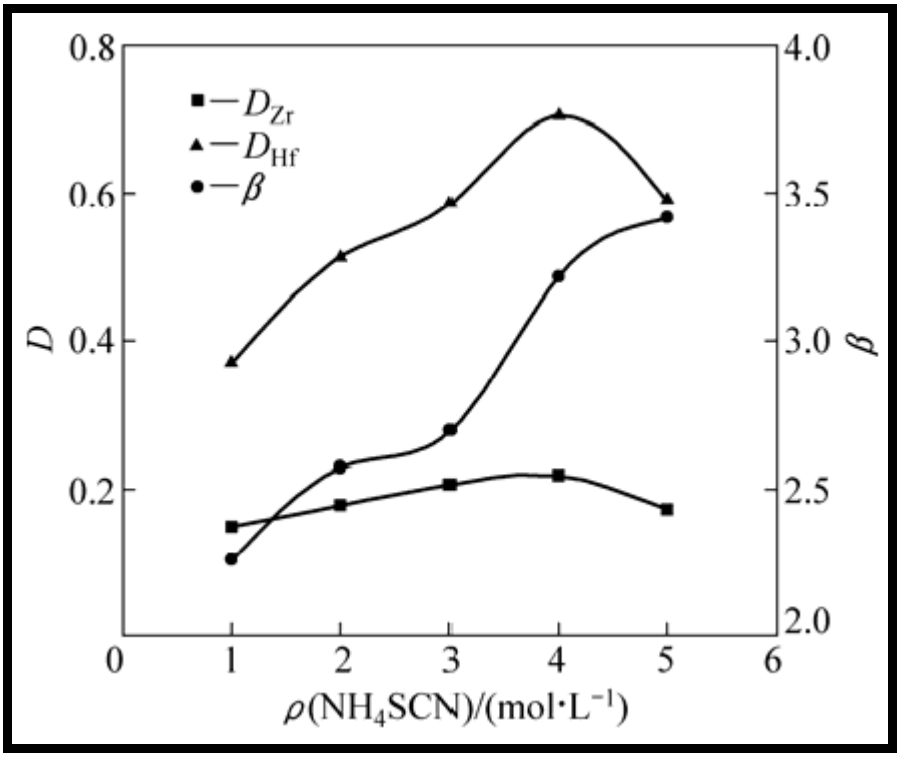


Figure 3.3: The effects of NH_4SCN concentration on distribution ratio(D) and separation factor (β) of Zr and Hf [94]

Banda *et al.*[95] investigated the separation of hafnium and zirconium in a sulphate matrix using two individual acidic extractants - di-(2-ethylhexyl)phosphoric acid (D2EHPA) (see **Table 3.6**) and Cyanex 272, or in the presence of LIX63. Their results indicated that the extraction process using only D2EHPA or Cyanex 272 had better selectivity between Hf and Zr compared to the mixtures of D2EHPA/LIX and Cyanex 272/LIX extractants. Hafnium was preferentially extracted over zirconium (see **Figure 3.4**) and the separation factor around 30 was obtained using D2EHPA and 4 mol/L H_2SO_4 solution.

[95] R. Banda, S. H. Min and M. S. Lee, Selective extraction of Hf over Zr from aqueous H_2SO_4 solutions by solvent extraction with acidic organophosphorous based extractants, *J. Chem. Technol. Biotechnol,* 2014, 89, 1712-1719

Table 3.6: Separation factor of Hf over Zr using D2EHPA 4.0 mol/L H_2SO_4 [95]

[D2EHPA], mol/L	D, Zr	D, Hf	$\beta = D_{Hf}/D_{Zr}$
0.01	0.009	0.27	30
0.03	0.15	2.02	13.5
0.05	0.61	8.23	13.5
0.08	2.53	36.27	14.5

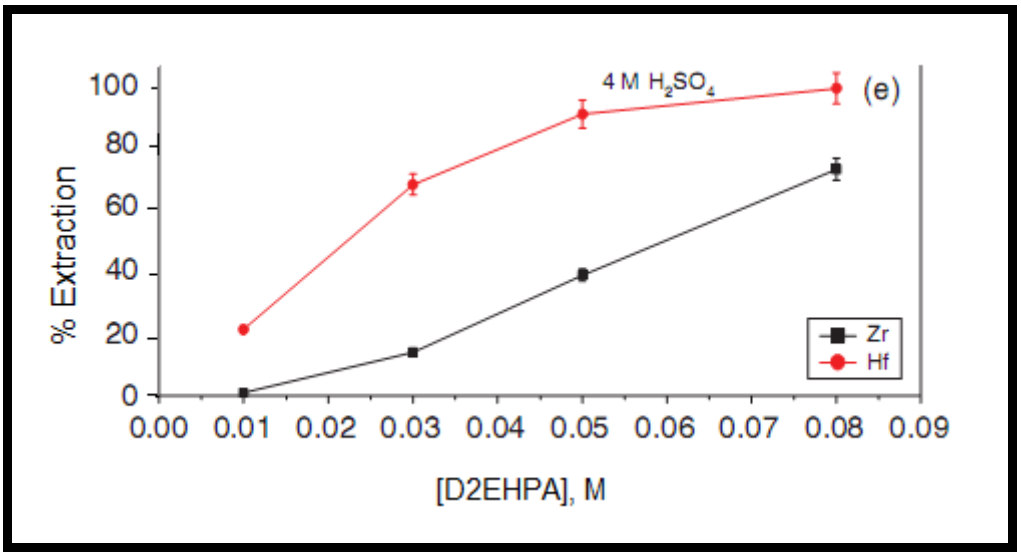


Figure 3.4: The effect of D2EHPA concentration on extraction of Hf and Zr at 4.0 mol/L H_2SO_4 [95]

Wang *et al.*[96] studied the separation of zirconium and hafnium from sulphuric acid with amine-based extractants. Different amines - Aliquat 336, Alamine 300, Alamine 308, Alamine 336 and TEHA were investigated. The highest separation, with a separation factor of 12.4, was achieved with Alamine 308 in 0.5 M H_2SO_4 (see **Table 3.7** and **Figure 3.5**).

[96] L. Y. Wang and M. S Lee, Separation of Zr and Hf from sulphuric acid solutions with amine-based extractants by solvent extraction, *Separation and purification technology*, 2015, 142, 83-89

Table 3.7: Results of separation factor of Zr and Hf under different concentrations of H_2SO_4 solutions and Alamine 308 in kerosene[96]

Alamine 308 (M)	Separation factor, β		
	0.3 M H_2SO_4	**0.5 M H_2SO_4**	**0.7 M H_2SO_4**
0.005	-	-	-
0.007	8.2	8.9	8.3
0.01	11.8	10.5	9.8
0.015	10.3	12.4	10.2
0.02	8.9	9.8	10.1
0.03	-	-	9.8

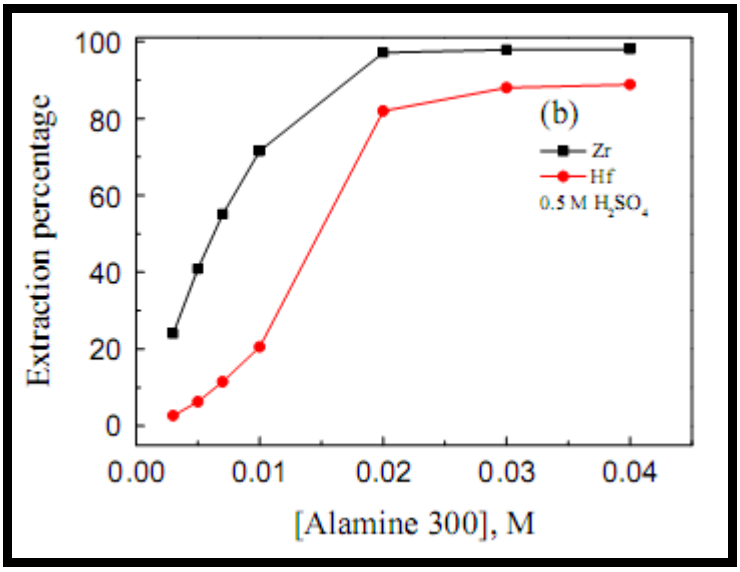


Figure 3.5: The effect of Alamine 308 concentration on the extraction of Zr and Hf from 0.5 M H_2SO_4 [96]

Taghizadeh *et al.*[97] also studied the separation of zirconium and hafnium, but using a mixture of TBP and Cyanex 923 as organic extractants. The extraction process was carried out in a $NaNO_3$ /nitric acid matrix. Their results indicated the preferential extraction of Zr below 3.5 M $NaNO_3/HNO_3$ in the presence of the TBP/Cyanex

[97] M. Taghizadeh, M. Ghanadi, E. Zolfonoun, Separation of zirconium and hafnium by solvent extraction using mixture of TBP and cyanex 923, *Journal of Nuclear Materials*, 2011, 412, 334-337

mixture (see **Figure 3.6**). The reported separation factor under these conditions was calculated as 186 (see **Table 3.8** below).

Table 3.8: Comparison of the extractants, loading capacity and separation factor for separation of Zr and Hf[97]

Experiments	Performance				
	Acid concentration in the feed solution (M)	Loading capacity of organic phase (60%v/v)	Extraction (%)		β= (Zr/Hf)
			Zr	Hf	
Usual TBP/HNO_3	7	20g/l	67	14	12
Novel method[b] or TBP/Cyanex	3.5	26.5 g/l	53	<1	186
Cyanex923 process	2.5	A	a	a	a

[a] = above 8 g/l zirconium, third phase is formed

[b] = metal concentration in the feed solution was 50 g/l

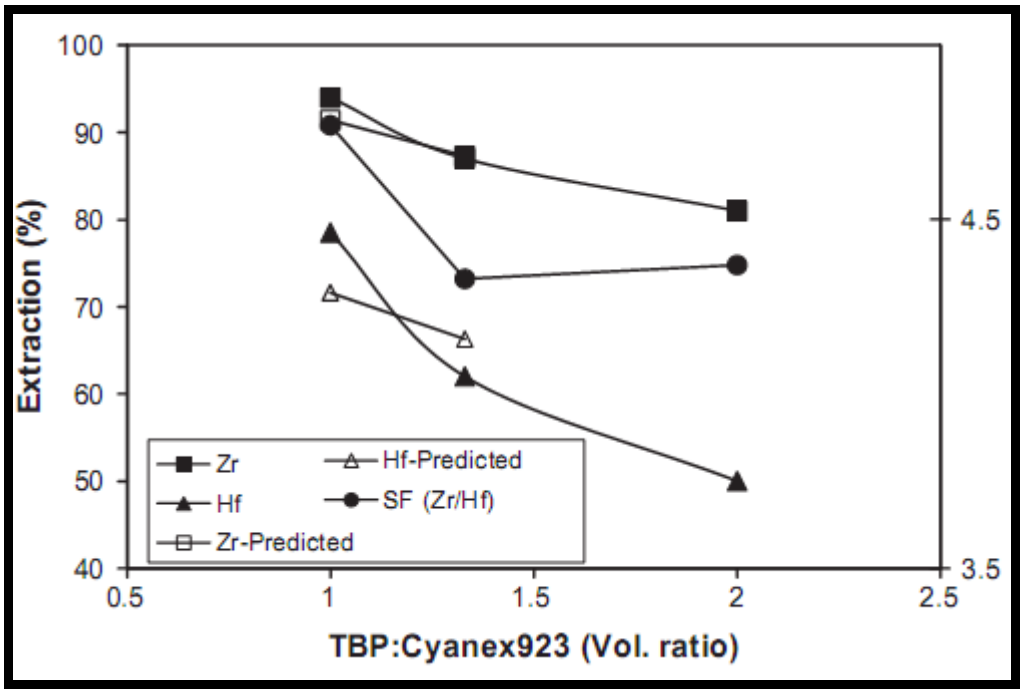


Figure 3.6: The effect of TBP/Cyanex 923 volume ratio on extraction of Zr and Hf[97]

3.3.3 Fractional crystallisation

Fractional crystallization was also used for the separation of Zr and Hf. This technique takes advantages of the difference in the solubility of similar inorganic salts of the two elements, especially the difference between the solubility of potassium hexafluorozirconate (K_2ZrF_6) and the analogous hafnium compound in aqueous solutions (see **Chapter 2, Section 2.6.3.1)**. The addition of HF and an excess of the cation in solution affects precipitation.[98] The application of fractional crystallization in the separation of Zr and Hf was popular in the 1940s, [99] but was quickly replaced by solvent extraction which was developed by Union Carbide in the 1950s [100] because of its ease, simplicity and speed to separate the two elements.[95] This method of separation involved several recrystallization stages (in the order of 16 - 18 stages) in order to obtain high purification.[98] Currently, fractional crystallization is regarded more suitable as a pre-concentration step for elements rather than a separation technique.

Hirota *et al.*[98] investigated the dissolution of the two salts ($K_2Zr(Hf)F_6$) (see **Section 3.2**) in different solvents such as water, hydrofluoric acid and a mixture of HF/HCl. They used 10 g of $K_2Zr(Hf)F_6$, added 100 mL of solvents to each sample and heated for one hour at 79.80 ^oC. The samples were cooled to 19.85 ^oC and then held for five hours at -0.15 ^oC. By using ICP-OES for analysis, the study found that Hf separated with higher efficiency than Zr using HF-HCl solution as solvent for crystallization.[98]

[98] K. Hirota, J. Wang, S. Araki, K. Endo, H. Yamamoto, Purification of Zr and Hf resources using cryatallization in HF-HCl solvent mixture, *World Academy of Science, Engineering and Technology International journal of Chemical and Molecular Engineering*, 2016, (3)

[99] G. Roza, Understanding the elements of the periodic table zirconium, 2009, 1st ed.

[100] H. C. Peterson, G. H. Beyer, Separating hafnium from zirconium, *Solvent Extraction with Tributyl Phosphate*, 1958, Vol. 50

3.4 Conclusion

The discussions in the above sections focused on some of the successful techniques (flux fusion, microwave-assisted digestion, ion exchange, solvent extraction and fractional crystallization techniques) in the dissolution of zirconium compounds, as well as, separation of zirconium and hafnium. Successful separations of Zr and Hf have been achieved from different sample matrices or starting materials, which include thiocyanate, chloride, nitrate and sulphate. Most of the separation methods that have been discussed involve multi-stage steps to achieve purification and are in all cases very time-consuming. The chemicals used too, can be environmentally harmful – especially in situations where HF is used. The main aim of this project was to investigate the possible separation of Zr and Hf in inorganic salts $(Zr/Hf)O_2$ and apply the optimum separation conditions to separate the two elements of interest in Plasma-Dissociated Zircon (PDZ).

4 Selection of Analytical techniques

4.1 Introduction

The separation of Zr and Hf usually requires tedious and time-consuming processes to isolate and purify the different elements from complex mixture solutions.[101] A literature study on the dissolution and separation of Zr and Hf was discussed in the previous chapter. The successful analysis of the two elements relies heavily on (i) the choice of the dissolution technique; (ii) the type of products formed in this process; as well as, (iii) the chemistry thereof.[102] The dissolution technique investigated in this study includes flux fusion using $NH_4F{\cdot}HF$, while separation techniques include acid leaching (using microwave-assisted digestion), ion exchange and solvent extraction. This chapter will discuss the dissolution, separation and analytical techniques that were used in this study to affect the analysis of Zr and Hf products (see **Chapter 5, Figure 5.1**).

4.2 Sample dissolution technique

All the analytical measurements (identification and quantification of all the elements) were performed on aqueous solutions containing all the analytes present in the

[101] X. J. Yang, C. Pin, A. G. Fane, Separation of hafnium from zirconium by extraction chromatography with liquid anionic exchangers, *Journal of Chromatographic Science*, 1999, Vol. 37

[102] M. Nete, Separation and purification of niobium and tantalum from synthetic and natural compounds, PhD, Thesis, Bloemfontein; University of Free State, 2013

samples and therefore required the complete dissolution of all the samples that were investigated. The proper selection of techniques that afforded the complete decomposition and dissolution of analytical samples were critical to the success of an analysis of the samples, as well as, the subsequent separation steps.[103] The unknown chemical composition of mineral samples and their chemical properties usually require drastic conditions to destroy its natural structure to free all the individual constituents for analysis.[103] In this study, flux fusion technique was investigated as a possible technique for the dissolution of zircon and PDZ.

Flux fusion dissolution

Flux fusion is commonly used for the digestion of rocks, ores, soil sediments, metal oxides, ceramics and cements which are highly resistant to acid attack under ordinary experimental conditions.[103] This technique involves the digestion of the sample with an alkali salt (flux) at a temperature which is slightly higher than the melting point of the flux. The efficiency of the reaction between the flux and the sample depends on (i) the type of flux (acid, base or redox); (ii) the melting temperature of the flux; and (iii) the sample to salt ratio (for example, 1:10). The molten flux/salt acts as a high concentrated ionic solvent which reacts at a very high temperature with the introduced mineral sample.[104] The fusions can be performed using oil baths, furnaces (see **Figure 4.1**) or burners.

[103] Sample dissolution, 2004, [Accessed on 17-10-2017]. Available from: https://www.epa.gov/sites/production/files/2015-05/documents/402-b-04-001b-13-final.pdf

[104] B. Cullum, T. Vo-dinh, *Handbook of spectroscopy*, 2014, (1), 3-14

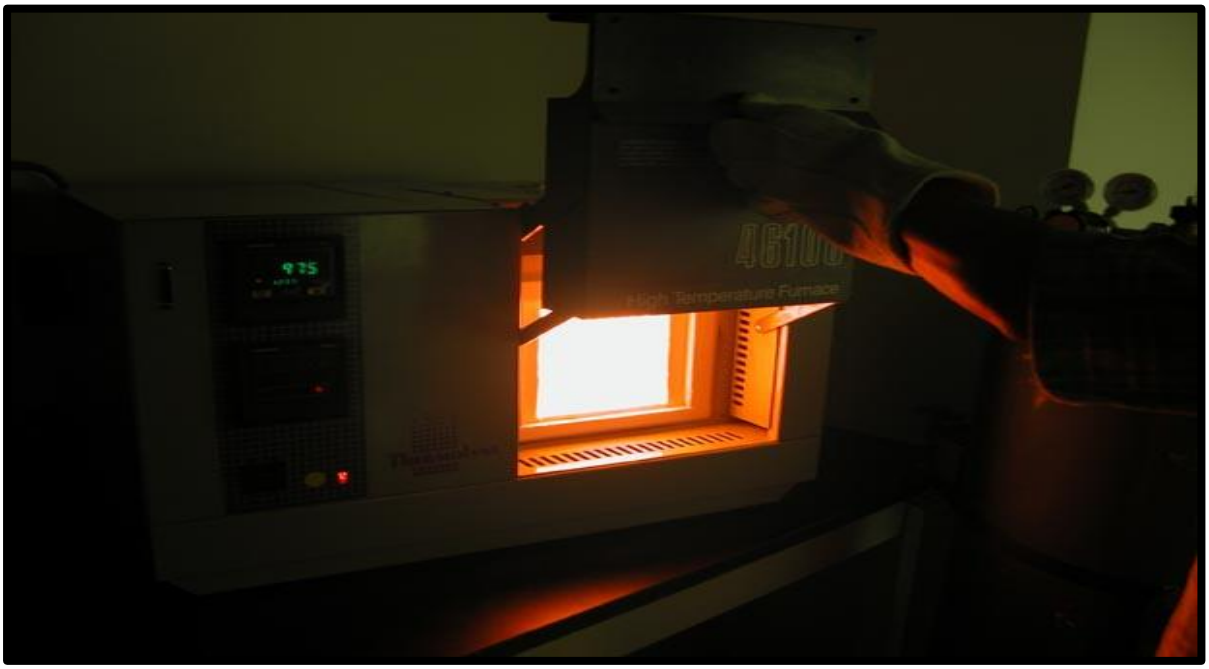


Figure 4.1: High temperature furnace used in flux fusion dissolution

The choice of crucibles and heat source is very important for the successful dissolution process and their selection depends on the type of salt (flux) used for the fusion due to the possible reaction (attack) between the flux and crucible which can damage the crucible thereby contaminating the sample (see **Table 4.1**) at high temperatures.[102] The melted mixture is cooled to room temperature and dissolved in water, or diluted acid or base solutions. This technique is also used for the dissolution of refractory materials which are highly unreactive towards common mineral acids. Fusion dissolution is relatively safe as it does not involve the use of dangerous concentrated acids and the sample digestion times are generally short, with an average digestion time of 30 minutes compared to most concentration acid dissolution methods which require much longer digestion times.[105] Moreover, correctly selected flux fusion methods usually produce completely dissolved sample, thereby enabling a complete sample analysis and possibly elemental separation.[103] However, high purity fluxes (alkali salts) are not always available and there is always the potential for sample contamination. Also, fluxes usually contain high

[105] E. Oliveira, Sample preparation for atomic spectroscopy: evolution and future trends, *J. Braz. Chem. Soc.,* 2003, Vol. 14

concentrations of Na, K or Li which are also known as the easily ionisable elements (EIE's), and have the potential to change the ICP flame temperature or background spectra (high intensity alkali metal spectra) and as such may cause changes in analyte intensities. This could lead to inaccurate elemental quantities in the analysed sample.[106] Additionally, crucibles made of metals such as Pt, Au, Ag, Fe, Ni or Zr are commonly used for metal oxide digestion or mineral ores and can in some instances, be very expensive.

The type of flux selected for the dissolution of samples is critically based on the chemical properties of the type of sample. For example, alkaline oxides will react better with acidic fluxes while metal samples (with low oxidation states) will react better with oxidising fluxes [106] to produce soluble products (see **Table 4.2**). In this study, $NH_4{\cdot}HF_2$ was found to be effective in the digestion of PDZ [107] and was therefore used for the digestion of the different Zr and Hf samples which were investigated.

[106] N. W. Chiu, J. R. Dean, C. W. Sill, Techniques of sample attack used in soil and mineral analysis, 1984

[107] M. M. Makhofane, J. L. Havenga, J. T. Nel, W. du Plessis, C. J. Pretorius, Manufacturing of anhydrous zirconium tetrafluoride in a batch reactor from plasma-dissociation zircon and ammonium bifluoride, *The Journal of the Southern Africa Institute of Mining and Metallurgy*, 2012, Vol.7A , 559

Table 4.1: Common fluxes and crucibles used for mineral dissolution [102]

Flux	Melting point (°C)	Type of crucible for fusion	Type of sample decomposed
$Na_2S_2O_7$ or $K_2S_2O_7$	403 or 419	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples
NaOH or KOH	321 or 404	Ni, Ag, glassy carbon	For silicates, oxides, phosphate and fluorides
H_3BO_3	250	Pt	For analysis of sand, aluminium silicates, titanite, natural aluminium oxide and enamels
NH_4HF_2 or KHF_2	125 or 239	Pt	For removal of silicon, the distraction of silicates and rare earth minerals and analysis of oxides of Nb, Ta, Ti and Zr

Table 4.2: Types of fluxes commonly used [106]

Alkaline fluxes	Acidic fluxes	Oxidising fluxes
Sodium carbonate	Sodium bisulfate	Sodium peroxide
Sodium hydroxide	Potassium bisulfate	Sodium nitrate
Potassium hydroxide	Sodium pyrosulfate	Potassium nitrate
Sodium peroxide	Potassium hydrogen fluoride	
Sodium tetraborate	Ammonium hydrogen fluoride	
Lithium metaborate		
Lithium tetraborate		
Potassium fluoride		
Sodium fluoride		
Lithium fluoride		

4.3 Separation and purification techniques

4.3.1 Acid leaching (using microwave-assisted digestion)

Microwave-assisted digestion was first developed in the mid-1970s and has now become a popular method for sample preparation.[108] Microwave-assisted digestion utilizes a combination of electromagnetic radiation and a mineral acid to dissolve the sample which is being investigated. Microwaves promote the rotation of specific molecules in a reaction mixture which results in increased molecular collisions and the generation of heat.[108] The technique is commonly used for the decomposition of both inorganic and organic samples which will be analysed using instruments such as ICP-OES/ MS or AA.

[108] Nadkarni R. A., Applications of microwave oven sample dissolution in analysis, *Analytical Chemistry*, 1984, Vol. *56*, (12), 2233–2237

Advantages of this technique include, the combination of high temperature at elevated pressures in a closed vessel to dissolve samples. Sample digestions are faster, cleaner and more reproducible compared to conventional hot plate digestion. The closed vessels prevent evaporative losses of volatile sample and/or the reaction products formed during the process.[109] Smaller amounts of reagents (compared to flux digestion) are used, thereby reducing the potential of sample contamination.[108] Disadvantages of microwave-assisted digestion include the cracking or potential explosion of digestion vessels due to excessive pressure build-up.[110]

The microwave has a rotor that holds the vessels firmly in place and has sensors which continously monitor the pressure in the sample vessels to ensure safe and precise reaction conditions.[111] Reactions take place in quartz or PTFE vessels which are highly resistant to acid attacks and are high temperature tolerant (see **Figure 4.2**).[112]

[109] K. A. Smith, M. S. Cresser, Soil and environmental analysis, *Modern Instrument Techniques*, 2004, 3rd ed.

