Quantification of hafnium in selected inorganic and organometallic compounds

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by

GONTSE ATLHOLANG ADELINE MALEFO

Supervisor

Prof. W. Purcell

Co-supervisors

Dr. J.T. Nel and **Dr. M Nete**

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Declaration

I declare that the thesis entitled "**THE QUANTIFICATION OF HAFNIUM IN SELECTED INORGANIC AND ORGANOMETALLIC COMPOUNDS**" submitted for the degree Magister in Analytical Chemistry, at the University of the Free State is my own original work and has not been previously submitted to any other institution of higher education in the Republic of South Africa or abroad. I further declare that all sources cited or quoted are indicated and acknowledged by means of a comprehensive list of references.

Signature…… **Date**……..…….

Gontse Atlholang Adeline Malefo

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Gontse Malefo

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LIST OF ABBREVIATIONS

ANALYTICAL EQUPMEMENT

ICP – OES	Inductively coupled optical emission spectroscopy
ICP – MS	Inductively coupled mass spectrometry
NAA	Neutron activation analysis
XRF	X-ray fluorescence
IR	Infrared
CHNS micro-analyser	Carbon, hydrogen, nitrogen, sulphur micro-analyser

CHEMISTRY TERMS

PTFE	Polytetrafluorethylene
CRM	Certified reference material
PDZ	Plasma-dissociated zircon
SARM62	Zircon reference sample
mp	melting point
PEG	polyethylene glycol
CPE	cloud point extraction process

SI UNITS

nm	Nanometer
ppm	Parts per million
pmol/kg	Picomole per kilogram
N	Normality

STATISTICAL TERMS

LOD	Limit of detection
LOQ	Limit of quantification
C.I	Confidence Interval
RSD	Relative Standard deviation
SD	Standard deviation
S_m	Standard deviation of the slope
Sc	Standard deviation of the intercept
r^2	Correlation coefficient

KEY WORDS

Hafnium

Zirconium

Zircon

Baddeleyite

Quantification

Hafnium oxide

Inductively coupled optical emission spectroscopy (ICP – OES)

Accuracy

Precision

1 MOTIVATION OF THE STUDY

1.1. BACKGROUND

The existence of hafnium eluded chemists for many years and was amongst the last elements on the periodic table to be discovered.[1,2] It was only discovered in 1923 by the Danish chemist, Dirk Coster and a Hunguarian chemist named Charles de Hevesy.[2] They identified the presence of hafnium in zirconium containing compounds by means of Henry Moseley‟s X-ray spectroscopy technique.[3] The element naturally occurs with zirconium in numerous mineral deposits as the mineral oxide not as a pure metal. Hf is produced as a by-product during the refining of zirconium,while ultra-pure hafnium metal is only produced through a complex refining process.[4] The element is normally found in concentrations between 1 and 3 % in a number of different zirconium mineral ores such as baddeleyite (ZrO_2), eudialyte (mineral containing minor hafnium), weloganite, painite ($CaZrAl_9O_{15}(BO_3)$), vlasovite and zircon ($(Zr,Hf)SiO_4$) amongst others.[5] However, it is mainly sourced from zircon ($(Zr,Hf)SiO_4$) resulting from the processing of the heavy mineral sands of igneous rocks.[4,5] Different hafnium containing mineral ores are shown in **Figure 1.1**.

[1] Hafnium, [Accessed 16-02-2015]. Available from: http://www.pamicon.net/hafnium-2/
[2] D.R. Holmes, ATI Wah Chang, ASM Handbook, Corrosion: Materials (ASM International), 13 B, p. 354 (2005)
[3] F.L. Pirkle, D.A. Podmeyer, ***Society for Mining, Metallurgy and Exploration***, 292, (1998)
[4] Rare Metals, Hafnium, [Accessed 03-03-2015]. Available from: http://www.avalonraremetals.com/rare_metals/hafnium/
[5] L.L Nkabiti., Method validation for the quantification of impurities in zirconium metal and other relevant Zr compounds, M.Sc. Dissertation at the Department of Chemistry, University of the Free State, RSA (2012)

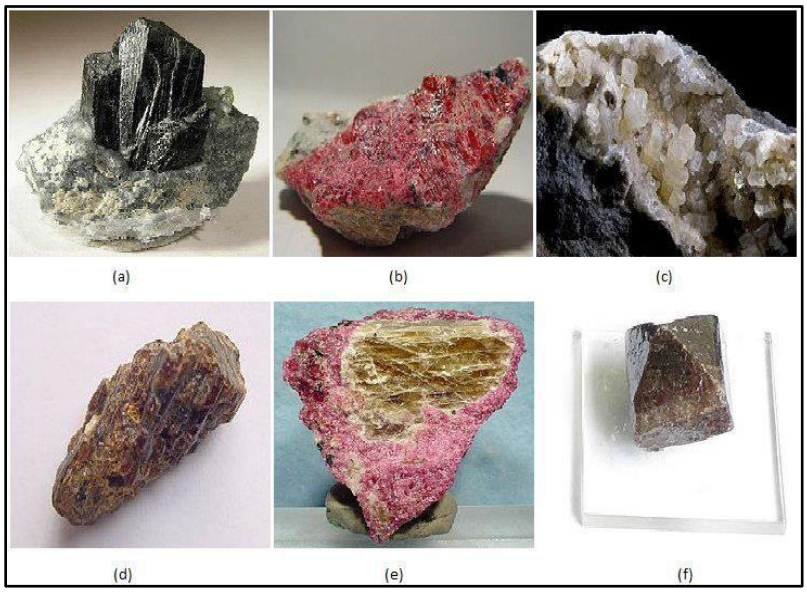

Figure 1.1: Hafnium–containing mineral ores: (a) baddeleyite, (b) eudialyte, (c) weloganite, (d) painite, (e) vlasovite, (f) zircon.[5]

The chemistry of hafnium and zirconium metals is very similar and is renowned to be two of the most difficult elements to separate. The separation of the two elements was originally developed by von Hevesey and V.T Jantzen through repeated recrystallization of the double ammonium or potassium fluorides.[6] The pure metallic hafnium was first prepared by van Arkel and de Boer[3-6] by the reduction of hafnium tetra-iodide with iodide over a hot tungsten filament. W.J Kroll later improved the original procedure of van Arkel and de Boer by reducing hafnium tetrachloride with magnesium.[7] Separation techniques which have been used for a successful separation of Zr and Hf include ion exchange, fractional precipitation, extractive distillation and solvent extraction techniques.[8] Of the above, extractive distillation and solvent extraction are commonly used in industrial separation process. The difficulty in separation and natural abundance techniques makes hafnium a scares commodity and very expensive.[9]

[6] W.M. Haynes, Handbook of Chemistry and Physics, 93, pp. 16 (2013)
[7] M. Smolik, H. Polkowska-Motrenko, Z. Hubicki, A. Jakobik-Kolon, B. Danko, ***Analytica Chimica Acta***, 806, p. 98 (2014)
[8] M. Makhofane, J.T. Nel, J.L. Havenga, A.S. Afolabi, ***The Southern African Institute of Mining and Metallurgy***, pp. 339 (2013)
[9] J. H. Schemel, ASTM Manual on Zirconium and Hafnium, pp. 3 - 5 (1977)

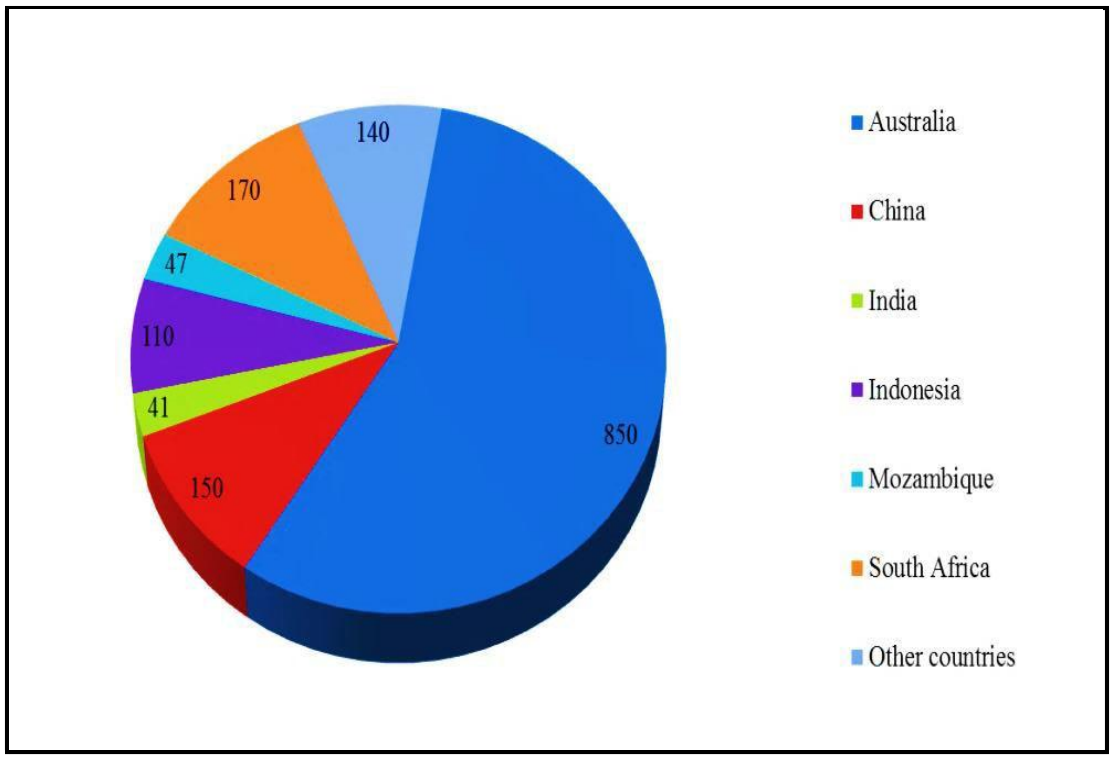

Figure 1.2: The world zircon production 2014(‘‘000 Tonnes).[10]

The production of zircon is critically important for the supply of hafnium. In 2014 the world‟s major production of zircon took place in Australia, South Africa and China,[10] as shown in **Figure 1.2**. Countries like Indonesia, Mozambique and India also commercially produce zirconium products from natural deposits of baddeleyite, which are also important sources of hafnium production.[10] Baddeleyite mining almost ceased to exist since then.

1.2. THE IMPORTANCE OF HAFNIUM

It is difficult to discuss the production, uses or chemical properties of hafnium without comparing it to zirconium. In a large number of zirconium applications, the hafnium is not even removed or separated from the zirconium due to the similarity of their chemical and physical properties, as well as the relative low concentration of Hf in the final products. Physical differences that do exist between the two elements are that Hf

[10] “Zirconium and Hafnium”, Mineral Commodity Summaries (US Geological Survey), pp. 188 - 189 (2015)

has twice the density of Zr and a relatively higher melting point. They also have different nuclear properties. Hafnium has a barn value (neutron absorption cross sectional area) of 104 cm^2 while Zr has a 0.184 cm^2 neutron absorption cross sectional area.[4]

One of the most important uses of zirconium metal is in the nuclear industry as cladding for the nuclear material in reactors. High corrosion resistance and low neutron cross section absorption of nuclear grade zirconium makes this metal ideally suited to be used in this highly robust environment.[1,3,11] Hafnium on the other hand is also used in the nuclear industry, but due to its high neutron absorption coefficient it is used as control rods in the nuclear process to control and regulate the nuclear reactions.[3,11] It is especially in this industry that ultra-pure Zr metal (Hf < 100 ppm) is needed to improve the efficiency of a nuclear reactor.

All hafnium compounds, including metal, oxides and salts have very high melting points and are extremely corrosion resistant and therefore have a wide variety of applications in industrial and nuclear technology.[11,12] The high corrosion resistance property of hafnium is a result of the produced protective film of oxide upon contact with air and makes it fairly resistant to attacks by most mineral acids. However hafnium is quite reactive with a variety of non-metals such as hydrogen, carbon and nitrogen to form brittle compounds at elevated temperatures, although is less reactive compared to zirconium.[1,13] The metal is extensively used in the super alloy industry in the development of high technology applications which include atomic power engineering and aerospace[14] and as control rods in nuclear submarines due to its ability to capture thermal neutrons.[1,14]

Hafnium is also used in the production of binary compounds which are among the best refractory materials known and are used as linings in the inside of high temperature ovens which include hafnium boride and hafnium oxide.[14] The exceptional uses of

[11] A. Bahattin, ***Mineral Research Exploration Bulletin,*** 109, pp. 75 - 79 (1989)
[12] M.T. Larrea, I. Gomez-pinilla, J.C. Farinas, ***Analytical Atomic Spectrometry***, 12, p. 1323 (1997)
[13] K.V.Sahira, ***International Journal of Engineering Science Invention***, 7, pp. 124 - 126 (2013)
[14] E.L. Dzidziguri, E.A. Salangina, E.N. Sidorova, ***Russian Metallurgy***, 5, p. 768 (2010)

zirconium and hafnium in the nuclear industries require an almost complete separation of the two metals and accurate quantification of these elements.[15]

1.3. AIM OF THE STUDY

In all beneficiation processes, from dissolution to separation, the three important factors to consider are the extent of dissolution, completeness of the recovery and the subsequent separation from each other and the associated impurities.[14] An integral component of the mineral beneficiation involves the determination or quantification of the concentrations of the different analytes at every step of the processing route. Several analytical techniques which include an inductively coupled plasma optical emission spectrometry (ICP-OES), radiometric and neutron activation analysis are the most frequently used techniques for the quantification of hafnium in zirconium ores during their separation attempts.[10] The choice of each technique is determined by several factors which include the capability of the instrument to accurately analyse all the elements of interest as well as the accompanying impurities and the availability of the instrument (See **Chapter 4**).

Hafnium is one of the less known or studied elements on the periodic table due to its similarity to zirconium and also due to the separation dilemma that exist between the two elements. The current study was prompted by the lack of knowledge of the chemistry of hafnium such as in solubilities and volatilities of compounds that distinguishes it from zirconium. The aim of the study was to investigate the dissolution of hafnium compounds, especially those that are similar to its occurrence in its natural state namely the oxide, using different digestion techniques. The study would also entail the dissolution of other hafnium compounds such as hafnium(IV) tetrafluoride and newly synthesized fluorido hafnate complexes which are easily dissolved in order to develop and validate the analytical procedures for hafnium compounds. In this respect "in-house" reference material will also be developed or synthesized in the absence of commercially obtained CRMs.

[15] L.A. Machlan, J.L. Hague, ***Journal of Research of the National Bureau of Standards-A. Physics and Chemistry***, 66A, p. 517 (1962)

The objectives of this study are to:

- Perform an in depth literature study on the dissolution and analytical techniques for the dissolution and analysis of hafnium compounds.
- Establish measurement traceability in synthesized and analysing hafnium reference materials.
- Develop digestion methods for hafnium oxide using different digestion methods such as open beaker, fusion and acid-assisted microwave digestion.
- Investigate the ability of the different analytical techniques such as ICP-OES and CHNS-microanalyser for the analysis of hafnium.
- Optimize analytical technique‟s operating conditions for the determination of hafnium at trace levels.
- Carry out method validation by performing the statistical calculations on the analytical data.

2 Overview of hafnium

2.1. INTRODUCTION

Hafnium was discovered in 1923 by Coster and de Heversy. It was predictedby D. Mendeleev (see **Figure 2.1**) as an element which has properties similar to, but heavier than titanium and zirconium.[16] The element was initially mistaken for celtium but later rectified using Mosely's law, which explains the energy dependency of the characteristic X-ray radiation upon the nuclear charge which proved that indeed the element was different to that of celtium. This newly found element was then named hafnium (see **Chapter 1**, **Section 1.1**).[17]

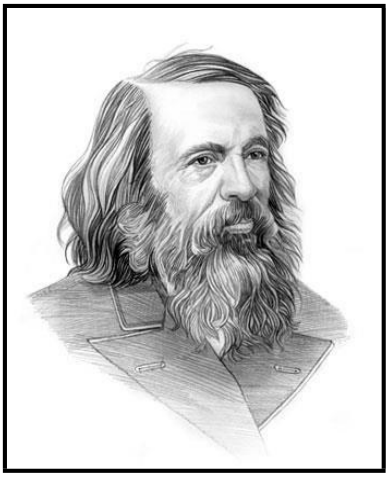

Figure 2.1: D. Mendeleev (1834–1907).[18]

Hafnium has a natural abundance of about 5.8 $mg.kg^{-1}$ (see **Figure 2.2)** and is the 45th most abundant element in the Earth's crust and it is estimated to make up about 0.00058 % of the Earth's crust.[13] The Hf content in soil is within the range of 1.8 to 18.7 $mg.kg^{-1}$, depending on the parent rock type. Generally, ground water contains less than 0.1 $\mu g.L^{-1}$ concentrations of Hf and about 0.008 $\mu g.L^{-1}$ is present in oceanic water.[19,20]

[16] M. Laing, ***Journal of Chemical Education***, 85, p. 63 (2008)
[17] N. Mehta, Textbook of Engineering Physics Part II, p. 56 (2009)
[18] Dimitri Mendeleev, [Accessed 21-05-2015]. Available from: http://www.elementalmatter.info/images/dimitri-mendeleev.jpg
[19] Hf - Hafnium, [Accessed 17-02-2015]. Available from: http://weppi.gtk.fi/publ/foregsatlas/text/Hf.pdf
[20] A. Kabata - Pendias, Trace Element in Soils and Plants, 3rd edition, p. 224 (2001)

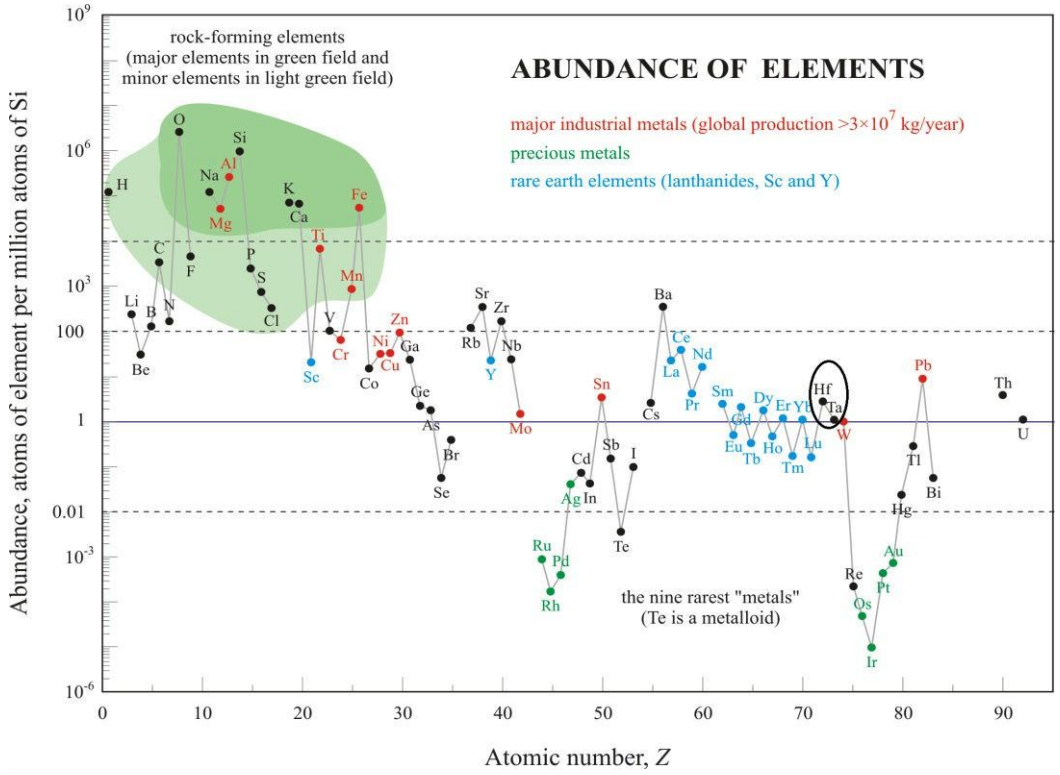

Figure 2.2: Relative abundance of elements in the earth's upper crust.[21]

Hafnium is always associated in nature with zirconium in numerous mineral deposits (see **Chapter 1**) as the mineral oxide and not as a pure metal. Although it is contained in about 40 known minerals, its most important sources are zircon $(Zr,Hf)SiO_4$ and baddeleyite ZrO_2 which contain ~3 % of hafnium.[22] However, some zircon mineral deposits (alvites and cyrtolites) containing up to 20 % of hafnium has been reported in Norway.[23] Furthermore, a scandium mineral throtveitte (also from Norway) and a namacotche zircon mineral from Mozambique were found to contain less Zr than Hf concentrations.[24]

A small amount of hafnium is also contained in mineral sands of igneous rocks, from which zircon is mainly sourced. Due to its physical and chemical inertness it is considered to be a common mineral found in sedimentary and metamorphic rocks[6,25,26], which are formed by the compression of sediments and the fusion of sedimentary or igneous rocks at high temperature

[21] Abundance of Elements in the Earth's Crust, [Accessed 11-06-2015]. Available from: http://upload.wikimedia.org/wikipedia/commons/thumb/0/09/Elemental_abundances.svg/1280px-Elemental_abundances.svg.png

[22] R.H. Nielsen, G. Wilfing, Ullmann's Encyclopedia of Industrial Chemistry, Hafnium and Hafnium compounds, pp. 2 - 5 (2000)

[23] A.M. Abdel – Gawad, ***The American mineralogist***, 51, pp. 464 - 465 (1966)

[24] A.A. Levinson, R.A. Borup, ***The American Mineralogist***, 45, p. 562 (1960)

[25] D.A. Brobst, W.P. Pratt, United States mineral resources, Geological survey professional, 820, pp. 713 - 721 (1973)

[26] E.A. Belousova, W.L. Griffin, S.Y. O'Reilly, N.I. Fisher, ***Contributions to Mineralogy and Petrology***, 143, p. 602 (2002)

and pressure, with approximately 75 % sedimentary rocks covering the Earth's surface.[27,28] The amount of zircon sand (and hence hafnium) is usually of low concentrations since it is found with other heavy minerals such as ilmenite, rutile, monazite, garnet, staurolite and kyanite.[6]

The major natural sources of zirconium (and hence hafnium) are found in Australia, South Africa and United State (see **Figure 2.3)** with smaller deposits dispersed all over the world. Although hafnium has some important industrial applications (see **Section 2.8**) quantitative estimates of Hf in different minerals have until recently been relatively little studied. Hafnium is also obtained as a by-product during the refining of zirconium from zirconium ore minerals and currently has low industrial demand.[10]

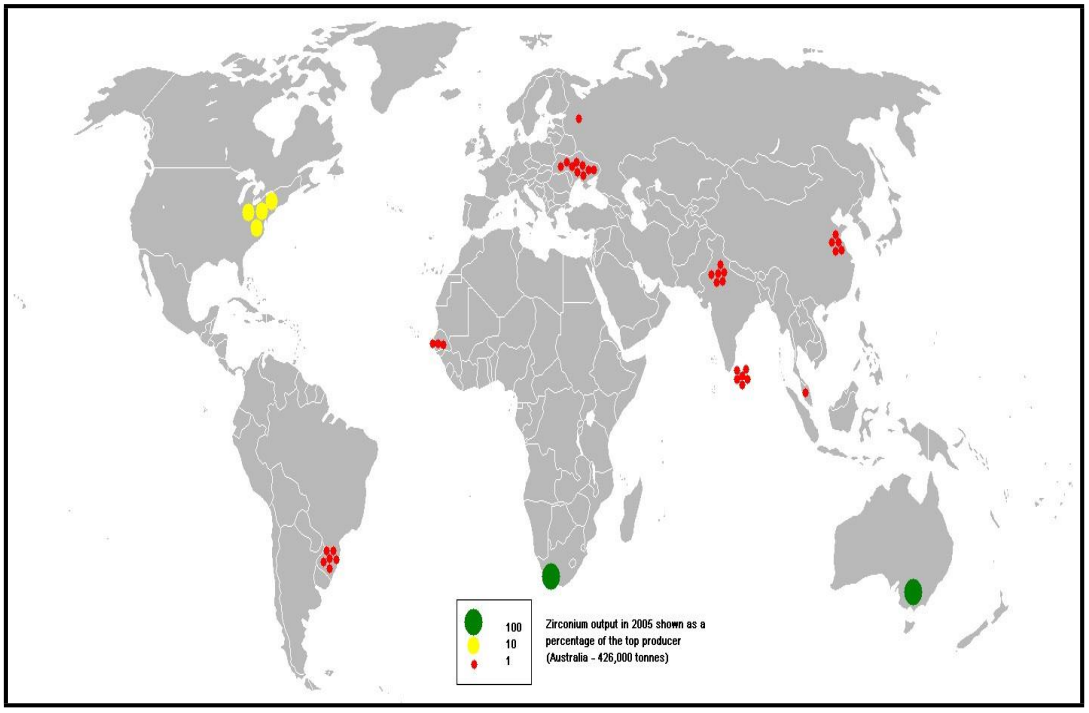

Figure 2.3: Geographical distribution of zirconium.[29]

The latest (2014) quantitative estimates of hafnium resources are not yet available.[10] The known hafnium reserves in 2010 are given in **Table 2.1**.

[27] Sedimentary rock, [Accessed 23-02-2015]. Available from: http://www.sciencedaily.com/articles/s/sedimentary_rock.htm
[28] J. Girard, Principles of Environmental chemistry, 3rd edition, pp. 15 - 16(2014)
[29] World Zirconium Producing Countries, [Accessed 20-05-2015]. Available from: http://www.mapsofworld.com/minerals/world-zirconium-producers.html#

Table 2.1: Zircon and hafnium reserves reported in 2010.[22]

Country	Zircon		Hafnium content of zircon reserve ('000 Tonnes)
	Production ('000 Tonnes)	Zircon reserve ('000 Tonnes)[e]	
Australia	480	32000	390
United State	135	15000	145
South Africa	135	15000	145
Brazil	18	4000	38
India	15	9000	85
Sri Lanka	5	3000	29
Malaysia	3	3000	29
World total (rounded)	791	81000	861

[e] – Estimated

2.2. HAFNIUM MARKET OVERVIEW

It is important to note that the market for Hf closely follows the market or the trends of Zr production and sales due to their close association in primary or natural resources. This implies that any increase or decrease in zirconium ore production inevitably lead to the same tendency for Hf. The only difference in the market for the two elements is that in many Zr applications the hafnium is not removed and sold as Zr due to the quantities present and also due to their chemical and physical similarities.

The leading producer of zircon is Australia with about 60 % of zircon's world production followed by 17 % in S.A and the U.S.A in 2010 (see **Table 2.1**). In Australia, zirconium is mainly produced by the Jacinth - Ambrosia heavy mineral sands mine situated in South Australia. However, the final zirconium products are processed at the Narngulu mineral separating plant, near Geraldton in the Eucla Basin which is situated in Western Australia[30](see **Figure 2.4**).

[30] Jacinth-Abrosia, Eucla Basin, South Australia. [Accessed 14-08-2015]. Available from: http://www.iluka.com/company-overview/operations/eucla-basin-south-australia

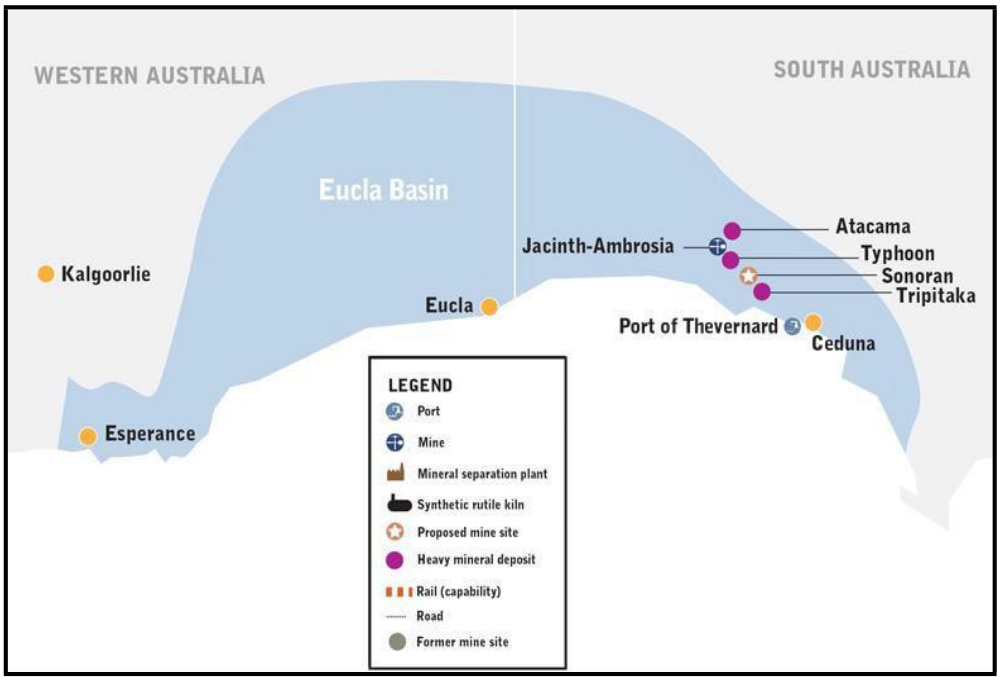

Figure 2.4: The Distribution of zirconium in Australia.[30]

In 2013, about 158 000 tonnes of zircon was produced from the heavy mineral sands in the Eucla Basin of South Australia while 136 000 tonnes were produced in the Perth Basin of Western Australia and the Murray Zircon mine situated in Victoria (see **Figure 2.5**). The production of zircon by the Murray Zircon mine which started in 2011 decreased to 60 000 tonnes in 2014 due to weak commodity prices and finally closed in 2015.[31,32] However, Murray Zircon then partnered with Image Resources Limited in the development of the Atlas and Boonanaring mineral sands deposit project in the Perth Basin of Western Australia.[31,33]

[31] "Zirconium and Hafnium", Mineral Commodity Summaries (US Geological Survey), p. 85.2 (2013)
[32] Murray Zircon to wind down operations in South Australia as falling commodity prices continue to bite, [Accessed 17-08-2015]. Available from: http://www.abc.net.au/news/2015-05-04/murray-zircon-to-wind-down-operations/6442770#,
[33] Boonanarring and atlas development project, [Accessed 17-08-2015]. Available from: http://www.imageres.com.au/index.php/projects/boonanarring-and-atlas-development-project.html,

Figure 2.5: Murray Zircon heavy mineral sands mine.[32]

The project which was approved by the Foreign Investment Review Board (FIRB) is expected to begin in 2016 with an annual zircon production of 35 000 tonnes with a mine-life expectancy of 10 years. About $20 million has been invested on this project with Murray Zircon having a 42 % share in the Image Resources' project.[34]

Another new development in zirconium production in Australia is the proposed Dubbo Zirconia (DZP) open-cut mine located near Toongi in the Central Western region of New South Wales Australia. The initial indication is that this mining development will produce zirconium, hafnium, niobium, tantalum, yttrium and rare earth elements with a mine-life expectancy of 70 years. The proposal was approved in February 2015 by the Planning Assessment Commission of Australia and the construction of DZP is expected to begin in the latter part of 2015.[35] Estimates indicate that this project alone will produce 16 000 tonnes zirconium dioxide, 4 900 tonnes of rare earth oxides and 3 000 tonnes of ferroniobium. An investment in this project totals about $1 billion and is mainly financed by Australia's Alkane Resources with financial backing from Credit Suisse, Sumitomo Mitsui Banking Corporation and Petra Capital.[35]

[34] FIRB approval granted for Image transaction, [Accessed 17-08-2015]. Available from: http://www.engineeringnews.co.za/article/firb-approval-granted-for-image-transaction-2015-08-07

[35] The Dubbo Zirconia Project, New South Wales, [Accessed 17-08-2015]. Available from: http://www.mining-technology.com/projects/the-dubbo-zirconia-project-new-south-wales/

In South Africa, zircon is mainly obtained from the beach-sands of Kwa-Zulu Natal (eastern coast of South Africa) in Richards Bay Minerals (RBM) belonging to Rio Tinto Iron & Titanium (RTIT) and Billiton Plc.[36] Zircon is also produced by Exxaro's Namakwa sands mining operations located on the west coast of South Africa. This operation started in 1994 and has since then been amongst the world's largest mineral sand operations. The Brand-se-Baai heavy mineral sands mine is located 385 km North of Cape Town while the mineral processing plant for zircon, rutile and ilmenite is located at Koekenaap, about 60 km away from the mine.[37] This mine has a life expectancy of 20 years with the expected annual zircon production of 160 000 tonnes per annum.[38] Exxaro Resources Limited also developed the Fairbreeze mine located in the south of Mtunizi. This mine replaced the Hillendale draft mine which ceased production in December 2014.[31] About R2.45 billion has been invested in the construction of the Fairbreeze mine and it is expected to start production in the mid-June 2015 with an annual zircon production of about 60 000 tonnes for a period of 15 years.[39] Another recent development in South Africa includes the Tormin project which began with the production of zircon and rutile concentrates in January 2014. This project will produce about 48 000 tonnes per year of non-magnetic concentrate grading 81 % zircon as well 11.6 % rutile over a 4-year life expectancy.[10]

Zirconium production in the USA as one of the major global suppliers is extremely unpredictable and mainly driven by the commodity market trends. For example, two of the older zirconium producing mines, one near Stony Creek, VA and the other one near Starke, FL which started mining operations in 1993, only produced zirconium ore until 2014. Operations at the Virginia mine stopped in April 2014 mainly due to economic and environmental challenges such as sustained weak market conditions and new federal government regulations faced by Central Appalachian mining industry[40] while the associated mineral separation plant operated at reduced capacity which reduced existing inventories.[10] In the middle of 2012 zircon mineral prices in the U.S.A decreased from the highs of $2 650 per