[110] Benefits of microwave digestion over open acid digestions, [Accessed on 12-10-2017]. Available from: http://lab-training.com/2014/01/19/benefits-of-microwave-digestion-over-open-acid-digestions/

[111] Microwave reaction system for sample preparation, [Accessed on 17-10-2017], Available from: https://acs.expoplanner.com/files/acsfall17/ExhibFiles/1056_2709_MicrowaveSynthesis_MultiwavePRO.pdf

[112]Theory of sample preparation using acid digestion, pressure digestion and microwave digestion, [Accessed on 10-01-2018]. Available from: file:///C:/Documents%20and%20Settings/uvp/My%20Documents/Downloads/MW_Theorie_Probenvorbereitung_PT_en.pdf

(a) (b)

Figure 4.2 (a) Microwave digester, (b) Rotor and vessels

4.3.2 Ion exchange separation

This technique was used to investigate the possible separation of Zr and Hf in a fluoride solution formed during the flux fusion dissolution of the samples. Ion exchange chromatography is used to afford the separation of inorganic ions and the separation is based on an exchange of different ions in the analyte solution (mobile) with those in the stationary phase. The stationary phase usually consists of resin beads synthesised from a polystyrene polymer which is cross-linked with divinylbenzene and which have free phenyl groups attached to the chain that can easily react to add ionic functional groups (see **Figure 4.3**) to the structure.[113] There

[113] Chemistry libretexts, [Accessed on 08-09-2017]. Available from:https://chem.libretexts.org/Textbook_Maps/Analytical_Chemistry_Textbook_Maps/Map%3A_Analytical_Chemistry_2.0_(Harvey)/12_Chromatographic_and_Electrophoretic_Methods/12.6%3A_Other_Forms_of_Liquid_Chromatography

are four types of ion exchange resins that are used in analytical chemistry (see **Table 4.3**).[114]

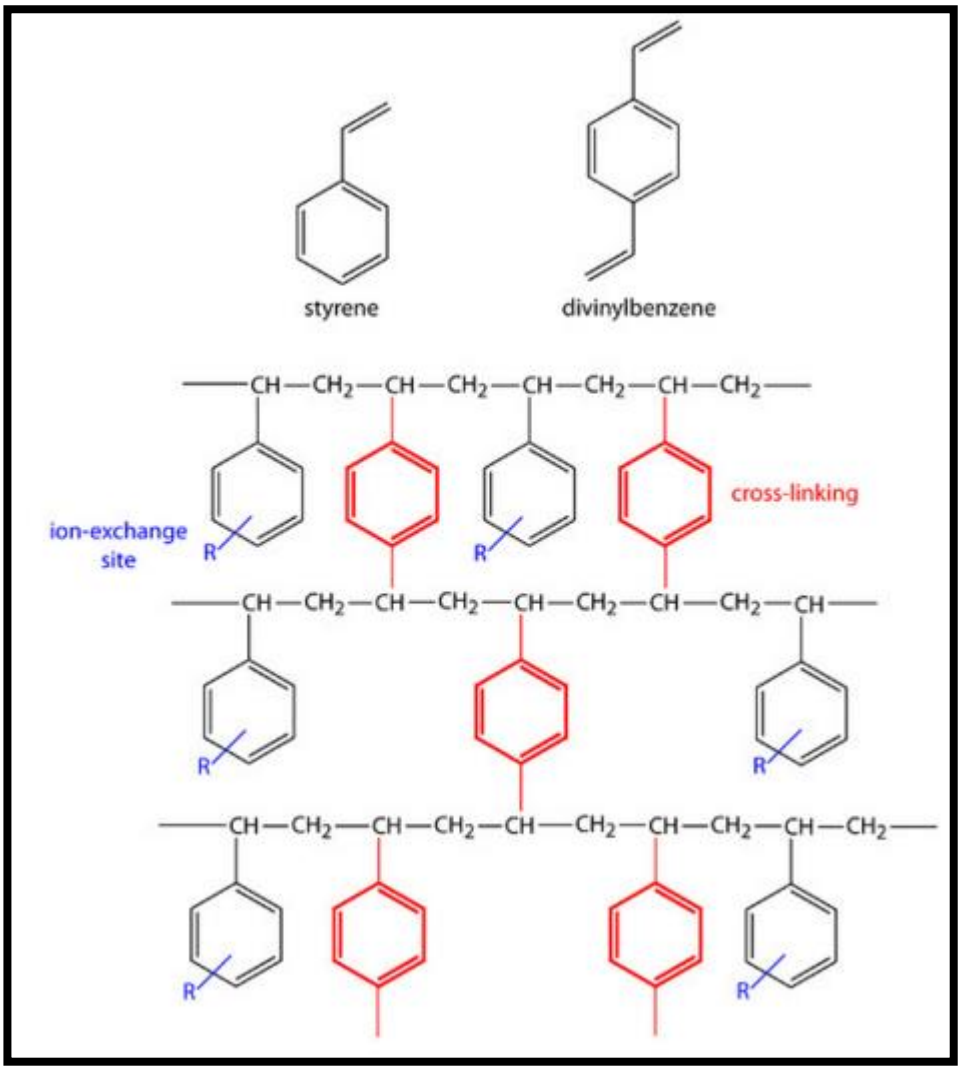


Figure 4.3: Structure of typical cation and anion resins[113]

[114] T. R. Dulski, Trace elemental analysis of metals: Methods and Techniques, New York, Marcel Dekker, 1999

Table 4.3: Types of ion exchange resins[114]

Exchange type	Ion exchange group	Buffer counter ions	pH range	Commercial samples
Strong acid cation	Sulfonic acid ($-SO_3^-$)	Na^+, H^+, Li^+	4-13	Amberlite IR-120, Amberlite IR-122, Dowex 50W-X8, Dowex 50W-X10
Weak acid cation	Carboxylic acid ($-COO^-$)	Na^+, H^+, Li^+	6-10	Amberlite IRC-50, Ionac CGC-270
Strong base anion	Quaternary amine ($-N(CH_3)_3^+$)	Cl^-, $HCOO_3^-$,CH_3COO^- ,SO_4^{2-}	2-12	Amerlite IRA-400, Amberlite IRA-410, Dowex 1-X8, Dowex 2-X8
Weak base anion	Primary amine ($-NH_3^+$), secondary amine and tertiary amine(DEAE)	Cl^-, $HCOO_3^-$, CH_3COO^- ,SO_4^{2-}	2-9	Amberlite IRA-45, Dowex 3

Some of the cation resins in **Table 4.3** have both strong and weak, as well as, protons which can be exchanged with other cations from the sample solution. The exchange reactions are illustrated below in **Equations 4.1 and 4.2**.[115] $RzSO_3^-$ and $RzCO_2^-$ in the equations represent the polystyrene polymer part of the resin.[115]

$$nRzSO_3^- H^+ + M^{n+} \rightleftharpoons (RzSO_3)_nM + nH^+ \quad 4.1$$

$$nRzCO_2^- H^+ + M^{n+} \rightleftharpoons (RzCO_2)_nM + nH^+ \quad 4.2$$

The anion exchange resins, both strong and weak, on the other hand, have anions which can be exchanged with other anions from sample solution (see **Equations 4.3 and 4.4**).[115] The $RzNR_3^+$ and $RzNH_3^+$ groups again represent polystyrene polymer

[115] G. D. Christian, Analytical Chemistry, Waltham, Mass., Xerox College Pub., 1971

part of the resins while the active/exchange sites are the amine groups attached to the polymer.

$$nRzNR_3^+Cl^- + A^{n-} \rightleftharpoons (RzNR_3)_nA + nCl^- \quad 4.3$$

$$nRzNH_3^+Cl^- + A^{n-} \rightleftharpoons (RzNH_3)_nA + nCl^- \quad 4.4$$

There are two methods of performing elemental separation using ion exchange which include batch or column exchange. With regard to batch exchange, the ion exchange resin and analyte solution are mixed in a glass-stopped flask or vessel. The exchange is then allowed to come to equilibrium, which results in the exchange of analyte ion and resin ion and then the solution is filtered (see **Equation 4.5**).[116] The quantitatively exchangeable ions between resin and aqueous solution depends on the weight distribution coefficient D (see **Equation 4.6**).[116]

$$Res\text{-}H^+ + Na^+ \overset{D}{\rightleftharpoons} Res\text{-}Na^+ + H^+ \quad 4.5$$

$$D = \frac{\text{mmoles sorbed solute per gram of dry resin}}{\text{mmoles solute in solution per mililiter of solution}} \quad 4.6$$

In column exchange, elution separation is in operation where a portion of sample is introduced at the top of the resin-containing column (see **Figure 4.4**). By adding the fresh portion of the mobile phase, it forces (gravity) the solvent containing sample down the column resulting in the absorption/exchange of the analyte ions (which have to be different for all the analyte ions) with that of the resin (exchangeable ions) between the mobile and stationary phase.[117] The continued addition of solvent forces the solute molecules to move down the column in a continuous series of transitions between mobile and stationary phase, which affect the concentration difference between the different analyte molecules (various bands in **Figure 4.4**) allowing for

[116] J. Fritz, G. Schenk, Quantitative analytical chemisty, Boston, Allyn and Bacon, 1966

[117] D. A. Skoog, D. M. West, Analytical chemistry, an introduction, New York, Holt, Rinehart and Winston, 1965, 2nd ed.

the separation of the mixture components. The separation of the solute ions is determined by the chemical nature of ions in the sample and the relative amount of the stationary and mobile phase in the column. The degree of separation of the constituents in the mixture is influenced by numerous experimental factors which incline the linear flow rate, column length, column packing, viscosity, type of eluent, volume of eluent, pH and temperature of the solutions.[117]

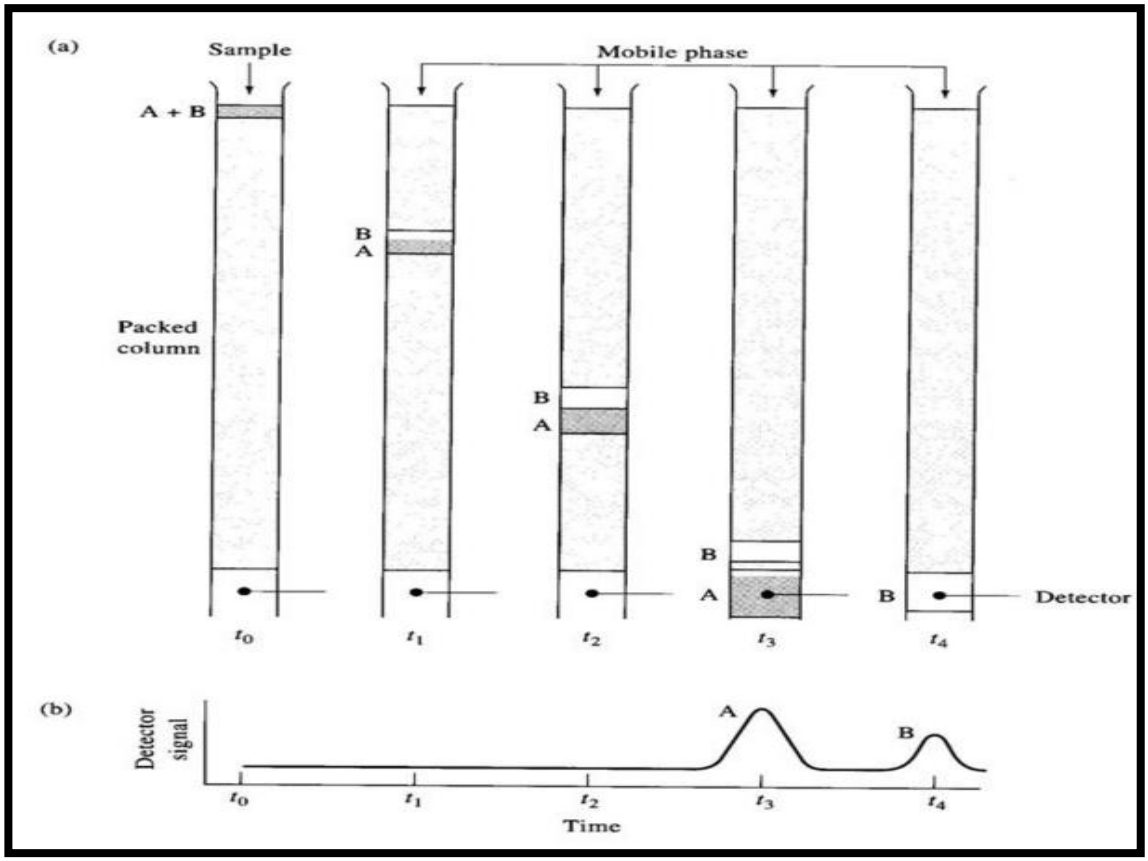


Figure 4.4: The elution chromatographic separation of a two-component mixture [118]

Successful separation of the different metals in solution depends on the difference between the ionic bonds (absorption) between mobile metal ions and the stationary counter ionic sites (see **Equations 4.7 and 4.8**).

$$A\ (mobile) \underset{}{\overset{K}{\rightleftharpoons}} A\ (stationary) \qquad 4.7$$

[118] Separation of a two-component mixture, [Accessed on 08-09-2017]. Available from: http://slideplayer.com/slide/8057990/25/images/10/Separation+of+a+Two-component+Mixture.jpg

Where K is distribution constant

$$K = \frac{[A]s}{[A]m} \qquad 4.8$$

$[A]_s$ = molar concentration of the solute in the stationary phase.

$[A]_m$ = molar concentration of the solute in the mobile phase.

The migration rates of solutes in the chromatography (see **Figure 4.4**) are determined by retention times (t_R). The definition of t_R is time interval between its sample injection onto a column and the appearance of its peak at the other end of the column (see **Equation 4.9**). **Figure 4.5** (below) indicates a typical chromatograph for two solute mixtures. However, **Figure 4.6** indicates a typical chromatograph of a solute where the small peak on the left represents a species that are not retained by the stationary phase and the large peak on the right is that of solute species. The t_M in **Figure 4.6** represents the time that un-retained species (dead time) spend in the mobile phase, while t_S represents the time the solute has been retained in the stationary phase.[122]

$$t_R = t_S + t_M \qquad 4.9$$

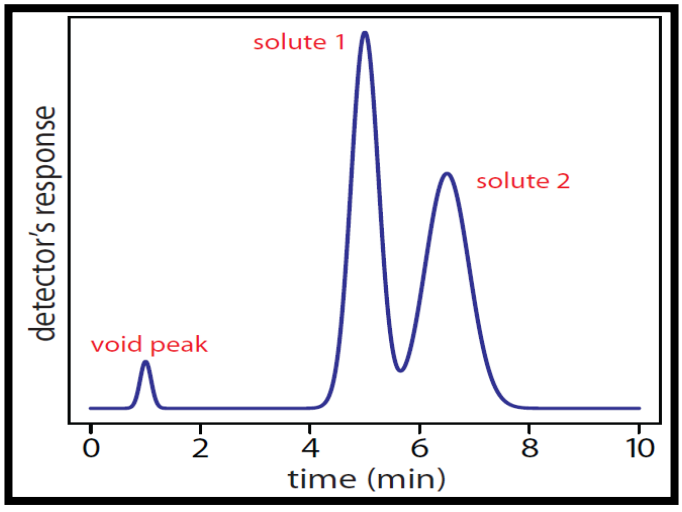


Figure 4.5: A typical chromatography for two solute mixtures [119]

[119] D. Harvey, Analytical chemistry, Boston: McGraw-Hill, 2000

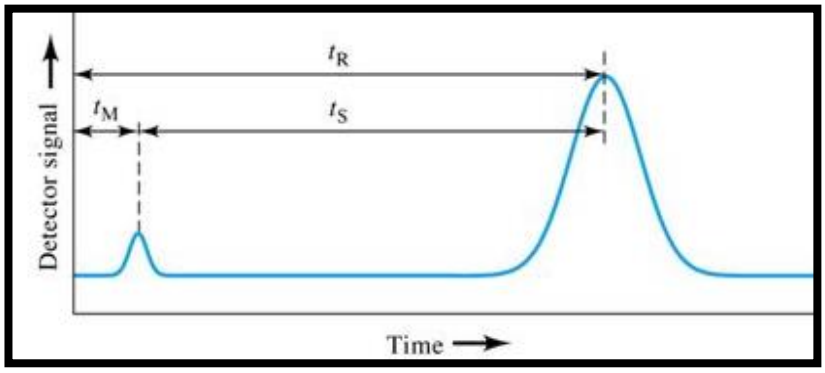


Figure 4.6: A typical chromatography of one solute in a one component mixture [122]

The retention factor (k') is the term used to measure the migration rates of solute on columns and is an important experimental (semi-quantitative) parameter that is defined by **Equations 4.10** and **4.11**.

$$k'_1 = K_1(V_S/V_M) \qquad 4.10$$

k'_1 can also be calculated using the information chromatogram in **Figure 4.6** using **Equation 4.11** where t_M is time taken to elute a non-absorbed marker through the column and t_R is time taken to elute a peak to its maximum height, while t_S is equal to $t_R - t_M$ [120]

$$k'_1 = \frac{(t_R - t_M)}{t_M} \qquad 4.11$$

A retention factor between one and ten are preferred since small values may indicate poor separation due to little or no retention (interaction) on the column. A small amount of solute is recommended for the best column separation to avoid the saturation of the resin which may lead to a loss of column efficiency and poorly shaped peak profiles.[117] The retention factor of sample ions can be altered by changing the chemical nature and concentration of the pairing ions.[121]

[120] D. T. Gjerde, L. Hoang, D. Hornby, RNA purification and analysis: Sample preparation, extraction, chromatography, Copyright Wiley-VCH Verlag GmbH and Co. KGaA, 2009

[121] S. J. Fritz, Factors affecting selectivity in ion chromatography, *Journal of chromatography A*, 2005, 8-17, 1085

The selectivity (or separation) factor (**α**) of two solutes **1** and **2** is defined as the ratio of the distribution constant of the more strongly retained solute **2** to the distribution constant for the less strongly held solute **1** (see **Equation 4.12**). This also indicates the relationship between the selectivity factor of two solutes and their retention factors (see **Equation 4.13**). Selectivity factor (**α**) should always be greater than unity and provide a measure of how well the column will separate the two solutes.[122]

$$\alpha = \frac{K_2}{K_1} \qquad \text{where K is distribution constant} \qquad 4.12$$

$$\alpha = \frac{k'_2}{k'_1} \qquad \text{where } k'_2 > k'_1 \text{ and k' is retention factor} \qquad 4.13$$

Optimum selectivity or separation may be achieved through the manipulation of different experimental factors which include particle size of the resin, column length, flow rate and concentration of the eluent. All of these factors may be changed in order to optimize the selectivity of separation.

The number of theoretical plates (N) is a measure of the column efficiency according to the Plate theory and can be calculated using **Equation 4.14** where the column length is divided by the plate height (H).[122]

$$N = \frac{L}{H} \qquad 4.14$$

or using **Equation 4.15** where w = the peak width on a chromatogram (**Figure 4.7**)

[122] D. A Skoog, D. M. West, F. J. Holler, S. R. Crouch, Fundamental of analytical chemistry, 2014, 9th Ed.

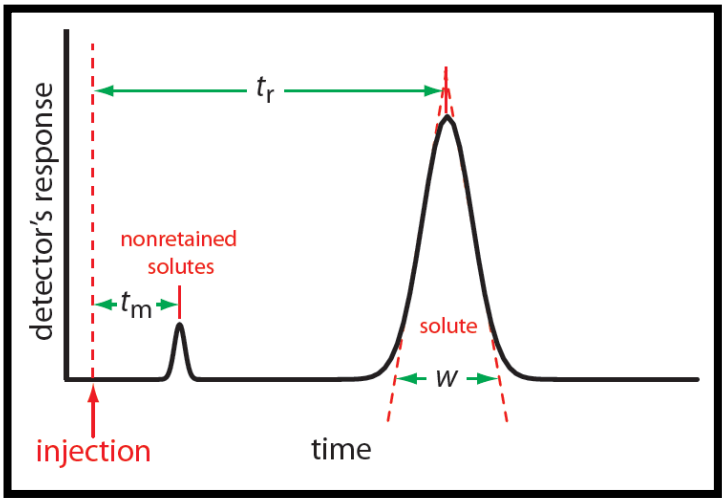


Figure 4.7: Chromatogram showing solute's retention time and peak width (w)[119]

$$N = 16\left(\frac{t_R}{w}\right)^2 = 5.54\left(\frac{t_R}{w_{1/2}}\right)^2 \qquad 4.15$$

The more the number of the theoretical plates available within a column, the more equilibrations possible, and the better the quality of the separation (see **Equation 4.15**).[122]

Ion exchange has some advantages, such as, simplicity of use (use of burettes); high selectivity of the resins and wide applicability in industrial processes. However, the method also has some disadvantages, such as, relatively slow separation process and sometimes high volumes of eluent/s are needed to complete the separation of targeted elements or analytes.[102]

The resolution of column tells one how far apart two bands are, relatively to the widths and provides the quantitative measure of the ability of the column to separate two solutes. A resolution value of Rs ≥ 1.5 between two peaks indicates that the sample solutes are well separated to a degree at which the height of each peak may be accurately measured (see **Figure 4.8** and **Equation 4.16**). [122]

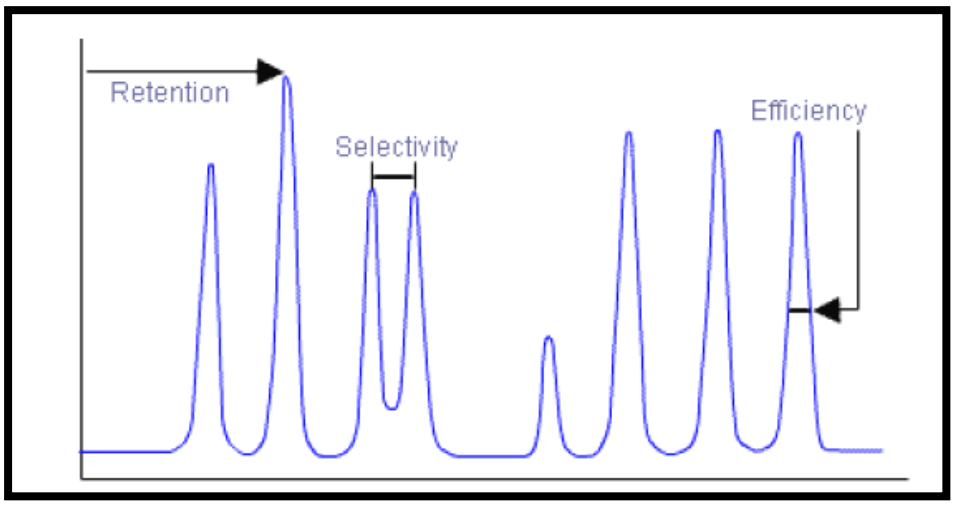


Figure 4.8: Resolution of two peaks [123]

$$R_s = \frac{2(t_{R2} - t_{R1})}{W_{s1} + W_{s2}} \qquad 4.16$$

Where retention time is $t_{R2} > t_{R1}$ and peak width, $Ws1 \approx W_{s2}$

[123] The theory of HPLC chromatography parameters, [Accessed from 11-02-2018]. Available from: http://www.chromacademy.com/lms/sco2/Theory_Of_HPLC_Chromatographic_Parameters.pdf

4.3.3 Solvent extraction separation

Solvent extraction (SX), is a technique that involves the distribution of a solute between two immiscible liquid phase – normally an aqueous and an organic phase. Solvent extraction was developed in 1842 by Peligot for the isolation of uranium in mineral ores using ethylacetate as an extracting solvent.[124] Advantages of this technique include the rapid and clean separation of both organic and inorganic substances. Moreover, the inexpensive and effective reagents make the scaling up of SX processes much easier in hydrometallurgical industries.[125]

The most common extracting solvents are Tributyl Phosphate (TBP), Trioctyl Phosphine Oxide (TOPO) and Methylisobutyl Ketone (MIBK). Extracting solvents are selected on the basis of their immiscibility with the aqueous phase and density. The separation process by SX on laboratory scale, involves vigorous shaking of the organic and aqueous solution mixtures in a separating funnel to enable transfer of the solutes between the two immiscible liquid phases and subsequent separation of the solutions based on their densities.[116] SX is generally a tedious process and sometimes involves several extraction steps, as well as, back-extraction steps to ensure separation and quantification. The technique may also require costly or large amounts of organic solvents and can generate large volumes of organic waste whereby its disposal is difficult and costly. Nevertheless, the re-use of the organic solvents are possible with distillation. Emulsion formation, however, can interfere with the phase-separation process.[126]

The success of SX separation is determined by distribution constant (K_D) and distribution ratio (D). The larger the K_D and D value, the better the transfer of the solute from the aqueous into the organic phase. The distribution constant describes

[124] S. M. Khopkar, Solvent extraction: Separation of elements with liquid ion exchangers, New Delhi: New Age International, Publishers, 2007

[125] S. Roy, Solvent extraction, Metallurgical and material engineering department, Jadavpur University, [Accessed on 23-11-2017]. Available: https://www.slideshare.net/DilipSaha1/solvent-extraction-51718683

[126] Separation techniques, [Accessed on 24-11-2017]. Available from: https://www.epa.gov/sites/production/files/2015-05/documents/402-b-04-001b-14-final.pdf

the equilibrium constant for the distribution of an analyte in two immiscible solvents of an extraction system (see **Equation 4.17 and 4.18**).[115]

$$S_{aq} \underset{}{\overset{K_D}{\rightleftharpoons}} S_{org} \qquad 4.17$$

$$K_D = \frac{[S]_{org}}{[S]_{aq}} \qquad 4.18$$

$[S]_{org}$ and $[S]_{aq}$ are the concentration of the solute in organic and aqueous phases respectively.