[36] G.E. Williams, J.D. Steenkamp, ***South African Institute of Mining and Metallurgy***, p. 183 (2006)
[37] Heavy Minerals Mining in South Africa, [Accessed 17-08-2015]. Available from : http://www.mbendi.com/indy/ming/hvym/af/sa/p0005.htm,
[38] Industrial Mineral Sands, [Accessed 17-08-2015]. Available from: http://www.miningreview.com/exxaro-among-mineral-sands-top-three/
[39] Planned Fairbreeze mine to benefit region and all stakeholders, [Accessed 17-08-2015]. Available from: http://www.exxaro.com/index.php/planned-fairbreeze-mine-to-benefit-region-and-all-stakeholders/
[40] Alpha Natural Resources Subsidiaries Announce Plan to Downsize West Virginia Mining Operations [Accessed 17-06-2015]. Available from: http://www.prnewswire.com/news-releases/alpha-natural-resources-subsidiaries-announce-plan-to-downsize-west-virginia-mining-operations-300028449.html

metric ton in 2011 and 2012 (see **Figure 2.6**) to $1 050 per metric ton in 2014. The high Zr prices in the 2011 and early 2012 could mainly be attributed to a 350 % increase in imports due to extremely high zircon demand by steel manufacturers and other industrial consumers and a decrease of about 71 % in exports due to reduced domestic production (see **Figure 2.6**).[10]

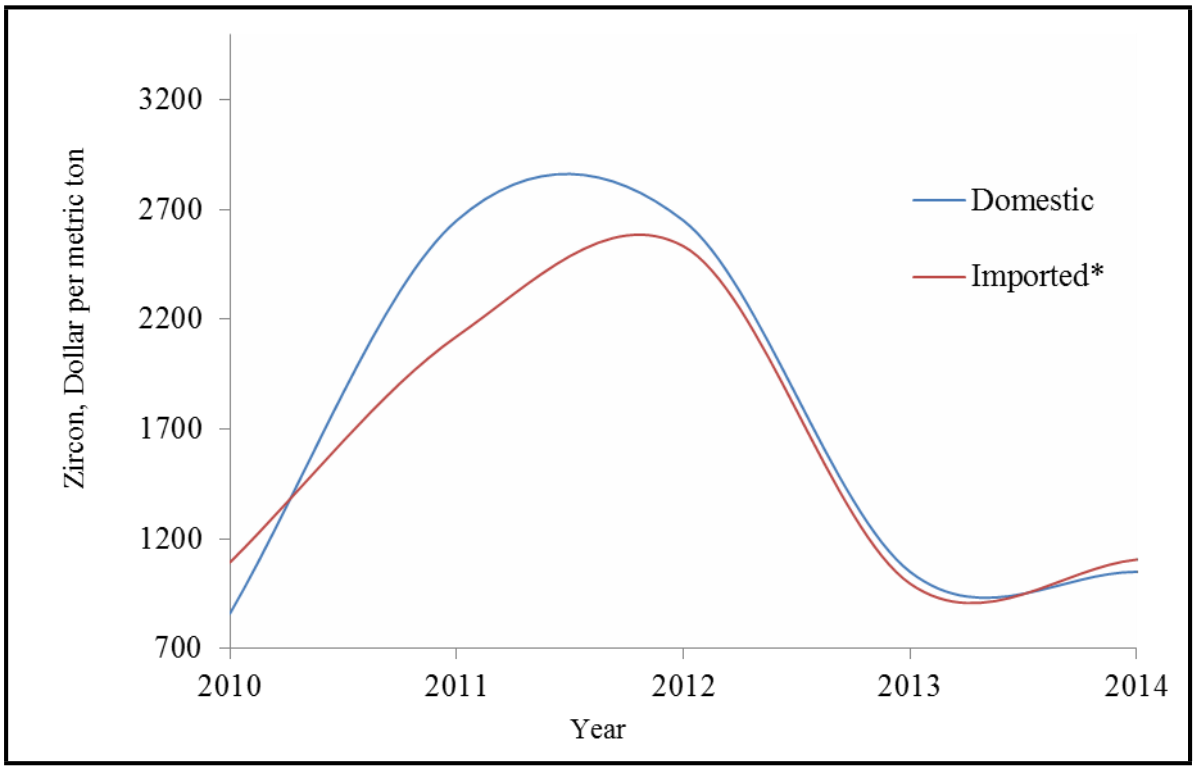

Figure 2.6: Annual average prices of zircon from 2011 to 2014[e], U.S.A.[10]

***Unit value based for the U.S.A imports for consumption from Australia and South Africa**

Recent expectation of an increase in zirconium demand prompted expansion of production capacity in the U.S.A. A new zircon plant (see **Figure 2.7**) was commissioned in 2014 by Southern Ionics Minerals Company for the processing of heavy mineral deposits as well as ancient beach sand ridge in Charlton and Brantley counties, Georgia. Production of zircon and titanium minerals is expected to begin in June 2015.[41] About 100 million U.S dollars have also been invested in this new Mineral Sand plant as well as in two new mines in Charlot (Mission South Mine) and Brantley (Mission North mine) counties which are expected to begin the production in the fourth quarter of 2015.[41]

[41] Zircon plant opened in US by Southern Ionics Minerals, [Accessed 03-06-2015]. Available from: http://imformed.com/zircon-plant-opened-in-us-by-southern-ionics-minerals/

Figure 2.7: Southern Ionics Minerals' new mineral sands plant.[41]

Southern Ionics Minerals will be the third zircon producer in the U.S.A after lluka Resources Ltd and DuPont Titanium Technologies. lluka which has been producing zircon since 1970s is set to end zircon production in the U.S.A by the end of 2015. Iluka produced about 50 000 tonnes of the U.S.A zircon in 2012. Production in this mine (Iluka) decreased to 39 000 tonnes in 2013 and further to 25 000 tonnes in 2014 which finally led to the mine's closure when appropriate commercial arrangements could not be negotiated.[41]

Worldwide, three other large projects involving heavy-mineral concentrate beneficiation started production in January 2014. In February 2014, the Kwale project in Kenya also began with zircon production and projection estimate about 30 000 tonnes per year zircon production over mine-life of 13-years. In March 2014, zircon production also began at the Grenade Cote project in Senegal and the first shipment of zircon was made in August of the same year. Estimates indicated 80 000 tonnes per year of zircon will be produced during a mine-life of more than 20 years. Heavy-mineral exploration and mining projects were also performed in Australia, Madagascar, Mozambique, Tanzania and Sri Lanka.[10,41] The imports of zirconium raw material from the U.S.A to different countries are distributed as shown in **Table 2.2**

Table 2.2: The distribution of zirconium raw material imports from the U.S.A to different countries (2012–2013).[10]

Zirconium mineral concentrates		Zirconium, unwrought, including powder		Hafnium, unwrought	
South Africa	60 %	Japan	49 %	France	50 %
Australia	35 %	Germany	31 %	Australia	23 %
Other	5 %	China	8 %	Germany	21 %
		France	6 %	Other	6 %
		Other	6 %		

2.3. THE EXTRACTION OF HAFNIUM FROM MINERAL ORES

Hafnium ores are very rare, but the commonly known ones include hafnon and alvite[4]. The metal is usually extracted as a by-product during the refining of zirconium from zirconium ore minerals (see **Chapter 1, Section 1.1**), with zircon being the primary source. Zirconium ore minerals are extracted by heavy mineral sands mining. An example of a heavy mineral sands mining operation, in South Africa, for some of the zirconium-containing minerals is shown in **Figure 2.8**.

Figure 2.8: Heavy mineral sands mining at Richards Bay Minerals (South Africa).[42]

Mineral sands can be mined by both dry and dredge (wet) mining techniques. Dry mining is normally useful for deposits that are shallow, contains hard bands of rock, or are in a series of unconnected ore bodies. Dredge mining is suitable for sediment deposited from flowing water.[43] Once the primary processing (mining and washing of ore) of zircon is completed, the sample is decomposed, which normally requires aggressive chemical reagents and high temperatures. The chemical inertness of zircon makes it a major obstacle to successfully dissolve zircon using conventional acid digestion techniques and as such various methods with different reagents have been developed to dissolve, separate and isolate zirconium and hafnium metal.[44] The dissolution methods reported so far include caustic fusion, fluorosilicate fusion, lime fusion and a two-step process involving carbiding and chlorination of the crude carbide.[44] A flow diagram illustrating the processes involved in the production of hafnium metal is shown in **Figure 2.9.**

[42] Coastal watchdog picks bone with mine [Accessed 20-05-2015]. Available from: http://zululandobserver.co.za/50995/coastal-watchdog-picks-bone-with-mine/
[43] Zircon Industry Asscociation, [Accessed 10-06-2015]. Available from: http://www.zircon-association.org/zircon-sand
[44] R.Nielsen, Ullmann's Encyclopedia of Industrial Chemistry, A28, p. 543 (1996)

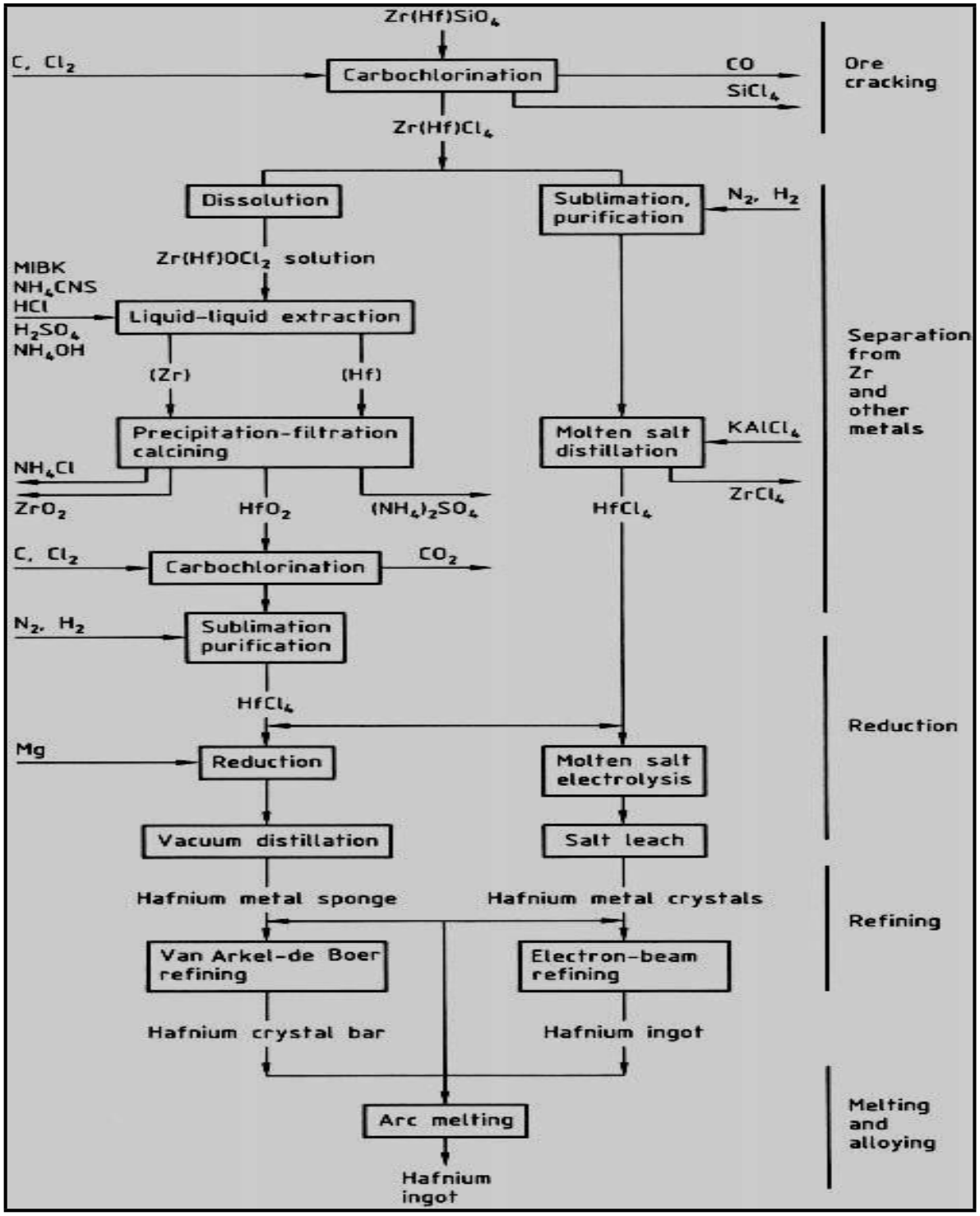

Figure 2.9: Flow diagram for the production of hafnium.[22]

The most well-known procedures for extracting hafnium from its zirconium mineral ores are carbochlorination and alkali extraction. The procedures are discussed in detail in the next paragraphs.

2.3.1. CARBOCHLORINATION EXTRACTION

This process involves the treatment of mixtures of zircon sand and carbon with chlorine gas in a fluidized bed reactor at temperatures of about 1200 °C (2192 °F). In this chemical process, carbon ensures the completion of the reaction and chlorine gas is used as the fluidizing medium (see **Equation 2.2**).[5,22] Moreover, when zircon is heated with carbon in the absence of chlorine gas at the temperature of 2500 °C, carbon acts as a reducing agent to produce (Zr,Hf)C according to **Equation 2.3**.

$$(Zr,Hf)SiO_4 + 4C + 4Cl_2 \rightarrow (Zr,Hf)Cl_4 + SiCl_4 + 4CO \qquad \textbf{(2.2)}$$

$$(Zr,Hf)SiO_4 + 3C \rightarrow (Zr,Hf)C + SiO + 3CO \qquad \textbf{(2.3)}$$

According to **Equation 2.2**, zirconium and hafnium tetrachlorides are recovered as a power and separated from the silicon tetrachloride as a by-product by cooling the gas mixture in a large volume space condenser to 200 °C. Zirconium and hafnium tetrachlorides have no liqiud phase at atmospheric pressure. Hence, they both condense as packed solids from the chlorinator product gas and collected in condensers above the condensation temperaure of silicate tetrachloride of about 20 °C. The $SiCl_4$ is then condensed as a liquid, purified and used in the production of pure silicon for the semiconductor industry, whereas the condensed Zr and Hf tetrachlorides are ready for zirconium and hafnium separation.[22] Fused oxide can also be carbochlorinated, according to **Equation 2.4**.

$$(Hf,Zr)O_2 + 2C + 2Cl_2 \rightarrow (Zr,Hf)Cl_4 + 2CO \qquad \textbf{(2.4)}$$

In the Kroll process (see **Chaper 1, Section 1.1**) Zr and Hf tetrachlorides are reduced with metal magnesium in a furnace at 800–850 °C (see **Equation 2.5**).

$$(Zr,Hf)Cl_4 + 2Mg \rightarrow Zr,Hf\ (metal) + 2MgCl_2 \qquad \textbf{(2.5)}$$

Pure hafnium product of > 99.9 % purity is produced after the purification of hafnium sponge (resulting spongelike material from **Equation 2.5**) at high temperature distillation where the magnesium chloride is removed.[22]

2.3.2. ALKALI EXTRACTION

The alkaline extraction entailes the fusion of the Zr/Hf mineral with different alkali salts such as caustic soda and sodium carbonate. The fusion melt is subsequently dissolved in water and dilute acid such as hydrochloric acid.[22]

2.3.2.1. Caustic fusion

Caustic fusion involves the mixing of zircon with sodium hydroxide and the subsequent fusion of the homogenous mixture proceeds at a temperature of about 650 °C. This results in the formation of either sodium zirconate and sodium metasilicate or orthosilicate depending on the mole ratios of the alkali, according to **Equation 2.6**. This melt is soluble in water.[22]

$$Zr(Hf)SiO_4 + 4NaOH \rightarrow Na_2Zr(Hf)O_3 + Na_2SiO_3 + 2H_2O \qquad \textbf{(2.6)}$$

2.3.2.2. Soda fusion

Soda fusion is accomplished at a temperature of about 1200 °C. In contrast to caustic fusion, the product formed is sodium zirconium silicate (see **Equation 2.7**) and is only soluble in strong acids. Hydrochloric acid is commonly used acid for the dissolution of the melt as indicated in **Equation 2.8**.[45]

$$Zr(Hf)SiO_4 + Na_2CO_3 \rightarrow Na_2Zr(Hf)SiO_5 + CO_2 \qquad \textbf{(2.7)}$$

$$Na_2Zr(Hf)SiO_5 + 4HCl \rightarrow 2NaCl + Zr(Hf)OCl_2 + SiO_2 + 2H_2O \qquad \textbf{(2.8)}$$

Relatively high zircon to sodium carbonate ratios (1:20) result in the formation of sodium zirconate and sodium silicate[45,46] according to **Equation 2.9**

$$Na_2Zr(Hf)SiO_5 + Na_2CO_3 \rightarrow Na_2Zr(Hf)O_3 + Na_2SiO_3 + CO_2 \qquad \textbf{(2.9)}$$

[45] Recovery of Zirconia from Zircon Sands, [Accessed 10-06-2015]. Available from: http://repository.up.ac.za/bitstream/handle/2263/27817/05chapter5.pdf?sequence=6&isAllowed=y

[46] Sample fusion, [Accessed 17-06-15]. Available from: http://www.inorganicventures.com/sample-preparation-fusion

2.4. SEPARATION OF ZIRCONIUM AND HAFNIUM

It is impossible to discuss the purification of hafnium sponge without taking into account its association with zirconium, as it is one of the impurities or minor elements in all zirconium minerals. As explained in **Chapter 1**, the separation of these elements is very challenging due to their similar chemical and physical properties and hence different separation methods have been developed. An overview of some of the most successful separation methods is presented in this section. The separation methods that will be discussed in detail are the most commonly methods used in the industrial separation process namely extractive distillation and liquid – liquid extraction.[24,45] Both separation methods require the initial chlorination of the primary zirconium and hafnium source (see **Equation 2.2**).

2.4.1. EXTRACTIVE DISTILLATION

In 1978, the French state company (Compagnie Europeene du Zircon) CEZUS started an industrial plant necessary for the production of zirconium and hafnium using the Besson's process (extractive distillation in molten salts). The method uses molten potassium chloroaluminate ($KAlCl_4$) salt as the solvent and is performed at atmospheric pressure.[47] The mixture $(Zr,Hf)Cl_4$ carbochlorination (see **Equation 2.4**) is first purified from trace-element impurities by sublimation prior to separation. Distillation is performed at 500 °C and the purified vapour is continuously introduced above the midpoint of the distillation column and dissolved in the descending solution of $KAlCl_4$ which have a temperature of 350 °C at that point in the distillation column.[22] The hafnium and zirconium tetrachloride are separated as the solvent circulates through the column with the more volatile $HfCl_4$ accumulating at the top of the column (higher vapour pressure) whereas the solution mixture of $KAlCl_4$ and $ZrCl_4$ remains in the bottom of the column.[22] $HfCl_4$ (top) and $ZrCl_4$ (bottom) are both removed from the distillation column thereafter using an inert gas such as nitrogen gas.[48] The remaining solvent containing different $Zr/HfCl_4$ ratio is pumped back into the midpoint of column (see **Figure 2.10**). This hafnium – depleted tetrachloride mixture is then reprocessed in the distillation column using the same method with various adjustments to produce pure hafnium tetrachloride at the top of the column and purified zirconium tetrachloride at the bottom.

[47] R.Banda, M.S. Lee, ***Department of Advanced Material Science and Technology, Institute of Rare Metal, Mokpo National University, Chonnam, Republic of Korea***, p. 201 (2014)

Further processing of the metal halides involves the use of the Kroll process to produce metallic hafnium and zirconium.[22,45]

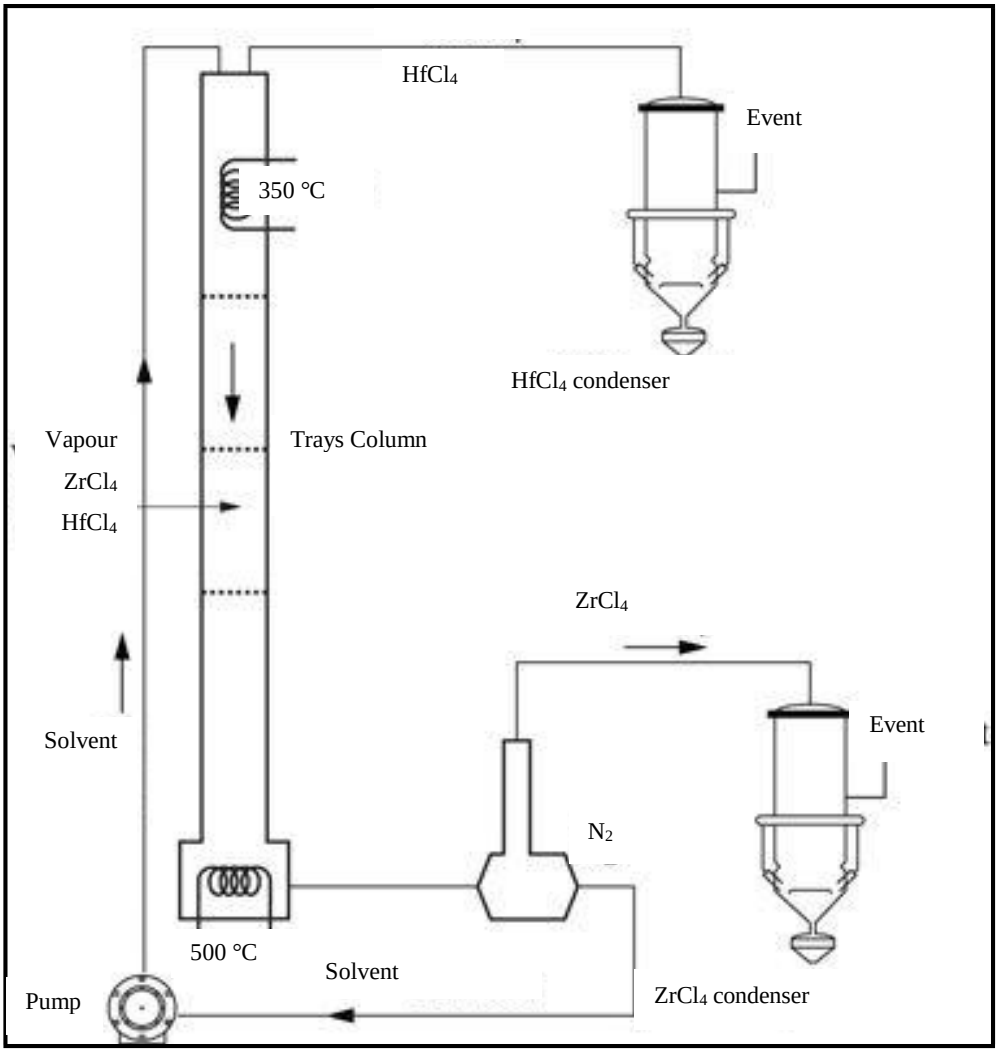

Figure 2.10: Extraction distillation of $ZrCl_4/HfCl_4$ by CEZUS.[48]

2.4.2. LIQUID-LIQUID EXTRACTION

Various liquid-liquid extraction separation methods exist and they all involve the use of different solvents. The selection of the extractant depends on the type or solution content of aqueous phase in which the Zr-Hf salt mixture is dissolved.[22] The commonly used solvents include the methyl isobutyl ketone (MIBK), TBP and ammine containing solvents. The solvent extraction process was originally developed in 1949 by Union Carbide at Oak Ridge National Laboratory. The method took advantage of the difference in the distribution of Zr and Hf between MIBK and HCl solvent media.[47] Appropriate amounts of thiocyanic acid

[48] A. Vignes, Extractive Metallurgy 3, pp. 11 - 12 (2011)

were dissolved in MIBK.[47] This resultant organic solution was mixed and shaken with the zirconium-hafnium dichloride aqueous solution for the separation of Hf from Zr. Hafnium is extracted into the organic solvent as a thiocynate complex leaving Zr in the aqueous solution.[47] It is then back extracted from the organic phase using dilute sulphuric acid.[47] The excess sulphuric acid in Hf solution is subsequently treated with gaseous ammonia, which reacts with thiocyanic acid and hafnium thiocyanate, the resultant hafnium hydroxide is calcinated to hafnium(IV) oxide at 1000 °C (see **Figure 2.11**).[47]

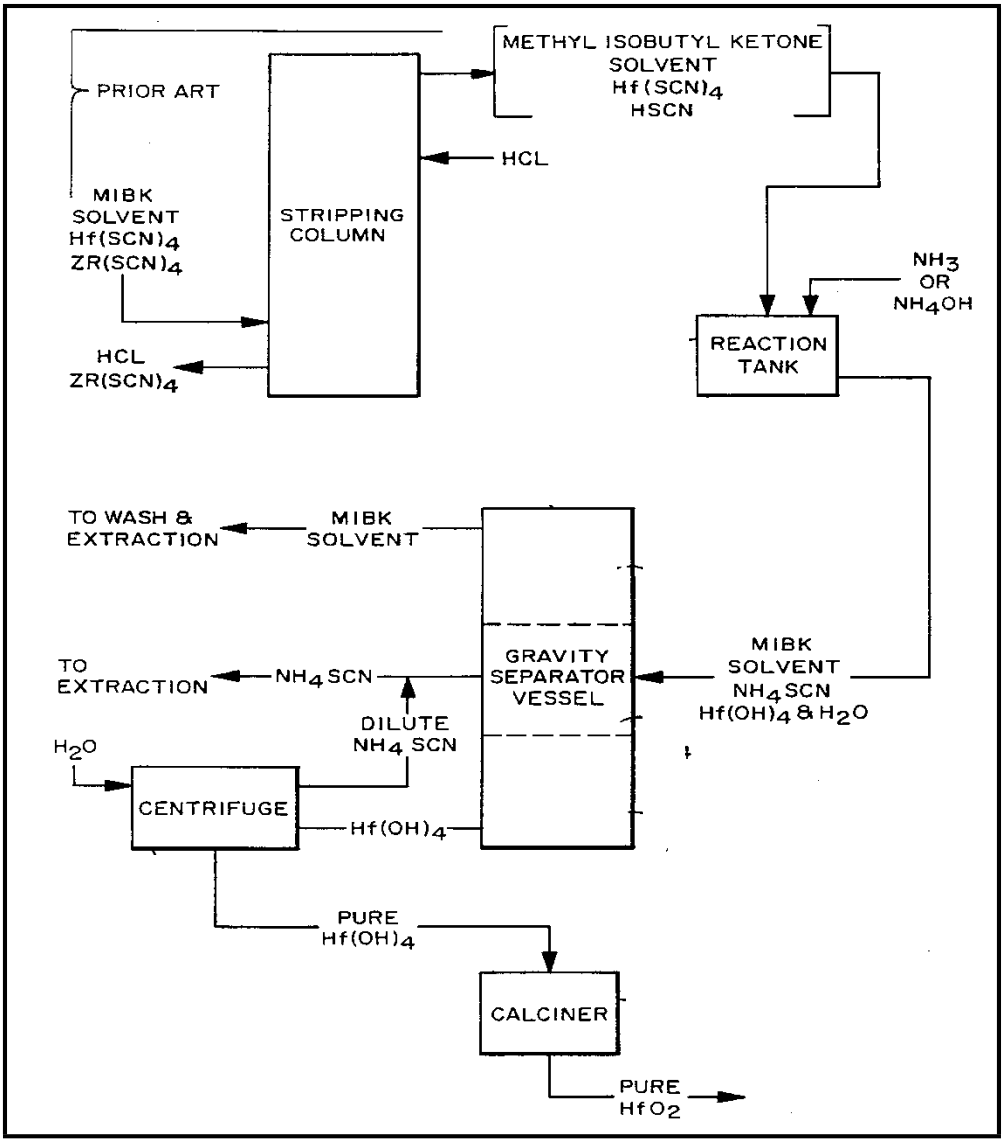

Figure 2.11: Recovery of hafnium from loaded extraction solvent.[49]

[49] Recovery of hafnium values from loaded extraction solvent**,** [Accessed 18-06-2015]. Available from: https://patentimages.storage.googleapis.com/pages/US4873072-1.png

2.5. HAFNIUM PRODUCTION

There are numerous methods used for the production of hafnium metal. The process includes i) chlorination and the conversion of the salt to metal by its reduction with magnesium followed by vacuum distillation for the removal of the magnesium and magnesium chloride (Kroll Process), and ii) electrowinning and refining of hafnium.

2.5.1. CHLORINATION AND KROLL REDUCTION

Hafnium dioxide isolated from the separation processes (see **Section 2.4**) is converted to the hafnium tetrachloride by a fluidized-bed carbochlorination process at a temperature of about 950 °C, according to **Equation 2.10**. The resultant hafnium tetrachloride is purified in a nitrogen-hydrogen atmosphere by sublimation to minimize the amounts of aluminium, iron and uranium impurities.[25]

$$HfO_2 + C + 2Cl_2 \rightarrow HfCl_4 + CO_2 \qquad (\mathbf{2.10})$$

The Kroll process which was developed in the 1950s by W.J Kroll at the Albany Bureau of Mines in the U.S.A in an effort to improve Arkel and de Boer's original method is used to produce pure metallic hafnium. According to the Kroll process hafnium tetra-iodide is reduced to metallic Hf using iodine over hot tungsten filament in Van Arkel iodide cell which is depicted in **Figure 2.12**

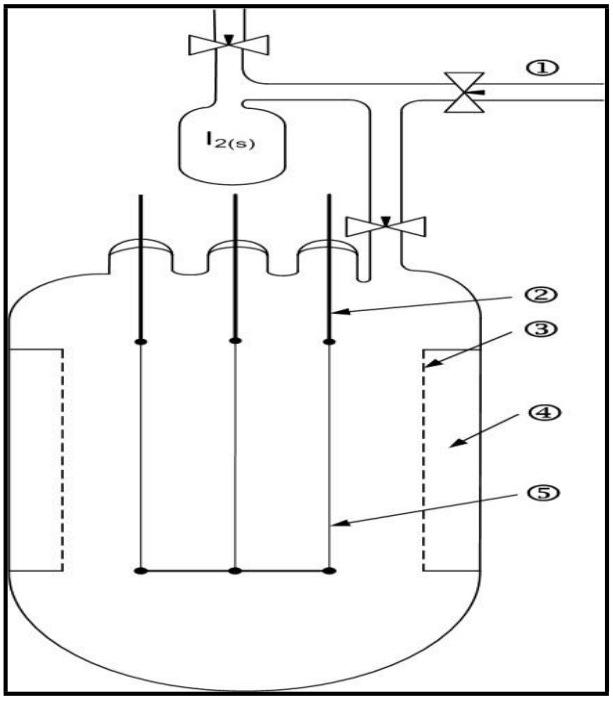

Figure 2.12: Schematic view of an apparatus used for the crystal bar process.[50]

Keys:

1. Pipe to vacuum pump
2. Electrode which heats the filament
3. Molybdenum screen
4. Chamber of the raw metal
5. Tungsten filament, on which the pure metal deposits

Currently the Kroll process is used for the production of nearly all commercial titanium, zirconium and hafnium metal from the metal chlorides, according to **Equations 2.11, 2.12** and **2.13**. In this method the hafnium chloride power is packed in a vertical cylindrical steel retort welded onto a stainless steel-lined steel crucible containing distilled magnesium ingots.[51]

$$ZrCl_4 + 2Mg \rightarrow Zr + 2MgCl_2 \qquad \textbf{(2.11)}$$

$$HfCl_4 + 2Mg \rightarrow Hf + 2MgCl_2 \qquad \textbf{(2.12)}$$

[50] Crystal bar process, [Accessed 03-08-2015]. Available from: https://en.wikipedia.org/wiki/Crystal_bar_process

[51] D. Royston, P.G. Alfredson, Australian Atomic Energy Commission, Research Establishment, pp. 1 – 4 (1970)

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2 \quad \textbf{(2.13)}$$

After cooling the upper part of the distillation furnace using coils in the lid, the lower part is then heated at about 850 °C.[22,27,51] Hafnium tetrachloride vapour is reduced by the molten magnesium as it sublimes out of the bottom part of the furnace forming hafnium metal sponge and magnesium chloride. After the reduction process the reaction products are separated with the unreacted magnesium and magnesium chloride concentrated at the upper portion of the furnace while the hafnium sponge remains in the lower part of the furnace. [27,51]

Due to a large difference in the density of magnesium chloride (2.32 $g.cm^{-3}$) and hafnium sponge (13.29 $g.cm^{-3}$), magnesium chloride is removed by mechanical separation.[22,27,51] Exposure to an air-helium mixture at a pressure of about 0.05 x 10^{-3} mm Hg prevents the rapid ignition of the hafnium sponge and allows for the slow oxidation of the metal surface, forming a protective layer (HfO_2) to the extent that the furnace could be opened and the hafnium sponge removed without any loss of material.[52] Handling, fragmentation and cleaning of the hafnium sponge is done in a helium atmosphere box.[51,52] Most of hafnium's applications (see **Section 2.8**) require hafnium sponge to be further purified using Van Arkel iodide cell (see **Figure 2.12**) to form hafnium crystal bar (see **Figure 2.13**) with purity of 99.99 %.