The distribution ratio (D) is the ratio of total solute concentration in each phase (see **Equation 4.19**). The completeness of separation of extraction must be proved by relating the percentage extraction (%E) with the distribution ratio (see **Equation 4.20**).

$$D = \frac{\left|[S]_{org}\right|_{Tot}}{\left|[S]_{aq}\right|_{Tot}} \qquad 4.19$$

$$\% E = \frac{100D}{D + (V_w/V_o)} \qquad 4.20$$

The distribution constant (**Equation 4.18**) can be expressed in terms of the experimental conditions on how solute is transferred from one solvent to another by demonstrating **Equation 4.21** below.[102]

$$q_n = \left(\frac{1}{K_D V_r + 1}\right)^n \qquad 4.21$$

Where q is the fraction amount of solute which remains in the aqueous layer after extraction; V_r is the ratio of organic volume to aqueous volume and n is the number of successive extractions.

The separation of metal ions by solvent extraction depends on the ability of the metal ions to form organic-like molecules (organometallic) which can be selectively extracted into the organic phase. This can be achieved by the addition of inorganic or organic ligands in either the aqueous or organic solvents to form a neutral compound with the metal ion of interest (see **Figure 4.9**).[127]

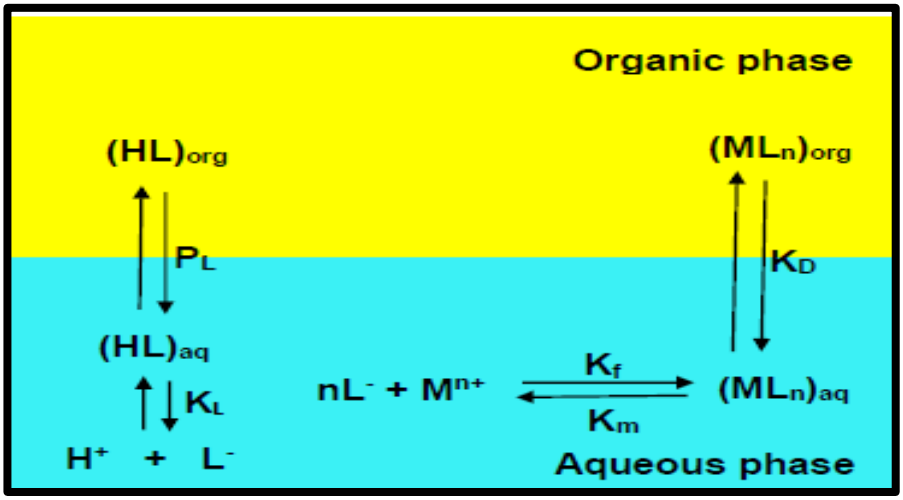


Figure 4.9: General solvent extraction process of metal complexes[128]

The extraction process in **Figure 4.9** can be summarised in one reaction (see **Equation 4.22**) with extraction ratio D (see **Equations 4.23 and 4.24**).

$$M^{n+}_{(aq)} + nHL_{(org)} \underset{}{\overset{D}{\rightleftharpoons}} ML_{n(org)} + nH^{+}_{(aq)} \qquad 4.22$$

[127] Liquid-liquid extractions, [Accessed from 28-07-2017]. Available from: https://chem.libretexts.org/Textbook_Maps/Analytical_Chemistry_Textbook_Maps/Map%3A_Analytical_Chemistry_2.0_(Harvey)/07%3A_Collecting_and_Preparing_Samples/7.7%3A_Liquid%E2%80%93Liquid_Extractions

[128] Liquid-liquid extractions, [Accessed from 28-07-2017]. Available from: https://chem.libretexts.org/Textbook_Maps/Analytical_Chemistry_Textbook_Maps/Map%3A_Analytical_Chemistry_2.0_(Harvey)/07%3A_Collecting_and_Preparing_Samples/7.7%3A_Liquid%E2%80%93Liquid_Extractions

$$D = \frac{[ML_n]_{org}[H^+]^n{}_{aq}}{[M^{n+}]_{aq}[HL]^n{}_{org}} \qquad 4.23$$

Where D is the extraction ratio for all species in solution; $[ML_n]_{org}$ is the concentration of the metal chelate in the organic layer; $[M^{n+}]_{aq}$ is the concentration of metal ions in the aqueous layer and $[HL]_{org}$ is the concentration of the chelating agent in the organic layer. Extraction ratio can also be summarised in four steps of extraction process (see **Equation 4.23**) namely, (i) the distribution of chelating agent between the aqueous and organic phases (P_L); (ii) the dissolution and dissociation of the chelating ligand in either the organic or aqueous phase (K_L); (iii) the dissociation constant of the neutral metal ligand in the aqueous phase(K_m); and (iv) the distribution of the metal compound between the two liquid phases (K_D). Each of the four steps of the extraction process must be in equilibrium (see **Appendix 1**).[115]

$$D = \frac{K_{D\,(MLn)}\ K_L{}^n}{K_m\ P_{L(HL)}{}^n} \qquad 4.24$$

Extraction constant of metal ions (D>>) is favoured when:

$K_D > 1$ which indicates that metal chelate should be highly soluble in the organic layer.

$K_L > 1$ shows that chelating agent should easily dissociate in the aqueous layer.

$K_m < 1$ indicates that metal chelate should be highly soluble in the aqueous layer.

Lastly $P_L < 1$ indicates that the chelating agent should be highly soluble in the aqueous layer. [102]

The measure of the ability of the system to separate the metal ions is determined by a separation factor (**α**) which refers to the ratio of the distribution constant A to the distribution constant B that were determined under identical experimental conditions (see **Equation 4.25**). The separation of the different metal ions is only achieved if **α**>1. The more that **α** deviates from unity, the easier it will be to obtain separation.

$$\alpha_{A,B} = \frac{K_{D(A)}}{K_{D(B)}} \qquad 4.25$$

4.4 Quantification technique

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is a multi-element analysis technique that is used for the detection of trace and major metals in different samples. This technique was first developed in the early 1960s. [129] Since then, ICP-OES has been used in conjunction with other procedures for quantitative analysis of numerous types of samples. The basic principle of the technique entails the dissociation and excitation of the constituent atoms and ions in a sample to higher energy levels using a plasma which generates temperatures of about 7000 K. [130] Upon the relaxation, the atoms emit light with characteristic wavelengths which can be used to identify and quantify its composition.

The main components of the ICP-OES include the sample introduction system, the torch assembly and the spectrometer. The sample introduction system consists of a peristaltic pump, Teflon™ tubing, a nebulizer and a spray chamber.[131] The peristaltic pump transports the sample into the nebulizer where it is mixed with the carrier gas to produce an aerosol that is then spritzed into a spray chamber as small droplets. Only >1 % droplets are carried into the plasma while 99 % droplets are collected and drained as indicated in **Figure 4.10**. There are numerous types of nebulizers and the

[129] Analytical techniques, Inductively coupled plasma, [Accessed on 11-01-2018]. Available from: https://upcommons.upc.edu/bitstream/handle/2117/93737/08CAPITOL6.pdf?sequence=8&isAllowed=y

[130] X. Hou, B. T. Jones, Inductively coupled plasma/optical emission spectrometry, *Encyclopaedia of Analytical Chemistry*, 2000, 9468-9485

[131] R.A Meyers, Encyclopaedia of Analytical Chemistry, 2000 9468 - 9485

most commonly used ones include: i) pneumatic; ii) ultrasonic; and iii) grid nebulizers.[131]

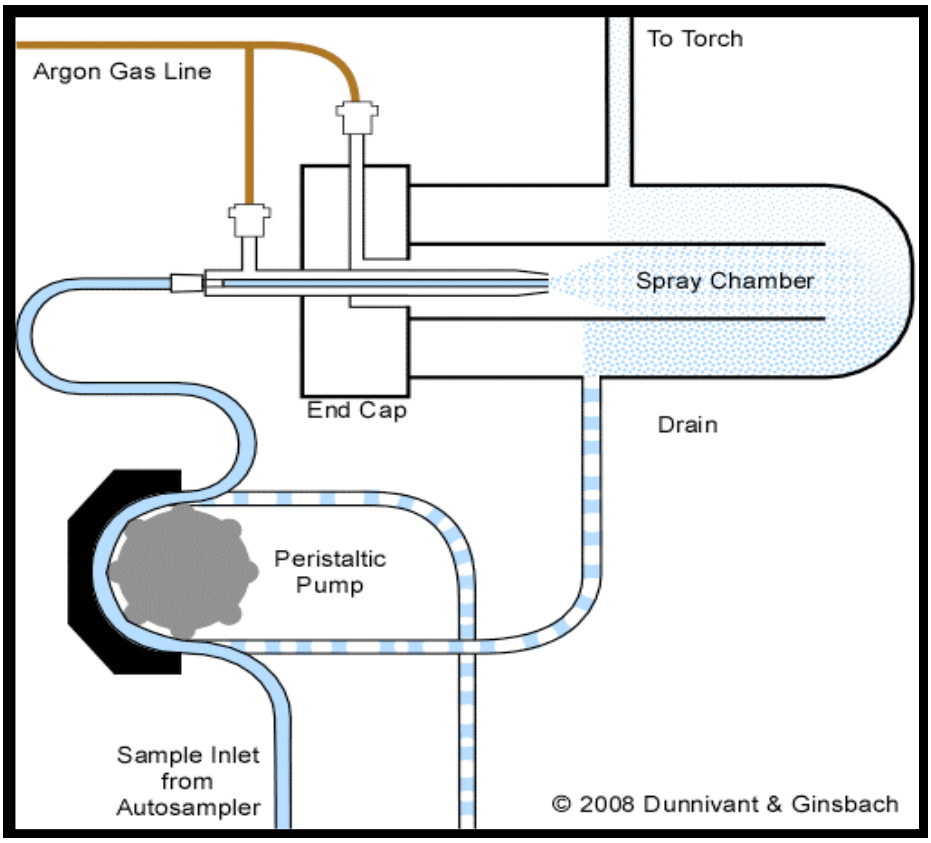


Figure 4.10: Sample introduction into ICP-OES[132]

Another important component of the ICP-OES is the plasma torch which consists of concentric quartz tubes with the inner tube containing the sample aerosol and argon support gas, while the outer tube contains flowing gas to keep the tubes cool. The induction coil wrapped around the tubes contains an oscillating current which is produced by a radio frequency generator to create an oscillating magnetic field.[129] An oscillating current in the ions and electrons of the support gas are caused by the magnetic field that is created in the induction coil, whereby those ions and electrons collide with other atoms in the support gas to create very high temperature plasma (see **Figure 4.11**).

[132] Components of an Inductively Coupled Plasma—Atomic Emission Spectrometry System (ICP-AES), [Accessed 03-09-2018]. Available from: http://people.whitman.edu/~dunnivfm/FAASICPMS_Ebook/CH3/3_3_2.html

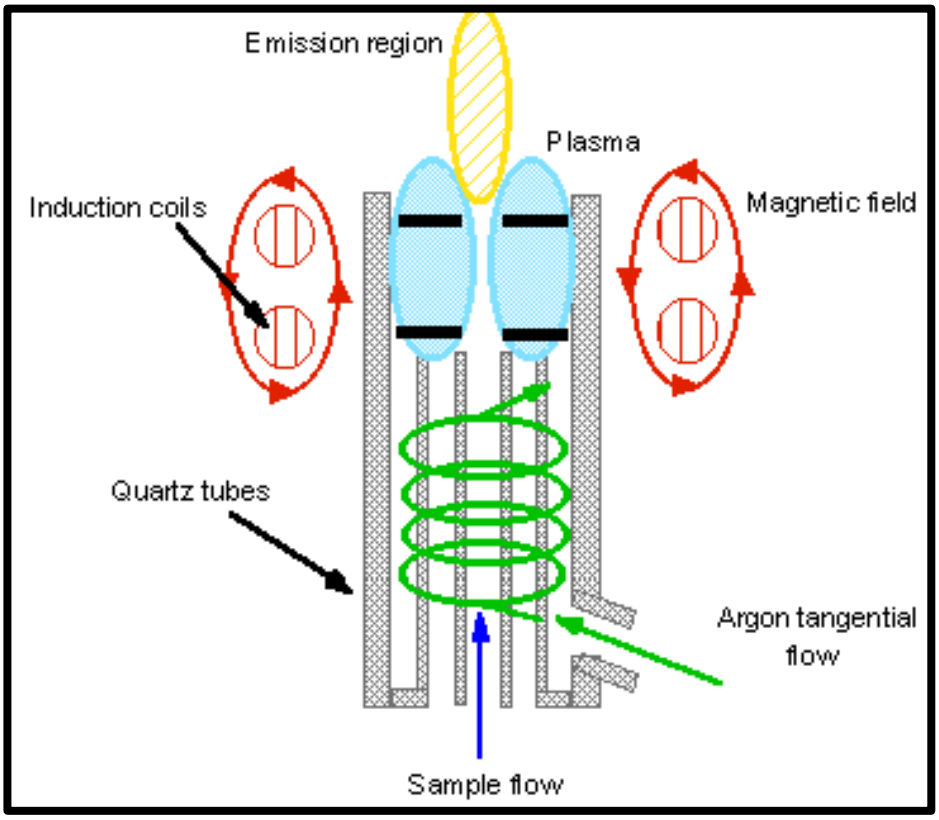


Figure 4.11: Schematic cross-section on ICP-OES[129]

The high temperature plasma which is produced according to **Equation 4.26** below, removes the sample from the aerosol and produces microscopic salt particles, which are then converted into a gas of individual molecules followed by dissociation into atoms. After the sample has been desolvated, vaporised and atomized, it undergoes ionization and excitation processes as illustrated in **Figure 4.12**.[102,131]

$$Ar(g) + Energy \longrightarrow Ar^{+} + e^{-} \qquad 4.26$$

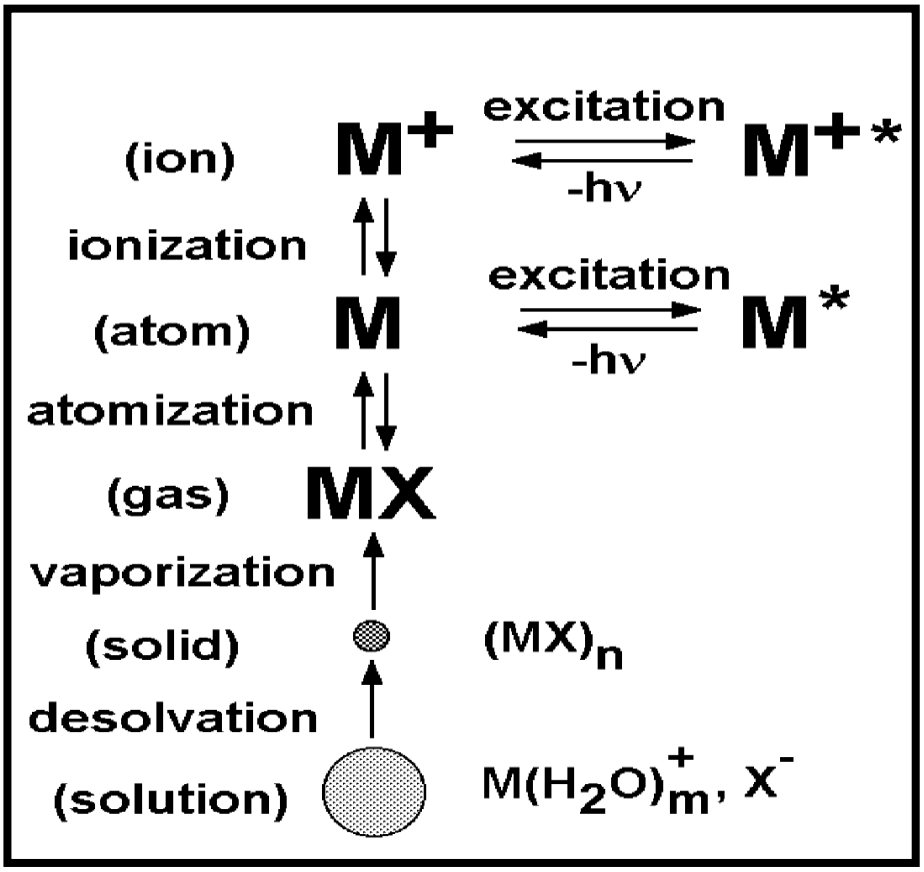


Figure 4.12: Introduction of the small droplet into the ICP-OES[131]

A plasma torch consists of three concentric quartz tubes for the argon flow and injection of the aerosol, namely, plasma flow, auxiliary flow and nebulizer flow (see **Figure 4.13**). The purpose of plasma torch includes, the evaporation of the solvent from the analyte salts, atomization of the atoms in the salt and the excitation of the ground state atom to a higher energy level.

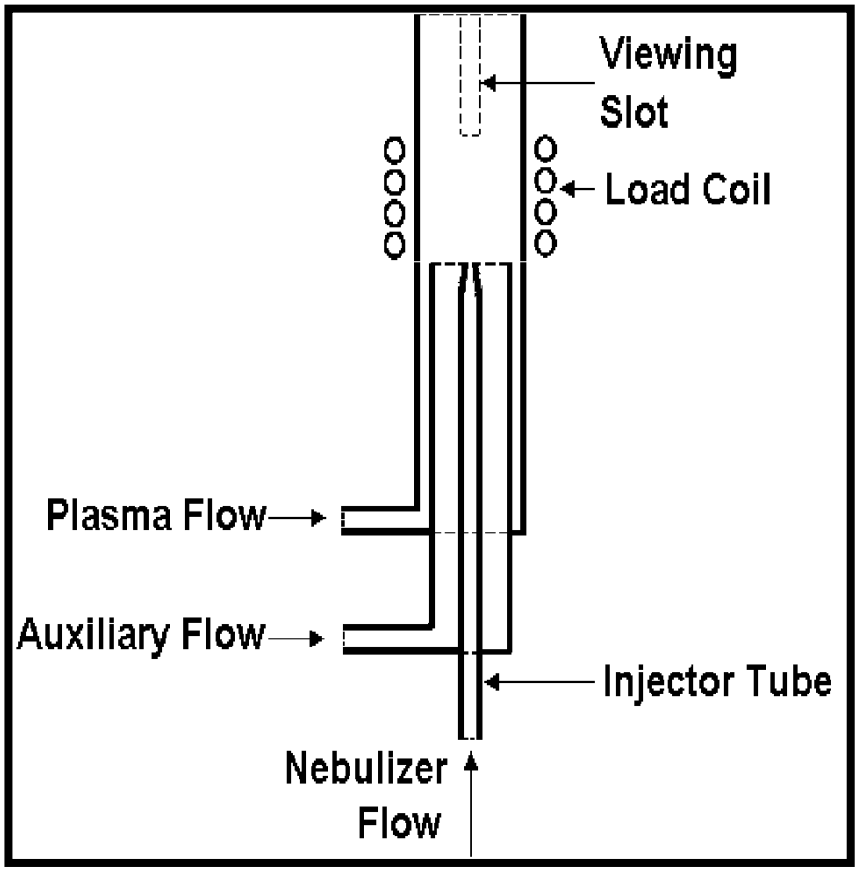


Figure 4.13: Illustration of plasma torch used in the ICP-OES[131]

ICP-OES has advantages that include the ability to identify and quantify all elements with the exception of argon, non-metals which include nitrogen and oxygen, artificially made elements such as Tc, as well as, halogens. It has the ability to simultaneously analyse a multi-element sample, use single solutions for the determination of trace and major elements, and has good precision (0.5-1 %) and accuracy. Furthermore, it has the capability to determine elements such as B, Be, S and P that are difficult to be determined by other techniques and lastly, the technique makes it feasible to analyse small sample sizes and small solution volumes (1-2 mL). However, this technique has some disadvantages too that include sample

preparation for analysis which are time-consuming while accurate analyses of trace elements in some sample types are limited by spectral interference.[133]

4.5 Method validation

It is good analytical practice to assess the validity of analytical procedures during their development for their reproducibility, reliability and accuracy of the analytical results. This process is called validation of the analytical method and should be a fundamental part of method development in analytical practice. Analytical methods can be effected by experimental parameters such as sample matrix and analyte concentrations.[134] It is therefore important that the newly developed procedures are validated for a number of different parameters which include robustness under different chemical conditions. Other parameters investigated in the validation process, include the linearity of the calibration curve, precision of analytical results, accuracy and limits of detection (see **Figure 4.14**).

[133] U. A. Lar, National centre for marine geosciences Nigerian geological survey agency, *Sediment Geochemistry: Laboratory Analytical Tools, Procedures and Precautions*, PHD, University of Jos-Nigeria

[134] C. C. Chan, H. Lam, Y.C. Lee, X. Zhang, Analytical method validation and instrument performance verification, John Wiley and Sons, Inc., Hoboken, New Jersey, 2004

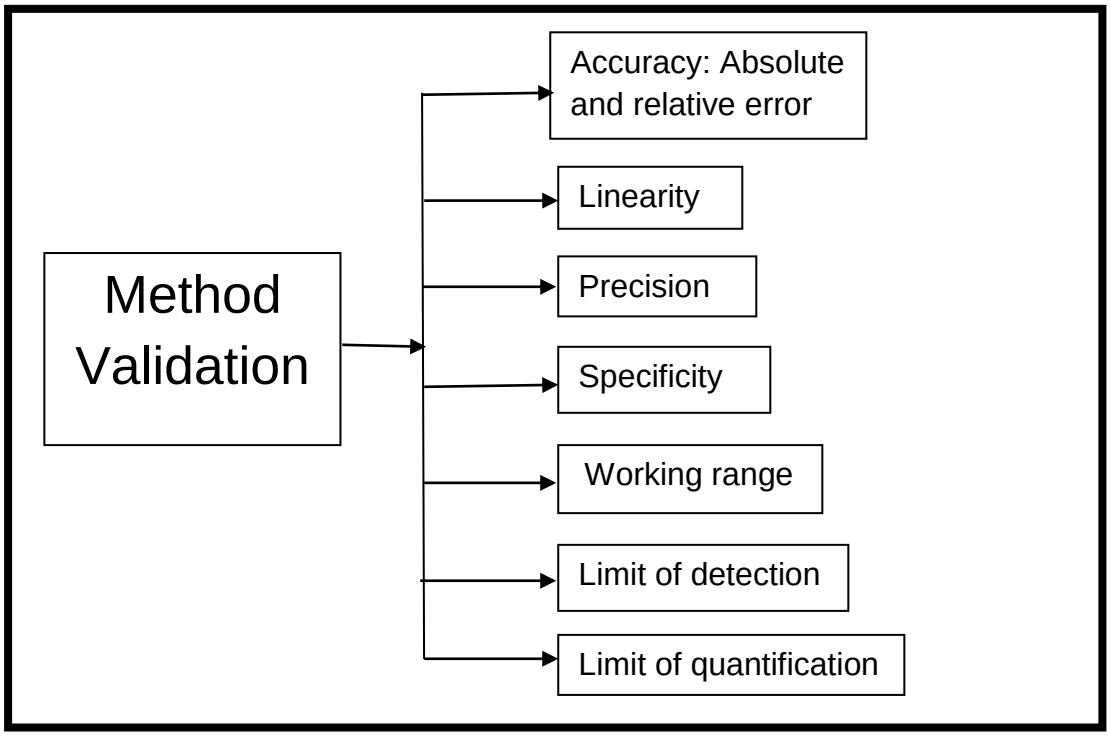


Figure 4.14: Method validation parameters.

4.5.1 Accuracy

Accuracy of the analytical method can depend on the available information. Normally, a Certified Reference Material (CRM) is used to determine the true or standard value of the different elements. CRMs include pure metals, metal salts or minerals. In these compounds, the elemental content of most of the elements of interest are accurately known. The experimentally obtained results of applying the newly developed method on the CRMs are compared with the certified values or the theoretically expected percentages to determine the accuracy of the method. However, many CRMs which match the matrix of the mineral sample are available and as such, the accuracy and precision of the results is judged by repeating the procedure several times to obtain an average value which can be regarded as a “true or accepted” value. Alternatively, the sample can be analysed by a different laboratory (inter-laboratory) or by a different analyst in the same laboratory using the same procedure or be analysed with different analytical techniques. In the presence

of an accepted or reference value, the accepted recovery range is recommended to be between 98 and 102 %.[135]

4.5.1.1 Absolute error (E)

The absolute error in the measurement of a quantity is the difference between the measured value and the true value (see **Equation 4.27**), where x_t is the true or accepted value of the quantity.

$$E = X_i - X_t \qquad 4.27$$

4.5.1.2 Relative error (E_r)

The relative error of a measurement is more useful than absolute error, it is expressed in percentage or parts per trillion (see **Equation 4.28**).

$$E_r = \frac{X_i - X_t}{X_t} \times 100\ \% \qquad 4.28$$

4.5.2 Linearity

The linearity of an analytical procedure is the ability to obtain test results of variable data that are directly proportional to the concentration of analyte in the sample. The working standard concentrations, as well as, the samples tested for accuracy, should be within the linear range. Linearity is usually demonstrated directly by dilution of a standard stock solution and at least, five diluted concentrations from stock solution are recommended. Linearity is evaluated by a least-squares fit of a plot of the obtained signals (intensity) as a function of analyte concentration. The variable data generated from linearity are used to calculate the following parameters, for example, the slope of the regression line, y-intercept and the linearity are acceptable when a correlation coefficient, r^2 of 0.997 and higher (closer to 1.0) is obtained (see **Figure 4.15**). The slope of the regression line provides an idea of the sensitivity of the regression while the y-intercept provides the analyst with an estimated variability/selectivity of the method.[134]

[135] P. De Bièvre, H. Günzler, Validation in chemical measurement, Springer-Verlag berlin Heidelberg, 2002

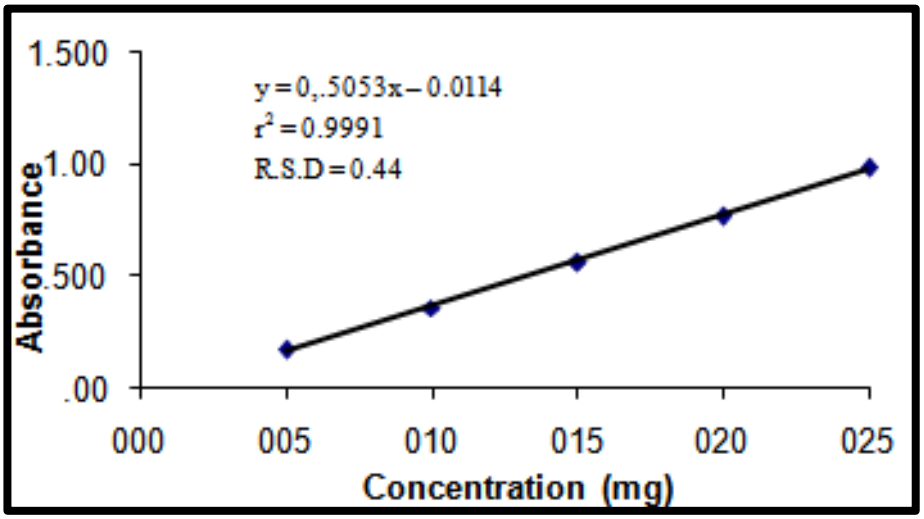


Figure 4.15 A calibration curve of good linearity, r^2 = 0.9991[136]

4.5.3 Precision

The precision of an analytical procedure is the closeness of agreement between independent test results obtained from multiple samples of the same homogeneous sample under a prescribed method. Precision is usually expressed in terms of the standard deviation (s), variance (s^2) and Confidence coefficient of Variation (CV) and is calculated using the average of a number of repeats (see **Equations 4.29 to 4.31**).[134]

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}} \qquad 4.29$$

$$s^2 = \frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1} \qquad 4.30$$

$$CV = \frac{s}{\bar{x}} \times 100\% \qquad 4.31$$

[136] Accessed on 11-01-2018. Available from:
http://article.sapub.org/image/10.5923.j.aac.20120206.02_010.gif

4.5.4 Specificity

Specificity defines the ability of the method to detect the analyte of interest in the presence of an interfering substance. The suitable identification tests should be able to discriminate between compounds of closely related structures which are likely to be present. Materials structurally similar to the analyte are tested to confirm that a positive response is not obtained.

4.5.5 The working range

The working range of an analytical procedure is the interval between the upper and lower levels of analyte that have been demonstrated and have suitable levels of precision, accuracy and linearity. Assay tests of drug substance require the minimum specified range of test concentration to be between 80 and 120 %.

4.5.6 The Limit of Detection (LOD)

The limit of detection is the lowest amount of analyte in a sample that can be detected but not necessarily quantified. It is estimated by signal to noise ratio of 3:1. LOD is calculated by using **Equation 4.32** where the value of **3** corresponds to a confidence interval of 99.7 %; **s** is the standard deviation of the blank solution; and **m** is the slope of the calibration.

$$LOD = 3 \times \frac{S}{m} \qquad 4.32$$

4.5.7 The Limit of Quantification (LOQ)

The limit of quantification is the lowest amount of analyte in a sample that can be quantified with suitable accuracy and precision. It is estimated by signal to noise ratio of 10:1. It is also based on evaluation and standard deviation of response and slope (see **Equation 4.33**). **Figure 4.16** illustrates the determination of LOD and LOQ.

$$LOQ = 10 \times LOD \quad 4.33$$

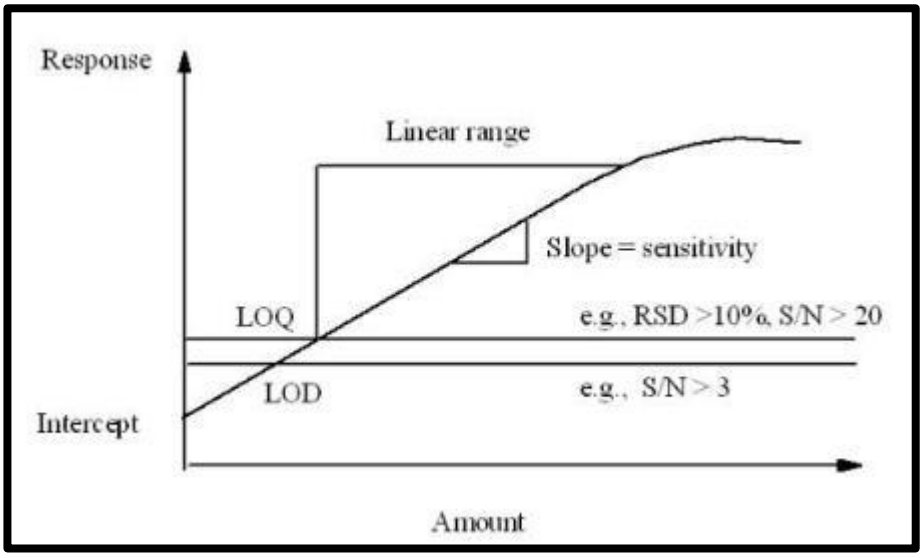


Figure 4.16: Determination of LOD and LOQ on a calibration curve

4.6 Conclusion

The analytical techniques discussed in this chapter were applied and investigated in the study. For instance, flux fusion technique was used for the complete dissolution of samples, such as, ZrO_2, HfO_2 and PDZ. The possible separation of zirconium and hafnium in zircon and PZD fluoride solution will be evaluated using acid leaching, ion exchange and solvent extraction. Zr and Hf quantification will be achieved using ICP-OES. Experimental results will be validated to ensure that the experimental procedure and analytical techniques adhere to analytical chemistry protocols.

5 Dissolution and separation of Zr and Hf from $(Zr/Hf)O_2$ mixtures and PDZ

5.1 Introduction

The dissolution of Zr and Hf from different primary zirconium sources (see **Chapter 3**, **Section 3.1**) often involves the use of either hazardous chemicals such as HF and NaOH[137] which are, environmentally unfriendly or uneconomical. This is due to the need for high temperatures during the mineral fusion process.[138] The difficulty to dissolve Zr/Hf minerals and some of their compounds is as a result of the chemicals' inertness of their oxides and silicate. The separation of Zr and Hf normally involve tedious and difficult processes due to their similarities of chemical and physical properties. Hydrometallurgical separation usually involves the conversion of the natural compounds into inorganic compounds such as halogen compounds followed by multi-stage separation steps.

This chapter covers all the aspects that were investigated to try and separate the Zr and Hf which were present in the different types of samples. This includes the dissolution, quantification and subsequent separation of the two elements from each other (**Figure 5.1**). Dissolution of the different samples was attempted using $NH_4F{\cdot}HF$, while selective separation was investigated with microwave-assisted acid digestion (leaching), ion exchange and solvent extraction. All the separation procedures were initially investigated on synthetic mixtures of Zr and Hf dioxide and

[137] G. J. Neuerburg, A method of mineral separation using hydrofluoric acid, *The American Mineralogist*, 1961, Vol.46, 1498

[138] S. Lubbe, R. Munsami, D. Fourie, Beneficiation of zircon sand in South Africa, *Journal of the South African Institute of Mining and Metallurgy*, 2012, 112(7), 583-588

the most successful or promising experimental conditions were applied to Plasma-Dissociated Zircon (PDZ). The metal oxides were selected to develop the methods based on the fact that the two elements of interest are present in the mineral as metal oxides in their most stable oxidation state (+4). At each step investigated in the study, from dissolution to separation, the resulting solutions were quantified for Zr and Hf content, using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Isolation of ZrO_2 after the separation process was done using precipitation technique.

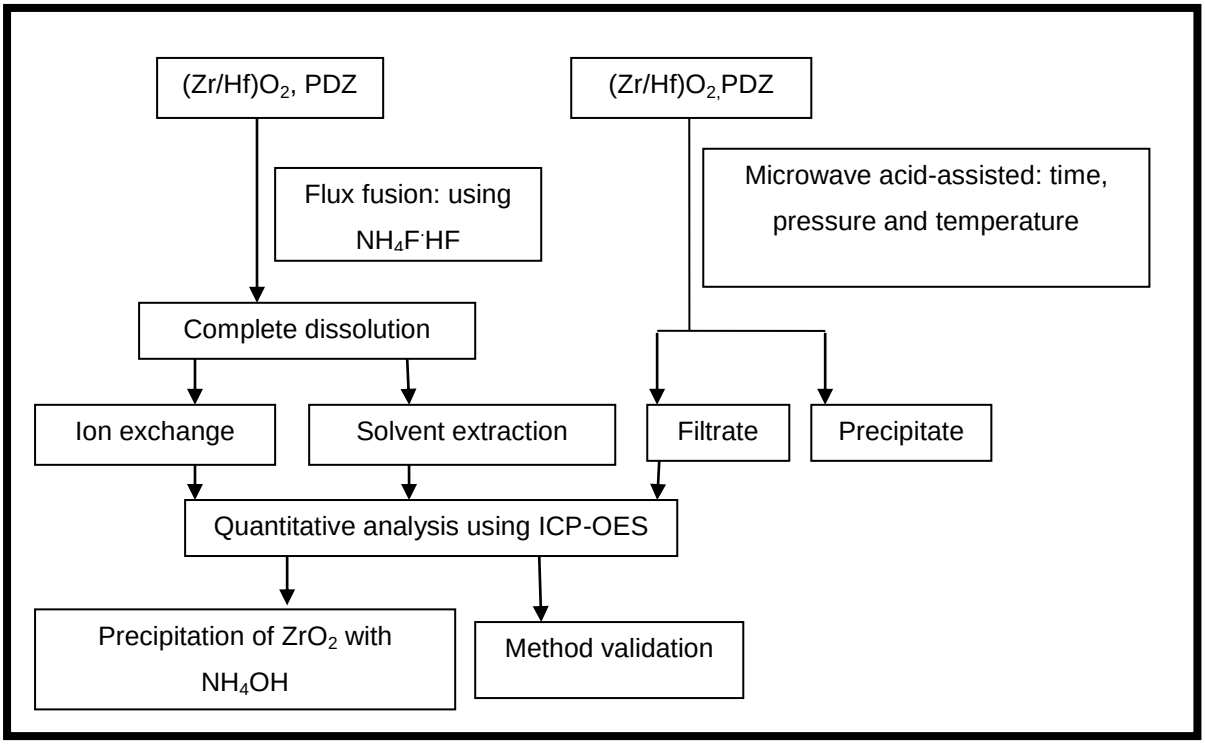


Figure 5.1: Schematic presentation of the different processes followed in this study

5.2 Equipment and reagents

Ultra-pure water, conductivity = 0.05 µS/cm, was used for all the analytical solution preparations. The water was purified in the laboratory using an ultra-reverse osmosis system from AJD Tranders (see **Figure 5.2**).

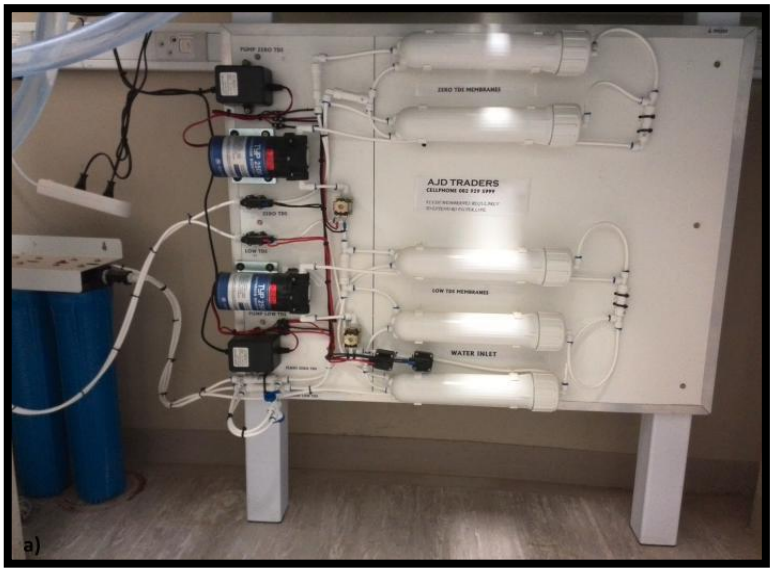


Figure 5.2 Ultra-reverse osmosis system

A Shimadzu AW320 electronic balance was used to weigh all the samples accurately to 0.1 mg at 25 °C under the certified ISO 9001 quality assurance system. Gilsom Pipetman micropipettes (100 – 1000 µL) and Brand pipetman (1 – 10 mL) were used for the accurate transfer of solutions, while Schott Duran grade (A) type and polytetrafluoroethylene (PTFE) volumetric flasks (brought from Merck) were used for sample preparations. Glass columns with an internal diameter of 1.2 cm were used during ion exchange separations, while a centrifuge bought from MSE (Measuring and Scientific Equipment) was used to remove any solid from the solution prior to analysis.

Microwave-assisted digestion of the PDZ was performed with an Anton Paar Perkin-Elmer Multiwave 3000 reaction system equipped with an 8SXF100 rotor and glass reaction vessels. The operating conditions for the microwave-assisted digestion of PDZ are given below in **Table 5.1**. Reaction vessels were cleaned using 8 mL of 55% HNO_3 in a microwave-heated oven for a period of 30 minutes prior to the sample digestion.

Table 5.1: Microwave-assisted digestion conditions for digestion of PDZ

Parameter	Condition
Power	600 watts
Ramp	15 min
Hold	90 and 135 min
Pressure rate	0.5 bar/sec
Temperature	240 °C
Pressure	60 bar
Reagents	98 % H_2SO_4
Volume of the reagent	8 mL

A Shimadzu ICPS-7510 spectrometer with a radial-sequential plasma source was used for the quantification of zirconium and hafnium in the different compounds during the study. The ICP-OES' operating conditions given in **Table 5.2** were maintained throughout the study.

Table 5.2: ICP-OES' operating conditions for the analysis of hafnium

Parameter	Condition
RF Power	1.2 kW
Coolant gas flow	14.0 L/min
Plasma gas flow	45 L/min
Auxiliary gas flow	0.5 L/min
Carrier gas flow	0.7 L/min
Sample introduction method	Peristaltic pump
Type of spray chamber	Glass cyclonic
Type of nebuliser	Concentric
Injector Tube diameter	3.0 mm

All reagents used during the study, along with their respective purities and purposes, are listed in **Table 5.3** below. All analyses were done in triplicates and the average values of the results were reported based on the standard deviations (last digit of the value) to show the uncertainty of the techniques.

Table 5.3: Chemicals and reagents used in this study for synthesis

Chemical	Formula	Purity, %	Purpose	Supplier
Reagents				
Zirconium and hafnium ICP standard in HNO_3 (5 % v/v, 1000 mg/L)			Calibration curves	Separation
Ammonium bifluoride	$NH_4F.HF$		Digestion	Merck Chemicals
Plasma-dissociated zircon	PDZ	Mineral	Digestion	NECSA
Zirconium oxide	ZrO_2	99	Digestion	Sigma Aldrich
Hafnium oxide	HfO_2	99	Digestion	Sigma Aldrich
Acids				
Nitric acid	HNO_3	55	Cleaning glassware	Associated chemical enterprises (ACE)
Hydrochloric acid	HCl	32	Separation and analysis	Associated chemical enterprises (ACE)
Sulphuric acid	H_2SO_4	98	Digestion, separation and analysis	Associated chemical enterprises (ACE)
Perchloric acid	$HClO_4$	70	Separation and analyisis	Associated chemical enterprises (ACE)
Ammonium hydroxide	NH_4OH	25	Precipitation	Associated chemical enterprises (ACE)

5.3 Quantification of Zr and Hf in $(Zr/HfO)_2$ and PDZ

5.3.1 Preparation of ICP-OES calibration solution and measurements

Hafnium (Hf) and zirconium (Zr) standard solutions were prepared from the original hafnium and zirconium standards of 1000 mg/L (see **Table 5.3**). Concentrations of Zr and Hf standards 1, 2, 4, 8 and 10 ppm were prepared in different acids - HCl, H_2SO_4 $HClO_4$ and HNO_3. The solutions were diluted with purified water and filled to the mark in 100.0 mL volumetric flasks. A blank solution was prepared, similar to the standard curve solutions (without analytes), by adding 5 mL of appropriate acid and diluting it with purified water and filled to the mark of 100.0 mL. All solutions were then allowed

to stand overnight, before ICP-EOS analysis. Quantitative analyses were performed at 343.823 nm and 277.336 nm for Zr and Hf respectively.[139]

5.3.1.1 Determination of Limit of Detection (LOD) and Limit of Quantification (LOQ) for selected elements

The limit of detections and quantifications (see **Table 5.4)** were determined using the standard deviation and slope of calibration curve for each element (see **Equations 4.32** and **4.33** in the previous chapter**)**. Ten replicates of the blank solution and three replicate measurements of the standard solutions[140] of the two elements in the different acids were obtained with ICP-OES (see **Appendix 2**). The standard curve was constructed from the determined slope and y-intercept.

[139] S. J. Lotter, Identification and quantification of impurities in zircon, PDZ and other relevant zirconium products, MSc, Thesis, Bloemfontein; University of Free State, 2008

[140] D. A Skoog, D. M. West, F. J. Holler, S. R. Crouch, Fundamental of analytical chemistry, 2014, 9th Ed.

Table 5.4: LODs and LOQs obtained for each element in the different acids

Element	Standard deviation of the blank	Slope	LOD (ppm)	LOQ (ppm)
HCl (32 %)				
Zr	0.0181	4.577	0.013	0.1301
Hf	0.0005	0.138	0.0111	0.111
H_2SO_4 (95-99 %)				
Zr	0.0019	0.889	0.0071	0.0706
Hf	0.0004	0.043	0.0306	0.3059
HNO_3 (65 %)				
Zr	0.0022	0.730	0.0098	0.0982
Hf	0.0004	0.035	0.0357	0.3574
$HClO_4$ (70%)				
Zr	0.0024	0.788	0.0102	0.1021
Hf	0.0008	0.040	0.0631	0.6308

5.3.2 Dissolution of $(Zr/Hf)O_2$ and PDZ by flux fusion using $NH_4F{\cdot}HF$

Approximately, 0.09 g ZrO_2 and 0.009 g of HfO_2 were accurately weighed (to 0.1 mg) and mixed in a platinum crucible. Ten times the mass (~1 g) of $NH_4F{\cdot}HF$ was added and homogenously mixed with the $(Zr/Hf)O_2$ mixture. The crucible was placed in the oven and heated to 200 ^oC (melting point of $NH_4F{\cdot}HF$ is 125 ^oC) [141] for 40 minutes. The resultant clear melt was allowed to cool to room temperature. The cold melt was dissolved with purified water (20 mL) with constant stirring on a hot plate and heated until the final volume was approximately 4 mL. The solution was then allowed to cool to room temperature and quantitatively transferred into a 100.0 mL PTFE volumetric flask. 5.0 mL of 32 % HCl was added to ensure matrix matching and then filled to the mark with purified water. The solutions were analysed for the Zr and Hf concentrations using ICP-OES and the results are given in **Table 5.5** (sample 1).

[141] M. Nete, Separation and purification of niobium and tantalum from synthetic and natural compounds, PhD, Thesis, Bloemfontein; University of Free State, 2013

The inaccurate recovery of the Hf prompted a slight variation in the dissolution of the resultant flux mixture. The clear melt was cooled to room temperature, 30 mL of 0.5 M H_2SO_4 was added and heated to 40 ^oC for 50 minutes to remove the fluoride ions as H_2SOF_2. The solution was then allowed to cool to room temperature and quantitatively transferred into 100.0 mL PTFE volumetric flasks. 5.0 mL of 32 % HCl was added to ensure matrix matching and then filled to the mark with purified water. The solutions were analysed for the Zr and Hf concentrations using ICP-OES and the results are given in **Table 5.5** (sample 2).

Table 5.5: Quantitative results of Zr and Hf after 40 minutes fusion digestion of the $(Zr/Hf)O_2$ with $NH_4F{\cdot}HF$ flux

Sample	Flux	Average Zr and Hf content in $(Zr/Hf)O_2$ (ppm)				% Zr and Hf recoveries (S.D)	
		Expected		Found			
		Zr	Hf	Zr	Hf	Zr	Hf
1	$NH_4F{\cdot}HF$	673	119	677	145	100.6(2)	121.2(9)
2*	$NH_4F{\cdot}HF$	606	132	607	131	100.1(2)	100(2)

* Addition of H_2SO_4 and volume decreased to 4 mL

The same procedure mentioned above on dissolution of the $(Zr/Hf)O_2$ mixture with $NH_4F{\cdot}HF$ was applied to the PDZ material. Visual inspection indicated complete sample dissolution. The results are presented in **Table 5.6**.

Table 5.6: Analytical results from ICP-OES for PDZ

Sample	Measurement	ICP-OES			
		% Element		% Metal oxide	
		Zr	Hf	ZrO_2	HfO_2
PDZ	1	48.8	1.21	66.0	1.43
	2	48.5	1.22	65.5	1.44
	3	49.1	1.20	66.3	1.41
	Average	**48.8**	**1.21**	**65.9**	**1.43**
	SD	0.3	0.01	0.4	0.01
	%RSD	0.6	0.96	0.6	0.96

5.3.3 Effect of fluoride on pure Zr and Hf standards mixture by using $NH_4F{\cdot}HF$ solution

It was also decided to investigate the possible influence of different amounts of $NH_4F{\cdot}HF$, and therefore fluoride ions, on the recovery of the two elements. The synthetic mixture of 4.0 ppm Zr and 4.0 ppm Hf were mixed with different volumes of $NH_4F{\cdot}HF$ solution (2, 4, 6 mL) and were transferred to 100.0 mL volumetric flasks. 5.0 mL HCl or H_2SO_4 was added to ensure matrix matching. The solutions were diluted with purified water and filled to the mark in 100.0 mL volumetric flasks for ICP-OES analysis. According to the results shown below in **Table 5.7**, fluoride ions in solution affect the recoveries of Hf in HCl matrix more than in H_2SO_4 matrix.

Table 5.7: Quantitative results of Zr and Hf metals from mixture of Zr/Hf standards and $NH_4F{\cdot}HF$ flux

Volume of $NH_4F{\cdot}HF$ (mL)	HCl matrix		H_2SO_4 matrix	
	% Zr and Hf recoveries (S.D)		% Zr and Hf recoveries (S.D)	
	Zr	Hf	Zr	Hf
0	100.4(1)	101.3(1)	100.8(4)	99(3)
2	86(2)	87(1)	101(2)	98(2)
4	86(2)	85(1)	101(3)	98(1)
6	82(2)	84(3)	100(2)	96.3(3)

5.4 Separation of Zr and Hf in both a synthetic $(Zr/Hf)O_2$ and PDZ mixtures

5.4.1 Microwave-assisted acid leaching of Hf in $(Zr/Hf)O_2$ and PDZ

A previous study by Malefo[142] indicates that HfO_2 completely dissolved in H_2SO_4 under certain microwave conditions, while a similar study by Löttor *et. al.*[139] on zircon and PDZ microwave dissolution indicated very poor Zr recovery. The current study investigated the possible selective leaching of Hf from Zr samples under microwave conditions using H_2SO_4 as solvent. Mixtures of 0.09 g ZrO_2 and 0.009 g HfO_2 were accurately weighed (to 0.1 mg) and quantitatively transferred into pre-cleaned glass reaction vessels and 8.0 mL of concentrated H_2SO_4 was added to each sample. The vessels were sealed and placed in the rotor which was subsequently placed in the microwave digestion system. Sample digestions were performed using the operating conditions in **Table 5.1**, and applying a digestion time variation (90 and 135 minutes). The residue was then separated from the solution by filtration and the filtrate was quantitatively transferred into a 100.0 mL volumetric flask and diluted to the mark with water. The solutions were subsequently analysed using ICP-OES. The same procedure described above on microwave acid leaching of Hf in the synthetic

[142]G. Malefo, Quantification of hafnium in Selected Inorganic and Organometallic Compounds, MSc, Thesis, Bloemfontein; University of Free State, 2016

$(Zr/Hf)O_2$ mixture using H_2SO_4 was also applied to PDZ. Inconclusive analytical results were obtained from the microwave digestion samples, therefore, this method for the possible Zr/Hf separation needs to be investigated further.