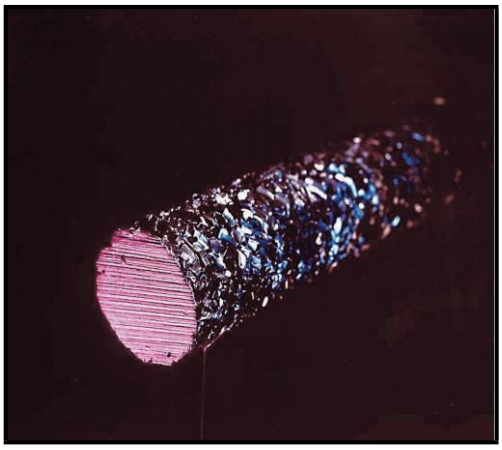

Figure 2.13: Hafnium crystal bar.[53]

[52] H.L. Gilbert, M.M. Barr, ***Journal of Electrochemical Society***, 102, pp. 244 - 245 (1955)
[53] Hafnium, [Accessed 03-06-2015]. Available from: http://www.mmta.co.uk/uploads/2013/01/09/133510_hafnium_mbm.pdf

Electrowinning and electron beam melting processes may alternative be employed to produce pure hafnium sponge. Electrowinning of hafnium has long been studied as an alternative to metallothermic reduction (see **Equation 2.4)**. The method involves the extraction of metals from their ores by electrolysis of aqueous solutions of their salts.[54] On the other hand, electron beam melting process takes place in molten pool under extremely high vacuum and it involves the evaporation of oxides[55] (see **Figure 2.14**). However, purification leaves behind interstitial impurities such as oxygen, carbon and nitrogen (see **Table 2.3**).

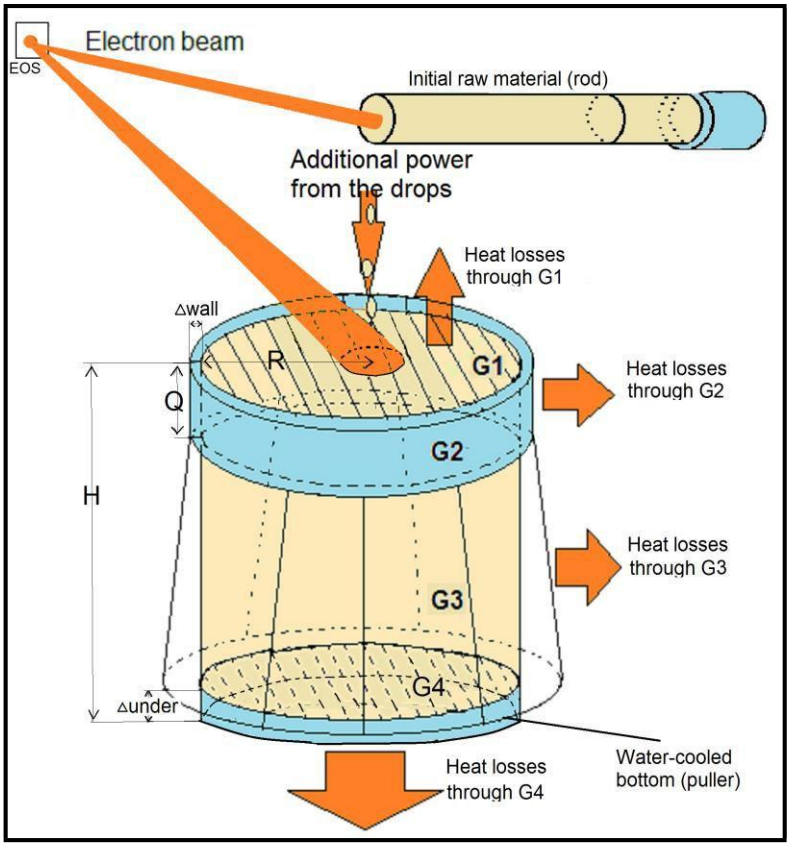

Figure 2.14: Schematic view of Electron-beam melting and refining process.[55]

Key:

G1. The top surface of the formed pure hafnium ingot

G2. The interface molten ingot/ water-cooled crucible side wall

G3. The interface ingot/ vacuum

G4. The interface ingot/ water cooled puller.

[54] D.R. Spink, C.P. Vijayan***, Journal of The Electrochemical Society***, 121, p. 879 (1974)
[55] K. Vutova, V. Donchev, ***Materials***,6 ,pp. 4627 - 4628 (2013)

Typical impurity levels of hafnium sponge from Kroll process, electrowinning hafnium crystal, electron-beam melting as well as Van Arkel crystal bar process are shown in **Table 2.3**.

Table 2.3: Typical impurity levels in parts per million for hafnium metal.[22]

Impurities	Kroll process sponge	Electrowinning crystals	Electron-beam melting ingots	Van Arkel-de Boer crystal
Oxygen	875	670	320	<50
Nitrogen	35	15	40	<5
Carbon	<30	40	<30	<30
Chlorine	100	50	<5	<5
Aluminium	200	10	<25	<25
Chromium	40	30	<20	<20
Iron	530	100	<50	<50
Magnesium	440	<10	<10	<10
Manganese	15	10	<10	<10
Nickel	<25	40	<25	<25
Silicon	25	<25	<25	<25
Titanium	<25	30	<25	<25

2.6. CHEMISTRY OF HAFNIUM

2.6.1. PHYSICAL PROPERTIES

Hafnium is a hard, heavy ductile slivery-white metal with an atomic mass of 178.49 $g.mol^{-1}$. It has a density of 13.29 $g.cm^{-3}$, a high melting point of 2 227 °C and a boiling point between 2 500 °C and 5 000 °C, depending on its purity.[56] Although physically and chemically similar to zirconium, hafnium has twice the density of zirconium, a higher phase transition temperature and a higher melting point. The metal is fairly resistant to attack by most mineral acids and has a high absorption cross section for thermal neutrons.[56] This physical property of capturing electrons is of great interest for hafnium and differs largely from zirconium which barely absorbs any neutron.[22] This is actually one of the few important

[56] B. Ludwig, M. Oliver, H. Richter, Encyclopedia of Metalloproteins, pp 937 - 938 (2013)

differences between the two transition metals which are located in Group 4 on the periodic table.[22,56] The most important physical properties of hafnium are listed in **Table 2.4**.

Table 2.4: Physical and Chemical properties of hafnium.[56]

Property	Hafnium	
Atomic Number	72	
Relative atomic mass	178.49 $g.mol^{-1}$	
Melting Point	2227 °C	
Boiling point	4602 °C	
Density	13.29 $g.cm^{-3}$	
Thermal conductivity (298 K)	23.0 $W\ m^{-1}\ K^{-1}$	
Coefficient of linear expansion (273-1273 K)	$5.9 \times 10^{-6}\ K^{-1}$	
Specific heat (298 K)	117 $J\ kg^{-1}\ K^{-1}$	
Thermal neutron absorption cross section	$1.04 \times 10^{-26}\ m^2$ (104 barns)	
Crystal structure	α-form Hexagonal close-packed	β-form Body-centered cubic
Temperature of transformation	1760 °C	

2.6.2. CHEMICAL PROPERTIES

Hafnium(IVb) is the first element in the third or late transition element series.[57] The atomic and ionic radii of Zr and Hf are almost identical and are due to lanthanide contraction (see **Figure 2.15**). Hafnium has an electron configuration of $[Ar]5d^26s^2$ compared to $[Ar]4d^25s^2$ for zirconium. Both metals display oxidation states of +II, +III and +IV with the latter the most stable oxidation state for both metals. The different oxidation states of both elements (Hf and Zr) involve the stepwise removal (oxidation) of the four valence electrons (s^2 and d^2 electrons) to form the different stable hafnium and zirconium compounds.[57]

[57] R.E. Krebs, The History and Use of Our Earth's Chemical Elements, 2nd edition, p. 147 (1922)

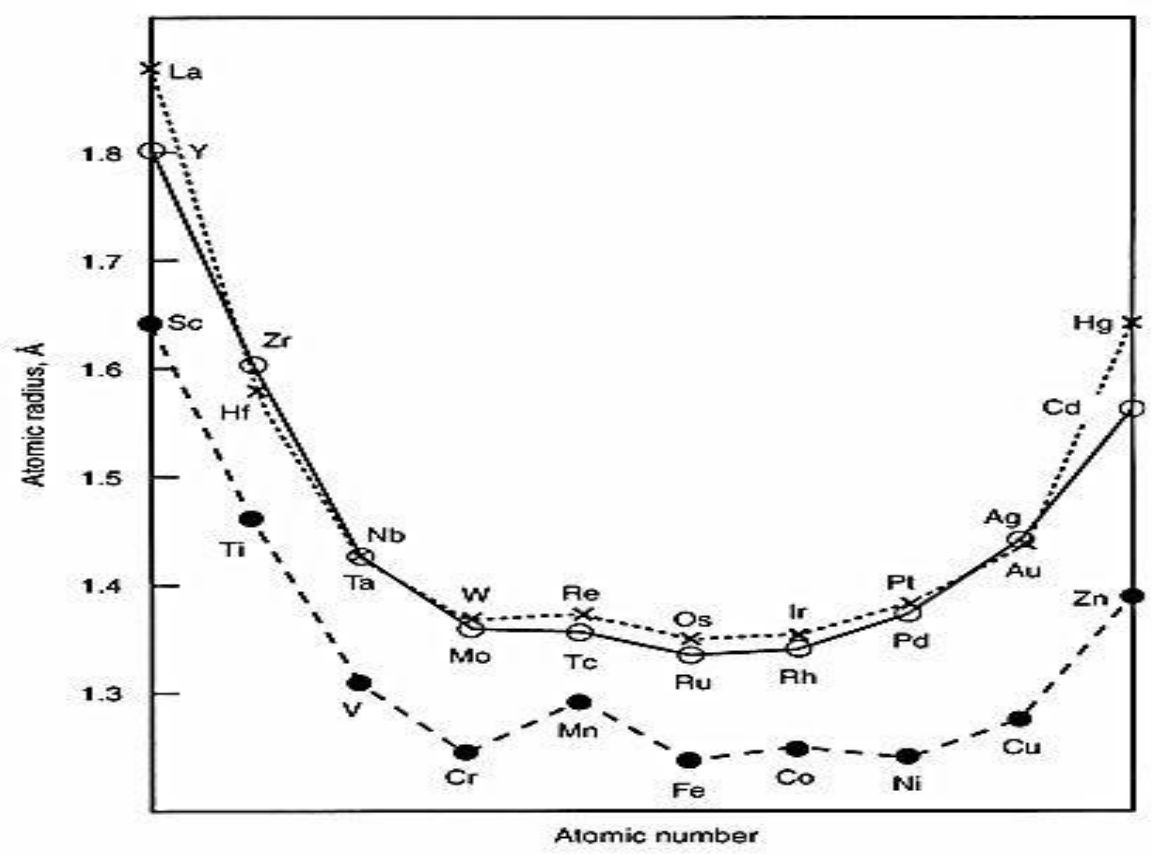

Figure 2.15: The similarity of atomic radii of Zr-Hf due to the lanthanide contraction.[56]

The different oxidation states and stereochemistry of zirconium and hafnium are given in **Table 2.5**.

Hafnium is chemically inert towards acid attack by most common mineral acids (similar to Zr). It is best dissolved in HF where the formation of anionic fluoro complexes is necessary for the stabilizing of Hf in solution.[56] Hafnium metal also resist attack by most concentrated alkalis however it reacts with halogens to form tetrahalides. It is also reactive towards a variety of non-metals such as hydrogen, carbon and nitrogen at elevated temperatures and form brittle compounds. Hafnium(IV) can be reduced to hafnium(III) and hafnium(II) in anhydrous molten halide. In aqueous solution, its valence state remains unchanged as +4 and do not seem to form any cationic complexes.[58]

[58] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th edition, pp. 777 - 778 (1988)

Table 2.5: Oxidation states and stereochemistry of zirconium and hafnium.[58]

Oxidation State	Coordination Number	Geometry	Examples
Zr^{II}, Hf^{II}, d^2	6	Octahedral	$ZrCl_2(PPh_3)_2$, HfO
Zr^{III}, Hf^{III}, d^1	6	Octahedral	$ZrCl_3$, $ZrBr_3$, ZrI_3, HfI_3
Zr^{IV}, Hf^{IV}, d^0	4	Tetrahedral	$ZrCl_4$(g), $Zr(CH_2C_6H_5)_4$
	6	Octahedral	Li_2ZrF_6, $Zr(acca)_2Cl_2$, $ZrCl_6^{2-}$, $ZrCl_4$
	7	Pentagonal	Na_3ZrF_7, Na_3HfF_7
		Bipyramid	$K_2CuZr_2F_{12}.6\ H_2O$
		Capped trigonal prism	$(NH_4)_3ZrF_7$
	8	Square antiprism	$Zr(acac)_4$, $Zr(SO_4)_2.4\ H_2O$
		Dodecahedral	$[Zr(C_2O_4)]^{4-}$, $[ZrX(diars)_2]$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

The hafnium metal ion exhibits a strong tendency to be hydrolysed due to its small ionic radii and high ionic charge and for example slowly hydrolyses and polymerizes in dilute hydrochloric acid. However, at lower acid solution concentrations the Hf ion undergoes extensive hydrolysis[59] (see **Equation 2.14**).

$$Hf(H_2O)_8^{4+} \rightarrow HfOH(H_2O)_7^{3+} + H^+ \qquad (\mathbf{2.14})$$

At approximately pH 2 hafnium hydrous oxide precipitates from aqueous solution and the degree of polymerization of Hf ion decrease.[59] Moreover, Hf is regarded as a hard Lewis acid metal and tends to bind stronger with hard basic groups such hydroxyl group compared to chloride ions.[59]

[59] L. Poriel, A. Favre-Réguillon, S. Pellet-Rostaing, M. Lemaire, ***Journal of Separation Science and Technology***, 41, p. 1930 (2006)

2.7. COMPOUNDS OF HAFNIUM

The study and knowledge of hafnium compounds is necessary for the development of separation methods for hafnium and zirconium, purification to the pure metal and for comparison of properties with similar zirconium compounds. Although the properties of inorganic hafnium and zirconium compounds are generally similar, small differences in chemical behaviour are more evident in their organometallic compounds.[5,58]

The most common binary compounds of hafnium such as hafnium oxide, hafnium carbide and hafnium halides are discussed in the following sections. Hafnium oxide is the most stable of the hafnium compounds and is probably the Hf compound found in all the mineral sources. The chemistry of HfO_2 is therefore a very important part in method development for Hf beneficiation. Hafnium halides on the other hand are extremely important for the separation of hafnium from zirconium during the production and purification stages of hafnium. Hafnium carbides on the other hand has extremely useful industrial applications and are the most refractory binary compound known and important for its applications as lining material for high temperature furnaces.[22]

2.7.1. HAFNIUM OXIDE

There two known oxides of hafnium namely hafnium monoxide (HfO with Hf in a rare +2 oxidation state) and hafnium dioxide (HfO_2). However, HfO_2 is the only stable oxide of hafnium and it is easily attacked by concentrated hydrofluoric acid at elevated temperatures. The metal oxide is formed by the ignition of hafnium metal or other hafnium compounds such as hafnium carbide, tetrachloride, sulphide, boride, nitrite or hydrous oxide.[60] The commercially available hafnium oxide which are produced by the separation of zirconium and hafnium transforms into tetragonal structure at about 1 700 °C. The tetragonal form is then converted to a cubic fluoride structure at about 2 600°C. This can be stabilized by the addition of erbium oxide, yttrium oxide, calcium oxide or magnesium oxide at lower temperatures.[60] Crystalline phases of HfO_2 are given in **Figure 2.16**. HfO_2 also reacts with concentrated sulphuric acid or alkali bisulphates to form various sulphates and it reacts with carbon chloride to form hafnium tetrachloride. The metal oxide also reacts with alkaline

fluorosilicates to form alkali fluorohafnates or alkalies to form alkaline hafnates at elevated temperatures and also react with carbon above 1 500 °C to form hafnium carbide.[60]

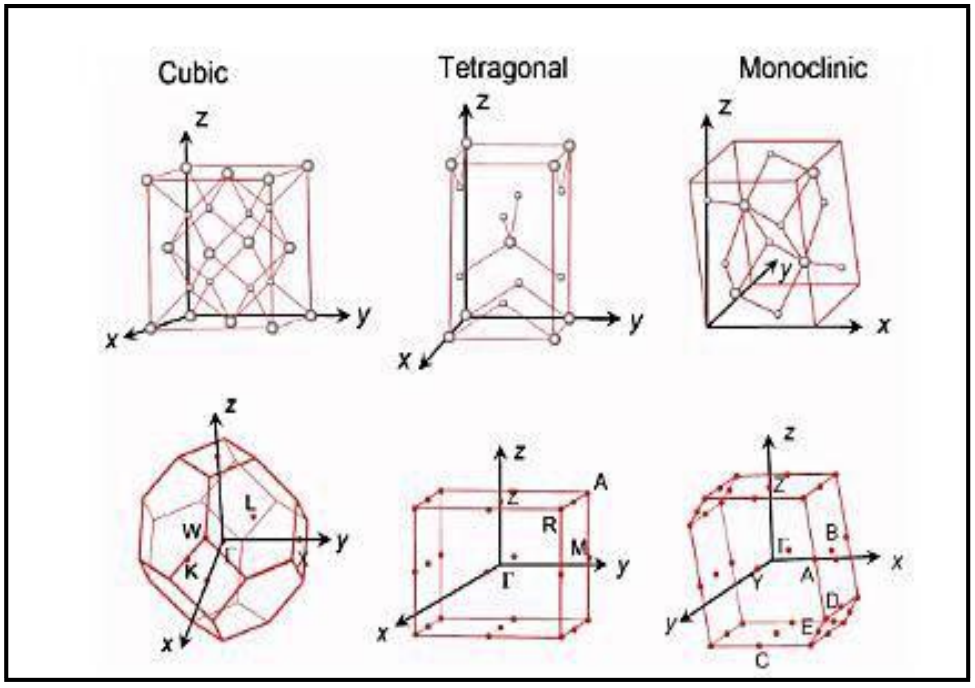

Figure 2.16: Crystal structures and their respective Brillouin zones for the crystalline phases of HfO_2.[61]

2.7.2. HAFNIUM CARBIDE

Hafnium carbide (HfC) is usually produced by the carbothermic reduction of hafnium oxide in an induction heated graphite-lined vacuum furnace. It can also be produced through the solid combustion in the presence of hydrogen and carbon at elevated temperatures.[62] Due to its extremely high melting point it can be referred to as ultra-high temperature ceramics.[62] The synthesis of HfC (see **Equation 2.14**) involves the reaction between carbon and some source of hafnium such as pure hafnium metal, metal hydride (HfH_2) or metal oxide (HfO_2). However, HfO_2 is considered to be the most suitable raw material for HfC synthesis mainly due to its affordability and thermodynamic stability. HfC powder is used for the fabrication of dense HfC ceramics.

[60] K. Othmer, Enclyclopedia of chemical technology, 12 , p. 445
[61] T.V. Perevalov, V.A. Gritsenko, S.B. Erenburg, A.M. Badalyan, H Wong,C.W. Kim, Journal of Applied physics, 101, p. 5 (2007)
[62] B. Matović, B Babić, D. Bučevac, M. Čebela, V. Maksimović, j. Pantić, M. Miljković, Ceramics International, 39, p. 719 (2013)

$$HfO_2 + 3C \rightarrow HfC + 2CO \quad (\mathbf{2.14})$$

Hafnium(IV) compounds usually exhibit high coordination numbers ranging between 4 and 8. This is mainly due to the relatively large and highly charged Hf_4^+ cation. In this regard the HfC compound consists of a nonstoichiometric carbide structure with the carbon atoms situated at the octahedral interstices of the hafnium metal lattice (see **Figure 2.17**).

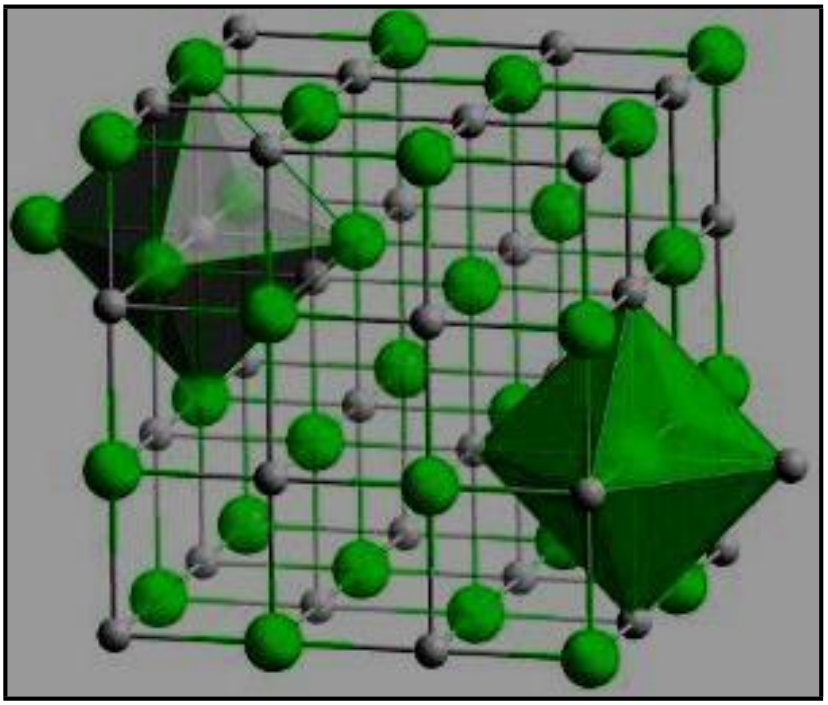

Figure 2.17: The crystal structure of Hafnium(IV) Carbide.[63]

2.7.3. HAFNIUM HALIDES

Metal halides in general are of great importance both in the primary-extraction processes of the metal from the different ores as well as in the refining of the metal to higher purity.[64] This is due to: (a) the high reactivity of halides towards many metal oxides to produce soluble metal halides, b) the difficulty in reducing many metal oxides to the metallic state, c) the metal halides are less refractory e.g. lower melting points and more prone to chemical manipulation, (d) oxides of carbide-forming metals cannot be reduced by carbon or carbon monoxide, (e) halogen compounds are less reactive (hydrolysis) than the oxides and can easily be separated and (f) metal halides have relatively high vapour pressures and distillation can be used to eliminate metallic impurities.[62]

[63] Hafnium Carbide, [Accessed 03-06-2015]. Available from: *http://www.chemicool.com/elements/images/300-hafnium-carbide.jpg)*

[64] Hafnium Production, [Accessed 11-06-2015]. Available from: (http://web.mit.edu/dsadoway/www/27.pdf).

Hafnium tetrachloride for example hydrolyses vigorously in water at room temperature to produce the stale oxide chloride (see **Equation 2.15**).

$$HfCl_4 + 9H_2O \rightarrow HfOCl_2.8H_2O + 2HCl \qquad \textbf{(2.15)}$$

$HfCl_4$ also reacts with electron donor ligands such as ethers, $POCl_3$ and CH_3CN and Cl^- ions to form six-coordinate species (see **Equation 2.16**).

$$HfCl_4 + 2Cl^- \rightarrow [HfCl_6]^{2-} \qquad \textbf{(2.16)}$$

The tetrachloride compound also reacts with diarsines to form $HfCl_4(diars)_4$ which has a dodecahedral type eight-coordinate structure. $HfCl_4$ can also react with carboxylic acids at 100 °C to form $Hf(RCO_2)_4$. Other halide compounds such as $ZrBr_4$, ZrI_4, $HfBr_4$ are comparable to $HfCl_4$, but with a main difference in the insolubility of HfF_4 in proton donor solvents such as methanol and CH_2Cl_2.[22]

Hafnium tetrafluoride is produced by the addition of stoichiometric amounts of hydrofluoric acid to hafnium oxychloride dissolved in 8M nitric acid. Hafnium tetrafluoride monohydrate is precipitated from the solution. The crystals are filtered and dried in a stream of anhydrous hydrogen fluoride gas.[22] Anhydrous hydrogen fluoride can substitute the chloride anions in hafnium tetrachloride or ammonium fluorohafnate can be heated to drive off ammonium fluoride to precipitate hafnium tetrafluoride.[22] A solution of hafnium tetrafluoride can also react with potassium fluoride in an acidic medium to crystalize potassium hexafluorohafnate (K_2HfF_6).[22] Other alkali metal hexafluorohafnates (Na_2HfF_6, Rb_2HfF_6 and Cs_2HfF_6) and the corresponding ammonium salts can be prepared in a similar way.[22] One of hafnium's major applications is in the nuclear industry (see **Chapter 1**, **Section 1.2**) due to its high neutron absorption coefficient. The metal is mainly used as control-rods in a nuclear reactor as well as in nuclear submarines (see **Figure 2.18**). In early reactors hafnium metal shaped in the form of a long crucible or hafnium covered in stainless steel were preferred as control rods due to their excellent hot-water corrosion resistance, good conductivity and its high thermal neutron absorption cross section. Currently, hafniumcontaining control rods have been replaced by stainless steel-clad silver-indium-cadmium as well as stainless steel-clad boron carbide control rods in some commercial nuclear power plants[22] due to the high cost and low availability of hafnium.

Hafnium is also used in gas filled and incandescent lights. It has other applications such as in plasma welding and arc cutting, microprocessors, CVD/PVD coating and lasers.[22] Some photographic flashbulbs also require the use of shredded hafnium foil rather than zirconium foil due to a higher intrinsic colour temperature and a greater light output that hafnium provides.[66,67]

Figure 2.18: Nuclear reactor rods being used in a submarine.[65]

Hafnium is also largely used as an alloying additive (1-2 %) in the production of high temperature nickel-based super alloys, due to its high melting point (2150 °C) and is used in the manufacturing of turbine blades in the combustion zone of jet aircraft engines.[22] Moreover, hafnium acts as an alloy component with elements such as niobium, tantalum and molybdenum. Hafnium containing niobium-based alloys are used as coatings for cutting tools while hafnium-tantalum-carbide has been used in the fabrication of rocket engine thruster nozzles. For example the main engine of the Apollo Lunar Modules in C130 consists of 89 % niobium, 10 % hafnium and 1 % titanium (see **Figure 2.19**). Hafnium is an excellent refractory material and produces excellent binary compounds when alloyed with elements such containing tantalum and molybdenum. Hafnium carbide and hafnium nitrite contributes highly to the market for refractory materials around the world due to their high melting points.[66]

[65] Hafnium, [Accessed 08-06-2015]. Available from: http://www.chemicool.com/elements/images/300-nuclear-sub.jpg

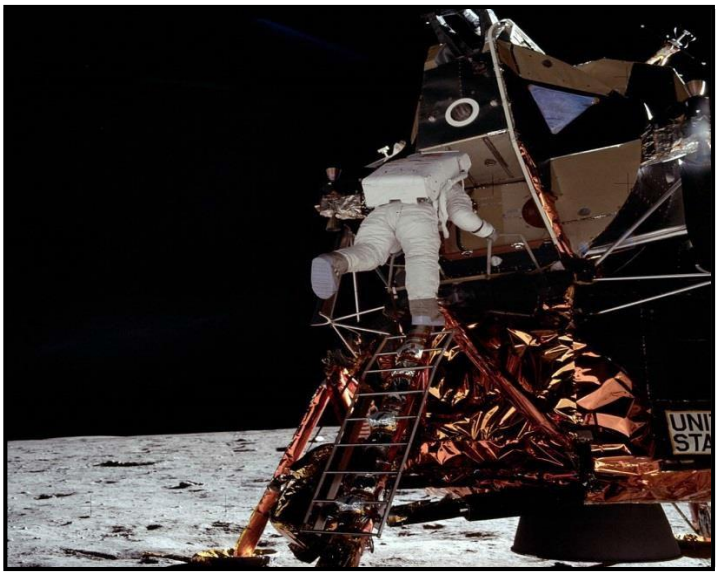

Figure 2.19: Hafnium-containing rocket nozzle of the Apollo Lunar Module in the lower right corner.[67]

The uses of hafnium alloys have been recommended to protect spent nuclear equipment and waste such as fuel storage racks, tanks as well as piping due to its inertness and ability to absorb neutrons.[67]

Hafnium dioxide also has important industrial uses and has been used as a special refractory oxide due to its high refractive index and low light absorption. The metal oxide is also suitable to be used as a hard, scratch-free coating for optical elements such as metal mirrors which are used in the near ultraviolet to infrared part of the spectrum.[67] Sputtering targets of hafnium and hafnium oxide are also used for coatings and specialised electronic applications in microprocessors.[57]

Hafnium tetrachloride has been used in the preparation of the first type of catalysts that produce high yields of high molecular mass isostatic polypropylene known as hafnium metallocene Ziegler-Natta-type catalysts. Hafnium tetrafluoride can also be used in the glass cladding of some heavy metal fluoride.[22]

[66] Hafnium: Small Supply, Big Applications, [Accessed 08-06-2015]. Available from: http://www.hardassetsinvestor.com/features/2572-hafnium-small-supply-big-applications.html?start=1 [67] Hafnium, [Accessed 08-06-2015]. Available from: http://en.wikipedia.org/wiki/Hafnium#/media/File:Apollo_AS11-40-5866.jpg

2.8. CONCLUSION

The unique properties of hafnium such as its high melting point and ability to capture neutrons make it an element of great interest and value in various industrial applications particularly in aerospace and nuclear industries. From the above discussion, it seems the possible applications of the metal in new technology may in future put demand stresses in the market compared to its supply growth. This market imbalance can only increase due to the difficulty in the extraction of hafnium and separation from zirconium minerals. Therefore, much effort is required in separating and producing hafnium of high purity. However, it is important to first developed robust and accurate analytical techniques for the accurate determination of Hf in the different matrices as well as final products. It is also important that the developed methods are cost-effective and less time consuming.

3 Dissolution and quantification techniques used for hafnium containing compounds - Literature review

3.1. INTRODUCTION

In a chemical analytical process there are 4 steps that can be identified for the quantitative determination of a sample namely; i) sampling, ii) sample preparation, iii) analyte isolation and iv) the quantitative determination of the isolated component/s.[58] Since the discovery of hafnium, by nature a chemically inert element, researchers have embarked on several scientific studies to develop effective digestion techniques for the dissolution of different hafnium raw materials such as zirconium ores. In order to quantitatively determine hafnium in the ores, samples or alloys as well as their impurities by utilizing wet chemistry techniques, it is of great importance to get the samples into solution. The most commonly used method for the dissolution of zirconium ores involves the use of HF, which is extremely toxic and allows a very limited exposure to operators as excessive exposure to it may lead to fatalities. Dissolution by HF is expected to dissolve all the hafnium containing compounds such as hafnium oxides. At the same time researchers also gave considerable attention to the accurate determination of Hf in different sample matrices. Analytical techniques which have been investigated include inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (MS), neutron activation analysis (NAA) and X-ray
fluorescence (XRF).[59]

This chapter gives an overview on available analytical methods which have been employed for the dissolution and determination of hafnium and other trace elements in various samples such as zirconium compounds, seawater and geological samples. A great challenge due to the physical and chemical similarities of hafnium and zirconium not only possess great challenge

[58] J. Minczewski, ***International Journal of Pure and Applied chemistry,*** 10, p. 567 (2009)
[59] S.M. Hasany, F.Rashid, A. Rashid, H. Rehman***, Journal of Radioanalytical and Nuclear Chemistry,*** 142, p. 505 (1990)

in the separation of these elements, but also the accurate quantification of the elements due to spectral interferences and coincidences.

3.2. METHODS OF DIGESTION

Researchers have investigated various digestion techniques for the decomposition of numerous samples which include minerals, metals and metal alloys containing hafnium. The digestion techniques that have been employed include flux fusion, acid leaching or acid dissolution and acid-assisted microwave digestions with various acids, salts and the combinations thereof.[60] The following section is an overview of the applications of these digestion techniques to hafnium containing samples and the results obtained with them.

3.2.1. OPEN VESSEL ACID DIGESTION

Open vessel acid digestion or wet ashing is one of the simplest and easiest ways to dissolve samples and is usually the starting point or the first method to be evaluated as dissolution technique. These methods only require the addition of acids at room or elevated temperatures to the sample to afford dissolution.

Bahattin[11] used a combination of HF and H_2SO_4 in the presence of ammonium sulphate to decompose zirconia. The addition of $(NH_4)_2SO_4$ to the reaction mixture was to elevate the H_2SO_4 boiling point and hence to try and improve its efficiency as a disintegration agent. Results indicate that the dissolution of the sample was still incomplete, resulting in poor Zr recoveries. Bastius[61] used a two-step procedure for the decomposition of zirconia. The samples were initially treated with a H_2SO_4 and $(NH_4)_2SO_4$ mixture followed by a HF and NH_4F mixture. Irrespective of the acid medium used, dissolution of zirconia by open vessel acid digestion remained ineffective with respect to the total dissolution of the sample and poor Zr recoveries were obtained. The dissolution method developed by Bahattin[11] and Bastius[61] focused more on the dissolution and Zr recoveries thereof of in zirconium dioxide and little attention was really given to the hafnium in the samples.

[60] Sample Dissolution, [Accessed 11-09-2015]. Available from: http://www.epa.gov/radiation/docs/marlap/402-b-04-001b-13-final.pdf
[61] H.Bastius, ***Ceramic Forum International***, 61, p. 140 (1984)

Liu *et al*.[62] investigated open-vessel acid digestion methods using HF-HNO_3-$HClO_4$ and HF-HNO_3-H_2SO_4 acid combinations for the dissolution of different geological samples. None of the methods could completely dissolve the sample or leach all the Hf and Zr in these geological samples. The dissolved/leached hafnium content was found to be in the range of 2.00 - 3.77 % in rocks, 2.41 - 4.08 % in stream sediments and 2.42 - 3.41 % in soils using both methods.