5.4.2 Ion exchange separation of Zr and Hf in (Zr/HfO_2) and PDZ after $NH_4F{\cdot}HF$ fusion

5.4.2.1 Ion exchange separation of Zr and Hf using different anion ion exchange resins

A literature study[143] has indicated that the most likely products after $(Zr/Hf)O_2$ reacted with $NH_4F{\cdot}HF$ in solution are the negatively charged ZrF_7^{3-} and HfF_7^{3-} anions (see **Equation 5.1**).

$$Zr(Hf)O_2{\cdot}SiO_2 + 8NH_4HF_2 \longrightarrow (NH_4)_3Zr(Hf)F_7 + (NH_4)_2SiF_7 + 3NH_4F + 4H_2O \qquad 5.1$$

Only anionic exchange resins were used in the subsequent separation of the two main elements, due to the existence of anions in solution. Three different anionic exchange resins, namely, Dowex Marathon wba; Dowex 21k; and Amberlite IRA-900 were used in this investigation to determine their effectiveness in the possible separation of Zr and Hf from their metal oxide parent samples. The different resins were added to the glass columns (burette) of 1.2 cm diameter as free flowing slurries prepared in water. The columns were packed up to a height of 20 cm above a cotton wool plug at the bottom of the column. The excess water was released from the column until the water level was about 2 cm above the resin bed.

Each resin was thoroughly washed by running not less than 10 mL of 0.1 M HCl through the resin prior to the elution of the sample. 5.00 mL sample aliquots of the $(Zr/Hf)O_2$ mixture (from **Paragraph 5.3.2**) was transferred to the columns and subsequently eluted with 0.1 M HCl (Cl^- ions act as exchanger). The effluents from

[143] M. M. Makhofane, J. L. Havenga, J. T. Nel, W. du Plessis, C. J. Pretorius, Manufacturing of anhydrous zirconium tetrafluoride in a batch reactor from plasma-dissociation zircon and ammonium bifluoride, *The Journal of the South Africa Institute of Mining and Metallurgy*, 2012, Vol.7A , 559

the columns were collected in 10.0 mL fractions into a 100.0 mL volumetric flask and diluted to the mark with water. The collected samples were left to stand for 24 hours before analysis by ICP-OES. The elution curves of the different resins are shown in **Figures 5.3** to **5.5**. All the three curves indicated a slight preferential elution of Zr over Hf with Hf eluted at a later stage (after a longer time). The strong resins, Dowex 21k and Amberlite IRA-900 showed a larger gap between the elution of Zr and Hf compared to the weak Dowex marathon resin. A decision was taken to proceed with the investigation and concentrate on Amberlite IRA-900 due to the larger difference between the two elution peaks.

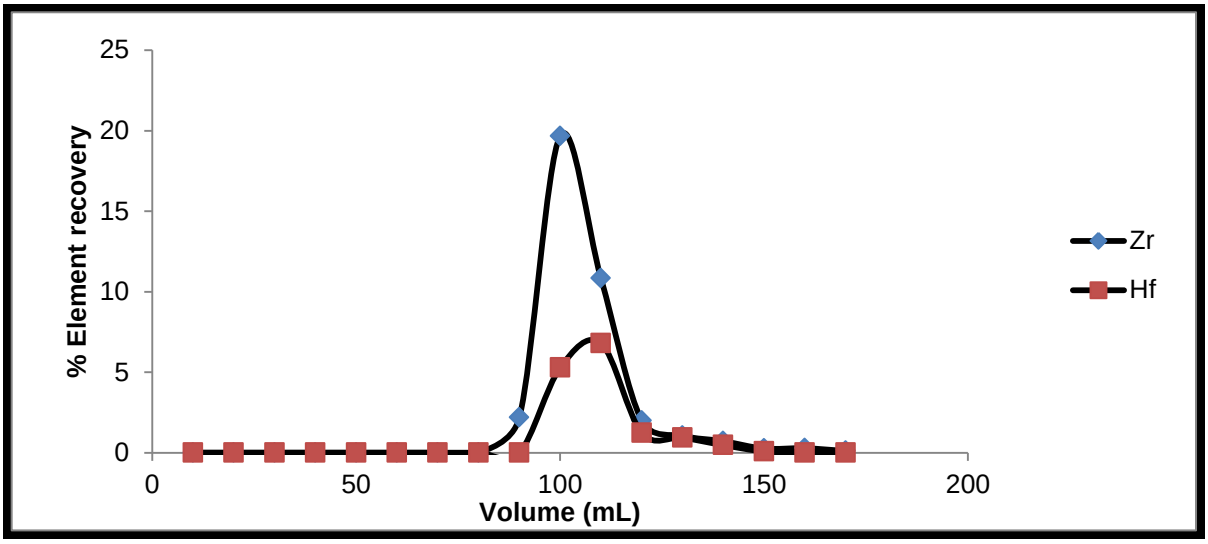


Figure 5.3: Elution behaviour of Zr and Hf using weak Dowex Marathon wba anion with 0.1 M HCl

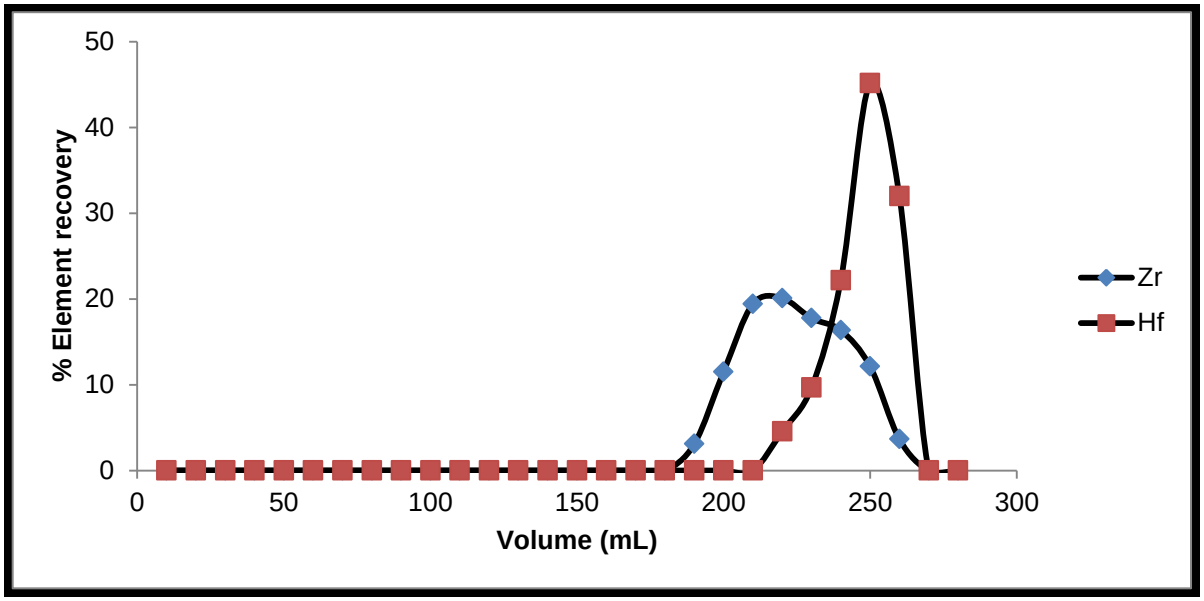


Figure 5.4: Elution behaviour of Zr and Hf using strong Dowex 21k anion with 0.1 M HCl

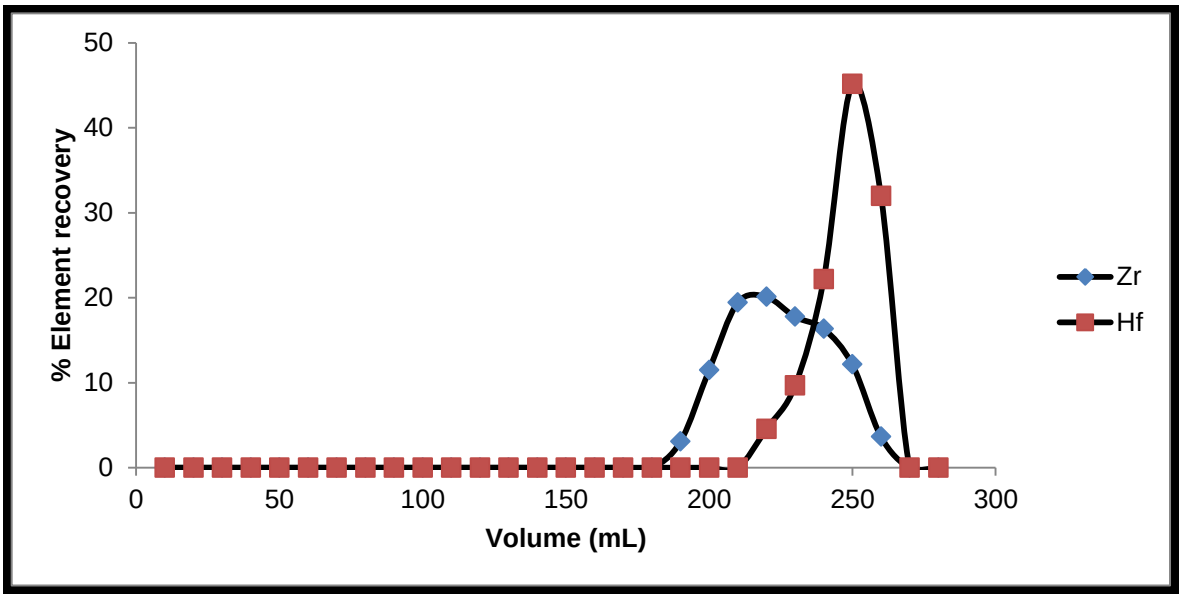


Figure 5.5: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion with 0.1 M HCl

5.4.2.2 Separation of Zr and Hf on strong Amberlite IRA-900 with perchloric acid

In this step of the investigation, the separation of Zr and Hf using ion exchange was investigated with Amberlite IRA-900 with perchloric acid ($HClO_4$) as eluent.[144] A sample aliquot of 5.00 mL of Zr/Hf (from **Paragraph 5.3.2**) was transferred to the packed column and subsequently eluted with 0.1 M $HClO_4$ (ClO_4^- ions act as exchanger). The effluent from the column was collected in 10.0 mL fractions into 100.0 mL volumetric flask and diluted to the mark with water. The collected samples were left to stand for 24 hours before analysis. The quantification was done using ICP-OES to determine the concentrations of Zr and Hf in each sample fraction. The elution curve of 0.1 M $HClO_4$ on strong anion is shown in **Figure 5.6**. 0.1 M $HClO_4$ elution indicated poor or no separation between Zr and Hf. Therefore, it was decided to end any further investigation with this acid and to continue with HCl, because it indicated better separation of two peaks than $HClO_4$.

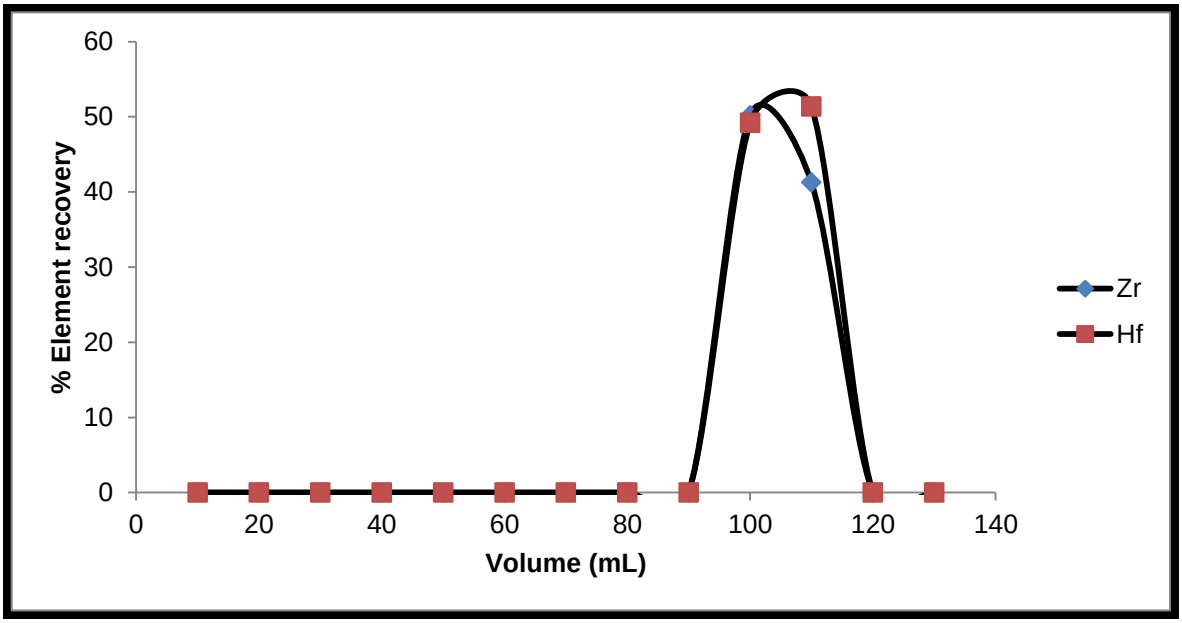


Figure 5.6: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and [$HClO_4$]

[144] E. M. Larsen, P. Wang, The ion exchange of zirconium and hafnium in perchloric acid with Amberlite IR-120, J. Am. Chem. Soc., 1954, 76(24), 6223-6229

5.4.2.3 Separation of Zr and Hf on strong Amberlite IRA-900 with hydrochloric acid (HCl)

5.4.2.3.1 Effect of 0.5 M hydrochloric acid

According to literature, it is indicated that Zr and Hf were separated by using high concentration HCl as eluent. [145] In this study, 0.5 M HCl was subsequently used to elute 5.00 mL aliquot of $(Zr/Hf)O_2$ (**Paragraph 5.3.2**) that was transferred to the packed column (**Section 5.4.2.1**). The effluent from the column was collected in 10.0 mL fractions into 100.0 mL volumetric flask and diluted to the mark with water. The collected samples were left to stand for 24 hrs before analysis. The analysis was accomplished using ICP-OES to determine the concentrations of Zr and Hf in each sample fraction. The recoveries of the two elements using the 0.5 M HCl eluent are 99(6) and 94(8) % for Zr and Hf respectively. The elution results at HCl concentration of 0.5 M showed simultaneous elution results for Zr and Hf (**Figure 5.7**) with little or no separation of the two elements under these acid conditions. Therefore, it was decided to discontinue the investigation with the 0.5 M HCl concentration.

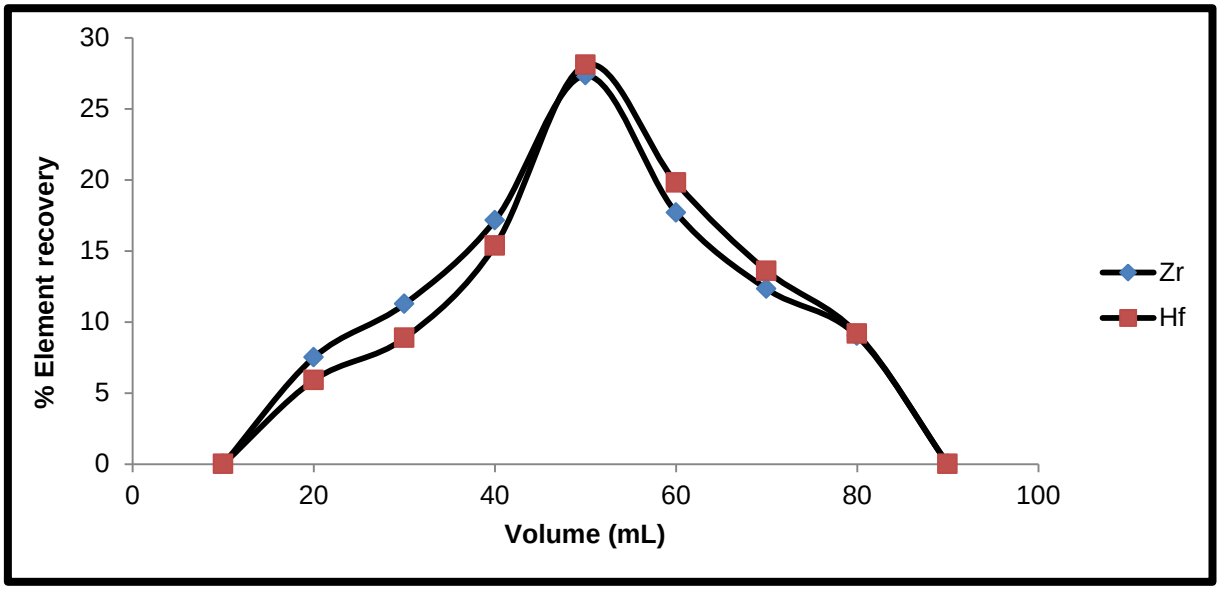


Figure 5.7: Elution behaviour of Zr and Hf using the strong Amberlite IRA-900 anion and 0.5 M HCl

[145] X. J. Yang, C. Pin, A. G. Fane, Separation of hafnium from zirconium by extraction chromatography with liquid anionic exchangers, Journal of Chromatographic Science, 1999, Vol.37, 171-179

5.4.2.3.2 Effect of flow rate using 0.3 M HCl concentration

The effect of flow rate was investigated to see if a change in this experimental condition can improve the separation of Zr and Hf. A sample aliquot 5.00 mL prepared as indicated in **Paragraph 5.3.2** was transferred to the three packed column mentioned in **Section 5.4.2.1** and subsequently eluted with 0.3 M HCl. The effluent from each column was collected in 10 mL fractions into 100.0 mL volumetric flask and diluted to the mark with water. The collected samples were left to stand for 24 hours before analysis. The analysis was done using ICP-OES to determine the concentrations of Zr and Hf in each sample fraction. The elution curves at flow rates of 0.67, 0.85 and 1 mL/min on strong anion Amberlite are shown in **Figures 5.8** to **10**. The effect of flow rate indicated slightly better separation at flow rate of 0.85 mL/min. Generally, there was no separation detected, therefore, it was decided to change the concentration of HCl to 0.1 M.

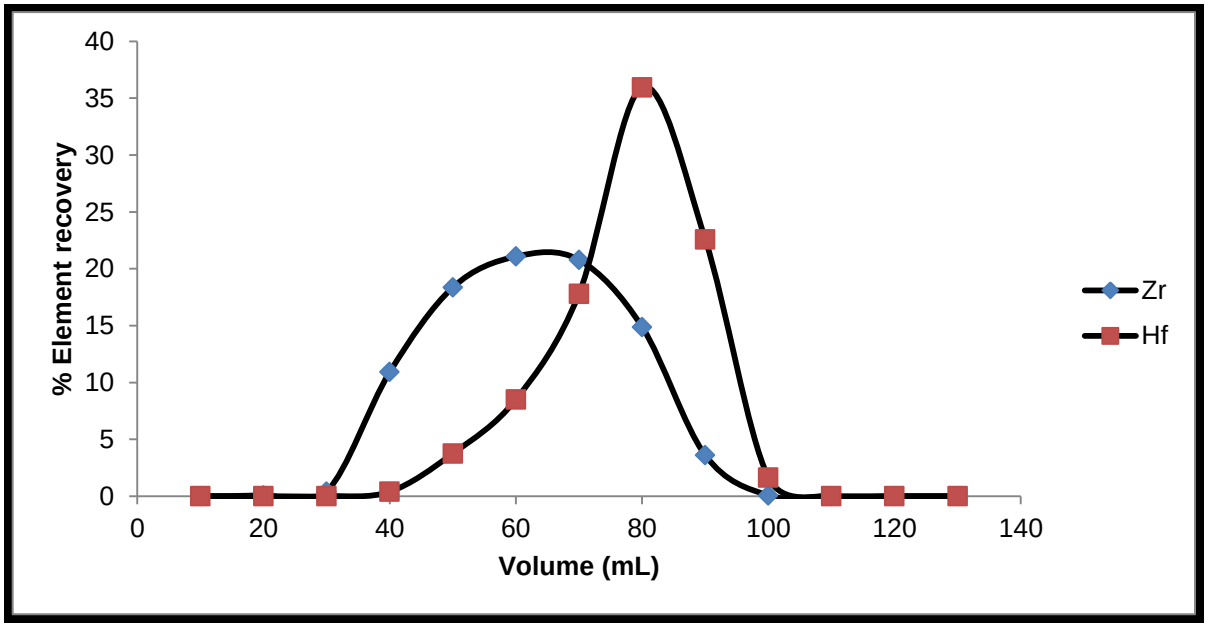


Figure 5.8: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.3 M HCl at 0.67 mL/min flow rate

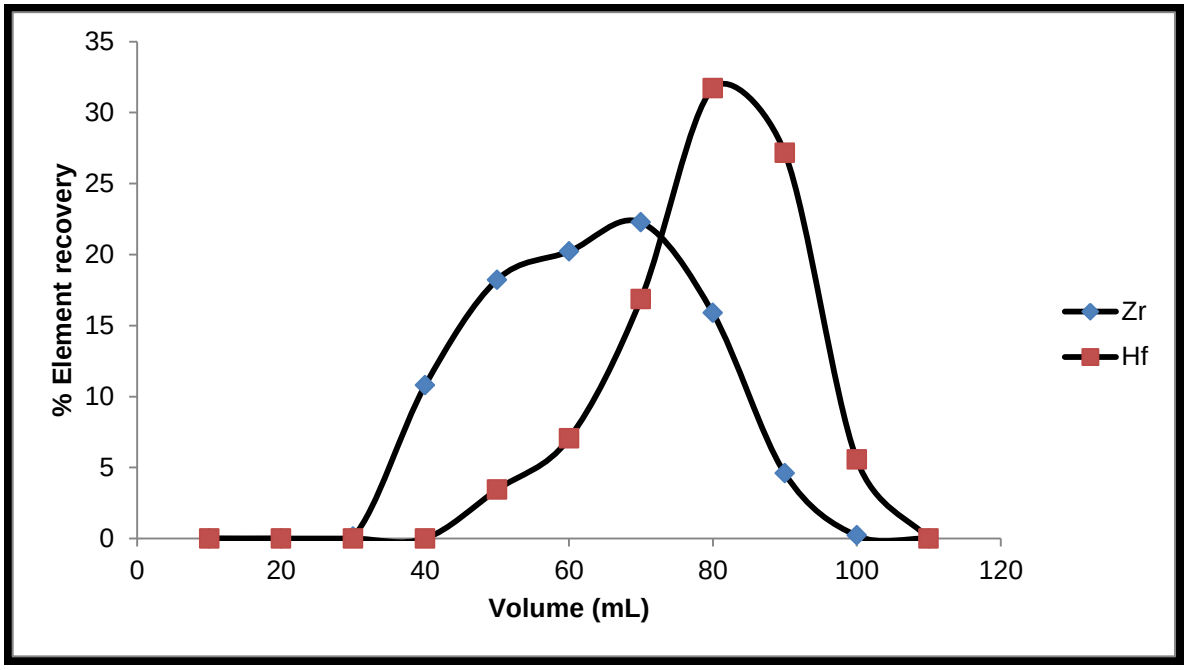


Figure 5.9: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.3 M HCl at 0.85 mL/min flow rate

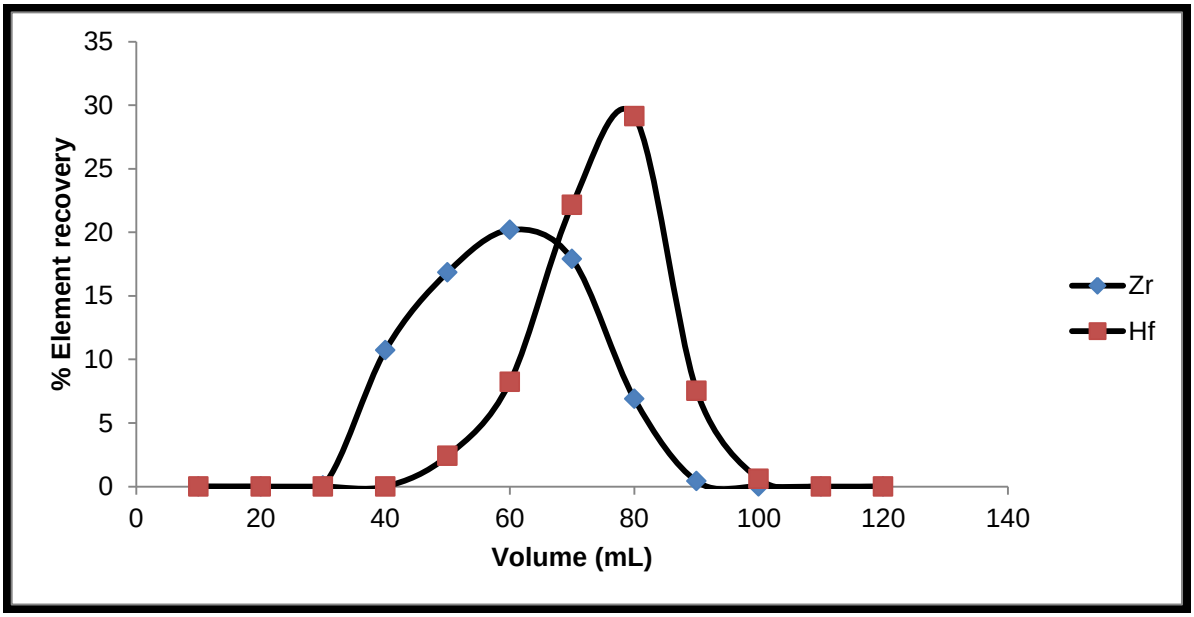


Figure 5.10: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.3 M HCl at flow rate of 1 mL/min.

5.4.2.3.3 Effect of column length using 0.3 M HCl concentration

The ion exchange columns were packed as indicated in **Section 5.4.2.1** to heights of 24 cm and the elution was carried out with 0.3 M HCl. The eluent from the columns were collected in 10.0 mL fractions into a 100.0 mL volumetric flask and diluted to the

mark with water. The collected samples were left to stand for 24 hours before analysis. The analysis was done using ICP-OES to determine the concentrations of Zr and Hf in each sample fraction. A poor elution curve was obtained when a column with a height of 24 cm was used with the strong anion Amberlite IRA-900 resin as shown in **Figure 5.11**. There was a slight difference in separation of Zr and Hf peaks compared to the shorter length of column (20 cm), but the separation was still poor. It was decided to maintain 20 cm length and change the concentration of acid to 0.1 M HCl.

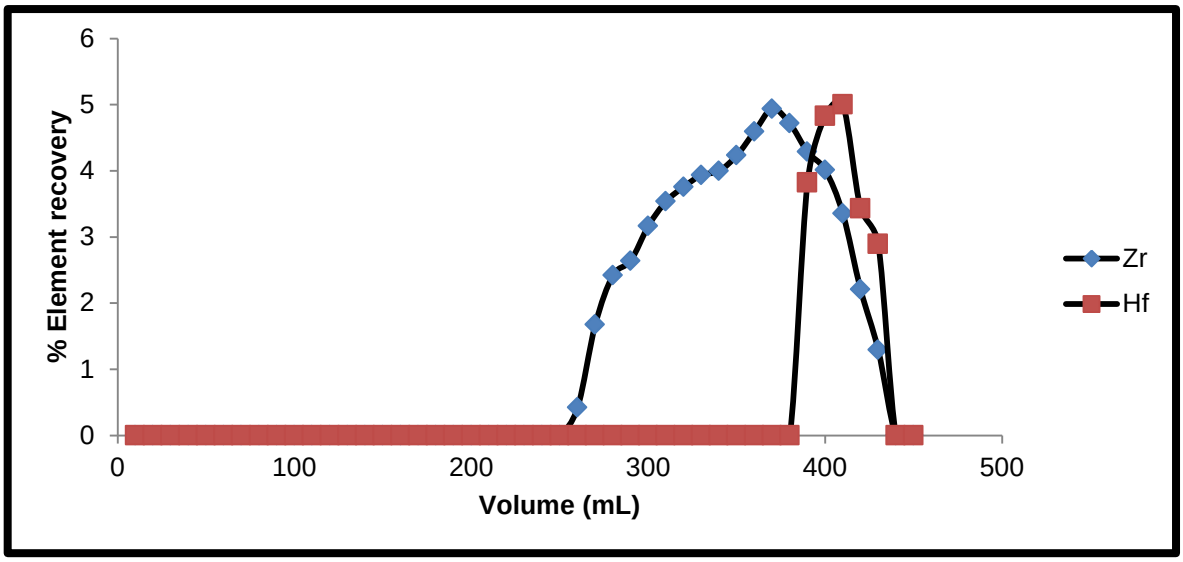


Figure 5.11: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.3 M HCl on a 24 cm packed column

5.4.2.3.4 Effect of flow rate using 0.1 M HCl concentration

The effect of flow rate was investigated to see if there was a change in the separation of Zr and Hf. The same procedure reported in **Paragraph 5.4.2.1** was used in collecting the sample for analysis using ICP-OES. The elution curve at flow rate of 1.5 mL/min on strong anion Amberlite is shown in **Figures 5.12** and 2.3 mL/min flow rate indicated that Zr and Hf were strongly absorbed by the resin, resulting in very poor elution curves and band broadening. It was therefore decided to change the concentration of 0.1 M to 0.05 M HCl.

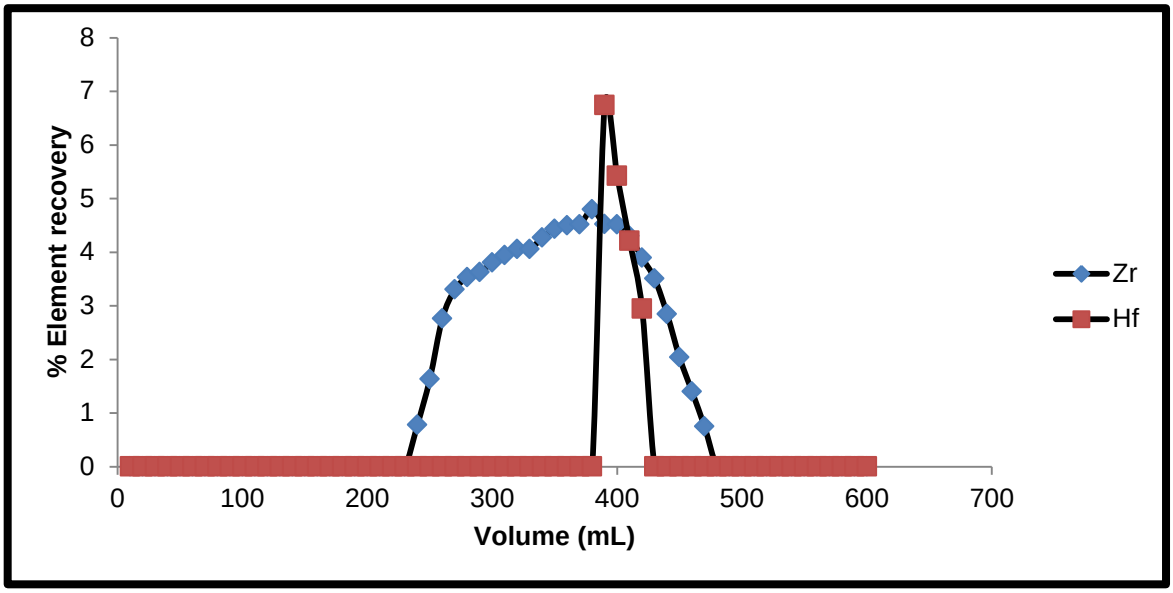


Figure 5.12: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.1 M HCl at flow rate of 1.5 mL/min

5.4.2.3.5 Effect of column length using 0.1 M HCl

The effect of column length was further investigated to check if there was a possible change in the separation of Zr and Hf by using 0.1M HCl instead of 0.3 M HCl (see **Section 5.4.2.3.3**). The ion exchange columns were packed to heights of 15 and 24 cm respectively, and the elution was carried with 0.1 M HCl. The same procedure indicated in **Section 5.4.2.1** was used in collecting the sample for analysis using ICP-OES. The elution curve of 15 and 24 cm column heights on strong anion Amberlite IRA-900 are shown in **Figures 5.13** and **5.14**. The separation was even less effective on the shorter column height (20 cm) compared to the longer column height (24 cm).

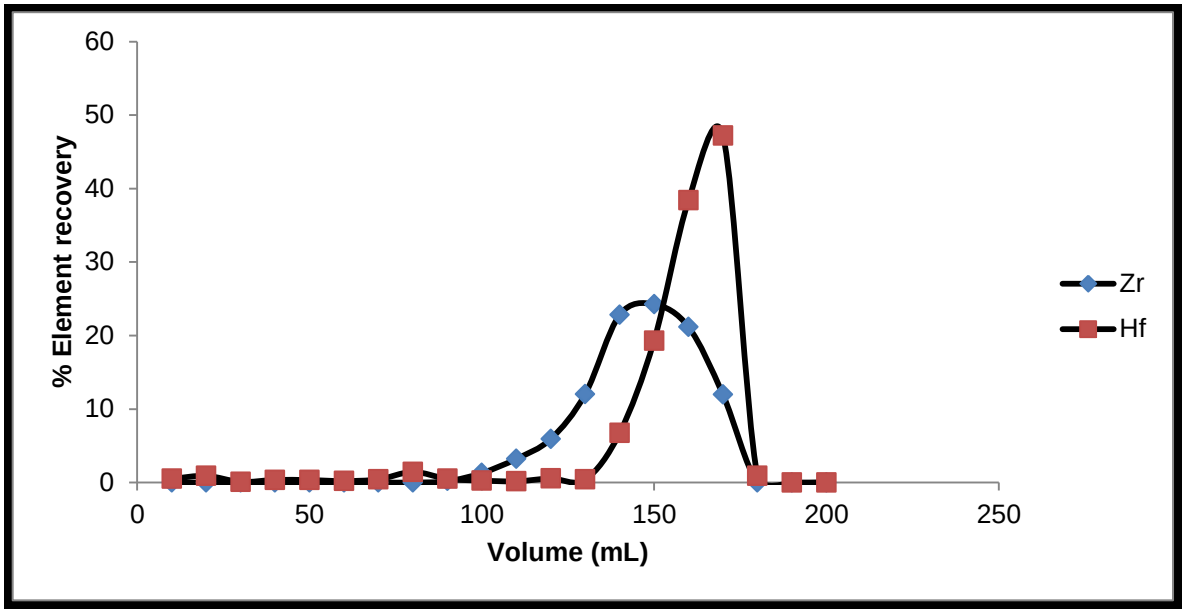


Figure 5.13: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.1 M HCl on a 15 cm packed column

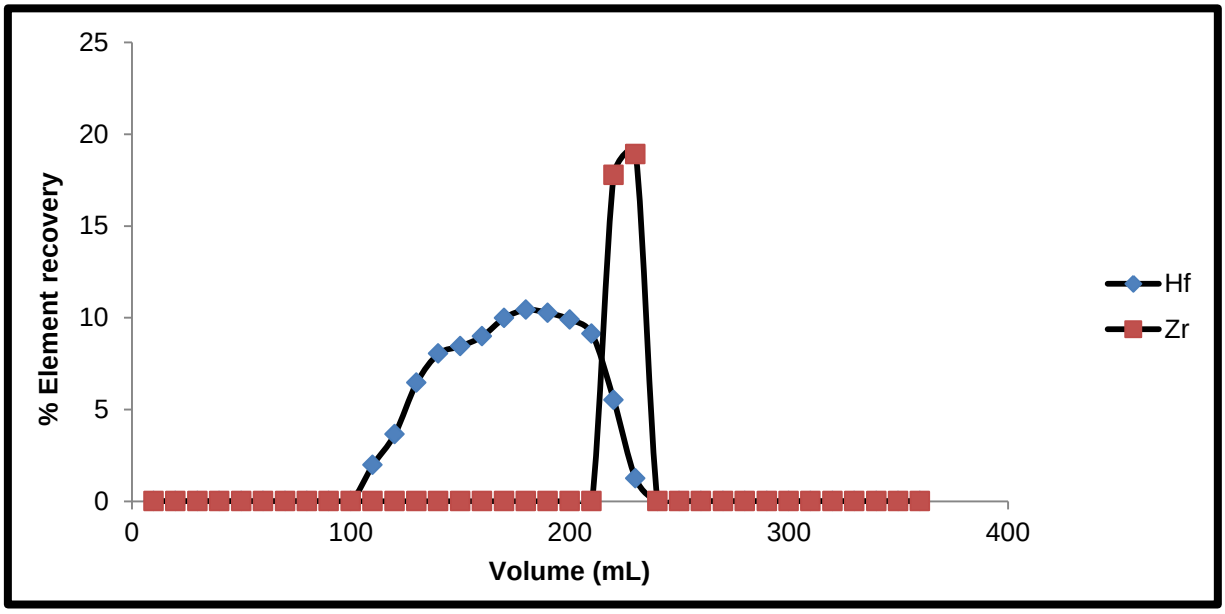


Figure 5.14: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.1 M HCl on a 24 cm packed column

5.4.2.3.6 Effect of sample volume using 0.05 M HCl concentration

In the next step, two different sample aliquots were investigated. A sample solution mixture of $(Zr/Hf)O_2$ (from **Paragraph 5.3.2**) was quantitatively transferred to the packed column and subsequently eluted with 0.05 M HCl. The effluent from the column was collected in 10 mL fractions into a 100.0 mL volumetric flask and diluted

to the mark with water. The collected samples were left to stand for 24 hours before analysis by ICP-OES. Samples of 5.00 and 3.00 mL were eluted with the 0.05 M HCl. The elution curve for a 5.00 mL sample volume is presented in (**Figure 5.15**).

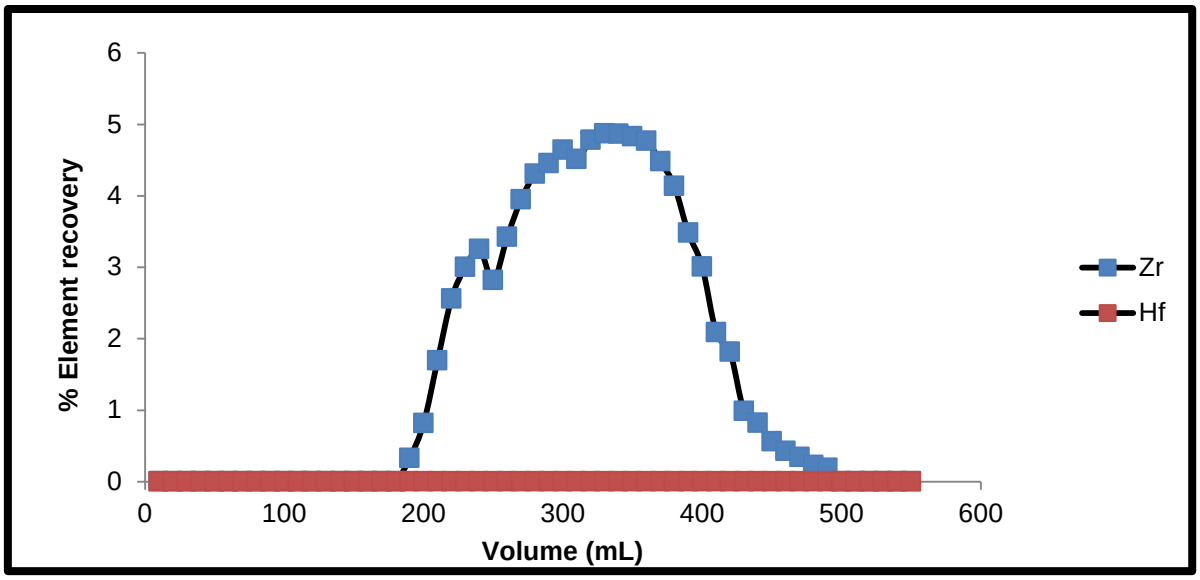


Figure 5.15: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.05 M HCl using 5.00 mL sample

A sample aliquot was reduced to 3.00 mL, to minimize the possible saturation of the resin which would also lead to poor separation of the two elements. The elution curve for the 3.00 mL volume is given in **Figure 5.16**. Generally, the sample volume showed no significant difference in the elution and separation of Zr and Hf. However, there is some observable difference in the peak width of the two elution curves with the 5.00 mL volume showing some slight peak broadening. The 0.05 M HCl selectively eluted only Zr, leaving the Hf stuck in the column. Therefore, the 0.05 M HCl elution on Amberlite IRA-900 was selected for the separation of Zr and Hf in PDZ.

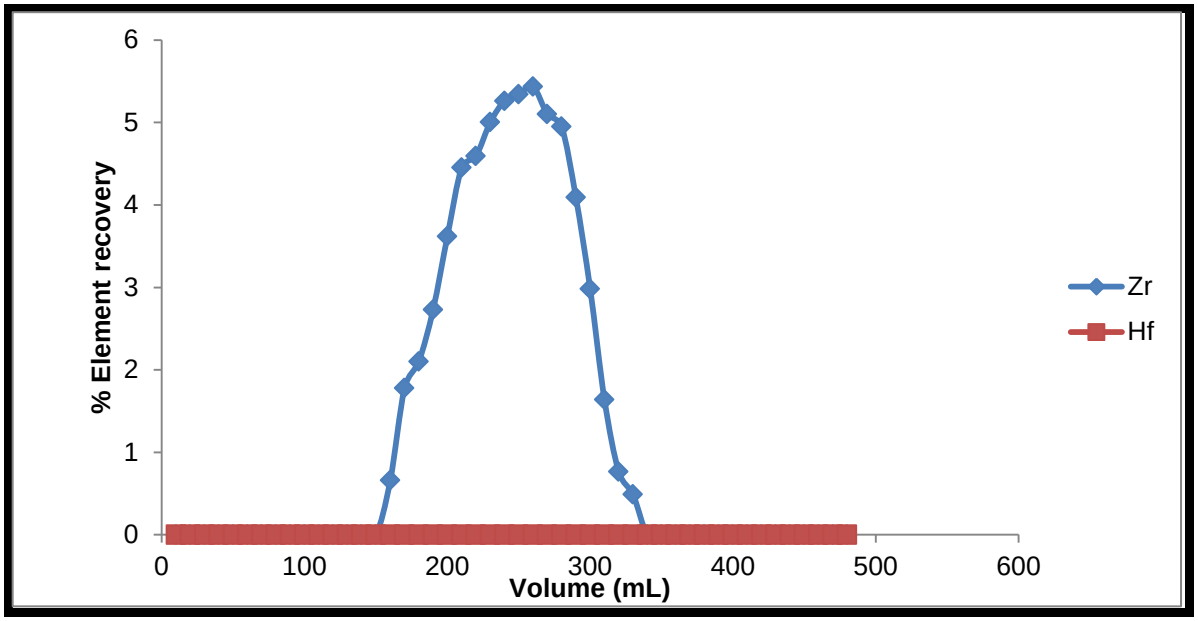


Figure 5.16: Elution behaviour of Zr and Hf using strong Amberlite IRA-900 anion and 0.05 M HCl using 3.00 mL sample

5.4.2.3.7 Separation of Zr and Hf in PDZ/$NH_4F{\cdot}HF$ matrix on Amberlite IRA-900 resin

The conditions for the separation of Zr and Hf obtained from **Section 5.4.2.3.6** above, were applied on the separation of Zr and Hf in PDZ. A sample aliquot of 3.00 mL (from **Paragraph 5.3.2**) was quantitatively transferred to the column packed with an Amberlite IRA-900 and subsequently eluted with 0.05 M HCl. The effluent from the column was collected in 10 mL fractions into a 100.0 mL volumetric flask and diluted to the mark with water. The collected samples were left to stand for 24 hours before analysis. Determination of Zr and Hf concentrations in each sample fraction were analysed using ICP-OES. A typical elution curve is shown in **Figure 5.17**, while the average recovery of triplicates is 24(6) % Zr.

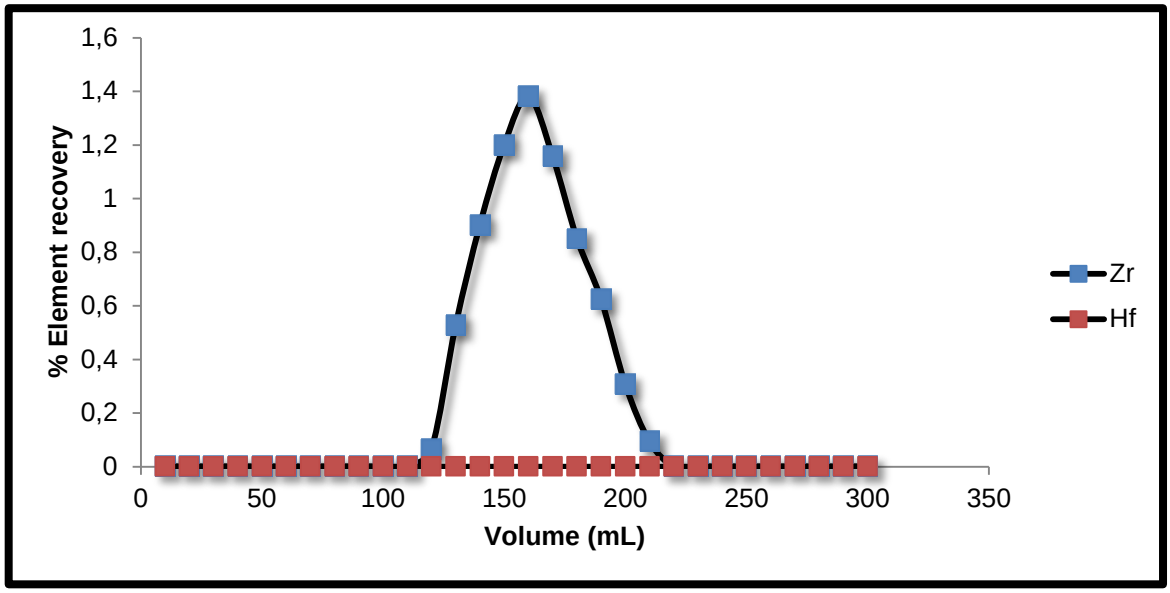


Figure 5.17: Elution behaviour of Zr from PDZ fluoride solution

5.4.3 Solvent extraction separation using the $NH_4F{\cdot}HF$ fused $(Zr/Hf)O_2$ mixture sample

5.4.3.1 Solvent extraction using different extractants

According to the literature study, extractants, such as, MIBK, TBP and amines have been used for the extraction of Zr and Hf.[146,147] Three different extractants, namely: methylamine, cyclohexyl amine and methyl isobutyl ketone (MIBK), were used in this study to determine the possible separation of Zr and Hf from their metal oxide parent samples. A 5.00 mL sample solution (containing Zr and Hf) from **Paragraph 5.3.2**, was pipetted into a separating funnel. The different concentrations of H_2SO_4, ranging from 2.0 to 8.0 M were used where 5.0 mL of each concentration was added, followed by 10.0 mL of different extractants. The extraction was performed by shaking the mixture for 10 minutes and subsequently allowing it to stand for 10 minutes for a liquid phase separation. These extractions were repeated three times

[146] X. Zhi-gao, W. Li-jun, W. Yan-ke, C. Ru-an, Z. Li, W. Ming, Solvent extraction of hafnium from thiocyanic acid medium in DIBK-TBP mixed system, *Trans. Nonferrous Met. Soc. China*, 2012, 22, 1760-1765

[147] L. Y. Wang and M. S Lee, Separation of Zr and Hf from sulphuric acid solutions with amine-based extractants by solvent extraction, *Separation and purification technology*, 2015, 142, 83-89

(n=3). All the extraction experiments were carried out at room temperature. The bottom aqueous layer was collected in a 100 mL beaker. The aqueous layer was heated on a hot plate at 50 ^{o}C for 30 minutes to evaporate any organic extractant and the solution was allowed to cool to room temperature. The solution was quantitatively transferred into a 100.0 mL volumetric flask. Zr and Hf concentrations were determined using ICP-OES (see **Figures 5.18** to **20**).