In another study, Roy *et al.*[63] used open vessel acid digestion with HF-HNO_3-$HClO_4$ for the dissolution of geological samples such as STM-1, NIM-L and AC-E. These samples did not completely dissolve and hafnium recoveries in the range of 80.0 – 92.3 % were reported and compared to the results obtained using flux fusion method (see **Section 3.2.2, Figure 3.1**). Recoveries of other elements such as Ti, Zr, Nb, Ta, Th and U in STM-1, NIM-L and AC-E samples were also generally inaccurate using open vessel digestion.

Kabannik and Popova[64] developed digestion methods involving a combination of flux and acid dissolution of hafnium germanides which are chemically very stable compounds. Decomposition of the germanides of various transition metals including titanium, zirconium and hafnium was achieved using various fluxes which included alkali and sodium peroxide, the sintering of a mixture of calcium oxide and potassium nitrate or sintering of calcium oxide and magnesium nitrate. Hafnium germanide was dissolved in a mixture of HF and HNO_3 and sintered with various mixtures such as barium carbonate and calcium oxide, magnesium oxide and sodium carbonate. Recoveries of 4.97, 4.37 and 2.86 % were reported for titanium, zirconium and hafnium in Ti_5Ge_3, Zr_5Ge_3 and Hf_5Ge_3 respectively. These results clearly indicate that the dissolution of the germanides is a great challenge, as indicated by this less than satisfactory recovery for the germanide, titanium, hafnium and zirconium.

3.2.2. DIGESTION BY FUSION

Flux fusion is a very popular dissolution technique in which highly inert materials/minerals are dissolved at elevated temperature in a water free environment. Alkali salts are normally heated to temperature above the melting point which then creates a highly concentrated, ionic liquid which can react either as a base/acid or oxidising agent to affect dissolution.

[62] Y.X. Liu, Q.X. Li, N. Ma, X.L. Sun, J. F. Bai, Q. Zhang, ***American Chemical Society***, 86, p. 11575 (2014)
[63] P. Roy, V. Balaram, A. Bhattacharaya, P. Nasipuri, M. Satyanarayanan, ***Current Science***, 93, pp. 1122 - 1125 (2007)
[64] G.T Kabannik, O.I. Popova, Chemical properties and analysis of refractory compounds, pp.54 - 56(1972)

Lundell and Knowles[65] reported the successful digestion of zircon and baddeleyite as hafnium source using borax ($Na_2B_4O_7.10H_2O$, melting point (mp) = 743 °C) fusion in a platinum crucible over a Meker burner. The resulting melt obtained from the borax fusion of the zircon and baddeleyite was thereafter dissolved in dilute HCl to ensure complete dissolution. Gaines[66] also recommended borax fusion for the digestion of hafnium raw materials. However, his method included the use of a fusion furnace and performed the fusion at a temperature between 1050 – 2000 °C for a period of 30 min instead of the Meker burner approach. He also used a different acid medium (mixture of HNO_3 and HF) to dissolve the melt to achieve complete dissolution.

Lötter *et al.*[67] performed flux fusion digestion using lithium tetraborate ($Li_2B_4O_7$, mp = 917 °C) to dissolve zircon reference sample (SARM62) and PDZ (plasma-dissociated zircon) in a platinum crucible at a fusion temperature of 1100 °C for 4 h. The melt was dissolved in dilute nitric acid. Lötter *et al.*[67] reported the chemical composition (obtained using ICP-OES) of both the dissolved SARM62 and PDZ and compared their results with the certified values. The results are reported in **Table 3.1**. Although good Zr recoveries (102.8 % in SARM62 and 99.5 % in PDZ) were obtained, the method was not suitable for the determination of Hf and highly unreliable Hf recoveries of 129.8 and 121.1 % in SARM62 and PDZ respectively were reported.

[65] G.E.F. Lundell, H.B. Knowles***, Journal of American Chemical Society***, 42, pp. 1445 - 1448 (1920)
[66] Samples Containing Zirconium or Hafnium, [Accessed 11-09-2015]. Available from: http://www.inorganicventures.com/samples-containing-zirconium-or-hafnium
[67] S. Lötter, W. Purcell, J.T. Nel, E. Snyders, ***The Southern African Institute of Mining and Metallurgy***, 112, pp. 73 - 75 (2012)

Table 3.1: Results obtained for the analysis of SARM62 and PDZ.[67]

Component	SARM62 certified value (mass %)	PDZ certified value (mass %)	SARM62 result (mass %)	PDZ result (mass %)
ZrO_2	64.2	65.3	66.0	65.0
SiO_2	32.8	32.6	44.0	27.0
HfO_2	1.31	1.33	1.70	1.61
TiO_2	0.13	0.12	0.15	0.41
Al_2O_3	0.88	0.07	1.40	0.60
Fe_2O_3	0.06	0.07	0.14	0.60

Roy *et al.*[68] used lithium metaborate fusion ($LiBO_2$, mp = 849 °C) digestion followed by the dissolution of the melts in HNO_3. This method also afforded complete sample dissolution and improved elemental recoveries were obtained when compared to open vessel acid digestion (incomplete dissolution) (see **Section 3.21**) Hafnium recoveries of 97.9(5), 98(4) and 102.4(6) % in STM-1, NIM-L and AC-E were reported. The accuracy of the results for all the elements analysed was determined by comparison of the experimental obtained percentages to the certified values as indicated in **Figure 3.1**. The analytical results generally indicated that the fusion digestion procedure produced more accurate results compared to the open vessel acid digestion due to complete dissolution of the sample resulting melt.

[68] P. Roy, V. Balaram, A. Bhattacharaya, P. Nasipuri, M. Satyanarayanan, ***Current Science***, 93, pp. 1122 - 1125 (2007)

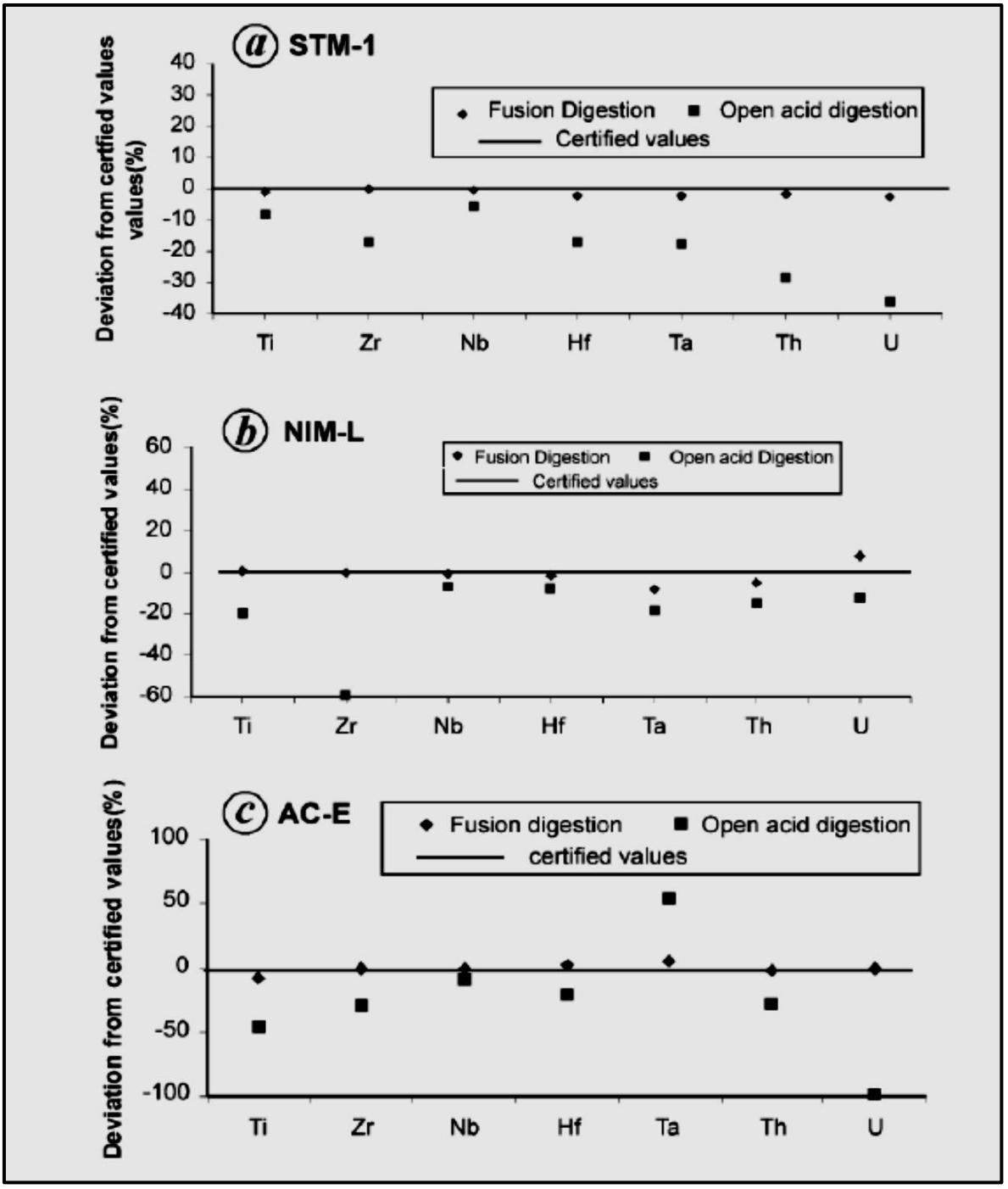

Figure 3.1: Deviation of values of open vessel and fusion digestion technique from certified values.[68]

Totland *et al.*[69] used lithium metaborate fusion for the digestion of different geological samples which included STM-1. The resulting melts were dissolved using a mixture of HF and $HClO_4$. The solutions were analysed using ICP-MS and Hf recoveries of 103.9(7) % in STM-1 were reported.

[69] M. Totland, I. Jarvis, K.E. Jarvis, ***Chemical Geology***, 95, pp. 39 - 47 (1992)

3.2.3. MICROWAVE ACID-ASSISTED DIGESTION SYSTEM

The ineffectiveness of open vessel acid digestion in ensuring a complete dissolution of zirconia and other refractive elements/ores have that been discussed in the previous paragraph. Microwave assisted digestion is one of the newer digestion techniques. The ability of this technique to digest samples at higher pressure and temperature in a contained environment with a minimum of solvent/acid adds to its efficiency and popularity as a dissolution method.

Ma and Li[70] developed a microwave acid-assisted digestion method for the dissolution of high purity zirconium dioxide which contains trace amounts of hafnium. Their study involved the use of different reagents including $(NH_4)_2SO_4$ and H_2SO_4 and HNO_3 and H_2SO_4 acid combinations at different microwave conditions. Complete zirconia dissolution was accomplished at a power of 630 W and 30 min reaction time using a mixture of $(NH_4)_2SO_4$ and H_2SO_4. Trace impurities in the zirconium dioxide samples were determined with ICP-OES and were found to be Fe, Hf, Mn, Na, Si and Ti. The developed microwave acid-assisted digestion method with a mixture of H_2SO_4 and $(NH_4)_2SO_4$ coupled with wavelet transform (a mathematical method used to eliminate spectral interferences) was found to be a fast and satisfactory quantitative determination of the low level impurities were obtained. The hafnium concentration was found to be approximately 100 times more than other recovered impurities (as expected). It was concluded that hafnium was the main impurity in zirconium dioxide samples (see **Chaper 1, Section 1.1**). Totland *et al.*[69] also used microwave acid-assisted digestion for the decomposition of geological samples including STM-1 and unexpectedly high hafnium recoveries of 107.5(3) % were reported in the STM-1 sample

In another study, Lötter *et al.*[67] quantitatively determined the amount of Hf, Zr, Al and Fe in zircon samples. In this study, a zircon sample was digested using a mixture of $(NH_4)_2SO_4$ and H_2SO_4. The digestion was performed at constant power of 1200 W with different heating temperatures and digestion periods. The results obtained by Lötter *et al.*[67] indicated that the choice of reagents has a great influence on the recovery of these elements. Microwave digestion using H_2SO_4 produced improved Hf and Zr recoveries in SARM62 and PDZ

[70] X. Ma, Y. Li, ***Analytica Chimica Acta***, 579, pp. 47 - 50 (2006)

samples compared to wet ashing and slightly improved Hf and Zr recoveries with combination of H_2SO_4 and $(NH_4)_2SO_4$ with microwave digestion (see **Table 3.2**). However, even these improved recoveries were still highly inaccurate contrary to reports by Bahattin.[11] He reported that mixtures of H_2SO_4 and $(NH_4)_2SO_4$ gave better Zr and Hf recoveries compared to the dissolution with only H_2SO_4, due to the elevated boiling point of H_2SO_4. Comparable recoveries were obtained for Hf and Zr as well as for Al and Fe. A relatively higher recovery of 83.77 % for Hf was obtained in PDZ in the absence of $(NH_4)_2SO_4$. Generally, the results obtained by Lötter *et al.*[67] for the microwave acid-assisted digestion technique have indicated that H_2SO_4 alone is a preferred dissolution reagent for both Zr and Hf. In addition, these results also showed a slight difference in solubilities of Hf and Zr in H_2SO_4 under specified microwave conditions with Hf being the more soluble constituent. Lötter *et al.*[67] also investigated the influence of the concentration of $(NH_4)_2SO_4$ on the leaching of PDZ constituents. The graphical representation of a relationship between the recovered content of hafnium and zirconium in SARM62 with varied amount of ammonium sulphate is shown in **Figure 3.2**. These results indicated that the percent recoveries of both Hf and Zr increased slightly with increasing the amount of $(NH_4)_2SO_4$. As similar relationship was observed for the amount of aluminium and iron that were recovered.

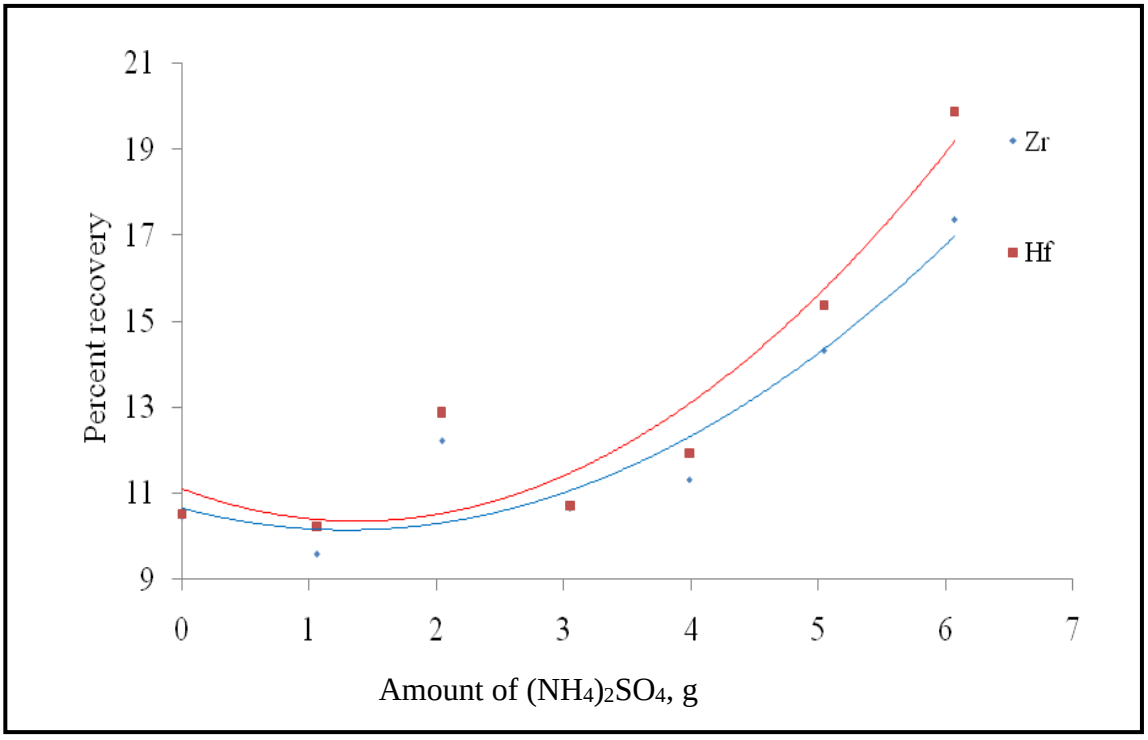

Figure 3.2: Zr recoveries in SARM62 as a function of the amount of $(NH_4)_2SO_4$ in the reaction mixture (Time = 30 min, temperature = 240 °C)

Table 3.2: The effect of varying amounts of $(NH_4)_2SO_4$ on the recovery of different elements in zircon samples.[67]

Sample	Mass $(NH_4)_2SO_4$, g	Percentage Recovery, %			
		Zr	Hf	Al	Fe
SARM62	0	10.44	10.51	94.19	99.52
SARM62	1.0596	9.57	10.23	145.58	140.94
SARM62	2.0449	12.21	12.88	158.20	149.26
SARM62	3.0507	10.64	10.71	140.33	142.69
SARM62	3.9895	11.30	11.94	130.20	140.47
SARM62	5.0484	14.31	15.36	145.03	153.57
SARM62	6.0737	17.36	19.88	141.81	138.73
PDZ	0	57.79	83.77	28.17	46.74

The effect of time on the digestion of zircon samples and Zr recovery using microwave acid-assisted dissolution was also included in the study by Lötter *et al.*[67] and the results are shown in **Figure 3.3**. The results clearly indicate that the Zr recovery improves with increased reaction time which range from 10 to 180 min. Again, this study paid little attention to the Hf recoveries in the zircon mineral.

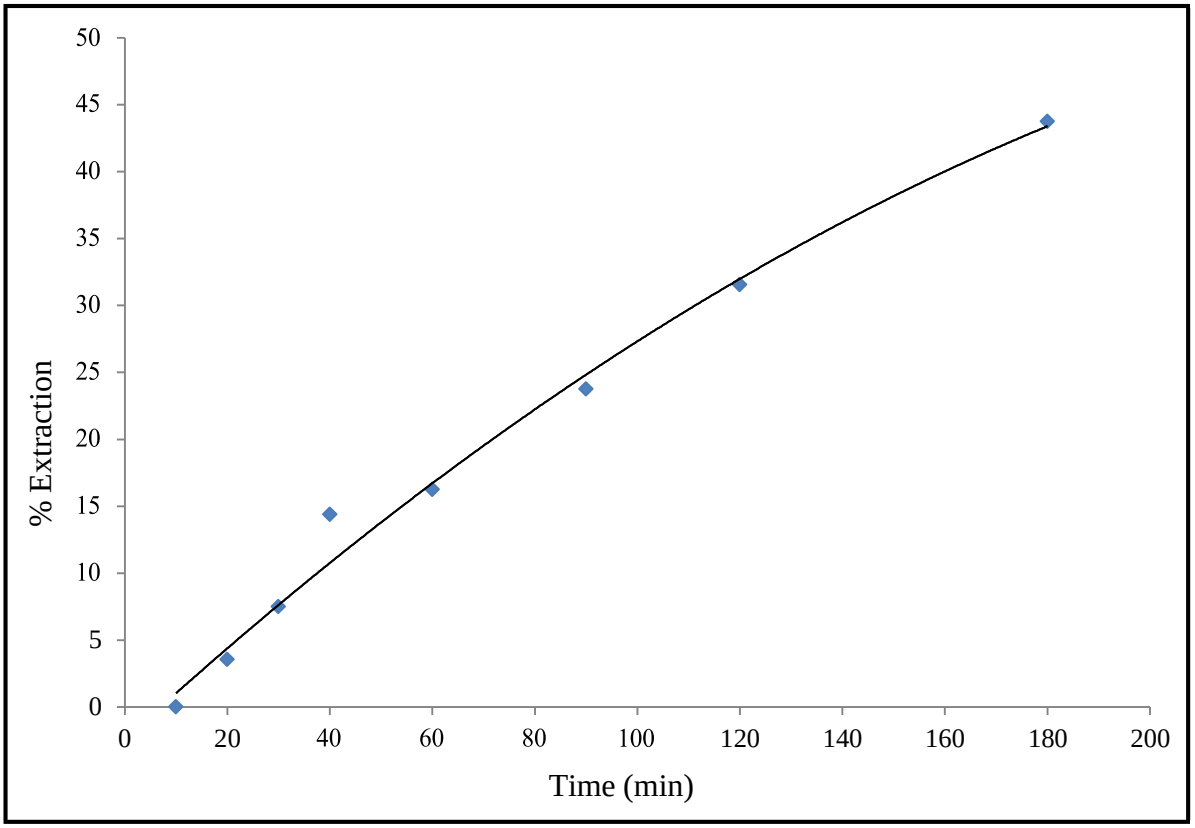

Figure 3.3: The effect of time on the Zr dissolution in PDZ in microwave system.[67]

3.2.4. DISSOLUTION OF HAFNIUM OXIDE BY RADIOACTIVE TRACER TECHNIQUE

Cooley and Banks[71] conducted a study on the aqueous solubility of hafnium oxide by radioactive isotope technique. Their study involved the investigation of the solubility of hafnium oxide in water by using hafnium 181, a α and γ emitter with a half-life of 46 days. Their results indicated that the solubility of HfO_2 increased after the addition of sodium sulfate or ammonium nitrate to the thermostated water-HfO_2 mixture. The dissolution was performed at different temperatures and the results indicated an increase of HfO_2 solubility with increase in temperature (see **Table 3.3)**

[71] R.A. Cooley, H.O. Banks, ***Journal American Chemical Society***, 73, p. 4022 (1951)

Table 3.3: Solubility of HfO_2 in H_2O at various temperatures.[71]

Temperature, °C	Mass of HfO_2 soluble in water, mg
34.6	2.3
49.7	2.8
60.0	2.9
70.3	3.2
89.7	4.7

These results suggest that a linear relationship exists between the temperature and the solubility of hafnium oxide (see **Figure 3.4**).

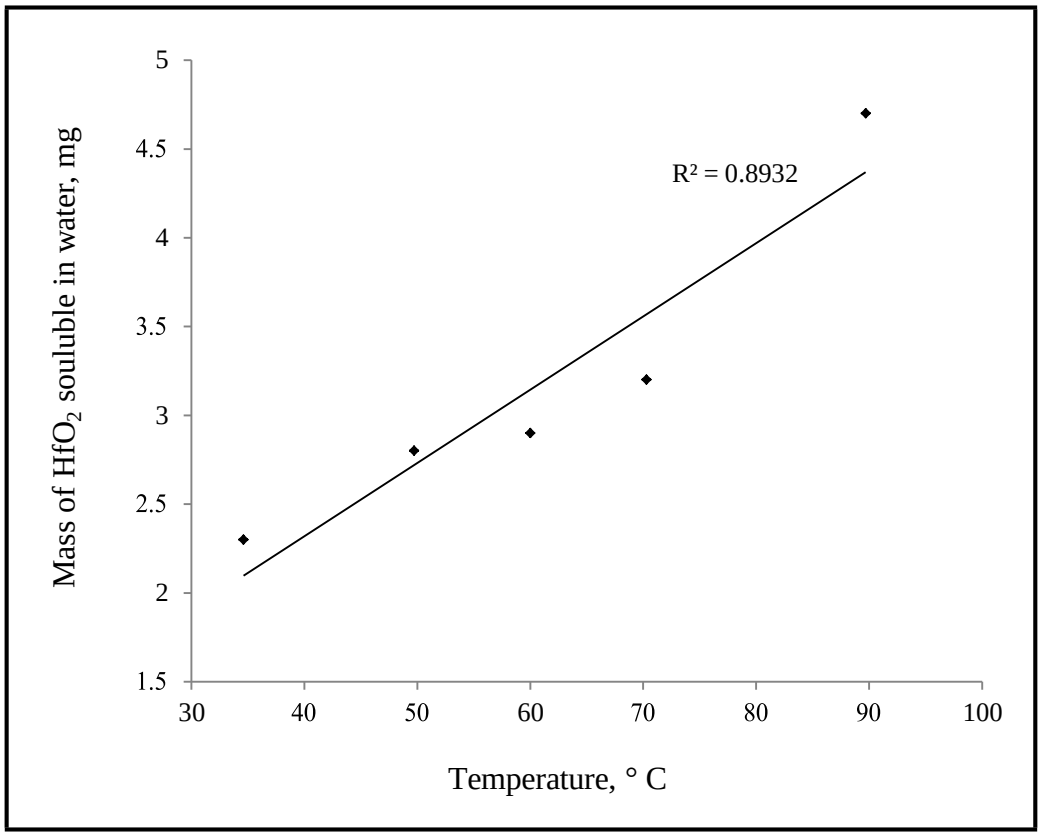

Figure 3.4: The relationship between temperature and the solubility of hafnium oxide in water

3.3. QUANTIFICATION OF HAFNIUM IN DIFFERENT CHEMICAL COMPOUNDS

Different analytical techniques which include ICP-OES, ICP-MS, NAA and XRF have been used to quantify hafnium in different samples which include zircon material ores, pure inorganic samples and metals. The literature survey of various spectrometric techniques used to quantify hafnium containing compounds is discussed in the following paragraphs.

3.3.1. DETERMINATION OF ZR/HF IN DIFFERENT SAMPLES USING ICP-OES AND ICP-MS

ICP-OES and ICP-MS are the most popular methods used for the analytical determination of hafnium in samples which include zirconium ores, geological and water samples. Smolik *et al.*[72] used ICP-OES to quantitatively determine hafnium in various zirconium inorganic compounds. The hafnium concentrations in the zirconium compounds are shown in **Table 3.4**. The hafnium content ranging from 2.49 to 3.17 % was reported which coincided with the concentration of hafnium normally found in nature (1 and 3 %, see **Chapter 1.1**). The results clearly indicate that the hafnium was not removed/separated from the Zr prior to the synthesis of these inorganic compounds cited in **Table 3.4**.

Table 3.4: Hafnium content in various zirconium compounds at various wavelengths by ICP-OES.[72]

Compound	Hf content as determined at different wavelengths, %					
	196.423 nm	227.716 nm	227.716 nm	232.247 nm	235.122 nm	Average
$ZrOCl_2.8H_2O$	2.50	2.46	2.50	2.49	2.49	2.50(1)
$Zr(SO_4)_2.4H_2O$	2.65	2.66	2.65	2.65	2.66	2.65(1)
$Zr(NO_3)_4.5H_2O$	3.14	3.16	3.17	3.16	3.20	3.17(2)

From **Table 3.4** it can also be concluded that the determination of Hf is not sensitive at the wavelength at which it was determined.

[72] Determination of hafnium in zirconium compounds using ICP-OES, [Accessed 16-09-2015]. Available from: http://www.pg.gda.pl/chem/InneJednostki/PTChem_/Roczniki_2007/smolik_jakobik.pdf

Smolik *et al.*[72] also used ICP-OES to investigate the effect of aqueous biphasic systems containing saturated solutions of salts such as sodium sulphate 1.5 %, sodium citrate (Na_3Cit) 4 % and aqueous solution of polyethylene glycol (PEG) 2.5 % on Hf determinations and the results are as shown in **Table 3.5**. These results indicated that solutions with sodium citrate (Na_3Cit) improve hafnium recoveries at all wavelengths. Their results indicated that the solution with 1.5 % Na_2SO_4 gave higher than expected hafnium recoveries (105.2 – 106.5 %). These high Hf recoveries could be due to contamination of the Hf sample by this additive (flux salt) or the influence of easily ionised Na which strongly emits (the yellowing flame) in the visible spectrum at these temperatures which may have resulted in enhanced analyte intensities.[73] The rest of the other salts produced lower Hf recoveries (see **Table 3.5**).

Table 3.5: Effect of different solutions on Hf determination in Zr matrix using ICP-OES.[72]

Λ, nm	**227.7**	**227.7**	**232.2**	**235.1**
Hf recovery, %				
PEG 2.5 %	82.2	83.0	81.8	83.8
PEG 5%	72.0	72.0	72.1	74.5
Na_2SO_4 1.5 %	106.5	105.2	106.4	105.2
Na_3Cit 4 %	93.0	92.0	92.7	92.3

Shariati and Yamini[74] used ICP-OES to quantitatively determine zirconium and hafnium using a cloud point extraction process (CPE) in which aliquots solution containing quinalizarine and Triton X-114 were kept at the pH of about 6. The wavelength lines of 282.023 and 343.823 nm were chosen for determination of hafnium and zirconium respectively. The effect of reagent concentration on the extraction of Zr and Hf complexes is shown in **Figure 3.5**.

[73] J.N. Baloyi, ***The Southern African Institute of Mining and Metallurgy***, p. 1 (2006)
[74] S. Shariati, Y. Yamini, ***Journal of Colloid and Interface Science***, 298, pp. 421 - 422 (2006)

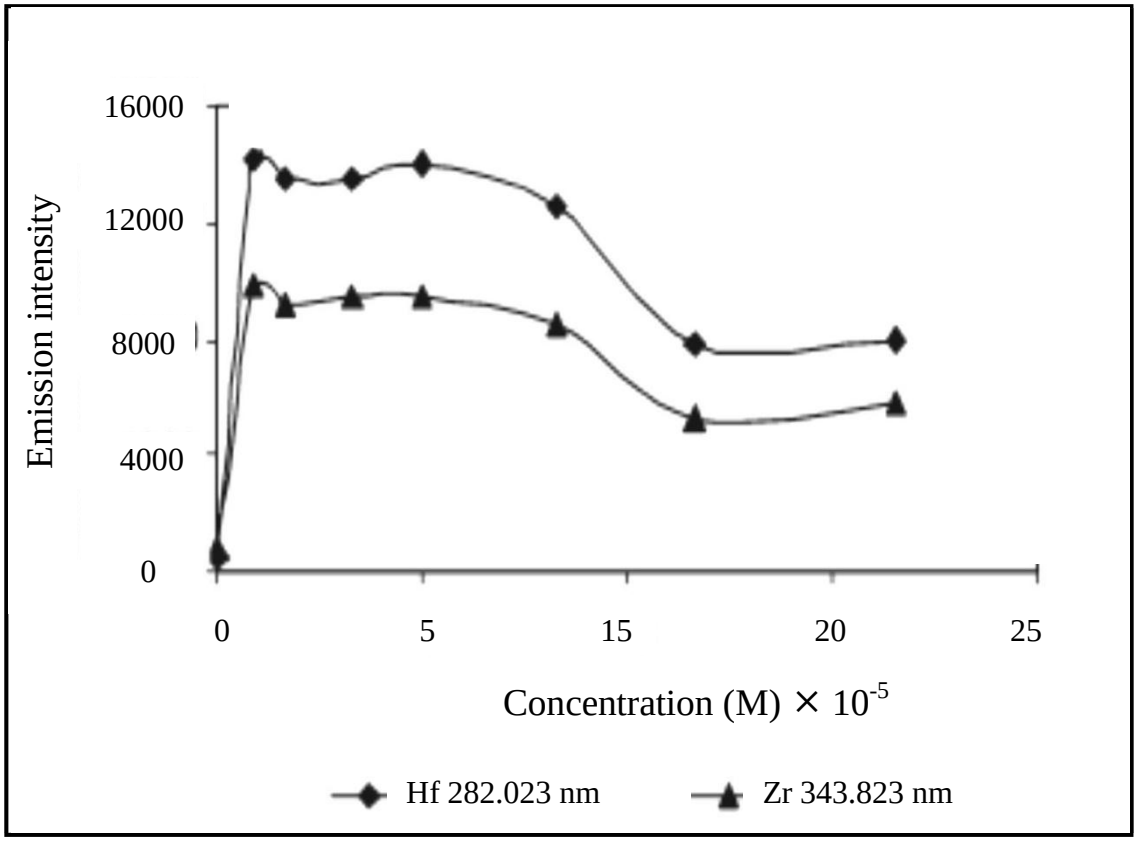

Figure 3.5: The effect of Triton X-114 reagent concentration on the extraction of Zr and Hf complexes.[74]

The effect of different metal ions on the determination of Zr and Hf with ICP-OES is shown in **Table 3.6**. Shariati and Yamini[74] reported hafnium and zirconium recoveries in excess of 95 % for most of the elements, but poor recoveries of 50.2, 77.4 and 90.2 % in the presence of Mn^{2+}, Fe^{3+} and Pb^{2+} respectively were reported. Zirconium recoveries were also found to be affected by the presence of the same elements. Hanh and Joseph[75] also studied the effect of other cations during the analytical determination of Hf and reported recoveries of 100 and 99.96 % in the presence of titanium (IV) and thorium (IV).

[75] R.B. Hanh, P.T. Joseph, ***Analytical Chemistry***, 28, pp. 2019 - 2020 (1956)

Table 3.6: Effect of interfering ions on the recovery of hafnium and zirconium.[74]

Ions	Concentration, ppm	Ion/ Zr or Hf ratio (w/w)	Recovery, %	
			Hf	Zr
Alkaline-earth metals	200	1000	95.1	97.4
Cd^{2+}	200	1000	97.4	99.2
Co^{2+}	200	1000	102.7	98.6
Ag^{+}	200	1000	102.4	96.7
Hg^{2+}	200	1000	95.4	97.0
Cr^{3+}	200	1000	100.0	96.8
La^{3+}	200	1000	96.5	88.4
	180	900	96.0	96.1
	150	750	96.1	99.2
Mn^{2+}	200	1000	50.2	65.1
	150	750	97.4	97.9
Cu^{2+}	200	1000	99.0	95.0
Ni^{2+}	200	1000	100.7	97.0
Zn^{2+}	200	1000	95.8	94.0
Pb^{2+}	200	1000	90.2	94.0
Al^{3+}	200	1000	97.0	96.6
Fe^{3+}	200	1000	77.4	75.0
Fe^{2+}	200	1000	102.1	101.7

Smolik and Jakobik-Kolon[76] separated Hf and Zr on a diphonix chelating ion exchange resin and subsequently determined the concentrations of Hf (196.36 nm) and Zr (251.304 nm) using ICP-OES and ICP-MS and the analytical results are given in **Table 3.7**. In general, the

[76] M. Smolik, A. Jakobik-Kolon, ***Analytical Chemistry,*** 81, p. 2686 (2009)

Hf results obtained with the two methods were very similar indicating similar capabilities in quantifying Hf in the samples.