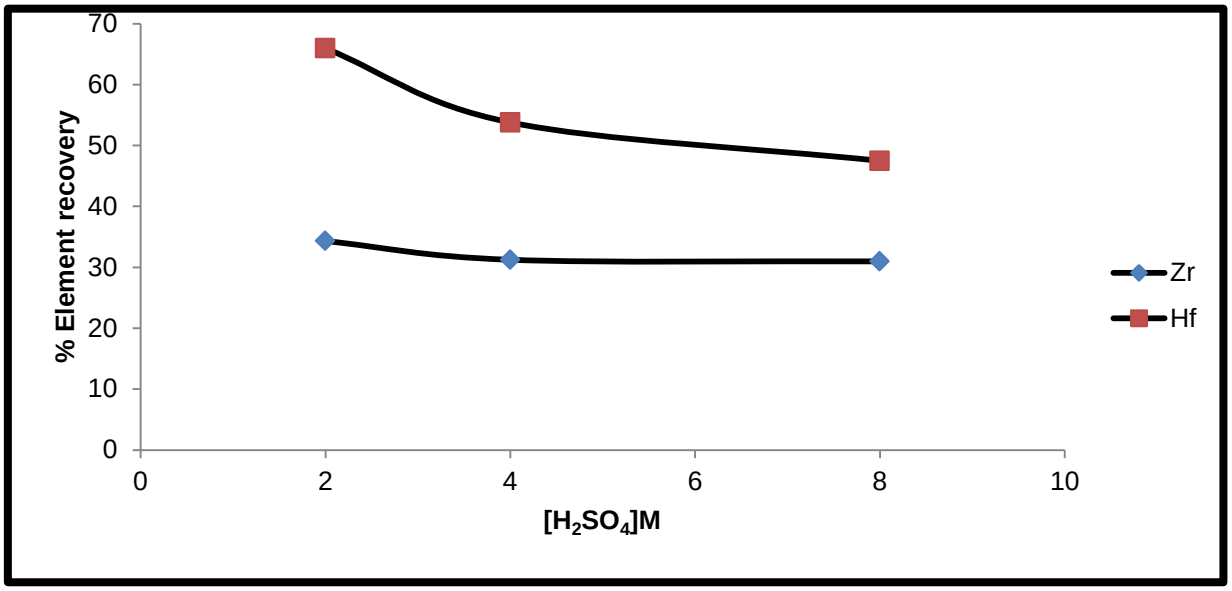


Figure 5.18: Extraction of Zr and Hf in aqueous solution from H_2SO_4 solutions using Methylamine, n = 3

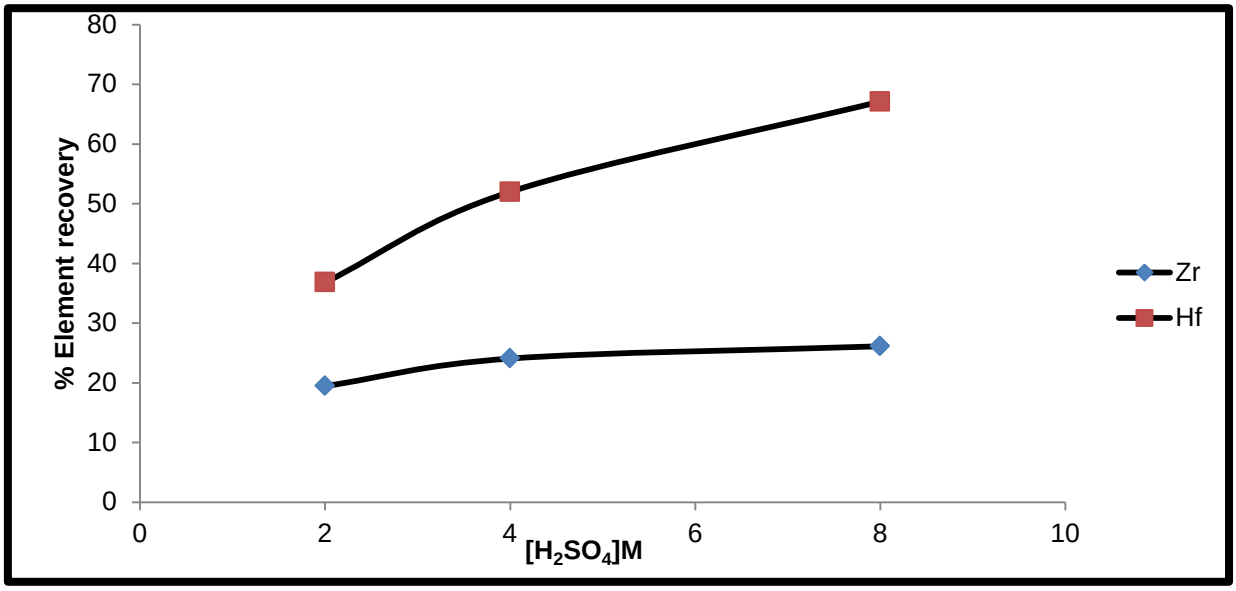


Figure 5.19: Extraction of Zr and Hf in aqueous solution from H_2SO_4 solutions using cyclohexyl amine, n = 3

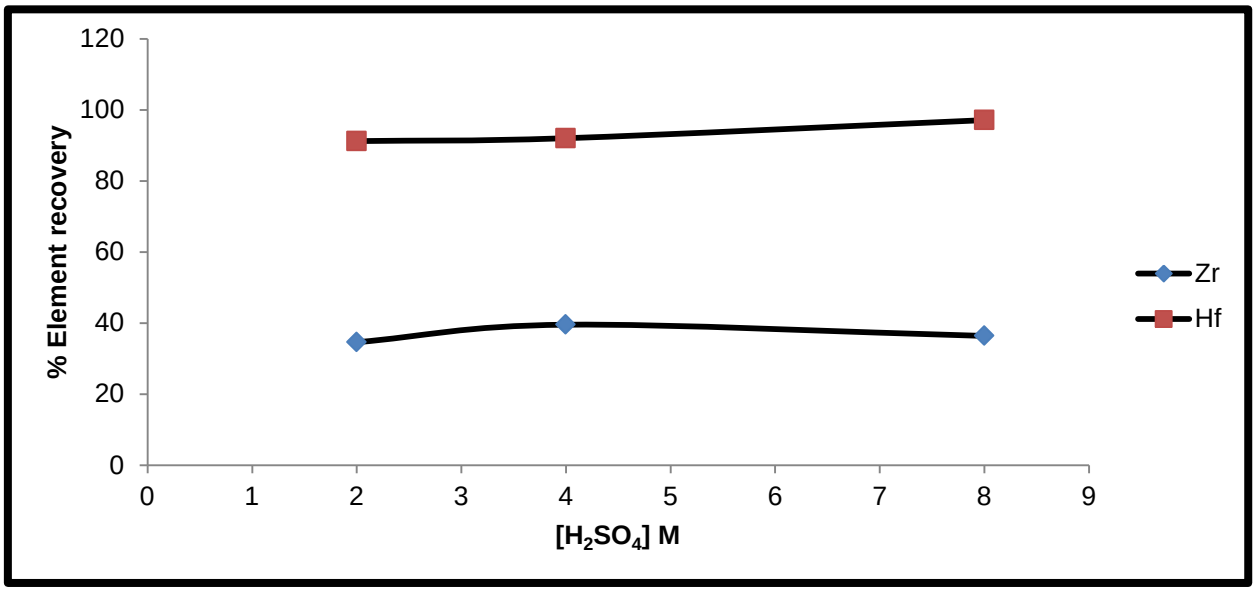


Figure 5.20: Extraction of Zr and Hf in aqueous solution from H_2SO_4 solutions using MIBK, n = 3

According to the results, MIBK extractant gave a promising separation, compared to other extractants investigated and it was decided upon to continue with MIBK for further investigation.

5.4.3.2 Solvent extraction using Methyl Isobutyl Ketone (MIBK)

In the next step, the extracting solvent MIBK was investigated for the separation of Zr and Hf. A 5.00 mL sample solution (from **Paragraph 5.3.2**) was pipetted into a separating funnel. A 5.00 mL of acid concentration, ranging from 2.0 to 8.0 M H_2SO_4 was added, followed by 10.0 mL of MIBK. The mixture was shaken for ten minutes and then allowed to stand for another ten minutes for phase disengagement. All the extraction experiments were carried out at room temperature. The bottom aqueous layer was collected in a 100 mL beaker. The aqueous layer was then heated on a hot plate at 50 ^oC for 30 minutes to evaporate any organic extractant (MIBK) dissolved. The solution was allowed to cool to room temperature. 5 mL of 0.5 M H_2SO_4 was added to the organic solution and evaporated to obtain an aqueous solution. The cold solutions in both the aqueous and organic phases were quantitatively transferred into 100.0 mL volumetric flasks and diluted to the mark with water. The concentrations of Zr and Hf in each solution were measured by ICP-OES in the aqueous solutions and the results are presented in **Tables 5.8** and **5.9**. The procedure was repeated for extraction in HNO_3 and for acid concentrations, ranging from 2.0 M to 8.0 M HNO_3 (**Table 5.10**).

Table 5.8: Results from solvent extraction for the separation of Zr and Hf using MIBK and H_2SO_4 for n = 1

H_2SO_4 (M)	**Average % recovery in aqueous layer**		**Average % recovery in organic layer**	
	Zr	**Hf**	**Zr**	**Hf**
2	69.84	94.18	7.98	10.47
4	71.99	96.80	7.97	11.16
8	72.91	101.67	6.68	8.88

The single extraction of the solution using H_2SO_4 gave unsatisfactory results, compared to the three extractions (see **Table 5.9**). The extraction in H_2SO_4 gave promising but incomplete separations.

Table 5.9: Results from the solvent extraction for separation of Zr and Hf using MIBK and H_2SO_4 for n = 3

H_2SO_4 (M)	Average % recovery in aqueous layer		Average % recovery in organic layer	
	Zr	Hf	Zr	Hf
2	36.37	97.12	67.11	18.59
4	39.53	92.03	66.03	10.08
8	34.61	91.22	65.40	3.77

The above procedure was repeated for the extraction in HNO_3. Acid concentrations, ranging from 2.0 to 8.0 M were investigated for three extractions. The results of these extractions are presented in **Table 5.10** which indicated incomplete extraction of both elements in HNO_3 as compared to H_2SO_4.

Table 5.10: Results from solvent extraction for separation of Zr and Hf using MIBK and HNO_3 for n = 3

HNO_3 (M)	Average % recovery in aqueous layer		Average % recovery in organic layer	
	Zr	Hf	Zr	Hf
2	97.72	109.62	1.71	5.43
4	92.75	107.28	3.11	7.00
8	87.60	99.51	1.72	4.79

5.5 Isolation of ZrO_2

The solutions enriched with Zr, obtained from ion exchange (see **Section 5.4.2.2.5**), were combined and concentrated by evaporating the solution. Ammonium hydroxide was added to precipitate Zr as $Zr(OH)_4$ which is indicated in **Equation 5.2**. The precipitate was separated from the solution by centrifugation, dried and calcinated at 950 ^oC for an hour.

$$2H_3ZrF_7 + 14NH_4OH \longrightarrow 2Zr(OH)_4 + 14NH_4F + 6H_2O \qquad 5.2$$

5.6 Quantification of Zr and Hf in the isolated product (ZrO_2)

Aliquots of approximately, 0.1 g of the isolated precipitate (from **Section 5.5**), were weighed in triplicate and mixed with $NH_4F{\cdot}HF$ in a ratio of 1:10 sample flux in a platinum crucible. The mixture was fused at 200 ^oC for 40 minutes. The molten sample was cooled to room temperature and then dissolved in water. The resultant solution was quantitatively transferred into 100.0 mL volumetric flasks, acidified with 0.5 M HCl to match with blank and standard solutions and subsequently, filled with water to the mark. Zr and Hf concentrations in solutions were analysed using ICP-OES and the results are reported in **Table 5.11**.

Table 5.11: Results for the quantification of Zr and Hf from the final isolated product

Sample	Replicate	% Metal oxide recovery	
		Zr	Hf
ZrO_2	1	84	0.119
	2	70	0.110
	3	79	0.113
	Average	**78**	**0.114**
	SD	7.0	0.004
	%RSD	8.9	3.914

5.7 Discussion of results

5.7.1 Determination of Limits of Detection (LOD) and Limits of Quantification (LOQ)

LODs were determined in order to detect the capability of the ICP-OES used in this study, to handle the low concentrations[148] of both Zr and Hf, especially in ion exchange elution and other processes. The LODs were determined for the most sensitive analytical lines - 277.336 and 343.823 for Zr and Hf respectively. LODs determinations were performed in different acid matrices. The LODs for Zr and Hf were calculated using **Equation 4.32**[149] and the values were found to range between 0.00706 to 0.01301 and 0.0111 to 0.0631 ppm (see **Table 5.4**) respectively. The LOQs of Zr and Hf were calculated using **Equation 4.33** in **Chapter 4**, and the values were between the ranges of 0.07061 to 0.13011 and 0.11095 to 0.6308 ppm respectively. All the LOD and LOQ values were found to be very high when compared with that indicated in the literature.[139] This might be caused by the aging of the equipment (old ICP-OES machine) which might cause the LODs to differ. The

[148] Guidance for the validation of analytical methodology and calibration of equipment used for testing of illicit drugs in seized materials and biological specimens, [Accessed on 08-03-2018]. Available from: https://www.unodc.org/documents/scientific/validation_E.pdf

[149] C. C. Chan, H. Lam, Y.C. Lee, X. Zhang, Analytical method validation and instrument performance verification, John Wiley and Sons, Inc., Hoboken, New Jersey, 2004

obtained LOD and LOQ values were generally lower than most of the concentrations obtained in different stages of the study which allowed for a wider analytical range.

5.7.2 Dissolution of $(Zr/Hf)O_2$ and PDZ using flux fusion

A successful digestion and subsequent dissolution of $(Zr/Hf)O_2$ and PDZ was achieved using $NH_4F{\cdot}HF$ fusion and subsequent dissolution in water. The dissolution procedure had advantages of low fusion temperature (200 ^{o}C); shorter fusion times (40 minutes); use of water; and with a stirring time of less than ten minutes, complete and quantitative dissolution of the reaction mixture was achieved (see **Paragraph 5.3.2**). According to the literature, the fusion products can be the soluble heptafluorides (see **Equation 2.17**, in **Chapter 2**). The analytical results obtained from this study (see **Table 5.5**), indicate recoveries of 100.6(2) % for Zr while the initial Hf recovery was far in excess (121.2(9) %) of what was theoretically possible. This inaccuracy of the Hf recovery was unexpected, however literature studies'[139,141] speculated about the possible influence of high fluoride concentrations on Hf recovery (**Paragraph 5.3.3** and **Figures 5.21** and **5.22**).

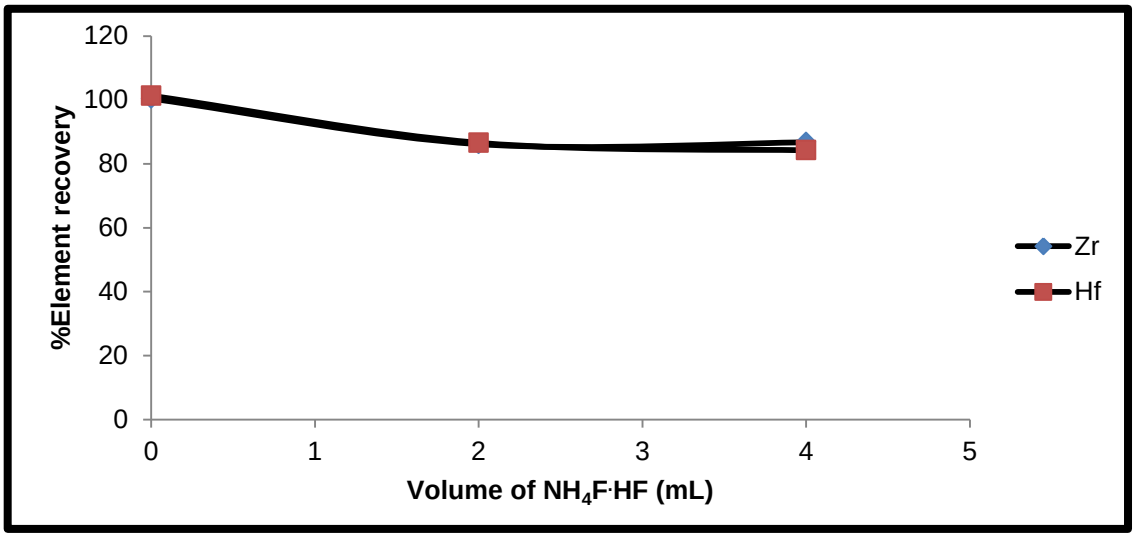


Figure 5.21: Effect of $NH_4F{\cdot}HF$ on recovery of Zr and Hf in HCl matrix

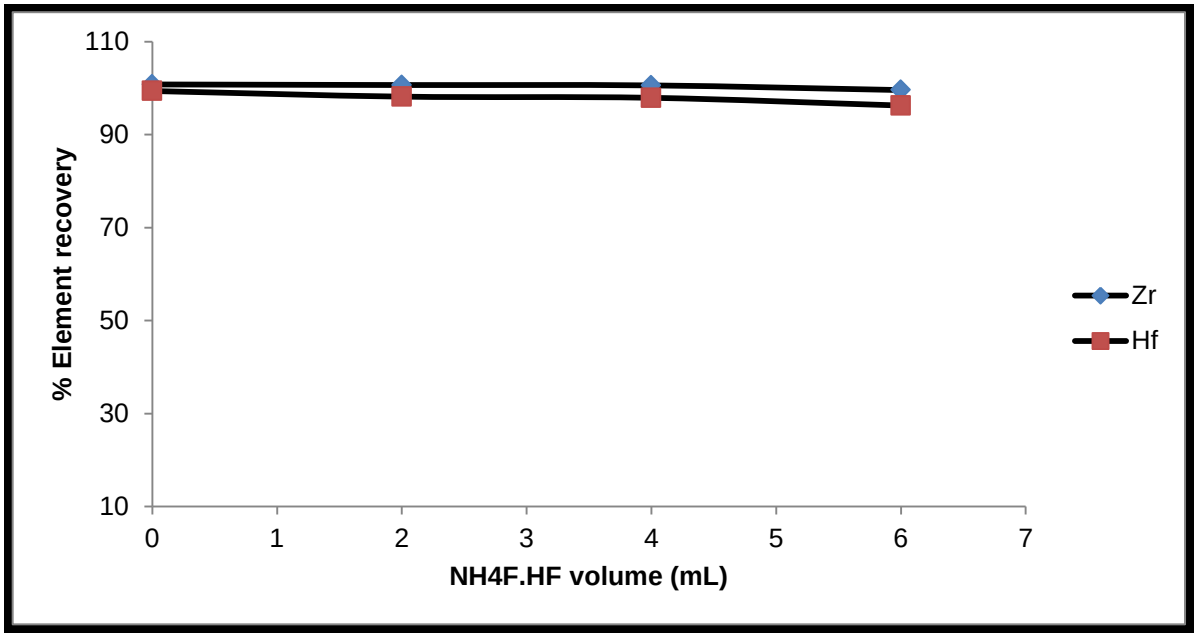


Figure 5.22: Effect of $NH_4F{\cdot}HF$ on the recovery of Zr and Hf in H_2SO_4 matrix

The excess of fluoride concentration was removed by the addition of concentrated H_2SO_4 and heating to remove the excess of F^- as volatile HF from the solution. This step brought the Hf recovery within an acceptable range and good recoveries for both Zr and Hf were obtained (100.1(2) % Zr and 100(2) % Hf) (**Figure 5.23**).

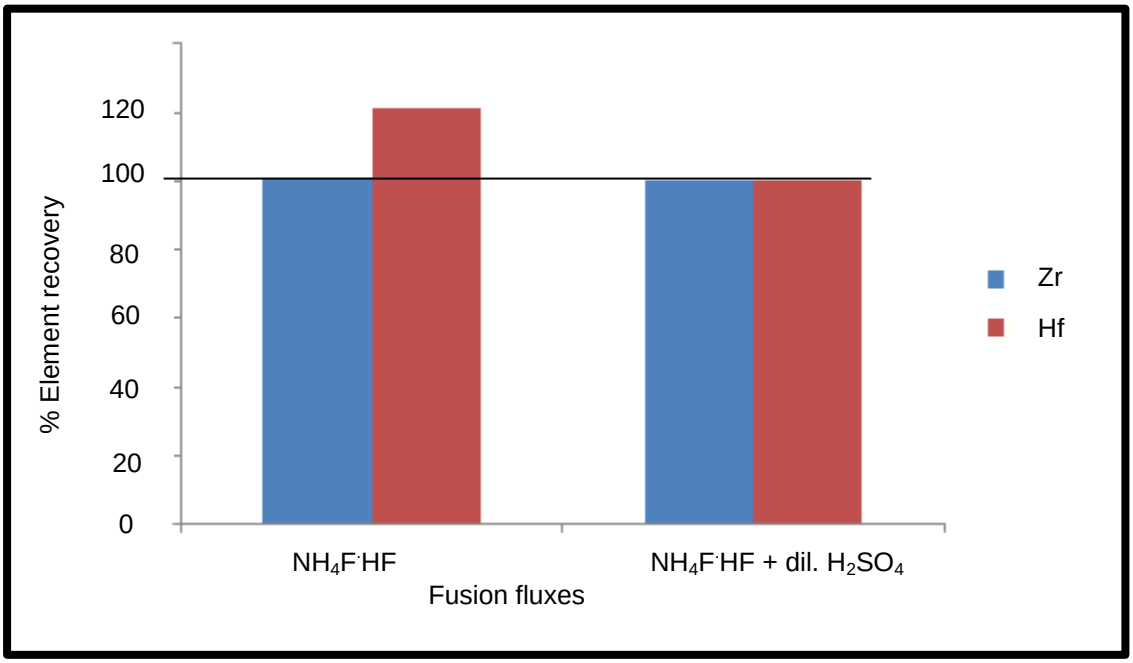


Figure 5.23: The recovery of Zr and Hf from $(Zr/Hf)O_2$

The analysis of PDZ (**Table 5.6**), indicates the presence of 48.2 % Zr (65.9(4) % ZrO_2) and 1.21(1) % Hf (1.43(1) % HfO_2) with relatively small percent RSDs. These quantitative results are comparable with those reported by Yamagata *et al.*,[150] for the same minerals which were reported as MO_2 % (M= Zr, Hf) in zircon.

5.7.3 Separation of Zr and Hf from $(Zr/Hf)O_2$ mixture using anion exchange resin

The separation of Zr and Hf using resins, such as, Dowex Marathon, Dowex 21k, and 0.1 M HCl, indicated poor separation factors of 0.88 and 1.08 respectively. It was decided to stop further investigation and just continue studies on Amberlite IRA-900 which gave a separation factor of 1.21. The separation of Zr and Hf using Amberlite IRA-900 and $HClO_4$ resulted in a very poor separation factor of 1.04, of which this acid was discontinued for further investigation, while HCl was continued. The chosen strong anion exchanger resin, Amberlite IRA-900 was used as a stationary phase

[150] C. Yamagata, J. B. Andrade, V. Ussui, N. B. Lima and J. O. A. Paschoal, High purity zirconia and silica powders via wet process: Alkali fusion of zircon sand, *Materials Science Forum*, 2008, Vol. 591-593, 771-776

while different HCl concentrations were investigated as mobile solvents. Different experimental factors that may affect this separation were investigated which include, HCl concentrations, mobile phase flow rate, column length and sample volume. Generally, the results indicated some preferential elution of Zr over Hf.

5.7.3.1 Effect of hydrochloric acid concentrations (HCl)

The results obtained from different concentrations of HCl revealed that the retention factor (k' calculated using **Equation 4.11**) decreased with the HCl concentration (**Figure 5.24**). Hf was the mostly retained species when compared to Zr, and as expected, there were more and similar desorption of the two elements as the acid concentration increased to 0.3 and 0.5 M respectively, but very poor or no separation was achieved under the investigated acid conditions (**Table 5.12**).

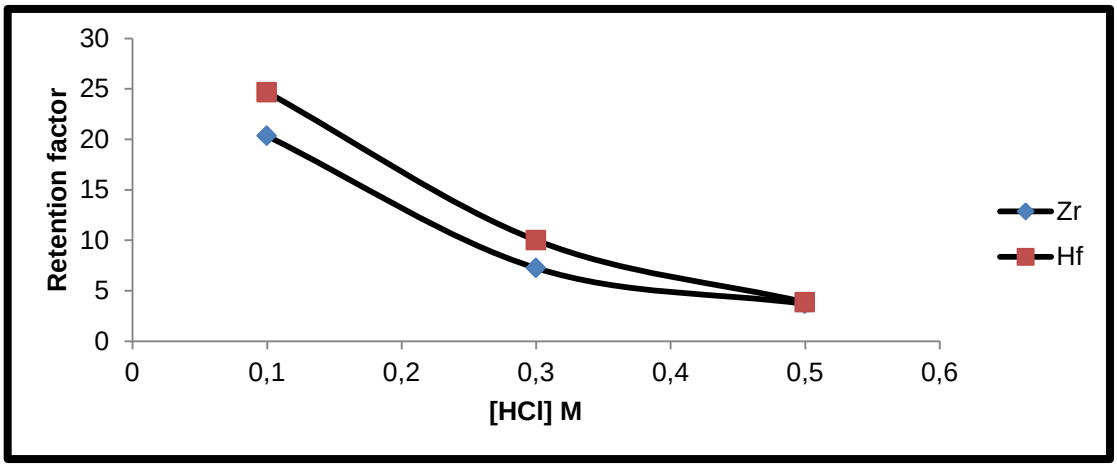


Figure 5.24: Effect of retention factor versus [HCl]

Table 5.12: Parameters calculated from the results obtained in an ion exchange chromatography

[HCl] M	Element	t_o	t_R	w	k'	$\alpha_{Hf/Zr}$
0.05	Zr	1	41	26	40	-
	Hf		-	-	-	
0.1	Zr	3	64	34	20.33	1.21
	Hf		77	21	24.66	
0.3	Zr	4	33	37	7.25	1.38
	Hf		44	23	10.00	
0.5	Zr	1	33	40	3.70	1.04
	Hf		34	46	3.86	

5.7.3.2 Effect of flow rate on 0.3 M HCl using Amberlite IRA-900

The separation of the two elements on a strong Amberlite IRA-900 resin was also investigated by varying the flow rates of the mobile solvent. Different flow rates, ranging from 0.67 to 1 mL/min. were studied for a column length of 20 cm. The preference of ion exchange for one of the ions present in the solution can also be expressed by the separation factor $\alpha_{Hf/Zr}$.[151] The results indicated slightly better separation at a low flow rate of 0.85 ml/min. ($\alpha_{Hf/Zr}$ = 1.51, see **Table 5.13**). Generally, there was poor separation for all different flow rates investigated (see **Figures 5.8**-**5.10**).