Table 3.7: Hafnium recovery in the different samples by ICP-OES and ICP-MS.[76]

Samples	Hafnium recovery, %	
	ICP-OES	ICP-MS
0 (feed solution)	80	82
3 (2.2 – 3.3 BVs)	n.d	66
4 (3.3 – 4.4 BVs)	33	31
5 (4.4. – 5.5. BVs)	12	12
6 (5.5. – 6.6 BVs)	12	12
7 (6.6 – 7.7 BVs)	22	16
8 (7.7 – 8.8 BVs)	24	31
9 (8.8 – 9.9 BVs)	30	31
10 (9.9 – 11.0 BVs)	40	41

n.d= not determined, or not reported

Roy *et al.*[68] studied the quantification of Ti, Zr, Hf, Th, and U in various samples including STM-1 and NIM-L (reference material) using ICP-MS after sample digestion using two different dissolution methods namely, open vessel and lithium borate fusion digestion (see **Figure 3.1, Section 3.2.1**). In another study, Totland *et al.*[69] used a mixture of HF and $HClO_4$ (see **Section 3.2.1**) for the dissolution of STM-1 (Hf containing geological sample) and subsequently analysed the solution using ICP-MS to quantitatively determine the trace elements, including hafnium in the sample. A hafnium recovery of 103.9(7) % in STM-1 was reported and which is comparable to the 97.9(6) % Hf reported by Roy *et al.*[68] for the same sample in HNO_3 solution (see **Section 3.2.1**).

Liu *et al.*[62] quantitatively determined hafnium in different geological samples using ICP-MS. Open-vessel acid digestion with $HF\text{-}HNO_3\text{-}HClO_4$ and $HF\text{-}HNO_3\text{-}H_2SO_4$ (see **Section 3.2.2**) were investigated. Hafnium content in the ranged between 2.00 - 3.77 %

in rock samples, 2.41 - 4.08 % in water stream sediments and 2.42 - 3.41 % in soils. Detection limit of 0.04 ʒg/g were reported.

McKelvey and Orians[77] used ICP-MS to quantitatively determine the amount of dissolved zirconium and hafnium in seawater. Prior to the ICP-MS analysis, the chelating ion-exchange resin was used for the extraction/pre-concetration of the dissolved Zr and Hf in the seawater. The detection limits of Zr and Hf were 0.21 and 0.03 pmol/kg respectively. The reported Zr concentrations were in the range of 41.8 pmol/kg to 280 pmol/kg with relative standard deviations (RSDs) between 2.5 and 7 %. Hafnium concentrations on the other hand were in the range of 0.28 pmol/kg to 1.4 pmol/kg and relative standard deviation of 9 and 22 % were reported.

In another study, Raso *et al.*[78] used the ICP-MS for the quantitative determination of various elements including hafnium in seawater. They used co-precipitation with iron-hydroxide to increase the elemental concentrations in seawater prior to ICP-MS measurement. The recoveries of zirconium, hafnium, yttrium and lanthanides ranging between 75 and 117 % with a relative standard deviation smaller than 10 % were reported.

3.3.2. DETERMINATION OF HAFNIUM IN DIFFERENT SAMPLES USING XRF AND NAA TECHNIQUES

Ricci[79] developed a XRF method for the determination of hafnium and zirconium in H_2SO_4 solutions. The solutions of Zr and Hf were pre-concentrated with iron solution to yield a transparent sample prior to its analysis. Hafnium recoveries of 100 and 100.9 % were reported for two samples (II and III) and 86.2 and 95.3 % for two other samples (I and IV) (see **Table 3.8**). Zirconium recoveries on the other hand ranged between 91.3 and 101.6 % and detection limits were calculated as 0.4 and 1.2 pg mL^{-1} for Zr and Hf respectively.

[77] B.A. McKelvey, K.J. Orians, ***Marine Chemistry***, 60, pp. 253 - 255 (1998)
[78] M. Raso, P. Censi, F. Saiano, ***Talanta***, 116, pp. 1087 - 1088 (2013)
[79] E. Ricci, ***Analytical Chemistry***, 52, pp. 1709 - 1710 (1980)

Table 3.8: XRF determination of Zr and Hf using $Fe(OH)_3$ co-precipitation method.[79]

Sample no:	Known concentration, ppm		Experimentally obtained concentration, ppm		Recovery, %	
	Zr	Hf	Zr	Hf	Zr	Hf
I	69.1	2.9	68.4	2.5	98.9	86.2
II	34.5	57.0	34.9	57.0	101.15	100
III	6.4	114	6.5	115	101.6	100.9
	6.9		6.3		91.3	
IV		8.6		8.2		95.3

Peralta-Zamora *et al.*[80] also used XRF for the determinations of Zr and Hf in solid samples. Two different methods were used for the preconcentration of the samples prior to XRF analysis, namely liquid-solid extraction with an anionic exchange resin modified with xylenol orange and precipitation with lanthanum. The results obtained using the two difference co-precipitation methods are shown in **Table 3.9**.

[80] P. Peralta-Zamora, L. Cornejo-Ponce, S. Bueno, J.W. Martins, ***Talanta***, 44, pp. 814 – 816 (1997)

Table 3.9: Determination of Zr and Hf in zirconium ore using XRF proposed methods.[76]

Replicate analyses	Extraction with modified resin, %		Precipitation with lanthanum, %	
	Zr	Hf	Zr	Hf
1	95.4	4.6	96.5	3.5
2	95.2	4.8	97.1	2.9
3	95.6	4.4	96.7	3.3
Average	95.4 ± 0.4	4.6 ± 0.4	96 ± 0.6	3.2 ± 0.6
RSD (%)	0.2	4.3	0.3	9.5

Smolik *et al.*[81] successfully dissolved zirconium sulphate in 2M HCl followed by Hf determination using different analytical techniques namely ICP-OES, ICP-MS and NAA (see **Table 3.10**). Relative standard deviations of results obtained using ICP-OES ranged from 29 to 253 % and from 18 – 38 % for both NAA and ICP-MS.

[81] M. Smolik, H. Polkowska-Motrenko, Z. Hubicki, A. Jakobik-Kolon, B. Danko, ***Analytical Chimica Acta***, 806, pp. 98 - 100 (2014)

Table 3.10: Determination of Hf in zirconium sulphate samples by NAA, ICP-OES and ICP-MS techniques.[81]

Sample code	Hafnium recovery, %		
	NAA	ICP-OES	ICP-MS
H3	1.0	1.1	0.9
H4	1.0	1.7	0.8
H5	0.9	0.9	1.1
H6	1.4	0.6	1.2
H10	6.6	8.2	7.6
G3	5.9	7.4	6.4
G4	6.8	8.2	6.8

Miura *et al.*[82] used NAA for the determination of hafnium in a zirconium metal sample using internal standardisation. The zirconium metal was first digested in mixture of H_2SO_4, HF and HNO_3 and then heated to evaporate HF. EDTA was added to the sample solution which was used as an internal standard method to ensure the homogeneity of the neutron flux. A Hf recovery of 52(1) % was reported.

A study on the quantitative determination of hafnium in mixtures of zirconium-hafnium hexachloro alkali compounds by NAA and XRF was conducted by Pickle *et al.*[83]. The study was aimed at developing a better technique for the determination of Hf. Both methods required prior separation of zirconium and hafnium. A separation method was therefore developed by using a mixture of $HfCl_4$ and $ZrCl_4$ in molten alkali chlorides (ACl where A= Li, Na, K, Rb, or Cs). Hf concentrations of 3.9 % and 4.0 % were reported for the two techniques. Analyses using these two techniques gave similar results. However, NAA required less sample preparation and was less time consuming compared to XRF. X-ray powder diffraction patterns were also used to follow the hydrolysis and conversion of chlorides to oxides as indicated in **Equation 3.1**.

[82] T. Miura, H. Matsue, T. Kuroiwa, ***Journal of Radioanalytical Nuclear Chemistry***, 282, pp. 50 - 51 (2009)
[83] C.A. Pickles, G.J. Kipouros, S.N. Flengas, ***Canadian Journal of Chemistry***, 61, p. 2189 (1983)

$$A_2(Zr,Hf)Cl_6 + 2H_2O \rightarrow 2(Zr,Hf)O_2 + 4HCl + 2ACl \quad (\mathbf{3.1})$$

(A = monovalent cation)

3.3.3. GRAVIMETRIC DETERMINATION OF HAFNIUM

Gravimetric and volumetric methods can be used for samples which contain large amounts of hafnium such as hafnium germanides. Kabannik and Popova[64] used gravimetric analysis for the determination of titanium, hafnium and zirconium in germanide compounds. Their method involved the use of barium chloride for the sintering of the dissolved hafnium germanides (see **Section 3.2.2)**.

Hanh and Joseph[75] developed a method for the analytical determination of hafnium using 1-naphthylglycolic acid. The developed method involves the precipitation of hafnium in hafnyl chloride (containing a minimal amount of hafnium oxide) with the addition of a standard solution with 0.1 M HCl and the 1-naphthylglycolic acid. Kumins used mandelic acid whereas Hillebrand and Lundell[65] used different reagents such as mandelic acid, cupferron and 1-Napthylglycolic acid to precipitate the hafnium as hafnium oxide from hafnyl chloride (see **Table 3.11**). The complete precipitation of hafnium was accomplished after the digestion period of 30 min on a water bath at 85 °C. The obtained dry precipitate was ignited in a platinum crucible and the results are given in **Table 3.11** for the precipitated amount of hafnium and zirconium oxides using different reagents including mendalic acid and cupferron.

Table 3.11: The precipitated amount of HfO_2 and ZrO_2 using different precipitants.[65]

Reagent Used	ZrO_2, g	HfO_2, g
Mandelic acid	0.0825	0.4875
Cupferron	0.0824	0.4876
1-Napthylglycolic acid	0.0826	0.4877

The same precipitation procedure, only with a different acid (H_2SO_4) was used to investigate the effect of acidity on the extent of hafnium precipitation. **Table 3.12** shows the weight of zirconium oxide formed after the igniting the precipitate. Similar results were obtained for hafnium oxide, indicating that a change in acid or its concentration does not have any effect on zirconium or hafnium recovery (see **Table 3.12**).

Table 3.12: The effect of acidity on the precipitation of hafnium oxide.[65]

Acid	Acid Concentration, N	ZrO_2 added, g	ZrO_2 found, g	Zr Recovery, %
HCl	0.1	0.0825	0.0824	99.88
	0.3	0.0825	0.0824	99.88
	0.5	0.0825	0.0824	99.88
H_2SO_4	0.36	0.0825	0.0824	99.88
	1.08	0.0825	0.0824	99.88
	1.80	0.0825	0.0823	99.76
	2.52	0.0825	0.0820	99.39

Zirconium and hafnium usually occur with iron, aluminium, titanium and rare earths as impurities in many of these mineral ores. The study by Hanh and Joseph[75] investigated the effect of these accompanying cations or impurities on the precipitation of hafnium and zirconium oxide (see **Table 3.13**). Standard solutions of zirconyl chloride were mixed with known amounts of the different cations and the precipitation of zirconium investigated. The same method was also used to determine the influence of these impurities on hafnium recovery.

Table 3.13: Effect of interfering ions on the recovery of hafnium and zirconium.[65]

Interfering ions	**Zirconium precipitate**		
	ZrO_2 added, g	**ZrO_2 found, g**	**Zr Recovery, %**
Aluminium (III)	0.0825	0.0826	98.84
Lanthanum (III)	0.0825	0.0827	99.71
Iron (III)	0.0825	0.0828	100.36
Titanium (IV)	0.0825	0.0829	100.48
Uranium (VI)	0.0825	0.0826	100.12
Thorium (IV)	0.0825	0.0824	100.58
Tin (IV)	0.0825	0.0826	101.45
Interfering cations	**Hafnium precipitate**		
	HfO_2 added, g	**HfO_2 found, g**	**Hf Recovery (%)**
Iron (III)	0.4875	0.4877	100.04
Aluminium (III)	0.4875	0.4877	100.04
Titanium (IV)	0.4875	0.4878	100.06
Thorium (IV)	0.4875	0.4873	99.96

In another study,[84] a Travancore zircon sample was digested by borax fusion and the melt was dissolved and Zr and Hf were precipitated with mandelic acid and with the sodium salt of 1-napthylglycolic acid and then converted to metal oxides (see **Table 3.14**). From the results in **Table 3.14** it is clear that there is not an appreciable difference in the recovery of hafnium and zirconium using mandelic acid and with the sodium salt of 1-napthylglycolic acid (48.12 and 48.08 % of Zr + Hf using mandelic acid and sodium salt of 1-napthylglycolic acid respectively).

[84] A.K. Mukherji, ***Analytical Chemistry,*** 36, pp. 1064 - 1065 (1964)

Table 3.14: The gravimetric analysis of a Travancore zircon sample.[84]

Zircon, g	Reagent	% $(Zr/Hf)O_2$ found	% (Zr/Hf) found
1.000	Mandelic acid	65.08	48.12
1.000	1-Napthylglycolic acid	64.95	48.08

Mukherji[84] evaluated a gravimetric analytical method to quantify zirconium and hafnium from their precipitation using different carboxylic acids such as trimesic, trimellitic and pyromellic acids as precipitants. Standard zirconium and hafnium nitrate solutions were acidified with warmed concentrated nitric acid followed by the addition of the carboxylic acid. The reaction mixture was heated at about 90 °C for a period of 20 min and a white product hafnium and possibly zirconium dioxide precipitated. The results obtained from this study are as shown in **Table 3.15**.

Table 3.15: Determination of hafnium content by gravimetric analytical method using various carboxylic acids.[84]

HfO_2 added, g	HfO_2 found, g	Hf recovery (%)
Precipitation with Trimesic Acid		
0.0173	0.0171	98.84
0.0343	0.0342	99.71
0.0509	0.0513	100.79
0.0692	0.0684	98.84
0.1372	0.0139	101.02
Average		99.84 ± 1.03
Precipitation with Trimellitic Acid		
0.0170	0.0171	100.59
0.0344	0.0342	99.42
0.0510	0.0513	100.59
0.0680	0.0684	100.59
0.1375	0.1368	99.49
Average		100.14 ± 0.62
Precipitation with Pyromellitic Acid		
0.0169	0.0171	101.18
0.0345	0.0342	99.13
0.0508	0.0513	100.98
0.0688	0.0684	99.42
0.1372	0.1368	99.71
Average		100.08 ± 0.93

The quantification of zirconium with the same method gave recoveries ranging from 99.84 to 100.14 %.

3.4. SYNTHESIS AND CHARACTERISATION OF HAFNIUM COMPLEXES

Another important aspect of analytical chemistry is the proper and thorough characterisation of the compounds that are investigated/studied. Techniques available for characterisation include IR spectroscopy and elemental analysis. The next few paragraphs will cover the characterisation of only a few Hf complexes cited in literature which was characterised with these techniques.

3.4.1. INFRARED SPECTROSCOPY

Antokhina *et al.*[85] studied the syntheses of different hafnium fluoro complexes. These researchers dissolved samples of HfF_4 (instead of HfO_2) in 40 % HF and constantly stirred the mixture on a hot water bath until completely dissolved. Colourless crystalline compounds were isolated after the evaporation of the resulting solution. The synthesized complexes were characterised using IR spectroscopy (see **Figure 3.6**) and the vibrational frequencies are reported in **Table 3.16**.

[85] T.F. Antokhina, T.A. Kaidaloya, N.N. Savchenko, L.N. Ignat'eva, ***Zhurnal Neorganicheskoi Khimii***, 57, pp. 1634 - 1638 (2012)

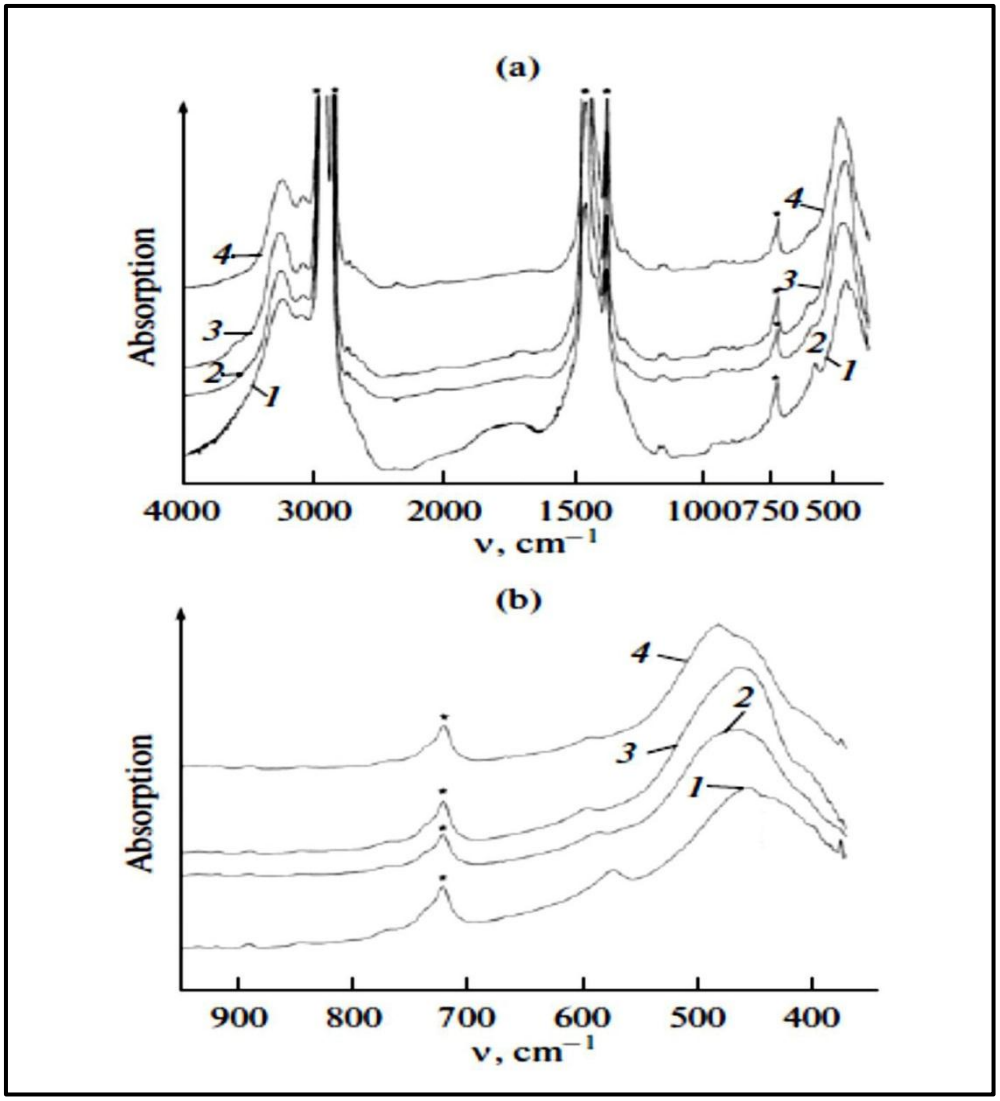

Figure 3.6: IR absorption spectra of hafnium fluoro complexes.[85]

Key:

a) 1 $(NH_4)_2HfF_6$
   2 $(NH_4)_6KHf_4F_{23}$
   3 $(NH_4)_6RbHf_4F_{23}$
   4 $(NH_4)_6CsHf_4F_{23}$

b) Expanded IR absorption spectra in the of 350 – 900 cm^{-1} region

The stretching frequencies of N-H bonds in ammonium groups were observed in the 3000 - 3300 cm^{-1} region (see **Table 3.16**). The vibration frequencies were observed within the region of 400 - 600 cm^{-1} for $(NH_4)_6MHf_4F_{23}$ (M = K, Rb, Cs).

Table 3.16: Infrared data of the synthesized hafnium and zirconium complexes.[85]

Complex	ν (N-H)	ν (A-F)
$(NH_4)_2HfF_6$	3226, 3080	565, 472
$(NH_4)_6KHf_4F_{23}$	3252, 3080	581, 487, 399
$(NH_4)_6RbHf_4F_{23}$	3257, 3207, 3077	583, 539, 482, 385
$(NH_4)_6CsHf_4F_{23}$	3247, 3077	586, 476, 381
$(NH_4)_6LiHf_4F_{23}$	3247, 3082	594, 574, 495, 460, 398
$(NH_4)_6NaHf_4F_{23}$	3254, 3082	593, 474, 458, 397
$(NH_4)_6LiZr_4F_{23}$	3240, 3080	588, 525, 484, 398
$(NH_4)_6NaZr_4F_{23}$	3247, 3080	584, 485, 398

Kharitonov *et al.*[86] on the other hand studied the characterisation of thiocyanate complexes of hafnium which involved the reaction of the mixture of $HfCl_4$ with KCNS in dilute HF solutions. Characterization of the product was also accomplished using IR spectroscopy (see **Figure 3.7**).

[86] Kharitonov, Yu Ya, I. A. Rozanov, and I. V. Tananaev. "***Bulletin of the Academy of Sciences of the USSR, Division of chemical science***, 12.4, p. 538 (1963)

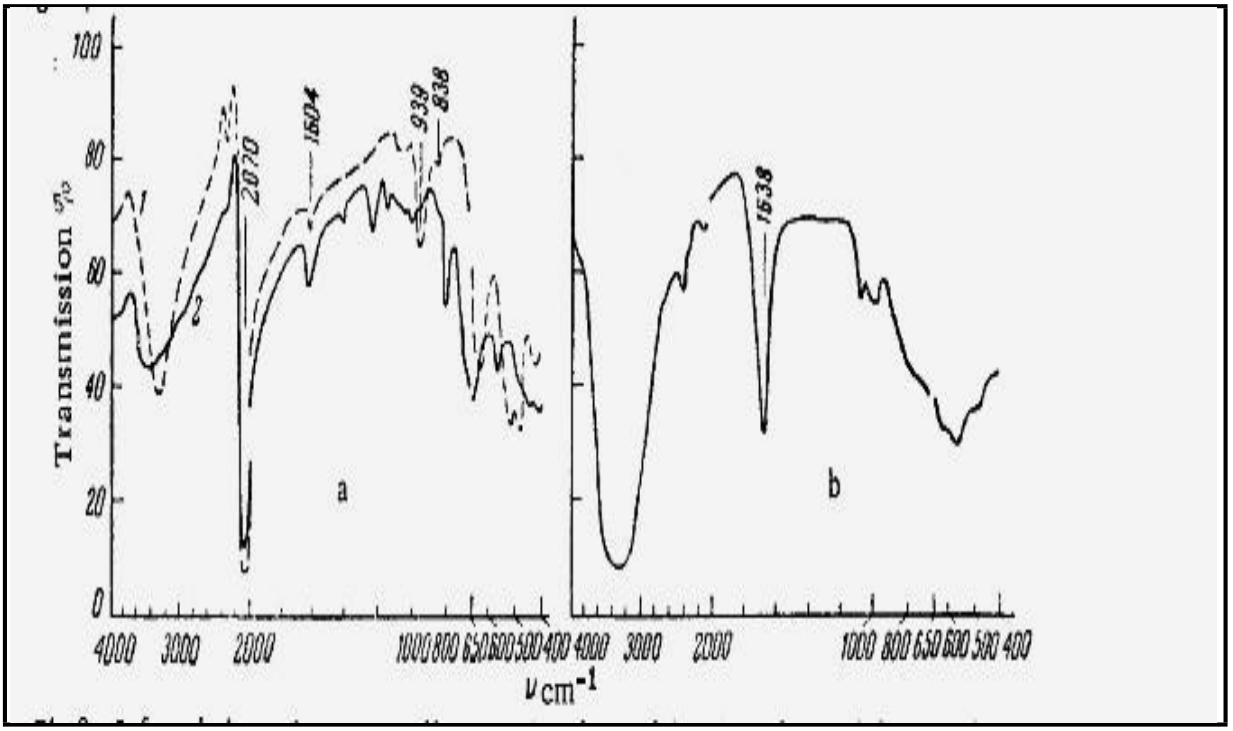

Figure 3.7: An infrared structure of a) $HfO(CNS)_2.CsCNS.2H_2O$ ( ) and thermal decomposition(----), (b) $HfOCl_2.8H_2O$.[87]

The ν(M=O) stretching frequencies of ZrO and HfO were observed in the 830 – 900 cm^{-1} region with HfO stretching frequencies slightly higher than that of the corresponding ZrO stretching frequency. Literature[87] has shown that if a thiocyanate group forms a bond with the central atom of the metal of the complex through a nitrogen atom, the absorption frequencies of S-C bonds lie in the region 694-748 cm^{-1} and M-N bond is in the 780 – 830 cm^{-1} region. The ν(CN) stretching frequencies of the NCS^- ligand are observed at ~ 2119 cm^{-1} for bridge and in the region 2050 – 2082 cm^{-1} for non-bridge thiocyanate group. In **Figure 3.7a** the S-C stretching frequency was observed at 800 cm^{-1}. HfO stretching frequency was not observed for $HfOCl_2.8H_2O$ complex while the broad water peak was observed within the region of 2400 – 3800 cm^{-1}.

[87] N.S. Kurnakov, Institute of General and Inorganic Chemistry, pp. 596 - 601 (1963)

3.4.2. X-RAY CRYSTALLOGRAPHY

X-ray crystallography is an important technique which is used for the characterisation of atomic and molecular structure of the synthesized solid complexes in three dimensional space.

Gerasimenko *et al*[88] have successfully synthesized hexafluorozirconates complexes with the addition of ammonium and rubidium fluorides to a solution of ZrO_2 and 40 % HF. The molar ratio of the cation to metal fluoride complex such as ammonium and rubidium fluorides were within the range of 0,5 - 2 in relation to the ZrO_2 amount. The structure (see **Figure 3.8**) of the complex was confirmed by X-ray crystallography using a SMART 1000 CCD diffractometer (Bruker Co.) and the cell parameters were determined as a = 7.635(1) Å, b = 13.079(1) Å and c = 22.507(3) Å in a Fmmm space group.

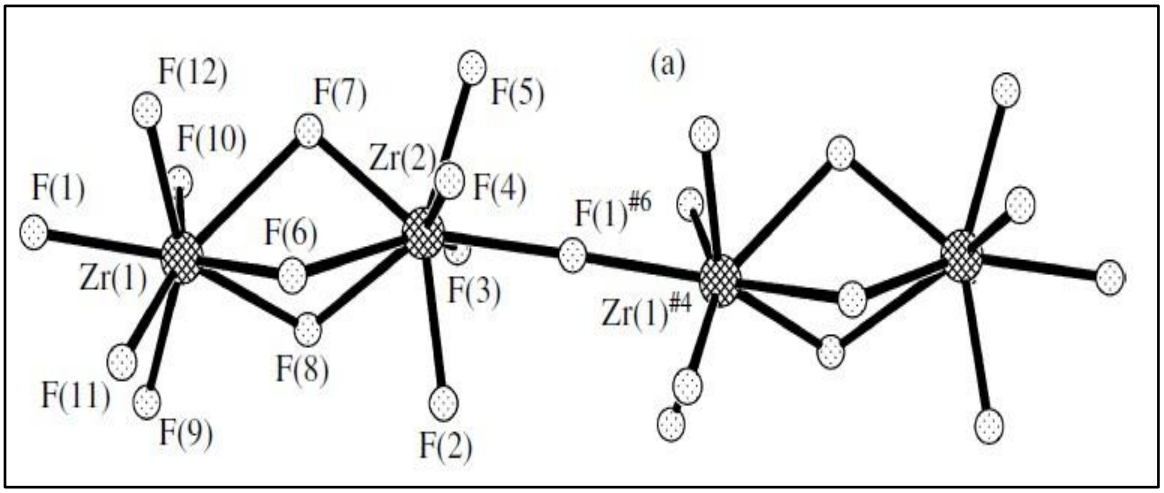

Figure 3.8: Crystal polymeric chain structure of $K_{1.218}(NH_4)_{0.782}ZrF_6$.[88]

Kavun *et al.*[89] investigated the crystal structure of ammonium hexaflourohafnate ($(NH_4)_2HfF_6$) complex using a SMART 1000 CCD diffractometer (Bruker Co.) The compound was found to be isostructural to ammonium hexafluorozirconate ($(NH_4)_2ZrF_6$) with the cell unit parameters of a = 13.3902(7) Å, b = 7.6850(4) Å, c = 11.6731(6) Å, space group $Pca2_1$, and Z = 8. The investigated structure of $(NH_4)_2HfF_6$ is given in **Figure 3.9**.

[88] A.V.Gerasimenko, V.Ya, Kavun, N.A. Didenko, A.B. Slobodyuk, N.F. Uvaron, V.I. Sergienko, ***Zhurnal Neorganicheskoi Khimii***, 52, p. 778 (2007)
[89] V.Ya. Kavun, A.V. Gerasimenko, V.I. Sergienko, R.L. Davidovich, T.F. Antokhina, ***Russian Journal of Coordination Chemistry***, 28, p. 631 (2002)

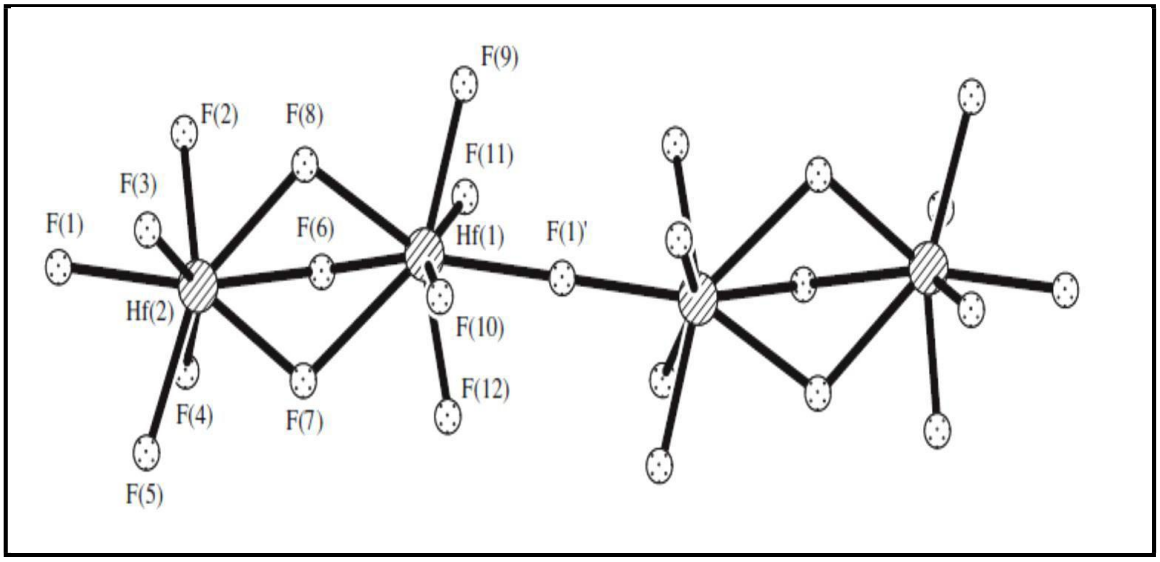

Figure 3.9: Crystal polymeric chain structure of $(NH_4)_2HfF$.[88] 6.

3.4.3. CHNS-ELEMENTAL ANALYSIS

Micro-chemical analysis is also a very useful method to determine the empirical or chemical formula of newly synthesized complexes.

Beweries *et al.*[90] studied the formation of hafnium complexes after the reaction of $Cp^*_2HfCl_2$ with lithium chloride and $Me_3SiC{\equiv}CSiMe_3$ in toluene. The reaction times were 10, 8 and 20 days for complexes (**1**), (**2**) and (**3**) respectively (see **Figure 3.10**). CHNS elemental analyzer was used for the identification of the light green crystal isolated for complex **1** and pale yellow crystal of complex **3**. Elemental data analysis of complex (**1**) and (**3**) are shown in **Table 3.17**.

Table 3.17: Characterisation of hafnium complexes, found (calculated).[90]

Complex	C (%)	H (%)
$C_{28}H_{48}HfSi_2$ (**1**)	54.22 (54.30)	7.66 (7.81)
$C_{28}H_{48}HfSi_2$ (**3**)	54.30 (54.30)	7.71 (7.81)

[90] T. Beweries, V.V. Burlakov, M.A. Bach, S. Peitz, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, B. Pathak, E. Jemmis, ***Angewandte Chemie International Edition***, 46, p. 6910 (2007)

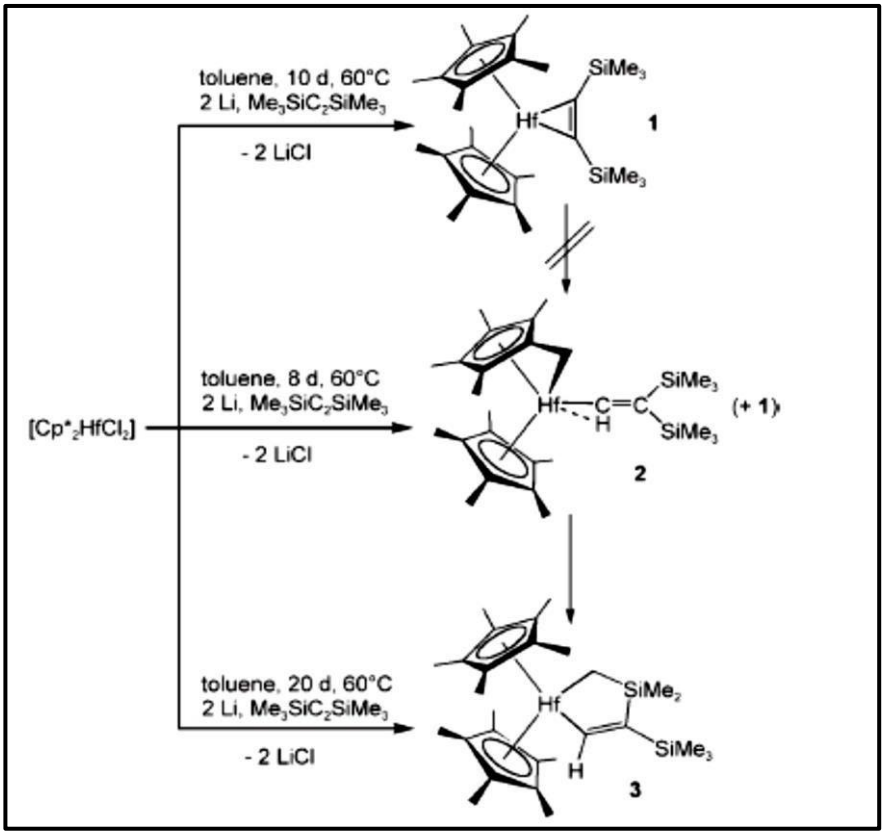

Figure 3.4: Synthesis of hafnium complexes **1**, **2** and **3.**[90]

A different study by Matsui *et al.*[91] involved the synthesis of hafnium complexes in toluene using $Hf(Ch_2Ph)_2$ and N-(2-pyrrolidene)-4-isopropylaniline as the starting materials. The solution was stirred at the temperature of -78 °C and additional toluene (5 mL) was added over a period of 5 min under argon. The solution was stirred continuously for 3 hours after which the solution was warmed to about -30 °C. The solution was evaporated at 0 °C and a crude orange solid product was obtained. Elemental analyzer was used to confirm the desired product. Elemental analysis data of the pyrrole-2-carboxyaldehyde product indicated the successful synthesis of the required product, found (calculated): C 79.21(79.19), H 7.60(7.67), N 13.20(13.26) %.

[91] S. Matsui, T.P. Spaniol, Y. Takagi, Y. Yoshida, J. Okuda, ***Dalton Transactions***, p. 2 (2000)

3.5. CONCLUSION

The quantitative determination of hafnium in various samples by analytical techniques such as ICP-OES and ICP-MS, were preceded by their dissolution using different digestion methods such as open vessel, fusion and microwave acid-assisted system. From the discussions in the previous sections, open vessel digestion technique turned out to be least effective in dissolving the hafnium containing compounds such as zirconia and inaccurate results were obtained. The literature study also showed that the most popular and successful digestion method used is flux fusion. However, the method has several disadvantages which could probably affect the recovery of the elements (and purity of the sample) such as sample cross contamination. This therefore prompted a shift to the use microwave acid-assisted digestion method (which is a closed system method) with reduced or no sample contamination. The method also has several advantages (see **Chapter 4**) which include short digestion periods and a low potential for sample contamination. However, very little research has been done with this technique for the digestion of Zr/Hf samples.

ICP-OES and ICP-MS techniques are the most commonly used techniques for the analytical determinations of hafnium in various samples including seawater and geological samples. These techniques (ICP-OES and ICP-MS) have several advantages over other analytical techniques (XRF, NAA). ICP-MS has lower detection limits and minimal spectral interferences. From the discussions in the above sections it appears that the analysis using both ICP-MS and ICP-OES is highly affected by the sample preparation procedure. For example, RSD values in some of the analyses were as high as 253 % (see **Section 3.3.2**). It is therefore extremely important to utilize sample preparation procedures such as matrix matching to minimize the matrix influence on the analytical method. NAA technique can be used for the direct determination of hafnium with low concentrations. It is however an expensive technique and has high photopeaks interferences. In addition, NAA and XRF require trace-matrix separation which is of great challenge for trace-elements such as hafnium in zirconium.

Newly synthesized hafnium complexes can successfully be characterised by IR spectroscopy, CNHS-microanalysis and X-ray Crystallography (see **Section 3.4**).

4 Dissolution and analytical techniques

4.1. INTRODUCTION

Different analytical techniques have been used during this study to quantify and identify hafnium in different hafnium containing samples. While a wide variety of analytical techniques does exist which can be used to quantify Hf in different matrices, the focus on this section and therefore in this study was the use of ICP-OES due to its high sensitivity, wide linear dynamic range and availability. Prior to the quantitative analyses by ICP-OES, it is mandatory to dissolve the samples which contain hafnium. Digestion techniques such as flux fusion, open vessel acid digestion and microwave acid-assisted digestion were used for sample dissolution and will also be discussed in the next few paragraphs.

This chapter reviews the analytical principles, equipment and techniques that have been used throughout the study. Techniques which were succesfully used for digestion such as open beaker followed by characterisation techniques such as of different such as IR (infrared spectroscopy), CHN microanalysis and X-ray crystallography as well as spectrometric techniques such as ICP-OES will be discussed in detail.

4.2. DIGESTION TECHNIQUES

Digestion techniques are necessary to convert the solid sample into water soluble species to afford its chemical characterisation, quantification of target elements as well as hydrometallurgical separation. Natural hafnium containing samples such as zircon and some synthetic compound such hafnium oxide and hafnium alloys are insoluble in water. Different mineral acids, salts or the combination thereof can be used to solubilise the solid samples into solutions. In this study, three different digestion techniques have been investigated namely, flux fusion, open vessel acid digestion and microwave acid-assisted digestion. The following sections give a detailed discussion on these three digestion techniques and their comparisons.

Solubility of these solid samples can be induced by three different chemical processes namely acid/base reactions, oxidation/reduction and finally complex formation. In acid/base reactions the mineral oxides react with the acid or base to produce water soluble species. In case of redox reaction, oxidizing agents are used to change the oxidation state of target element to produce new metal species with a new oxidation state which is water soluble. Complex formation can be a combination of the above two processes to produce water soluble metal complexes.

4.2.1. OPEN VESSEL DIGESTION

Open vessel digestion is one of the simplest and oldest digestion techniques that have been used for sample decomposition at relatively low temperatures and its normally falls within the acid/base category.[91] Different acids that can be used in open vessel digestion are listed in **Table 4.1**. The method involves the heating of the sample with constant stirring at a certain temperature until the analyte of interest is dissolved or completely leached.[91] Although different mineral acids may be used for sample dissolution in an open vessel, literature study[61] has shown that HF is highly effective in achieving a total dissolution of mineral samples such as zirconium ores. It can be used singularly or in combination with other reagents such as H_2SO_4 and NH_4F.[60, 91] A slurry can also be prepared using solutions of salts, base, acid and/or combinations thereof. In cases where a complete dissolution of the sample is not attained after heating and stirring for a desired time the residual sample is filtered and the leachable components are determined in the filtrate.

[91] S. Mitra, Sample Preparation Techniques in Analytical Chemistry, p. 231 (2004)

Table 4.1: Different acids that can be used in open vessel digestion.[60, 91, 92]

Acids	Uses
HCl	• Converts the metal to soluble chloride salts • Dissolve sedimentary rock and removes the organic material
H_2SO_4	• Effective oxidizer for decomposing organic materials • Digest oxides, hydroxides, carbonates and various sulphide ores
HNO_3	• Converts oxide, hydroxide, chlorides, carbonate or metal to soluble nitrates however it has a low oxidising potential
HF	• Dissolves silica and other silicates to form fluorosilicic acid that can dissociate to silicate tetrafluoride and hydrogen fluoride in the presence of heat • Digest oxides and ores of Nb, Ta, Ti and Zr
Aqua regia	• Dissolves soils, sediments and sludges
$HClO_4$	• Extreme oxidizing agent • It attacks most elements however due to its explosion hazard it is often used in conjunction with other acids such as H_2SO_4 and HNO_3

Open vessel acid digestion is preferably used for samples which are easily dissolved such as hafnium salts. It is the least effective digestion technique for the dissolution of chemically inert hafnium containing compounds as compared to flux fusion (see **Section 4.2.2**) and microwave acid-assisted digestion techniques (see **Section 4.2.3**). In addition to the incomplete dissolution due to chemical inertness of the samples, other factors such as sample loss due to votalisation may lead to low percentage recoveries.

4.2.2. FLUX FUSION

Flux fusion is generally used for samples that are highly resistant to chemical attack by commonly used mineral acids. This method makes use of molten salts as dissolution agent normally at elevated temperature and with the exclusion of water. Fusion may be carried out

[92] I. Akyar, Wide Spectra of Quality Control, p. 59 (2011)

in a sand bath, oil bath, in a furnace or over a Bunsen burner.[60] The technique involves the homogenous mixing of a basic, acidic or non-oxidising salt (flux) such as $Na_2B_4O_7$ with a sample in a suitable crucible and heating the mixture to a temperature higher than the melting point of the fluxes or alkali salts (see **Table 4.2**).[93] Mass ratios of 1:10 sample: flux is preferable for sample decomposition to limit the possible impurity built up (in the sample) from the added flux. The high salt content of the flux may also have other negative effects on the analysis of the samples such as it may block the nebulizer and led to high background signals in optical measurements.[60] The choice of the flux for the decomposition of the sample is influenced by the sample properties such as its acidity or basicity, refractory elements within the sample and fusion temperatures. For example, the decomposition of refractory oxides, silicates and silica-containing samples normally require the use of fluxes such as $Na_2B_4O_7$, $Li_2B_4O_7$ or NH_4HF_2 due to their ability to increase the analyte's solubility. After the dissolution or reaction process the melt is cooled to room temperature before acid or base dissolution. The melt produced by flux fusion should be soluble in water, basic or acidic solutions depending on the chemical properties of the analyte salt which is produced during the flux fusion reaction.[93]

[93] T.R Dulski, A manual for the chemical analysis of metals, pp. 83 - 87 (1996)

Table 4.2: The most commonly used fluxes for decomposition of hafnium containing compounds.[93, 94]

Types of fluxes		Melting point, °C	Notes
Acidic fluxes	Sodium pyrosulphate	403	
	Ammonium bifluoride	125	
	Lithium tetraborate	920	Necessary for casting borax glass for XRF spectrometry
	Potassium pyrosulphate	419	Can exceptionally be used to fuse metal directly
Basic Fluxes	Sodium hydroxide	321	
	Sodium carbonate	853	Ensures the conversion of cationic constituent of the analyte to carbonates or oxides that are soluble in different mineral acid
	Sodium carbonate + borax		The analyte's solubility is increase by the addition of the mixture of sodium carbonate + borax
Non oxidizing fluxes	Sodium tetraborate	878	
Oxidizing fluxes	Sodium peroxide	675	Suitable for decomposition of Cr, Sn and Zr minerals

[94] Spectroflux, [Accessed 11-10-2015]. Available from: https://www.princeton.edu/~cavalab/tutorials/public/AlfaOxideFluxes.pdf

In this study the flux fusion of hafnium samples were carried in the high temperature furnace shown **Figure 4.1**. The furnace can attain temperatures of up to 1100 °C and enables the investigation of a variety of fluxes with high melting point as listed in **Table 4.2**.

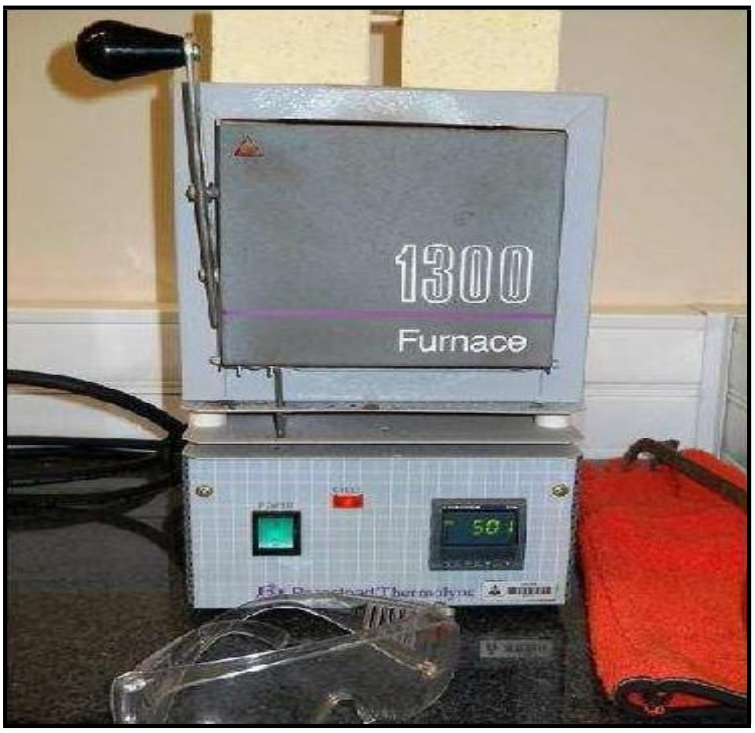

Figure 4.1: High temperature furnace for flux fusion

4.2.3. MICROWAVE ACID-ASSISTED SYSTEM

This method of digestion normally allow for higher and uniform heating in a closed environment. Microwaves are electromagnetic radiation with frequencies and wavelengths within the range of 300 MHz and 300 GHz and 0.001 – 0.3 m and are situated in the region between infrared and radio spectra in the electromagnetic wave spectrum (see **Figure 4.3**).[95] This technology utilises frequencies in the range of 0.915 and 2.45 GHz used for industrial, scientific and medical purposes to avoid possible interferences with telecommunications frequencies.[95] Microwave radiation was first used in 1975 as the source of heat for the decomposition of both organic and inorganic samples in Erlenmeyer flasks without pressure control.[60]

[95] C. Leonelli, P. Veronesi, G. Cravatto, Microwave-assisted Extraction for Bioactive Compounds, pp. 1 - 4 (2013)

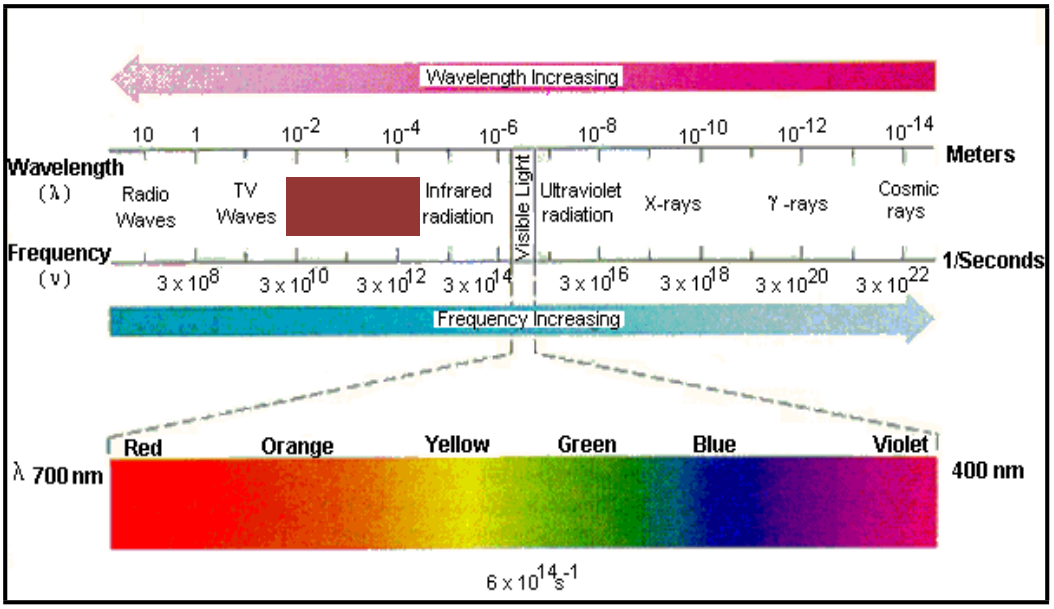

Figure 4.2: Electromagnetic wave spectrum.[96]

Microwave acid-assisted techniques can be used for the digesting of different types of samples such as rocks, soil, pure metals, metal oxides or plant material under controlled conditions such as pressure, temperature and time in either closed or open vessel.[60] The use of closed vessel microwave digestions (see **Figure 4.4**) only started in the 1980s with the aim of increasing the solubility of the samples within a shorter reaction time at relatively high temperatures and pressure and has recently gained preference over the open system due to its unique advantages.[97]

Digestion of the sample is carried out in either Teflon™ or glass vessels depending on the sample properties and the reagents used.[60, 95] Although shorter reaction time makes it an ideal digestion method, safety measures should be taken into consideration due to increased pressure which may result in explosion. Danger of explosion can be reduced by performing digestion with solvent-free reactions mainly intended for organic syntheses.[95]

[96] The atom and electromagnetic radiation, [Accessed 28-09-2015]. Available from: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/

[97] C.O. Kappe, D. Dallinger, S.S. Murphree, Practical Microwave Synthesis for Organic Chemistry: Strategies, Instruments and Protocols, p. 4 (2009)

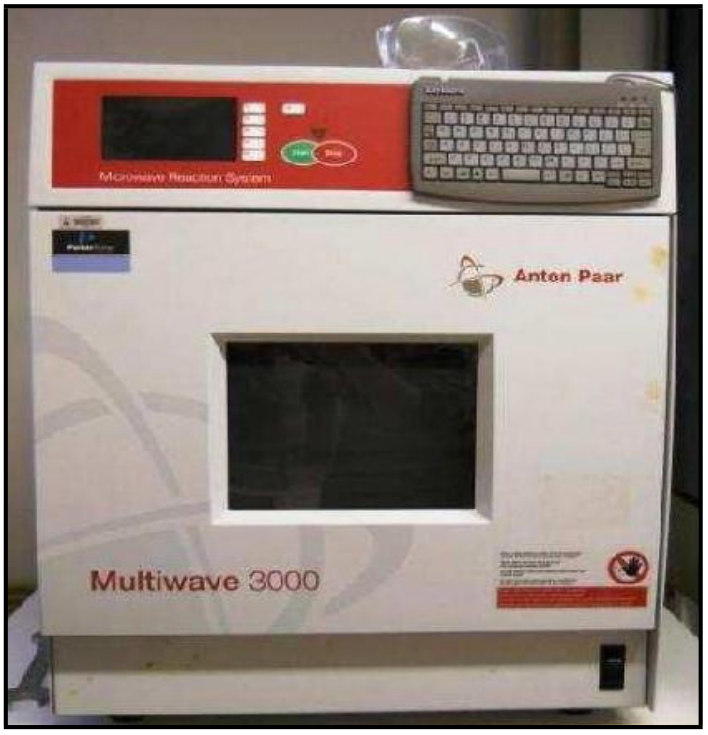

Figure 4.3: High pressure and temperature closed microwave acid-assisted system

A summary of the different digestion techniques, indicating their advantages and disadvantages are given in **Table 4.3**.

Table 4.3: A summary of advantages and limitations of different digestion techniques

Open acid digestion	Flux fusion	Closed acid digestion
Maximum temperature limited by the solution's boiling point	Maximum temperature limited the sample and the flux type	Maximum temperature: 260 - 300 °C
High acid consumption	Reduced acid consumption	Reduced acid consumption
Loss of volatile elements	Loss of volatile elements	Little or no loss of volatile elements
	Sample contamination high risks	Reduced potential of sample contamination
High digestion period	Reduced digestion period	Shorter digestion period
Reduced potential for injury and explosions	Unlikely to cause explosions	High potential for injury and explosions
Cost effective	Moderate cost	Capital Expensive
Various acid can be used	Various reagents can be used	The use of acids depends on the microwave vessels used
Incomplete dissolution of chemically inert samples	It likely to decompose chemically inert samples, However, it is intensive labour and requires large amount of the sample. Auto fusion equipment is available but capital expensive	Improved sample dissolution

Microwave technology has gained enormous popularity over the years since its introduction in 1980s, mainly due to its advantages (see **Table 4.3**) and the reported research using this technique on organic synthesis has steadily increased as shown in **Figure 4.4**. The growth in the number of publications which used microwave-assisted organic synthesis (MAOS) with non-thermally microwave effects and MAOS at the monitored temperature are shown in **Figure 4.4**.

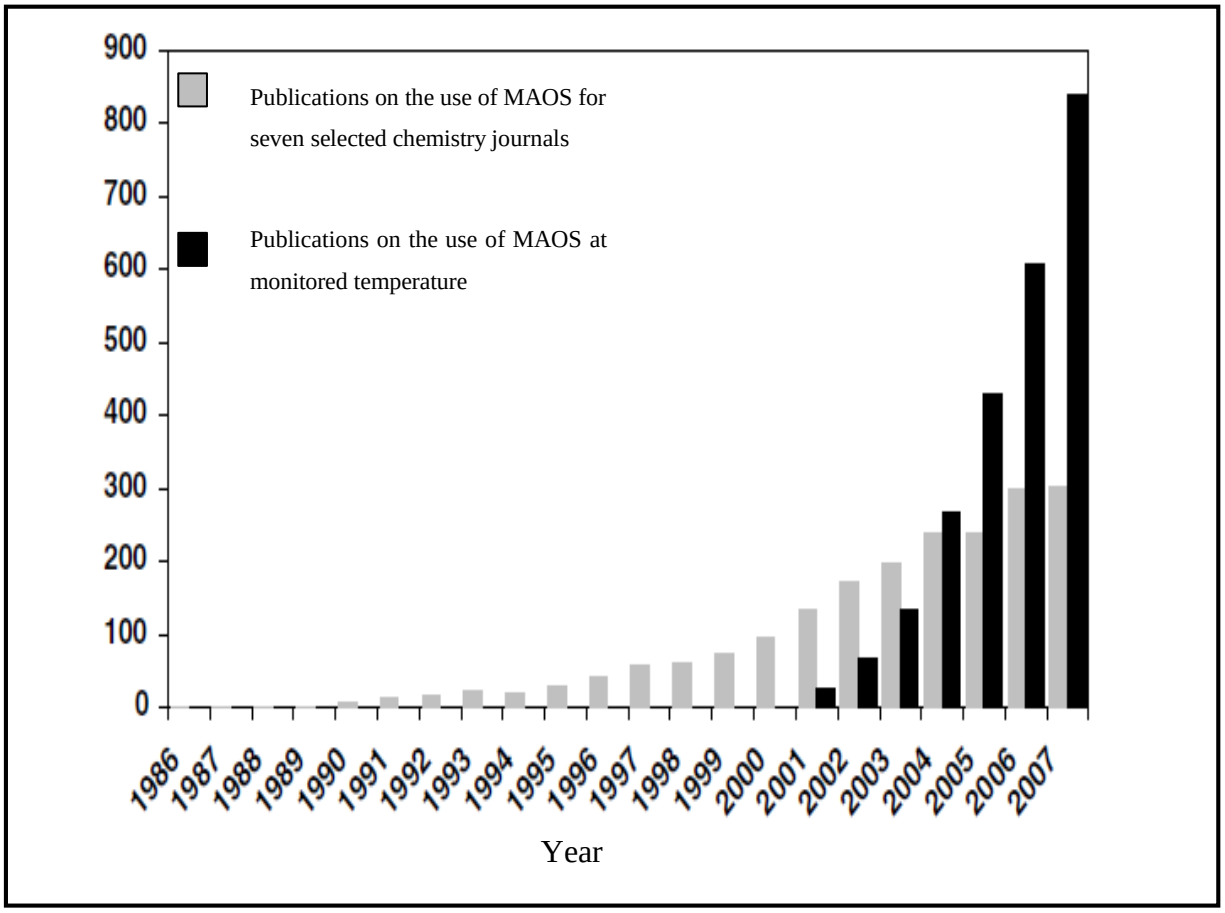

Figure 4.4: The reported number of publications from 1986 to 2007 on the use of microwave systems.[97]

4.3. ICP-OES ANALYTICAL TECHNIQUE

Analytical techniques such as ICP-OES, ICP-MS, XRF and NAA may be used for the quantitative determination of major and trace metallic elements in different sample matrices (see **Chapter 3, Section 3.2**). However, the discussion in this chapter will only focus on ICP-OES technique mainly due to its extensive use in this study. The discussion will also include comparisons of ICP-OES in terms of sensitivity and cost effectiveness to other analytical techniques.

ICP-OES is an emission technique that was developed in mid 1960s by Greenfield *et al*. and has been commercially available since 1974 and is widely used due to its multi-elemental analysis capabilities.[98] Over 70 elements (see **Figure 4.5**) can be analysed simultaneously

[98] C.B Boss, J.K Fredeen, Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, pp. 1 - 26 (1997)

using this technique. ICP-OES uses a plasma as temperature source with temperatures ranging between 6000 and 10000 K which allow for the complete excitation and atomization of elements of interest in the nebulised spray. Argon gas is commonly used in ICP-OES technology as carrier and plasma source. The technique involves the emission of electromagnetic radiation (light) at a specific wavelength which is unique to each element.[99]

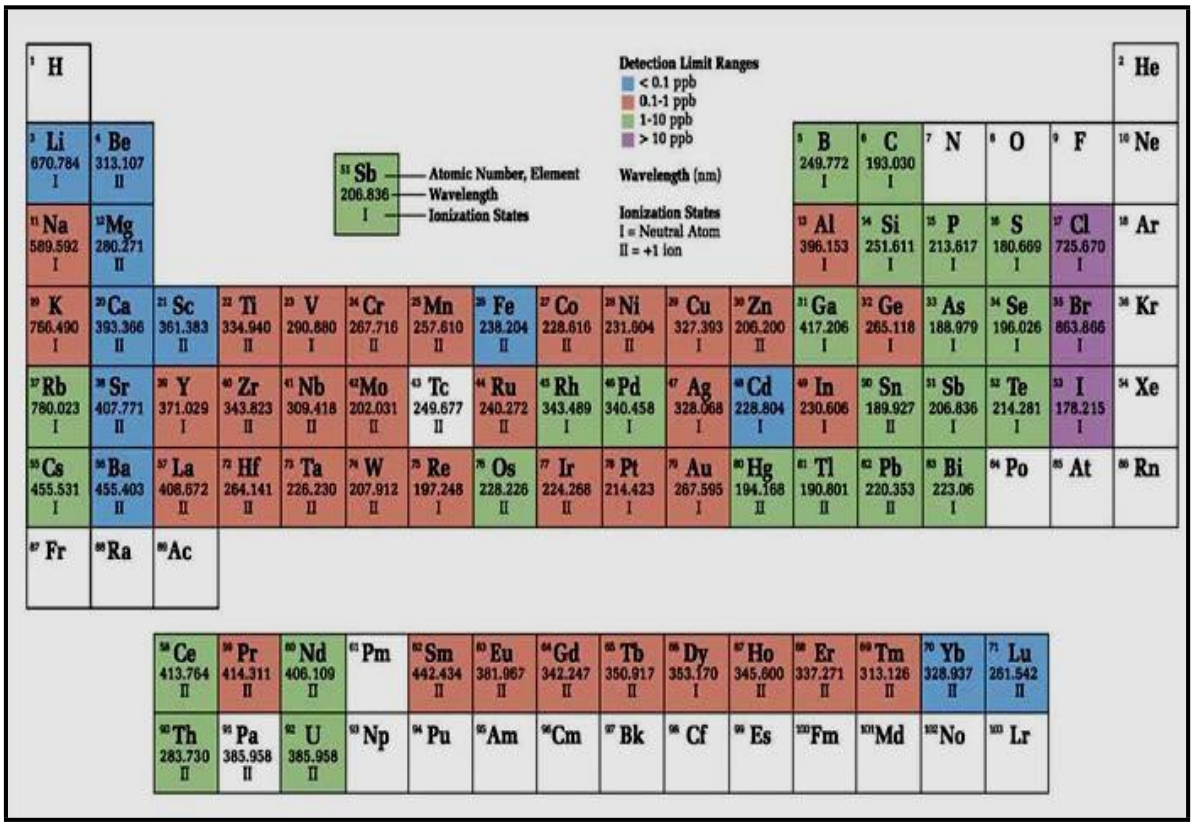

Figure 4.5: Periodic table showing elements that are detectable by the ICP-OES.[100]

The main components of the ICP-OES include the sample introduction system, the torch assembly and the spectrometer (used to measure the emission of light). The sample introduction system consists of a peristaltic pump, Teflon™ tubing, a nebulizer and a spray chamber.[101] The peristaltic pump transports the sample into the nebulizer where it is mixed with the carrier gas to produce an aerosol that is then sprayed into a spray chamber as small droplets. These droplets are then carried into the plasma while the large droplets are collected and removed into to the drain as indicated in **Figure 4.6**. There are numerous types of

[99] M Nete, Separation and purification of niobium and tantalum from synthetic and natural compounds, Ph.D. Dissertation at the University of the Free State, Bloemfontein, SA (2013)
[100] Elemental Analyses by ICP-OES, [Accessed 4-11-2015]. Available from: http://www.unn.ru/chem/ism/files/applecture21(2).pdf
[101] R.A Meyers, Encyclopedia of Analytical Chemistry, pp. 9468 - 9485 (2000)

nebulizers, the most commonly used ones include i) pneumatic, ii) ultrasonic and iii) grid nebulizers.[101]

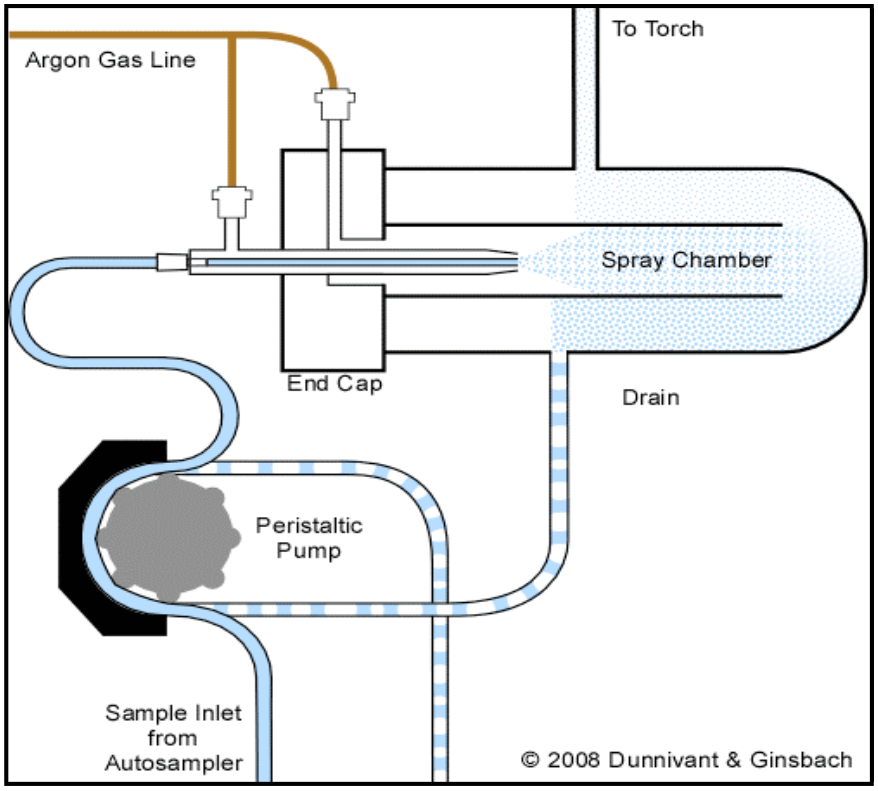

Figure 4.6: Sample introduction into ICP-OES.[102]

The high temperature plasma which is produced according to **Equation 4.3** removes the sample from the aerosol (desolvate) and produces microscopic salt particles, which are then converted into a gas of individual molecules (vaporisation) followed by dissociation into atoms (atomization). After the sample has been desolvated, vaporised and atomized it undergoes excitation and ionization processes as illustrated in **Figure 4.7**.[99, 101]

$$Ar(g) + Energy \longrightarrow Ar^{+} + e^{-} \qquad (\mathbf{4.3})$$

[102] Components of an Inductively Coupled Plasma—Atomic Emission Spectrometry System (ICP-AES), [Accessed 11-10-2015]. Available from: http://people.whitman.edu/~dunnivfm/FAASICPMS_Ebook/CH3/3_3_2.html

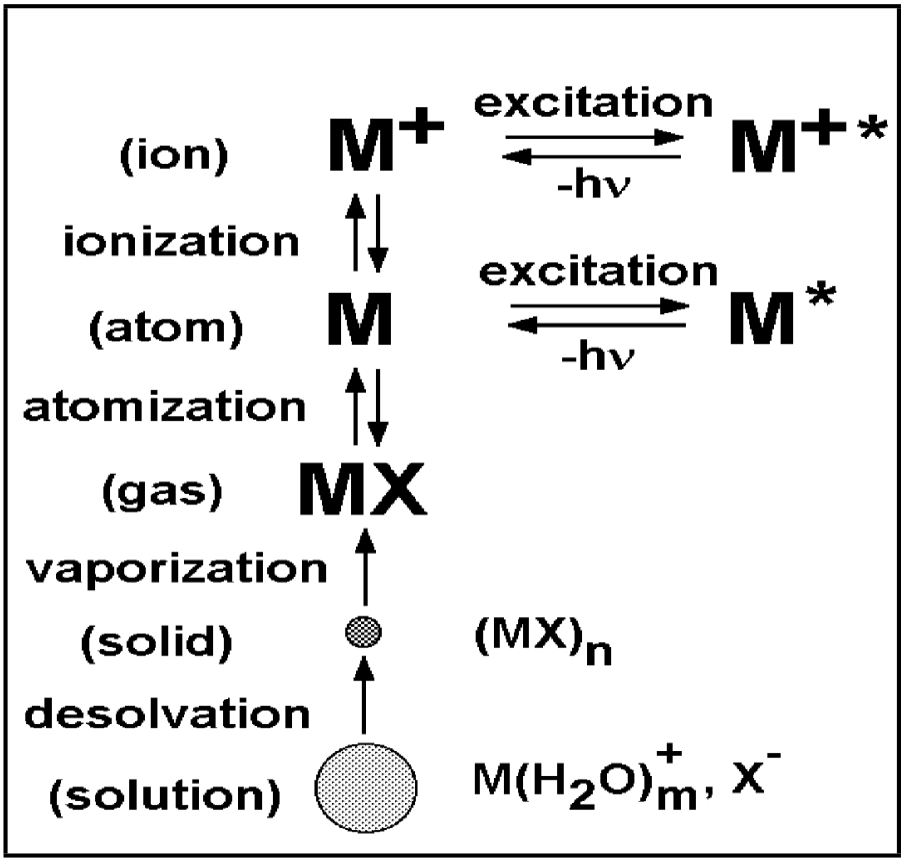

Figure 4.7: The introduction of the small droplet into the ICP RF discharge.[101]

Another important component of the ICP-OES is the plasma torch (see **Figure 4.8**). The torch is centred within a water-cooled induction coil coupled to a radio frequency (RF) generator which is used to sustain the plasma by the energy from RF generator device. This RF generator provides the load coil with power of about 700 – 1500 W creating an oscillating magnetic field around the torch at the rate relative to the frequency of the RF generator. At high temperatures all elements are thermally excited and the light is emitted at their corresponding wavelengths.[101, 102] A plasma torch consist of three concentric quartz tubes for the argon flow and injection of the aerosol namely; outer (plasma flow), intermediate (auxiliary flow) and inner tube (nebulizer flow). The purpose of the plasma torch includes i) the evaporation of the solvent from the analyte salts, ii) atomization of the atoms in the salt and iii) the excitation of the ground state atom to a higher energy level. The argon gas enters through the intermediate and outer tubes and flows tangentially as it goes upward. The sample is carried into the centre of the plasma through the inner tube.[101, 102]

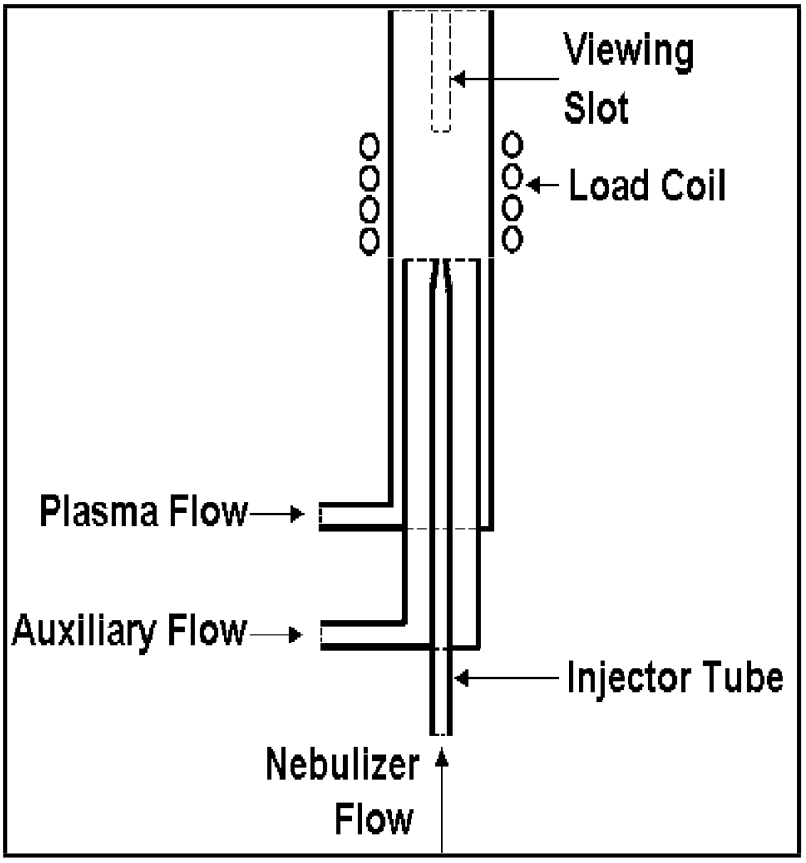

Figure 4.8: Schematic presentation of plasma torch used in the ICP-OES.[101]

ICP-OES has several advantages such as simultaneous multi-elemental analyses and low detection limit (1 - 10 ppb range). One of its disadvantages is that it only allows for wet chemical analyses.[98] Other advantages and disadvantages of the ICP-OES are summarised in **Table 4.4**.