[151] E. C. B. Felipe, H. G. Palhares and A. C. Q. Ladeira, Separation of Zirconium from hafnium by Ion Exchange, *2013 International Nuclear Atlantic Conference-INAC*, 2013

Table 5.13: Chromatographic parameters calculated from the effect of flow rate

[HCl] M	Element	Flow rate(mL/min)	t_o	t_R	w	k'	$\alpha_{Hf/Zr}$
0.3	Zr	1	4	33	37	7.25	1.38
	Hf			44	23	10	
	Zr	0.85	17	52	58	2.06	1.51
	Hf			70	40	3.12	
	Zr	0.67	5	32	34	5.4	1.41
	Hf			43	23	7.6	

5.7.3.3 Effect of the column length on Amberlite IRA-900 eluted with 0.3 M HCl

The poor separation between Zr and Hf and the observed tailing in both Hf and Zr elution curves (**Figures 5.11)** prompted an investigation into the effect of the column length. In order to reduce the tailing, the column packing was increased from 20 to 24 cm. The results of elution on this longer column height indicated a slight difference in the separation of Zr and Hf, with a separation factor 1.26 compared to the 20 cm column height ($\alpha_{Hf/Zr}$=1.21). Therefore, it was decided that the column height should be kept at 20 cm.

5.7.3.4 Effect of flow rate on 0.1 M HCl using Amberlite IRA-900

Different flow rates ranging from 1.5 to 2.3 mL/min. were investigated on the column length of 20 cm. The results indicated a slightly better separation at a lower flow rate 1.5 mL/min ($\alpha_{Hf/Zr}$= 1.19, **Figure 5.12**) while at 2.3 mL/min, Zr and Hf were strongly held by the resin. Generally, there was no separation from both flow rates.

5.7.3.5 Effect of the column length on Amberlite IRA-900 eluted with 0.1 M HCl

Due to poor separation between Zr and Hf and the observed tailing in both elements' elution curves (**Figures 5.12**), it triggered an investigation into the effect of the column length. The column packing was lowered to a height of 15 cm from 20 cm (**Figure 5.13**). The results of elution on this shorter column height indicated an even

poorer separation of Zr and Hf with the separation factor, 1.14 compared to the 20 cm column height ($\alpha_{Hf/Zr}$=1.21). The column was also packed to 24 cm height ($\alpha_{Hf/Zr}$= 1.24, **Figure 5.14**), the separation factor of both 20 and 24 cm heights indicated a slight difference in the separation of both peaks. Therefore, it was decided that the column height should be kept at 20 cm.

5.7.3.6 Effect of sample volume on the Amberlite IRA-900 resin

The results of the elution of a 5.00 mL sample with 0.05 M HCl on Amberlite IRA-900, indicated a selective elution of Zr and a complete retention of Hf. However, the Zr recoveries were unsatisfactorily low and in order to improve the elution and recovery for the Zr compound, the volume was reduced to 3.00 mL. The results of this study indicated slightly sharper elution curve (less width broadening compared to the 5.00 mL), but no improvement in Zr recovery was achieved (**Figures 5.15** and **5.16**).

5.7.4 Separation of Zr and Hf from PDZ using anion exchange chromatography

The separation of Zr and Hf in PDZ on a strong anion exchange Amberlite IRA-900 resin, was investigated using the 3.00 mL sample volume, 0.05 M HCl mobile solvent, 20 cm column length and 0.85 mL/min. flow rate. Zr was eluted from the column with an average recovery of 24(6) % and RSD = 25.9 % (see **Figure 5.17**). However, this method still has a challenge of producing low Zr recoveries.

The isolated Zr compound was precipitated with ammonium hydroxide, dried and calcinated at 950 ^{o}C. The white resultant powder (ZrO_2) was re-dissolved using flux fusion and $NH_4F{\cdot}HF$ flux and finally analysed with ICP-OES. An average Zr recovery of 77.8(7) % was obtained with an RSD of 8.86 %. The sample was also found to contain 0.11 (0) % of Hf with an RSD of 3.91 %. This separation method indicated that there was a possibility of obtaining pure ZrO_2 from PDZ fluoride solution, using fewer steps as seen in **Section 1.1**, **Chapter 1**.

5.7.5 Separation of Zr and Hf using MIBK from $(Zr/Hf)O_2$ solution

Although the ion exchange procedure resulted in a purer Zr compound, the low Zr recoveries, generally, render this method impractical. The solvent extraction technique (which is also commonly used according to literature[152,153]), was also investigated to try and isolate a purer Zr product with reasonably good quantities. The single extraction indicated almost similar extractions of Zr and Hf at all H_2SO_4 concentrations with a slight preference toward Hf (see **Table 5.8**). The results of the three extractions using MIBK as an extractant from H_2SO_4 solutions indicated that Zr was preferentially extracted into an organic layer, leaving Hf in an aqueous layer (see **Table 5.9**). This is contrary to what was observed during a single extraction of the elements. By increasing the number of extractions, Zr was more extracted at 8.0 M H_2SO_4 (see **Table 5.14**). Distribution constant and separation factor for incomplete extraction were determined using **Equations 4.17** and **4.24** in **Chapter 4**. Extraction from HNO_3, on the other hand, indicated some Hf extraction preference over Zr although the Hf recoveries in the organic phase were very low (**Table 5.10**).

Table 5.14: Distribution constant and separation factor of Zr and Hf between aqueous and organic layers from different $[H_2SO_4]$ where n=3

$[H_2SO_4]$M n=3	$[Zr]_{aq}$	$[Hf]_{aq}$	$[Zr]_{org}$	$[Hf]_{org}$	K_D (Zr)	K_D(Hf)	$\alpha_{Zr/Hf}$
2	242.68	88.56	456.69	16.10	1.88	0.18	10.35
4	263.15	81.93	453.25	8.96	1.72	0.11	15.75
8	232.72	84.23	444.82	3.86	1.91	0.05	41.66

[152] X. Zhi-gao, W. Li-jun, W. Yan-ke, C. Ru-an, Z. Li, W. Ming, Solvent extraction of hafnium from thiocyanic acid medium in DIBK-TBP mixed system, *Trans. Nonferrous Met. Soc. China*, 2012, 22, 1760-1765

[153] R. Banda, S. H. Min and M. S. Lee, Selective extraction of Hf over Zr from aqueous H_2SO_4 solutions by solvent extraction with acidic organophosphorous based extractants, *J Chem Technol Biotechnol,* 2014, 89, 1712-1719

5.7.6 Chemical characterization of the isolated ZrO_2 product after ion exchange separation

The isolated product after the separation of Zr and Hf in a PDZ sample, using ion exchange, was quantified for Zr and Hf content (**Table 5.11**). This step was extremely important to evaluate the possible removal of the Hf from the initial starting material. A comparison of the Zr content in the original PDZ (48.8 %) to the 77.8 % in isolated ZrO_2, confirms the removal of a lot of the impurities in the separation step. The initial Hf content was determined as ~ 2.5 %. Results in **Table 5.11**, indicate the presence of 0.11 % Hf which relates to 0.14 % Hf in the final product – an order of magnitude reduction (~ x18) in Hf concentration which is extremely promising for the improvement of the Zr quality, especially for nuclear applications. A major drawback of this method is the low ZrO_2 yield which was obtained after the separation and isolation steps.

5.8 Method Validation

Good calibration curves were obtained for both Zr and Hf with good linearity, R^2 values, ranging from 0.9993 to 0.9998. Analytical results indicate reproducible analysis of Zr and Hf in the $(Zr/Hf)O_2$ mixture in a fluoride matrix. However, Hf recoveries were constantly abnormally higher than the expected 100%. Accuracy was, therefore, considered not good for Hf which indicated that the analysis might be affected by high fluoride concentration of flux in relation to the small amount of hafnium present in the sample as it is indicated in literature studies[139,141]. The speculation is of the possible influence of high fluoride concentrations in solution. The t-value of Zr and Hf were determined to observe the reproducibility of analytical results using ICP-OES (see **Table 5.15**), where the t-value of Zr is accepted while t-value for Hf is rejected at 95% confidence interval. By dissolving the flux samples with diluted H_2SO_4, Zr and Hf recoveries were found to be reproducible (**Table 5.16**).

Table 5.15: Validation of Zr determination in $(Zr/Hf)O_2$ using flux fusion with $NH_4F{\cdot}HF$

Validation Criteria	Parameter	HCl	
		Zr	Hf
Recovery	Mean % (s)	100.6(1)	121.2(9)
Precision	RSD (%)	0.19	0.77
Working range	Calibration curve	1 – 10 ppm	1 – 10 ppm
Linearity	R^2	0.9997	0.9999
Sensitivity	Slope	2.4561	0.0999
Selectivity	S_m	0.0476	0.0476
Error of the slope	y- intercept	0.2981	0.0182
Specificity	S_c	0.0476	0.0476
Theoretical mean mass (μ) ppm		673.0	119.3
Experimental mean mass ($\bar{X}$) ppm		677	145
Standard deviation of the mass		2.8	3.3
t-test		2.5	13.4
T_{crit} at 95 % confidence interval		4.3	4.3
Decision		Accepted	Rejected

S_m = Standard deviation of the slope

S_c = Standard deviation of intercept

Table 5.16: Validation of Zr determination in $(Zr/Hf)O_2$ using flux fusion with $NH_4F{\cdot}HF$

Validation Criteria	Parameter	HCl	
		Zr	Hf
Recovery	Mean % (s)	100.1(2)	100(2)
Precision	RSD (%)	0.24	1.90
Working range	Calibration curve	1 – 10 ppm	1 – 10 ppm
Linearity	R^2	0.9997	0.9999
Sensitivity	Slope	4.5772	0.1383
Selectivity	S_m	0.0476	0.0013
Error of the slope	y- intercept	0.2535	0.0036
Specificity	S_c	0.1762	0.000
Theoretical mean mass (μ) ppm		606	132
Experimental mean mass ($\bar{X}$) ppm		607	131
Standard deviation of the mass		12.7	27.2
t-test		0.14	-0.06
T_{crit} at 95 % confidence interval		4.3	4.3
Decision		Accepted	Accepted

S_m = Standard deviation of the slope

S_c = Standard deviation of intercept

5.9 Conclusion

A mixture of commercial ($(Zr/Hf)O_2$) and PDZ, successfully dissolved using a flux fusion method and $NH_4F{\cdot}HF$ flux. The melt easily dissolved in the water. $NH_4F{\cdot}HF$, as a fluoride source, has several advantages (over the commonly used HF) which include, its lower corrosiveness to equipment, easy to handle and store qualities, as well as, cheap price. The Zr recovery from the fluoride fused $(Zr/Hf)O_2$, indicates that, Zr was quantitatively dissolved and recovered. However, in the case of Hf, recovery indicates that the Hf was dissolved but the analysis was affected by the high concentration of flux in relation to the small amount of hafnium present in the sample which gave inaccurate results. While fluoride fused $(Zr/Hf)O_2$ dissolved in diluted H_2SO_4 and evaporated to dryness, it highlighted the quantitatively recoveries of both

Zr and Hf. Acid leaching was investigated using microwave acid digestion and inconclusive analytical results were obtained. This method for the possible Zr/Hf separation, however, needs to be further investigated.

In ion exchange separation of Zr and Hf using Amberlie IRA-900 and low concentration of HCl, using single stage separation, was found to be effective in eluting Zr while holding Hf. However, the recovery of the isolated Zr was extremely low, indicating that a significant concentration of Zr was still adsorbed by the resin under the investigated acid conditions. The recovery of ZrO_2 also indicated very low Hf content present which proves the partial separation of both elements.

Solvent extraction was also investigated using MIBK, while methylamine and cyclohexylamine solvents and the results indicated incomplete separation of Zr and Hf. As indicated in the results from SX using MIBK solvent, the distribution ratio increased with the concentration of H_2SO_4 and number of extractions and more Zr compounds were extracted into the organic layer than Hf compounds. It was decided not to investigate further on PDZ. The evaluation of developed analytical techniques for beneficiation of Zr and Hf from $(Zr/Hf)O_2$ and PDZ is summarised in **Table 5.17**.

Table 5.17: Evaluation of beneficiation processes

Process	Condition	Evaluation	
		Zirconium	Hafnium
Dissolution of $(Zr/Hf)O_2$ or PDZ using $NH_4F{\cdot}HF$	Complete dissolution of both samples	√√	
	Complete recovery of Zr and Hf	√√	√√
Separation of Zr and Hf	Separation of Zr from Hf by acid leaching	√	√
	Separation of Zr from Hf by ion exchange	√√	
	Separation of Zr from Hf by using solvent extraction	√	√
Purification of Zr	Purification and isolation of ZrO_2	√	

√√ means successful

√ means not successful

6 Evaluation of the study and future studies

6.1 Introduction

This chapter will evaluate the achievements of the study against the aim/objectives set in **Chapter 1**, **Section 1.2** and **1.3**, as well as, any future research that could emanate from this study.

6.2 Evaluation of the study with regard to the main objectives

The primary objective of this project was to investigate the possible separation of Zr and Hf in inorganic salts $(Zr/Hf)O_2$ using ion exchange and solvent extraction, and consequently apply the optimum separation conditions between the two elements of interest in Plasma-Dissociated Zircon (PDZ). The individual objectives as outlined in **Chapter 1**, **Section 1.3** are:

- To develop an energy efficient and economically viable dissolution method for zirconium (Zr) and hafnium (Hf) oxides and Plasma-dissociated plasma (PDZ);
- To improve analytical techniques for accurate analysis of zirconium and hafnium in the different matrices;
- To quantitatively determine zirconium and hafnium concentrations in different sample matrices;

- To develop procedures for separation of Zr and Hf in inorganic salts $(Zr/Hf)O_2$ mixtures and develop the optimum conditions to the separation of Zr and Hf in PDZ;
- To validate methods of all the developed analytical techniques in order to assess their reliability in accordance with good laboratory practices.

This study is considered successful in achieving its individual objectives reiterated above. This achievement is based on the outcomes discussed in **Chapter 5**. A mixture of commercial $(Zr/Hf)O_2$), as well as, PDZ were successfully dissolved using flux fusion with $NH_4F{\cdot}HF$ as flux. The melt easily dissolved in the water. The concentration of zirconium and hafnium in both samples were quantitatively determined using ICP-OES. The analytical results obtained from $(Zr/Hf)O_2$ mixture indicated the recoveries of 100.6(2) and 121.2(9) % for Zr and Hf respectively. Hf recovery indicated that the analysis was affected by high fluoride concentration of flux in relation to the small amount of hafnium present in the sample which gave inaccurate results. The excess of fluoride concentration and fluoride ions (F^-) were removed by the addition of concentrated H_2SO_4 and heating processes respectively. These steps brought the Hf recovery within an acceptable range and good recoveries of (100.1(2) % Zr and 100(2) % Hf. The advantages of this dissolution method include a low fusion temperature (200 ^oC), shorter fusion times (40 minutes), and a water soluble melt which dissolve within 10 minutes. This dissolution method is considered more environmentally friendly, compared to HF. It is anticipated that the $NH_4F{\cdot}HF$ flux fusion produces fluorinated zirconium and hafnium compounds which imparted enough chemical differences between the two metals and allowed for their subsequent separation. The same experimental conditions were subsequently applied on the PDZ. Complete dissolution was obtained and both Zr and Hf were quantified using ICP-OES. The percentage of Zr and Hf in the PDZ compared favorably with those obtained in previous studies.

With regard to the development of procedures for the separation of Zr and Hf from fluoride solution of metal oxides and PDZ, techniques such as acid leaching, ion exchange and solvent extraction were investigated. The results from acid leaching

were inconclusive and the possible Zr/Hf separation using microwave digestion requires further investigation.

Meaningful Zr and Hf separation was achieved using ion exchange chromatography. The Amberlite IRA-900 anion exchange resin successfully separated substantial amounts of Zr and Hf in both the metal oxides and PDZ samples with 0.05 M HCl as eluent using only a single separation step. In these conditions, the Hf was strongly retained by the Amberlite resin, whereas, the Zr eluted more readily from the column. The obtained Zr recoveries from PDZ were found to be disappointingly low, compared to the Zr recoveries obtained in the salt $(Zr/Hf)O_2$. The elemental analysis of the isolated ZrO_2 after the separation process indicated very low Hf content, confirming the partial separation of both elements. This analysis pointed to the possible development of a separation process to obtain pure ZrO_2 from PDZ fluoride solution using fewer steps than the usual multi-steps discussed in **Chapter 1**.

Solvent extraction was also investigated for Zr and Hf separation as an alternative to ion exchange due to its low Zr recoveries obtained with the ion exchange separation method. This method, however, proved to be less successful than the ion exchange method.

With regard to the validation of the analytical results using ICP-OES, most of the results obtained for the Zr and Hf quantification in the inorganic salt ($(Zr/Hf)O_2$), were accepted at the 95 % confidence interval. However, other results indicated poor precision and accuracy of Hf, hence, the null hypothesis was rejected.

6.3 Future research

Based on the results obtained in this study, possible future studies may concentrate on the following aspects:

- The optimisation of separation conditions due to the relatively low zirconium recoveries obtained for the PDZ separation;
- The possible use of the Dowex 21k exchange anion resin which displayed some potential for the separation of Zr and Hf in a fluoride solution;
- The dissolution of PDZ in other flux mediums, such as, borate salts and the investigation of the separation of Zr and Hf in these new chemical environments;
- Microwave-assisted digestion of PDZ and the possible separation of the two elements based on dissolution differences under these conditions;
- In-depth investigation into the chelation (using organic ligand, containing a combination of sulphur and nitrogen co-ordination sites) of the metal ions (in PDZ matrix) and their subsequent extraction or separation of Zr and Hf from these mixtures.

Appendix 1

Solvent extraction from **Chapter 4**, **Section 4.4.3**.

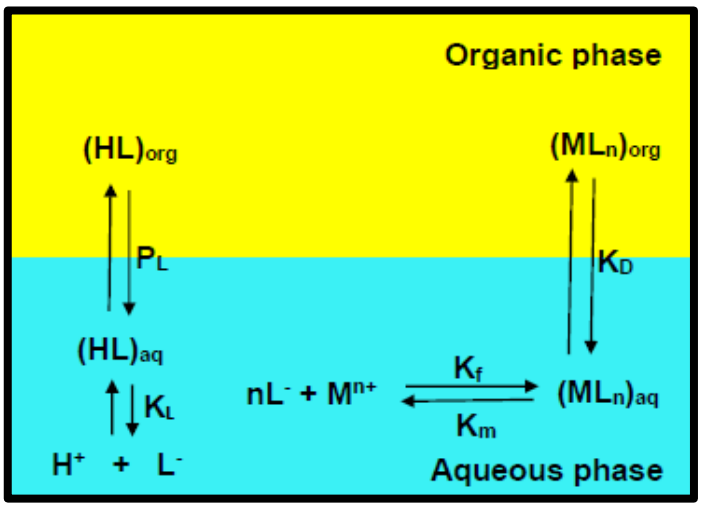


Figure 4.9: General solvent extraction process of metal complexes

For a chelating reagent, HL reacts with a metal ion M^{n+} to produce a neutral complex ML_n (see **Equation 4.22**), which represents the overall reaction during extraction process (see **Figure 4.9**).

$$M^{n+}_{(aq)} + nHL_{(org)} \underset{}{\overset{D}{\rightleftharpoons}} ML_{n(org)} + nH^{+}_{(aq)} \qquad 4.22$$

With

The extraction constant (D):

$$D = \frac{[ML_n]_{org}[H^+]_{n\ aq}}{[M^{n+}]_{aq}[HL]_{n\ org}} \qquad 4.23$$

or

$$D = \frac{K_{D(MLn)}K_L{}^n}{K_m P_{L(HL)}{}^n} \qquad 4.24$$

Equation 4.22 represents the four equilibrium steps that are happening in the extraction process (see **Figure 4.9**) which is indicated in **Equation 4.24(1)** to **4.24(8)**.

$$ML_{n(aq)} \underset{}{\overset{K_D}{\rightleftharpoons}} ML_{n(org)} \qquad 4.24(1)$$

With

$$K_D = \frac{[ML_n]_{org}}{[ML_n]_{aq}} \qquad 4.24(2)$$

Where K_D is the distribution constant of the metal chelate between two immiscible layers.

$$HL_{(aq)} \overset{K_L}{\rightleftharpoons} H^+_{(aq)} + L^-_{(aq)} \qquad 4.24(3)$$

With

$$K_L = \frac{[H^+]_{aq}[L]_{aq}}{[HL]_{aq}} \qquad 4.24(4)$$

Where K_L is the dissociation constant of the chelating agent in the aqueous layer.

$$ML_{n(aq)} \overset{K_m}{\rightleftharpoons} M^{n+}_{(aq)} + nL^-_{(aq)} \qquad 4.24(5)$$

With

$$K_m = \frac{[M^{n+}]_{aq}[L^-]^n_{aq}}{[ML_n]_{aq}} \qquad 4.24(6)$$

Where K_m is the dissociation constant of the neutral metal chelate in the aqueous phase.

$$HL_{(aq)} \overset{P_L}{\rightleftharpoons} HL_{(org)} \qquad 4.24(7)$$

With

$$P_L = \frac{[HL]_{org}}{[HL]_{aq}} \qquad 4.24(8)$$

Where P_L is the distribution constant of the chelating agent between the organic and the aqueous layers.

To obtain distribution ratio from liquid-liquid extraction of metal ion (**Figure 4.9**), **Equation 4.24(2)** is divided by **4.24(6)** and **4.24(4)** divided by **4.24(8)** to give the following **Equation 4.24(9)** and **4.24(10)**.

$$\frac{[ML_{n]org}}{[M^{n+}]_{aq}} = \frac{K_D}{K_m} [L^-]^n{}_{aq} \qquad 4.24(9)$$

$$[L^-]_{aq} = \frac{K_L}{P_L} \times \frac{[HL]_{org}}{[H^+]_{aq}} \qquad 4.24(10)$$

By further substitution of **Equation 4.24(10)** into **4.24(9)** give the formula of D by solving the equation (see **Equation 4.24(11)**).

$$D = \frac{[ML_n]_{org}[H^+]^n{}_{aq}}{[M^{n+}]_{aq}[HL]^n{}_{org}} = K_D \frac{[H^+]^n{}_{aq}}{[HR]^n{}_{org}} \quad \text{where } K_D = \frac{[MR_n]_{org}}{[M^{n+}]_{aq}} \qquad 4.24(11)$$

Appendix 2

Number of replicates	$HClO_4$		HCl		H_2SO_4	
	Zr	Hf	Zr	Hf	Zr	Hf
1	0.436532	0.053918	1.85204	0.062642	0.450661	0.053618
2	0.433097	0.054469	1.86761	0.063026	0.450673	0.05416
3	0.438324	0.053954	1.88317	0.062602	0.449883	0.054678
4	0.437159	0.052782	1.88317	0.063914	0.447497	0.054096
5	0.434277	0.054294	1.88317	0.0624	0.448749	0.054286
6	0.434153	0.053476	1.89873	0.062481	0.44885	0.053882
7	0.439625	0.053727	1.89873	0.062542	0.452304	0.054002
8	0.438298	0.054198	1.89873	0.062299	0.452706	0.054915
9	0.434863	0.054881	1.9143	0.062562	0.448181	0.054185
10	0.43985	0.05553	1.89873	0.062824	0.452642	0.054625
Mean (SD)	0.436618	0.054123	1.887838	0.062729	0.450215	0.054245
SD (Blank)	0.002416	0.000757	0.018046	0.000465	0.001901	0.000394
Slope	0.7808	0.0396	4.577	0.138	0.8885	0.0425
LOD	0.010211	0.063083	0.013011	0.011095	0.007061	0.030593
LOQ	0.102111	0.630833	0.130105	0.110954	0.070606	0.305929

Number of replicates	HNO_3		$HClO_4$	
	Zr	Hf	Zr	Hf
1	0.444397	0.053665	0.436532	0.053918
2	0.447512	0.054162	0.433097	0.054469
3	0.447753	0.053976	0.438324	0.053954
4	0.447978	0.054516	0.437159	0.052782
5	0.447681	0.054213	0.434277	0.054294
6	0.45047	0.054439	0.434153	0.053476
7	0.445607	0.054567	0.439625	0.053727
8	0.450661	0.05418	0.438298	0.054198
9	0.445111	0.055011	0.434863	0.054881
10	0.449688	0.054627	0.439850	0.055530
Mean (SD)	0.447686	0.054336	0.4366178	0.0541229
SD (Blank)	0.002173	0.000378	0.002416	0.000757
Slope	0.7303	0.0349	0.7808	0.0396
LOD	0.009819	0.035742	0.010211	0.063083
LOQ	0.098191	0.357421	0.102111	0.630833