Table 4.4: Disadvantages and advantages of the ICP-OES technique.[98, 100-103]

Advantages	Disadvantages
High sensitivity	Not suitable for the analyses of low level alkalis (less than 1-5 ppm) and halogens
Easy and rapid qualitative analysis	Matrix and spectral interferences as a result of the line rich spectra of most elements
Good precision (RSD 0.5 - 2 %)	Volatile organic solvents may cause damage to the generator
Minimal chemical interferences as a result of high temperature	High capital cost
Wide linear dynamic range (10^5 – 10^6 orders of magnitude)	

4.4. INFRARED SPECTROSCOPY

Infrared spectroscopy is an absorption technique used for the identification of chemical species by recording the vibration of different chemical bonds within a molecule and has been commercially available since 1970s. In the electromagnetic spectrum (see **Figure 4.2**), the IR region is situated in the lower energy side of the UV region with a wavelength range of $7.8x10^{-5}$ – $3 x 10^{-2}$ cm. The IR region is divided into three parts namely near ($7.8x10^{-5}$ - $3x10^{-4}$ cm), mid ($3x10^{-4}$ – $3 x 10^{-3}$ cm) and far infrared ($3 x 10^{-3}$ - $3 x 10^{-2}$ cm) (see **Figure 4.9**). However, only the mid region (400 – 4000 cm^{-1}) of the IR spectra is used for the chemical qualitative analyses of chemical molecules. In addition, this region has energy (photons) in the range of 1-10 Kcal/mol which is enough to cause vibration activation in molecules which are covalently bounded. The IR energy is necessary for the excitations in the vibration motion of molecules which are then recorded and displayed as stretching frequencies over the range that is been investigated.[104]

[103] L. Ebdon, E.H Evans, An Introduction to Analytical Atomic Spectrometry, p. 107 (1998)
[104] Online edition for students of organic chemistry lab courses at the University of Colorado, Boulder, Dept. of Chem. and Biochem., Chapter 15, Infrared Spectroscopy: Theory, pp. 156 - 162 (2002)

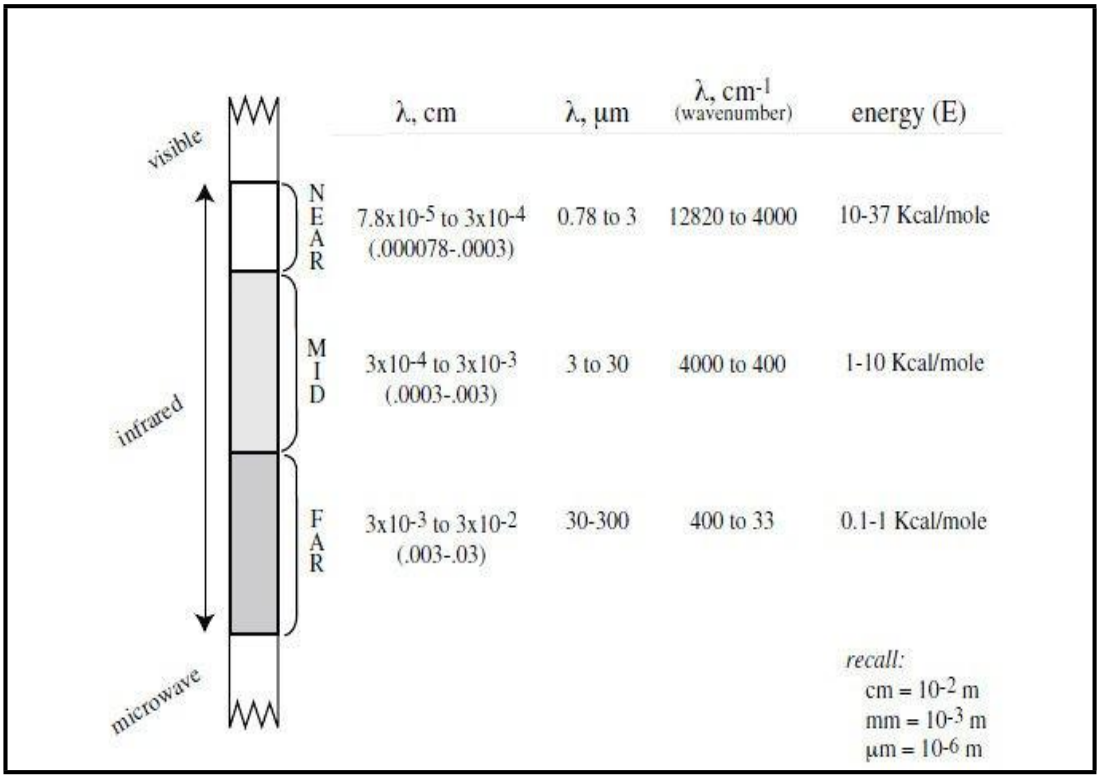

Figure 4.9: The IR regions of the electromagnetic spectrum.[104]

There are two types of molecular vibrations namely the stretching (symmetric and asymmetric stretch) and bending vibrations (scissoring, rocking, wagging and twisting)[104] as indicated in **Figure 4.10**. Both vibration types can be mathematically predicted. The prediction of stretching vibration employs the application of Hookes' Law which relates the frequency (ν) of the vibration of the spring to the mass (m) and force constant of the spring (k) according **Equation 4.4**.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad (\mathbf{4.4})$$

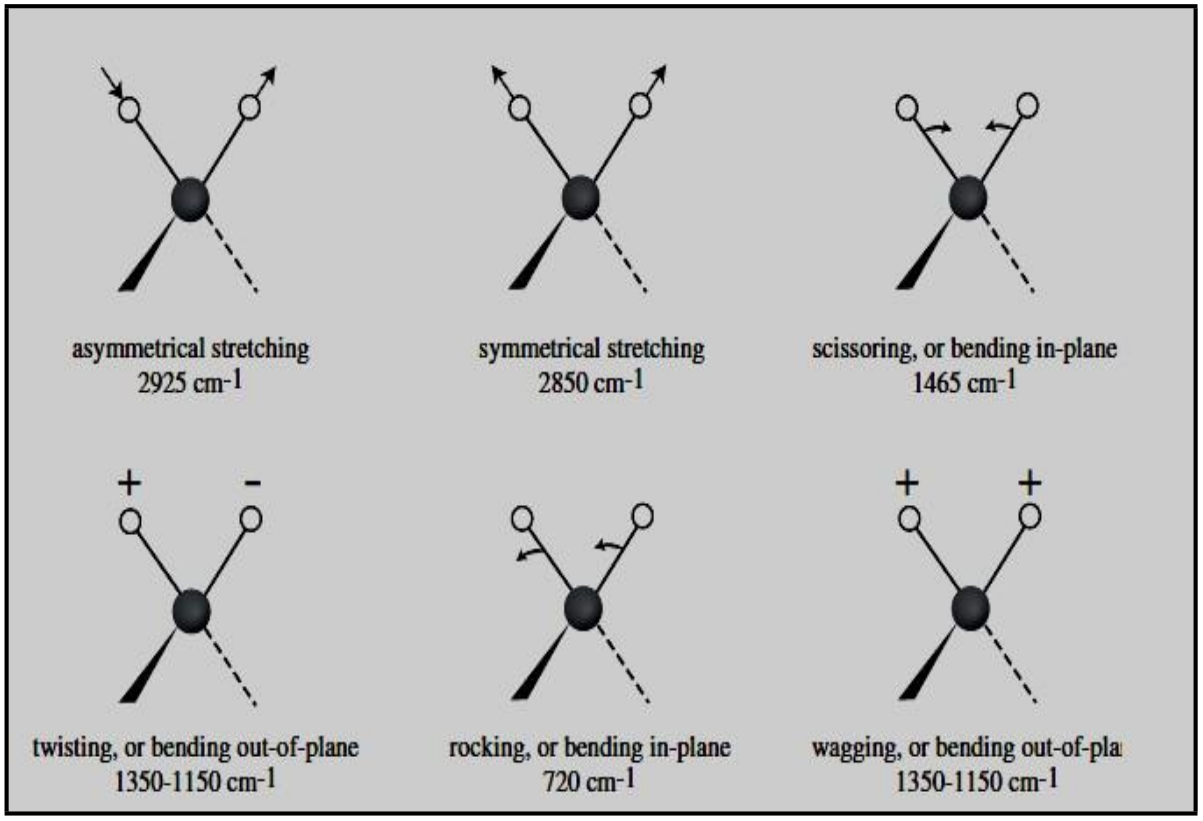

Figure 4.10: Vibration type of -CH_2 group.[104]

An example of the display or output of the vibration of chemical bonds within a molecule is given in **Figure 4.10**. Both types of vibrations are depicted in **Figure 4.11**, with the bending vibrations at about 400 to 1000 cm^{-1} and the double bond stretching vibration in the region between 1500 and 2000 cm^{-1}.[104] The IR spectroscopy has an advantage of showing a unique fingerprint spectrum for the analyzed compound and it requires a small amount of the sample.

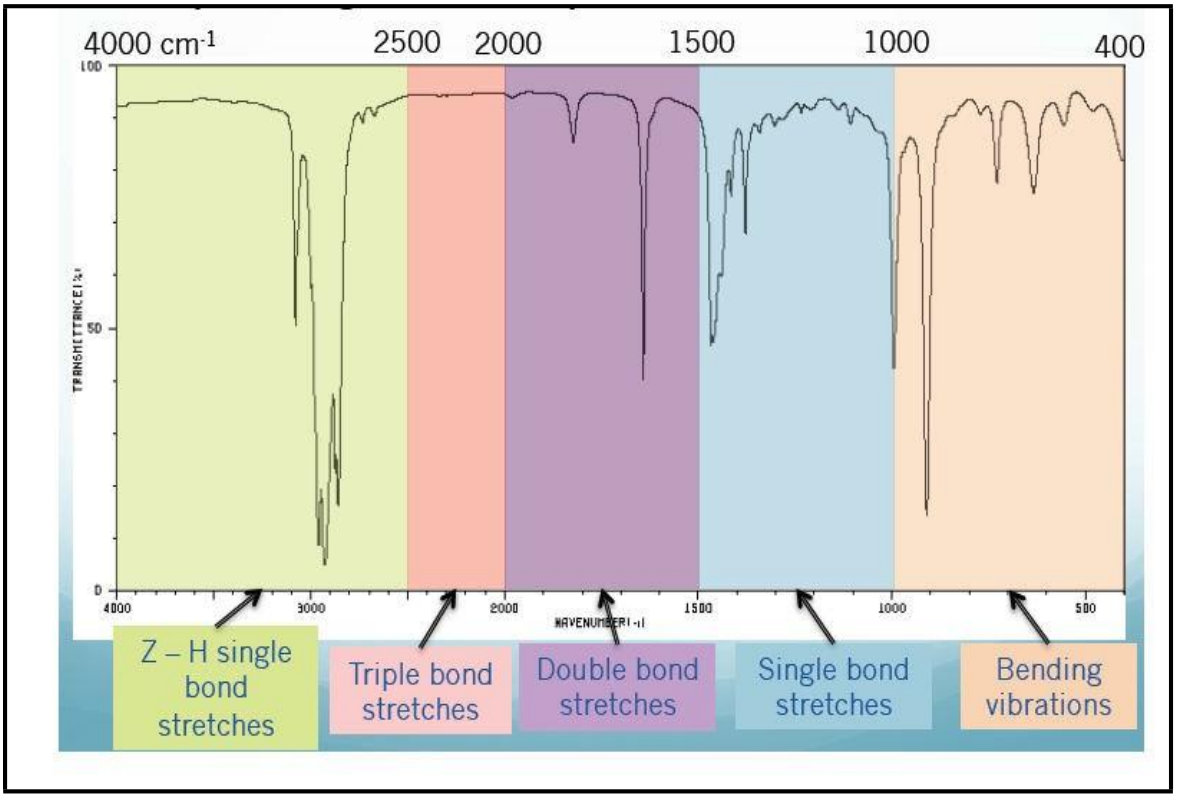

Figure 4.11: IR spectrum with correlation peaks.[105]

4.5. X-RAY CRYSTALLOGRAPHY

Crystallography is a powerful technique used to determinate the molecular structures of synthetic complexes by X-ray diffraction. It was initially developed in 1985 by Wilhelm Röntgen who studied the nature of X-rays which are produced through the collision of a high energy charged particle with matter.[106] The X-ray region is situated in the lower energy side of the UV region in the electromagnetic spectrum (see **Figure 4.2**) with wavelengths ranging between 0.01 and 10 nm.[107] In 1912, Lawrence and William Bragg discovered the diffraction phenomena of X-rays by crystals and thereafter derived Bragg's Law to determine the structure of crystals (see **Figure 4.12**). Bragg's Law relates the wavelength of X-rays to the angle of reflection[108] according to **Equation 4.5**.

[105] Infrared Spectroscopy**,** [Accessed 11-10-2015]. Available from: http://ecas.wvu.edu/chemvideos/pages/234/IR%20Lecture%20Slides.pdf
[106] J. Hannavy, Encyclopedia of Nineteenth-Century Photography, p. 1205 (2008)
[107] K. Wetzig, C.M Schneider, Metal Based Thin Films for Electronics, p. 93 (2003)
[108] X-ray diffraction, Bragg's Law and Laue equation, [Accessed 3-11-2015]. Available from: http://electrons.wikidot.com/x-ray-diffraction-and-bragg-s-law

$$n\lambda = 2d\sin\theta \qquad (4.5)$$

Where,

n = an integer determined by the given order or reflection

λ = the wavelength of x-rays

d = spacing between the planes in the atomic lattices and

θ = the angle between incident ray and lattice planes

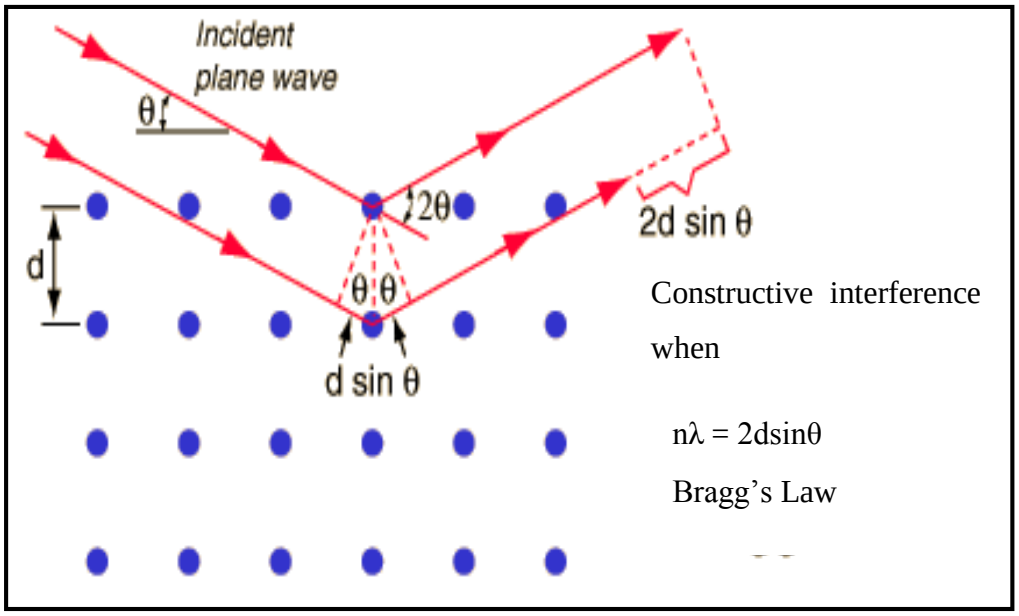

Figure 4.12: Bragg's Law for X-ray diffraction.[108]

The X-ray crystallography involves the deposition of a crystal compound through an X-ray beam. The X-rays are scattered by the atoms within the chemical compound and undergoes constructive interference according to Bragg's Law (see **Equation 4.5**) to produce a diffraction pattern which is then mapped onto the electron density map to give the information on the arrangement of atoms in the crystal (see **Figure 4.13**).[109]

[109] X-Ray diffraction**,** [Accessed 03-11-2015]. Available from: https://commons.wikimedia.org/wiki/File:X_ray_diffraction.png

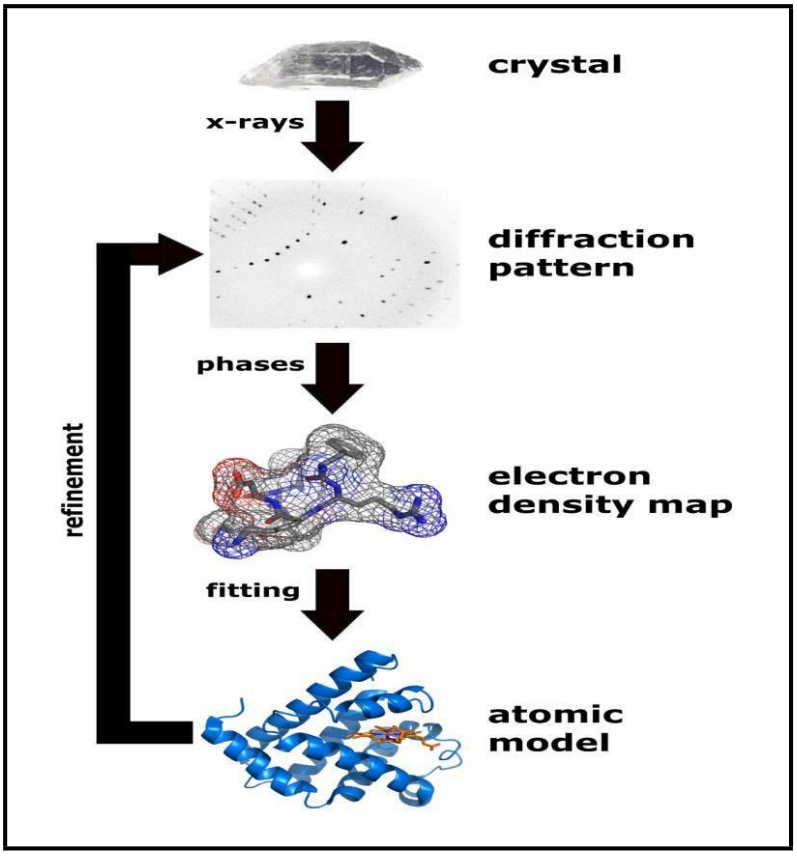

Figure 4.13: Steps followed in the determination of a molecular structure by X-ray crystallography.[109]

Although X-ray crystallography is not suitable for examining solutions or the behavior of molecules in solution, the technique has several advantages which includes the determination of a molecular structure in a three dimensional space and a high atomic resolution obtained for crystals that are well-diffracting and also its exact empirical or molecular mass which is critically important for analytical chemists.[110]

4.6. CHNS MICROANALYSER

CHNS microanalyses is a technique used to characterise (elemental analysis) compounds containing carbon, hydrogen, nitrogen and sulphur and has been in use for over thirty years.[111] Other than in chemical industry it also has applications in pharmaceuticals, oil-related products, catalysis and food industries.[112] The basic set up or construction for the CHNS

[110] J.D. Guzman, Labtimes magazine, p. 68 (2010)
[111] K.J Etherington, A Roger, P Hemming, Lab-Plus International magazine, p. 26 (2006)
[112] M. Thompson, The Royal Society of Chemistry: Analytical Methods Committee, 29, pp. 1 - 2 (2008)

elemental analyses is as shown in **Figure 4.14**. This technique involves five steps namely i) sample introduction in a tin capsule, ii) introduction of the sample within the tin capsules into the combustion chamber and the addition of oxygen which oxidises the C, H, S and N within the sample to CO_2, H_2O, SO_2 and N_2+ NO_x respectively (see **Figure 4.15**), iii) the transportation of the gaseous products by helium (carrier gas) to the detector, iv) absorption of excess oxygen and reduction of NO_x to elemental N_2 in the silcon tube packed with copper granules and v) the detection of the analytes and elemental analysis (%) of C, H, N and S.[112] The temperature of combustion is about 950 °C for the simultaneous CHNS analyses in an environment that is enriched with oxygen.[112, 113]

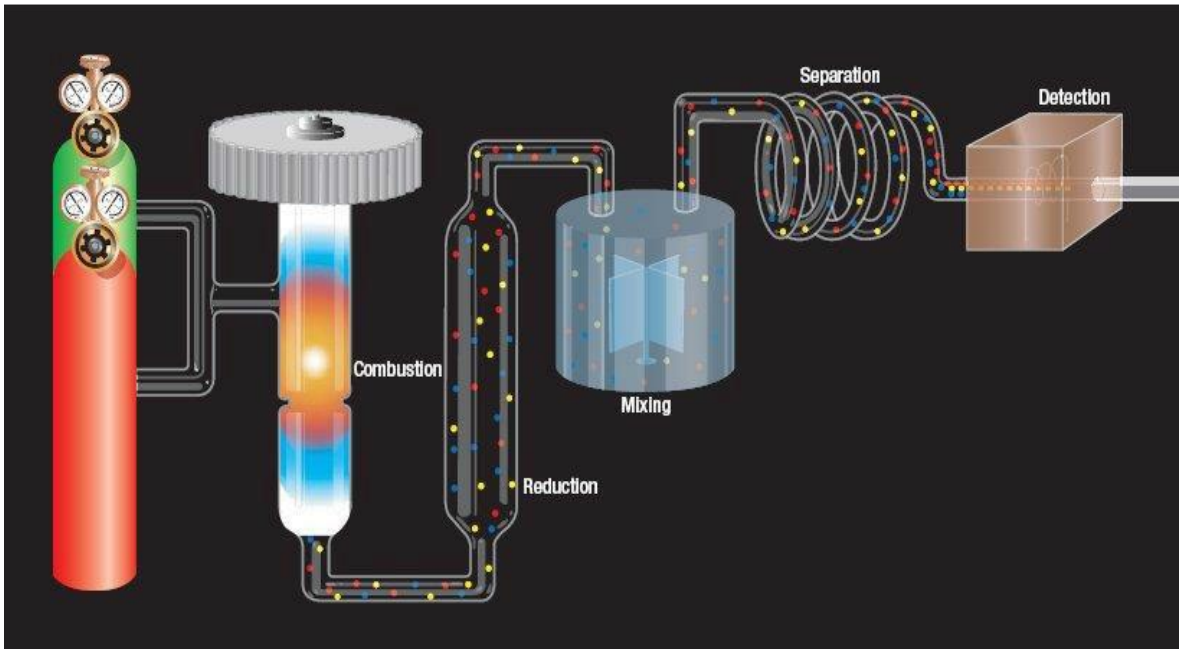

Figure 4.14: The basic set up for a CHNS micro-analyser.[113]

[113] Basic Theory of Elemental Analysis, [Accessed 11-10-2015]. Available from: http://www.qub.ac.uk/schools/SchoolofChemistryandChemicalEngineering/FileStore/InternalForms/ASEPAnalyticalServicesandEnvironmentalProjects/Filetoupload,404656,en.pptx.

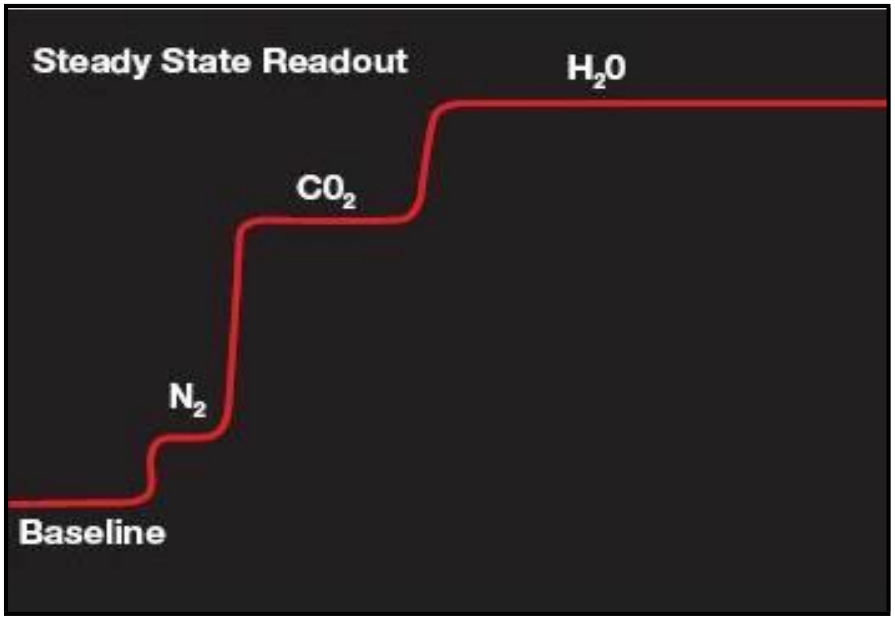

Figure 4.15: Stages followed in the formation CO_2, H_2O, N_2 and N-oxides.[113]

CHNS microanalyser requires accurately weighed but small amount of sample which is one of its advantages. Other advantages include simultaneous quantification of C, H and S under identical conditions and analysis of less than 8 min is required per sample.

4.7. CONCLUSION

Different dissolution techniques namely open vessel, flux fusion and microwave acid-assisted digestion have been used for sample decomposition of chemically inert compounds prior to analyses by ICP-OES. The most suitable and advantageous dissolution technique was identified as microwave acid-assisted and this is mainly due to its short digestion period and minimised sample contamination (see **Table 4.2**). Flux fusion was also used where the acid digestion techniques did not yield complete sample dissolution. Fusion digestion has an advantage of completely dissolving many chemical inert samples which include HfO_2. However, this technique is usually energy intensive and results in cross contamination of the sample by the flux salt. ICP-OES was used for Hf analyses in different solution matrices due to its availability, ability to simultaneously analyse more than one element, high sensitivity and low detection limits (see **Table 4.3**). Synthesized compounds were characterised using IR spectroscopy, X-ray crystallography ICP-OES and the CHNS microanalyser.

5 Method development for the digestion and quantification of hafnium containing compounds

5.1. INTRODUCTION

The aim of this study (see **Chapter 1, Section 1.3**) was to develop a suitable method of digestion and dissolution for hafnium containing compounds with the focus being on the chemically inert HfO_2. This dissolution method development is extremely important for accurate analysis of hafnium in different sample matrices (see **Chapter 5.4**). The samples that were investigated include HfO_2, $HfCl_4$, and the newly synthesized fluorohafnate and thiocyanate complexes namely sodium, potassium, rubidium, cesium, ammonium, tetramethyl ammonium, and tetraphosphenyl hexafluorohafnate and hafnyl thiocyanate.

In this section, an in-depth experimental study of the techniques used for the digestion and dissolution of hafnium containing compounds will be discussed in detail. This discussion will be followed by the an in-depth discussion of different analytical techniques such as ICP-OES, CHNS-micro analyser and infrared spectroscopy(IR) which were used to characterise and quantify hafnium in different hafnium containing compounds. The scheme indicating the dissolution and analyses of hafnium compounds in this study is given in **Figure 5.1**.

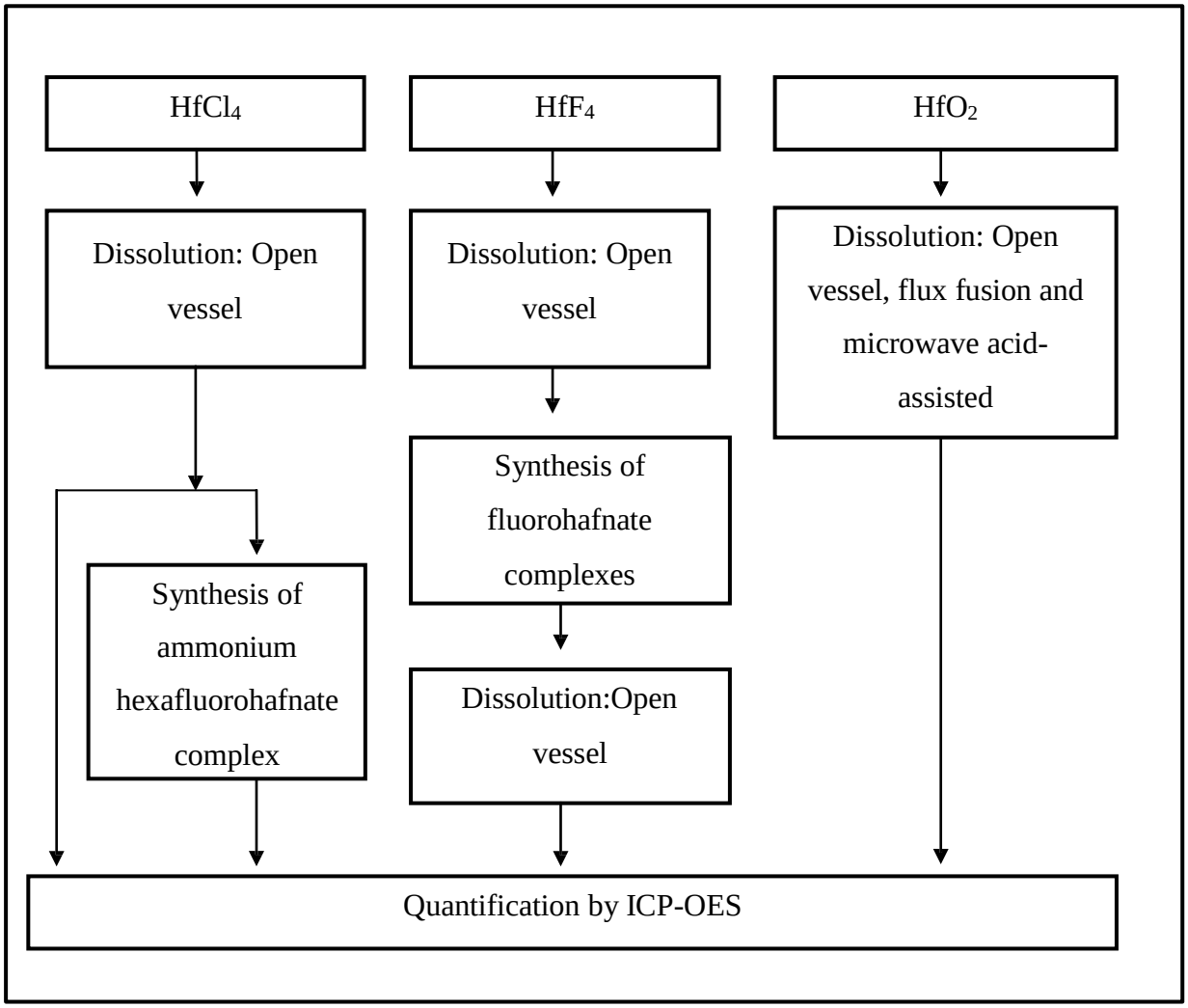

Figure 5.1: Scheme indicating the decomposition and quantification of hafnium samples in this study

5.2. GENERAL EXPERIMENTAL PROCUDURES

5.2.1. EQUIPMENT AND REAGENTS

All chemicals and reagents used during the study (with their respective purities and purpose) are listed **Table 5.1**.

Table 5.1: Chemicals and reagents used in this study for synthesis

Chemical	Formula	Purity, %	Purpose	Supplier
Reagents				
Hafnium ICP standard in HNO_3 (5 % v/v, 1000 mg/L)			Calibration curves	Sigma Aldrich
Potassium thiocyanate	KSCN	-	Synthesis	Saar Chemicals
Sodium fluoride	NaF	99	Synthesis	Saar Chemicals
Sodium tetraborate	$Na_2B_4O_7$	99	Digestion	Merck Chemicals
Ammonium bifluoride	NH_4HF_2	-	Digestion	Merck Chemicals
Hafnium tetrachloride	$HfCl_4$	98	Reference material	Sigma Aldrich
Hafnium tetrafluoride	HfF_4	99.9	Synthesis and Validation	Sigma Aldrich
Cesium fluoride	CsF	98	Synthesis	Sigma Aldrich
Hafnium oxide	HfO_2	99	Digestion	Sigma Aldrich
Tetraphenylarsonium chloride,	$(PPh_4)Cl$	98	Synthesis	Sigma Aldrich
Ammonium fluoride	NH_4F	98	Synthesis	Sigma Aldrich
Rubidium fluoride	RbF	99.8	Synthesis	Sigma Aldrich
Sodium hydroxide	NaOH	98	Digestion	Sigma Aldrich
Potassium fluoride	KF	-	Synthesis	Sigma Aldrich
Ammonium hydroxide	NH_4OH	25	Synthesis	Sigma Aldrich
Ammonium sulphate	$(NH_4)_2SO_4$	-	Digestion	Sigma Aldrich
Acids				
Nitric acid	HNO_3	55	Cleaning glassware	Sigma Aldrich
Nitric acid	HNO_3	65	Digestion and analysis	Sigma Aldrich
Hydrochloric acid	HCl	32	Digestion and analysis	Sigma Aldrich
Aqua regia	3 HCl: 1 HNO_3	-	Digestion	Sigma Aldrich
Sulphuric acid	H_2SO_4	98	Digestion and analysis	Sigma Aldrich

5.2.2. GENERAL EQUIPMENT

5.2.2.1. Weighing

All the samples were accurately weighed to 0.1 mg at 20 ± 2 °C using a Shimadzu AW320 electronic balance certified under ISO 9001. All experimental samples and reagents which were used in the study were weighed by adding the sample to a pre- weighed poly top glass vial.

5.2.2.2. Glassware and water purification equipment

Schott Duran type (50 and 100 mL) beakers were used for the sample digestion and synthesis of hexafluorohafnate and hafnyl thiocyanate complexes respectively. The Blau brand grade (A) volumetric flasks (100.0 and 200.0 mL) were used for sample dilutions and accurate volume measurements. Brand Transferpettes type (1000 ȝL and 10 mL) micro-pipettes from Lasec with an accuracy of ±0.01 mL were used for the accurate transfer of solutions into volumetric flasks. An ultra- reverse osmosis system from ADJ Traders (see **Figure 5.2**) was used for purification of water which was used in all cases throughout the study. The conductivity of pure water using a Hanna DIST 4 (HI 98304) conductivity meter was measured as 0.04 mS/cm.

Figure 5.2: a) Ultra reverse osmosis system and (b) water storage tanks

5.2.2.3. Microwave equipment

An Anton Paar Perkin-Elmer Multiwave 3000 reaction system (see **Figure 5.3)**, equipped with an 8SXF100 rotor and polytetrafluoroethylene (PTFE) reaction vessels was used for the acid dissolution of the different fluoride containing samples. Non-fluoride containing samples such as HfO_2 were dissolved using glass reaction vessels in the same microwave reaction system. The operation conditions for acid-assisted microwave digestion of hafnium oxide with various reagents are given in **Table 5.2**. Prior to the digestion reaction, the reaction vessels were cleaned using 8 mL of 55 % HNO_3 in a microwave heated oven for a period 30 min.

Figure 5.3: Anton Paar Perkin-Elmer Multiwave 3000 microwave reaction system

Table 5.2: Microwave operating conditions for the acid-assisted microwave assisted digestion of hafnium oxide

Parameter	Condition
Power	600 and 800 watts
Ramp	15 min
Hold	45, 55 min
Pressure rate	0.5 bar/sec
Temperature	240 °C
Pressure	60 bar
Reagents	*Aqua regia*, HCl (32 %), HNO_3 (65 %), H_2SO_4 (98 %)
Volume of the reagent	8 mL

5.2.2.4. ICP-OES spectrometer

A Shimadzu ICPS-7510 ICP-OES instrument with a radial-sequential plasma spectrometer was used for the wet chemical analysis of different hafnium containing compounds. **Table 5.3** shows default conditions of the emission intensity measurement that were used for all the analysis.

Table 5.3: ICP-OES operating conditions for the analysis of hafnium

Parameter	Condition
RF Power	1200 W
Coolant gas flow	14.0 $L.min^{-1}$
Plasma gas flow	45 $L.min^{-1}$
Auxiliary gas flow	0.5 $L.min^{-1}$
Carrier gas flow	0.7 $L.min^{-1}$
Sample introduction method	Peristaltic pump
Type of spray chamber	Glass cyclonic
Type of nebuliser	Concentric
Injector Tube diameter	3.0 mm

5.2.2.5. Characterisation of hafnium compounds

A Digilab Scimitar Series IR spectrometer was used for the infrared characterisation of the newly synthesised complexes and IR spectra were recorded within the range of 4000 – 200 cm^{-1}. A Truspec micro CHNS analyser from LECO was used for the elemental analyses of C, H, N and S in the synthesized hafnyl thiocyanate complex. The structural analysis of the synthesized hafnium complexes using X-ray crystallography was performed at the Nelson Mandela Metropolitan University.

5.2.3. GENERAL EXPERIMENTAL PROCEDURE

Purified water (see **Section 5.2.2.2**, **Figure 5.2**) was used for sample dilutions after acid digestion followed by filtration. The Hf analysis was performed with ICP-OES at the selected wavelength of 277.336 nm. This particular Hf emission was selected based on the absence of interfering elements in all the Hf samples, the sensitivity of the line as well as the absence of any influence of the acid matrix used in the Hf samples. The analyses of samples were performed in triplicate (unless otherwise stated) and the final results are reported with standard deviations to indicate the uncertainty of the mean value.

5.2.3.1. Flux fusion

A high temeperature fusion furnace shown in **Figure 5.4** was used for flux fusion of hafnium samples at fusion temperature(1020 °C) above the temperature of fluxes.[11]

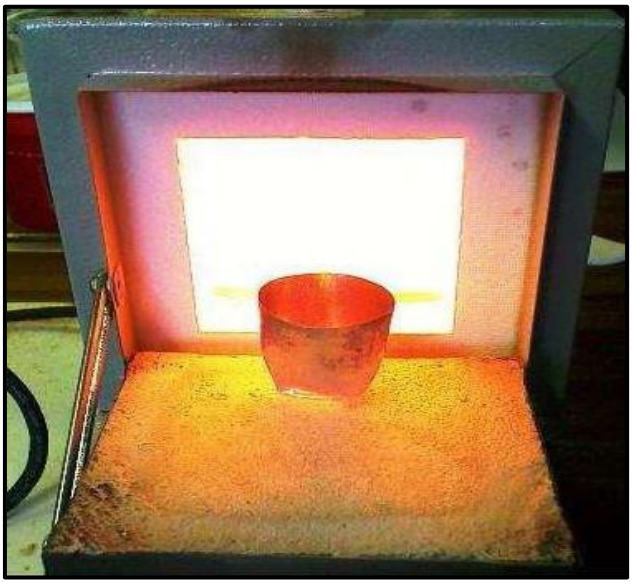

Figure 5.4: Pt crucible in fusion furnace at 1020 °C

The resulting white clear melts from the flux fusion experiments were subsequently dissolved in a minimum amount of H_2SO_4 (2.5 mL) for a period of 30 and 90 min for both NaOH and $Na_2B_4O_7$ and 90 min for NH_4HF_2 with constant stirring.

5.2.3.2. Elemental analysis (CHNS)

Analysis by a CHNS-microanalyser entailed the initial running of the blanks (analysis without a sample) until stable readings of N, C, H and S were obtained. Upon reaching stable instrument conditions, a calibration standard (sulfamethazine, EDTA) of approximately ~2 mg were weighed into a tin capsule and analysed along with accurately weighed masses of the hafnyl thiocyanate for the determinations of C, N and S content.

5.3. QUANTIFICATION OF HAFNIUM IN HAFNIUM COMPOUNDS

5.3.1. PREPARATION OF CALIBRATION STANDARDS FOR ICP-OES ANALYSIS

Hf calibration standards were prepared from the original Hf ICP standard solution of 1000 mg/L (see **Table 5.1**) for the analysis of Hf using ICP-OES. Four sets of Hf standards of concentrations of 0, 0.4, 1, 2, 5 and 10 mg/L were prepared in different acid solutions namely, HNO_3, HCl, *aqua regia* and H_2SO_4. A blank solution used for background corrections was prepared by adding 2.5 mL of appropriate acid (HNO_3, HCl, *aqua regia* and H_2SO_4) and the flasks were filled to the mark with purified water. All solutions were allowed to stand for a day before ICP-OES analysis to obtain homogenized and stable solutions.

5.3.1.1. Determination of LOD and LOQ of hafnium

The calibration solutions in **Section 5.3.1** were also used for determinations of the limit of detection (LOD) and quantification (LOQ). For this purpose, the intensity measurements for all the standards were performed in triplicate while ten replicates measurements were performed on the blank solutions[113]. Linear curves with the correlation coefficients (R^2) of 0.9998, 0.9994, 1.000 and 0.9999; gradients of 0.0130, 0.0161, 0.0133 and 0.1096 ppm^{-1} were obtained for Hf standard solutions acidified with HNO_3, HCl, *aqua regia* and H_2SO_4

[113]D.A Skoog, D.M West, F.J Holler and S.R Crouch, Fundamentals of analytical chemistry, 8th edition, pp 90-146 (2004)

respectively. The LOD and LOQ of Hf using the different acids were calculated using standard deviation approach according to **Equation 5.1** and **5.2**[113] and are reported in **Table 5.4**.

$$LOD = \frac{s}{m} \times 3.3 \quad (\mathbf{5.1})$$

where *s* is the standard deviation and m is the slope of the calibration curve.

$$LOQ = LOD \times 10 \quad (\mathbf{5.2})$$

Table 5.4: Hafnium intensities in different acid matrices and the calculated LOD and LOQ at 277.336 nm

Replicate Number	HCl	HNO_3	*Aqua regia*	H_2SO_4
1	0.0214	0.0232	0.0224	0.0147
2	0.0214	0.0230	0.0223	0.0148
3	0.0219	0.0232	0.0222	0.0148
4	0.0223	0.0229	0.0226	0.0147
5	0.0220	0.0228	0.0217	0.0150
6	0.0213	0.0230	0.0222	0.0152
7	0.0223	0.0228	0.0221	0.0146
8	0.0217	0.0228	0.0223	0.0149
9	0.0216	0.0231	0.0219	0.0147
10	0.0223	0.0229	0.0220	0.0149
Mean(S.D)	0.0218(3)	0.0229(1)	0.0221(2)	0.0148(1)
Slope	0.0130	0.0161	0.0133	0.1096
LOD	0.0985	0.0322	0.0649	0.0051
LOQ	0.9846	0.3215	0.6491	0.0510

5.3.2. OPEN VESSEL (WET ASHING) DISSOLUTION OF HAFNIUM TETRACHLORIDE

In the absence of a certified reference material (CRM) or standard reference material the evaluation of the accuracy of Hf analysis after digestion and dissolution was performed by determining the recovery of Hf in commercial $HfCl_4$ which is a simple matrix, has a known Hf content and is easily soluble in an acidic environment.

Hafnium tetrachloride samples in the range of 0.01125 - 0.01518 g were accurately weighed and transferred to 50.0 mL glass beakers. 2.5 mL of different acids (65 % HNO_3 and 98 % H_2SO_4) were added to each glass beaker. The solutions were heated for 30 min to approximately 70 °C for 65 % HNO_3 and 120 °C for 98 % H_2SO_4 to ensure the complete dissolution of hafnium tetrachloride as indicated by visual inspection. The solutions were allowed to cool to room temperature, then quantitatively transferred to

100.0 mL volumetric flasks and filled to the calibration mark with purified water. 10.0 mL aliquots of these solutions were subsequently transferred to 100.0 mL volumetric flasks and filled to the mark with purified water. These diluted solutions were analyzed for Hf concentrations using ICP-OES and the results are given in **Table 5.5**.

Table 5.5: Quantification of Hf in $HfCl_4$ in different acid medium

Sample Number	Hafnium content, ppm		% Hf recoveries
	Expected	Found	
65 % HNO_3			
Replicate 1	7.449	7.289	97.83
Replicate 2	7.840	7.634	97.37
Replicate 3	8.459	8.311	98.25
Average			97.81
Standard deviation			0.44
98 % H_2SO_4			
Replicate 1	6.270	6.250	99.68
Replicate 2	6.498	6.480	99.72
Replicate 3	6.690	6.720	100.5
Average			99.95
Standard deviation			0.43

5.3.3. OPEN VESSEL (WET ASHING) DISSOLUTION OF HAFNIUM TETRAFLUORIDE

Three portions of hafnium tetrafluoride (~0.01 g) were accurately weighed (to 0.1 mg) and transferred into 50 mL glass beaker. 2.5 mL of 98 % H_2SO_4 was added and the mixture was heated to temperature of 120 °C for 30 min with constant stirring to ensure the complete dissolution of hafnium tetrafluoride and visual inspection indicated the complete dissolution of the sample. After cooling to room temperature, the solutions were quantitatively transferred

to 100.0 mL volumetric flasks and filled to the mark with purified water for ICP-OES analysis and the results are presented in **Table 5.6**. The analytical results indicated the complete recovery of Hf using 98 % H_2SO_4 as acid and it was therefore used as this acid medium for the dissolution of the rest of the prepared hafnium complexes (see **Section 5.3.4.2**) when hafnium tetrafluoride was used as the starting material.

Table 5.6: Quantification of Hf in HFf_4 dissolved in 98 % H_2SO_4 (λ = 277.33 nm)

Sample Number	Hafnium content, ppm		Hf recovery, %
	Expected	Found	
Replicate 1	1.645	1.643	99.89
Replicate 2	1.619	1.615	99.77
Replicate 3	1.603	1.597	99.65
Average			99.77
Standard deviation			0.12

5.3.4. PREPARATION OF FLUOROHAFNATE COMPLEXES

5.3.4.1. Preparation of potassium hexafluorohafnate

Three portions of potassium fluoride of approximately 0.7 g (accurately weighed to 0.1 mg) were dissolved in 75 mL of purified water. Approximately 1.5 g portions of hafnium tetrafluoride was accurately weighed and transferred in small quantities to each potassium fluoride solution while stirring at a monitored temperature of 70 °C after 0.5 mL of 48 % HF (to create acidic medium with common anion effect) was added to the mixture. All the hafnium(IV) tetrafluoride salts were completely dissolved after about 30 min. The mixture was left to cool to room temperature and colourless crystals of potassium hexafluorohafnate were obtained after 4 days.

The other hafnium hexafluoro complexes (see **Table 5.7**) were prepared using the same method described in the preparation of potassium hexafluorohafnate. The isolated compounds include those of cesium, rubidium, tetraphenylphosphonium, tetramethylammonium and sodium hexafluorohafnate. The proposed reaction for these syntheses is as follows (see **Equation 5.3**);

$$HfF_4 + 2F^- \longrightarrow HfF_6^{2-} \xrightarrow{2M^+} M_2HfF_6 \qquad \textbf{(5.3)}$$

where, M = Na^+, K^+, Rb^+, Cs^+, $N(CH_3)_4)^+$ and $(PPh_4)^+$

The method described in **Section 5.3.4.1** did not succeed in the successful synthesis of the ammonium hexafluorohafnate (the complex did not crystalline), hence a different method was used (see **Section 5.3.4.3**).

Table 5.7: Mass of compounds used for the production of different hexafluorohafnate complexes

Expected Crystal Compound	Cation Donor	Mass range of HfF_4, g	Mass range of donor, g	Volume of 48 % HF, mL
Na_2HfF_6	NaF	1.75–1.81	0.58 -0.19	0.5
Rb_2HfF_6	RbF	0.18-0.21	0.09-015	0.5
Cs_2HfF_6	CsF	0.14–0.16	0.06–0.09	0.5
$[N(CH_3)_4]HfF_5.H_2O$	$N(CH_3)_4F$	0.65–0.72	0.05 -0.08	0.5
$(PPh_4)_2HfF_6\ 2H_2O$	PPh_4Cl	0.09–0.12	0.04-0.06	2

5.3.4.2. Characterisation of the different hafnium hexaflouro complexes with IR spectroscopy

The IR spectra of the different hafnium metal complexes (M_2HfF_6 where M = Na^+, K^+, Rb^+, Cs^+, NH_4^+, PPh_4^+ and $[N(CH_3)_4]^+$ were recorded and are reported in **Figure 5.5** and **5.6**. The ν(Hf-F) stretching frequencies of the of hafnium metal alkali hexafluoro complexes is given in **Table 5.8** while those for the ammonium type cations complexes is given in **Table 5.9**.

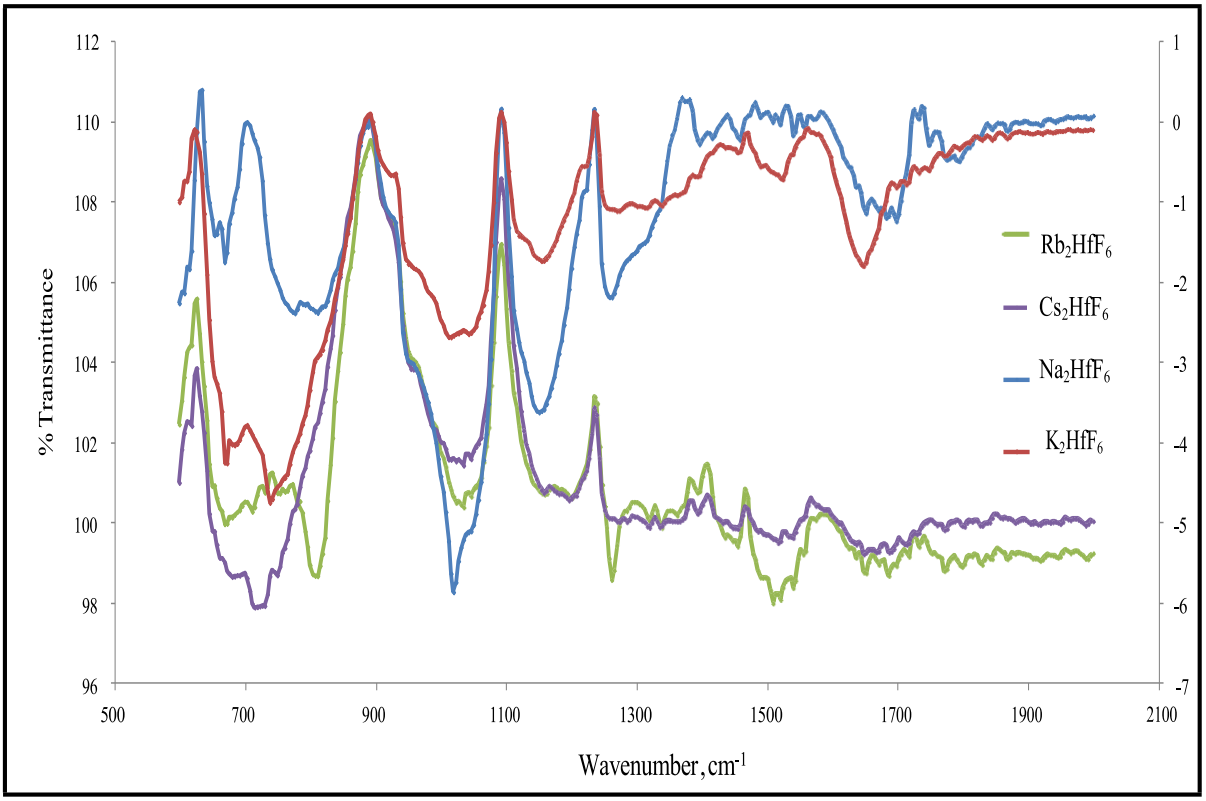

Figure 5.5: IR spectra of the different alkali metal hexafluorohafnate complexes with monocations

Table 5.8: ν(Hf-F) stretching vibrations of the metal alkali hafnium hexafluoro complexes

Expected Hf complexes	ν(Hf-F), cm^{-1}
Na_2HfF_6	668
K_2HfF_6	737
Rb_2HfF_6	734
Cs_2HfF_6	746

5.3.4.3. Preparation of ammonium hexafluorohafnate.[114]

Hafnium tetrachloride (1.5 g, 0.005894 moles) was dissolved in water (5 mL) with constant stirring with the formation of $HfOCl_2$ according to **Equation 5.4**;

$$HfCl_4 + H_2O\ (l) \longrightarrow HfOCl_2\ (aq) + 2HCl\ (aq) \qquad \textbf{(5.4)}$$

The obtained hafnyl chloride ($HfOCl_2$) solution was diluted with water (2 mL). Hafnium precipitated as hafnium hydroxide ($Hf(OH)_4$) upon slow addition of ammonium solution (4 mL) with constant stirring according to **Equation 5.5**.

$$HfOCl_2 + H_2O + 2NH_4OH \longrightarrow Hf(OH)_4 + 2NH_4Cl \qquad \textbf{(5.5)}$$

Hafnium hydroxide was filtered and the residual cake was washed with several portions of cold water. A hot solution of ammonium bifluoride (10 mL) was added to the filtrate as indicated in **Equation 5.6**;

$$Hf(OH)_4 + 3NH_4HF_2 \longrightarrow (NH_4)_2HfF_6 + NH_4OH + 3H_2O \qquad \textbf{(5.6)}$$

An excess amount of ammonium bifluoride (as the source of fluoride ions to ensure the highly soluble HfF_6^{2-} anion) was added and the mixture was heated to 70 °C with constant stirring for 20 min. The solution was cooled to room temperature and filtered to obtained colourless crystals of ammonium hexaflourohafnate.

[114]Preparation of ammonium hexafluorozirconate – $(NH_4)_2ZrF_6$, [Accessed 19-11-2015]. Available from: http://oxfordchemserve.com/preparation-of-ammonium-hexafluorozirconate-nh42zrf6/

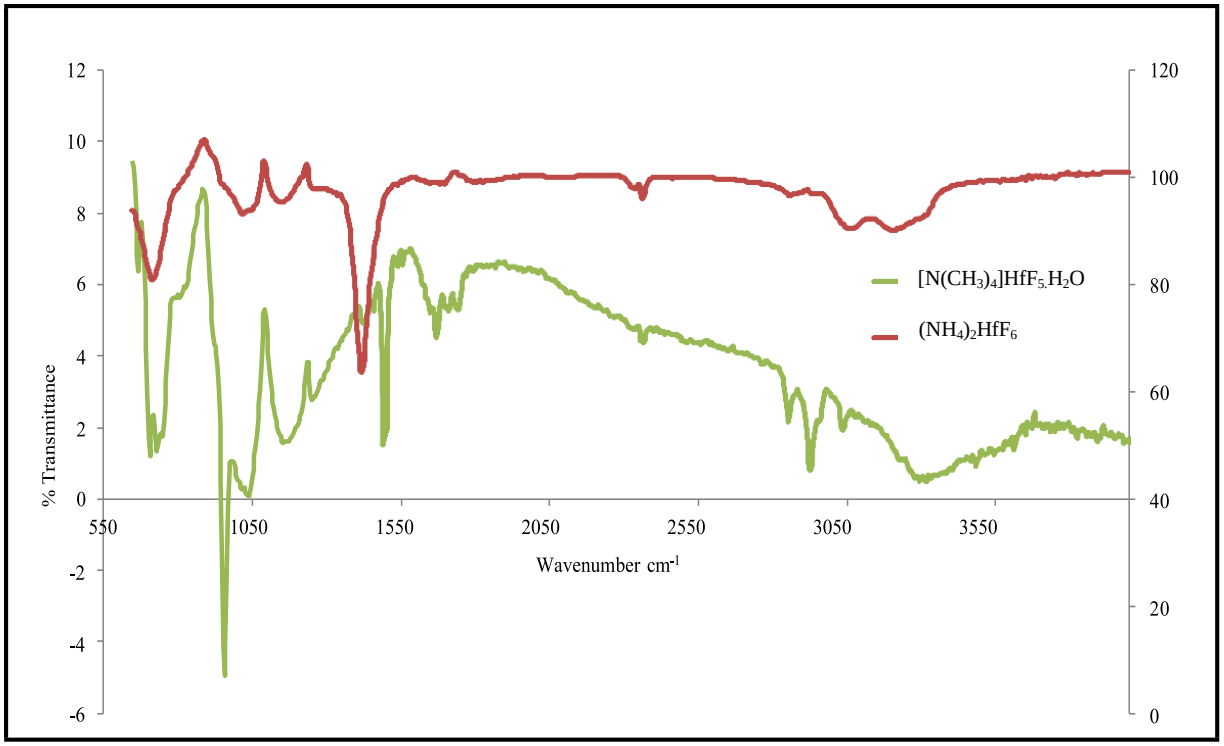

Figure 5.6: IR spectra of $[N(CH_3)_4]HfF_5.H_2O$ and $(NH_4)_2HfF_6$

Table 5.9: Infrared data of the synthesized of hafnium complexes

Expected Hf complexes	ν(Hf-F), cm^{-1}	ν(N-H), cm^{-1}	ν(O-H), cm^{-1}
$(NH_4)_2HfF_6$	731	3209, 3055	
$([N(CH_3)_4]HfF_5.H_2O$	723	3028	3286

5.3.4.4. Open vessel digestion of hafnium hexafluorohafnate complexes

Hafnium complexes (0.0138 – 0.0154 g) prepared in **Section 5.3.4** were accurately weighed in glass vials and quantitatively transferred to glass beakers containing 10.0 mL 98 % H_2SO_4. The sample completely dissolved in concentrated H_2SO_4 and was quantitatively transferred to 100.0 mL volumetric flasks and filled with purified water. 10.0 mL aliquots of these solutions were subsequently transferred to 100.0 mL volumetric flasks and filled to the mark with purified water. These diluted solutions were analyzed for Hf concentrations using ICP-OES and the results are presented in **Table 5.10**.

Table 5.10: Summary of ICP-OES results of the some of the synthesized hafnium complexes dissolved in H_2SO_4

Expected complex	Average hafnium content, ppm		% Hf recoveries(S.D)
	Expected	Found	
K_2HfF_6	3.859	3.847	99.7(1)
Rb_2HfF_6	2.637	2.738	98(3)
Cs_2HfF_6	5.221	5.338	102(2)
$(NH_4)_2HfF_6$	8.131	7.463	103(3)
$(PPh_4)_2HfF_6.2H_2O$	2.637	2.738	102(3)
Na_2HfF_6	8.385	8.010	92(2)
$[N(CH_3)_4]HfF_{5.}H_2O$	4.474	3.737	79(6)
$[N(CH_3)_4]_2HfF_{6.}H_2O$	4.330	3.737	94.7(5)

5.3.4.5. X-ray crystallography of the isolated complexes

A Bruker Kappa Apex II X-ray diffractometer system from the Nelson Mandela Metropolitan University was used to measure the intensity of the synthesized complexes. Data collection for the determination of the X-ray structure determination of some of successfully synthesized hafnium complexes suitable for X-ray crystallography were obtained for only four of the synthesized complexes namely K_2HfF_6, Rb_2HfF_6, Cs_2HfF_6 and $(PPh_4)_2HfF_6.2H_2O$. The radiation source was a fine-focus sealed tube emitting molybdenum Kα radiation at a wavelength 0.71073 nm with ω and ϕ-scans at 293 K. SIR 97 was used to solve all of the structures and SHEXL 97 for refinement. The structures of the successful synthesized complexes are reported as thermal ellipsoids in the different figures. The crystallographic data of these complexes are given in **Table 5.11** and the structures are individually and comprehensively discussed in **Section 5.5.2** and **5.5.3**.

Table 5.11: Crystallographic data and refinement parameters for the different hafnium compounds synthesized

Chemical formula		**K_2HfF_6**	**Rb_2HfF_6**	**Cs_2HfF_6**	**$(PPh_4)_2HfF_6.2H_2O$**
Compound name		Potassium hexafluorohafnate	Rubidium hexafluorohafnate	Cesium hexafluorohafnate	Tetraphosphenyl hexaflourohafnate
Formula weight		370.69	1762.25	558.31	1058.26
Wavelength Mo Kα		0.71073	0.71073	0.71073	0.71073
Crystal system		Orthorhombic	Monoclinic	Trigonal	Triclinic
Space group		Cm	C2/c	P-3m1	P-1
Cell length (Å)	a	6.5459 (7)	21.4921 (4)	6.3482	10.0723
	b	11.3836 (12)	6.5616 (1)	6.3482	11.0591
	c	6.8580 (7)	16.0741 (4)	4.9779	21.1870
Cell angle (°)	α	90	90	90	75.749 (2)
	β	90	101.590 (1)	90	77.842 (2)
	γ	90	90	120	71.111 (2)
Cell volume ($Å^3$)		511.03 (9)	2220.59 (5)	173.75	2142.06 (19)
Z		4	4	1	2
Theoretical density (g/cm^3)		4.818	5.271	5.336	1.641
F (000)		656	2754.8	236	1054
Absorption coefficient		22.080	29.710	25.366	2.582
Theta range for data collection		3.58 to 28.23	2.587 to 28.326	3.706 to 25.242	2.48 to 28.30
Index ranges		$-8 \geq h \geq 8$	$-28 \geq h \geq 20$	$-8 \geq h \geq 7$	$-12 \geq h \geq 13$
		$-14 \geq k \geq 15$	$-8 \geq k \geq 8$	$-8 \geq k \geq 8$	$-13 \geq k \geq 14$
		$-8 \geq l \geq 9$	$-21 \geq l \geq 21$	$-6 \geq l \geq 6$	$-25 \geq l \geq 28$
Refinement method		SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Data/ Restrain/ Parameters		370/0/30	2756/0/160	184/0/13	10553/6/548
Goodness of fit on F^2		1.265	1.127	1.295	1.075
Final R indices		$R_1 = 0.0301$, $wR_2 = 0.0831$	$R_1 = 0.0395$, $wR_2 = 0.1096$	$R_1 = 0.0911$, $wR_2 = 0.2027$	$R_1 = 0.0152$, $wR_2 = 0.0401$
R indices (all data)		$R_1 = 0.0301$, $wR_2 = 0.0831$	$R_1 = 0.0426$, $wR_2 = 0.1126$	$R_1 = 0.0912$, $wR_2 = 0.2033$	$R_1 = 0.0165$, $wR_2 = 0.0401$

5.3.5. PREPARATION OF HAFNYL THIOCYANATE

Three portions of hafnium tetrachloride of approximately 1.2 g (accurately weighed to 0.1 mg) were each dissolved in 7.0 mL of purified water with constant stirring. To the obtained hafnyl chloride ($HfOCl_2$) solution[114] approximately 2 g potassium thiocyanate was added in portions with constant stirring at temperature of 60 °C for 30 min. The mixture was left to cool down to room temperature to allow for crystallization of the product. After 3 days white crystals were isolated.

5.3.5.1. Infrared analysis of hafnyl thiocyanate

The IR spectrum of hafnyl thiocyanate is given in **Figure 5.7**. The complex was also characterized with IR and elemental analysis and the results are given in **Table 5.12.**

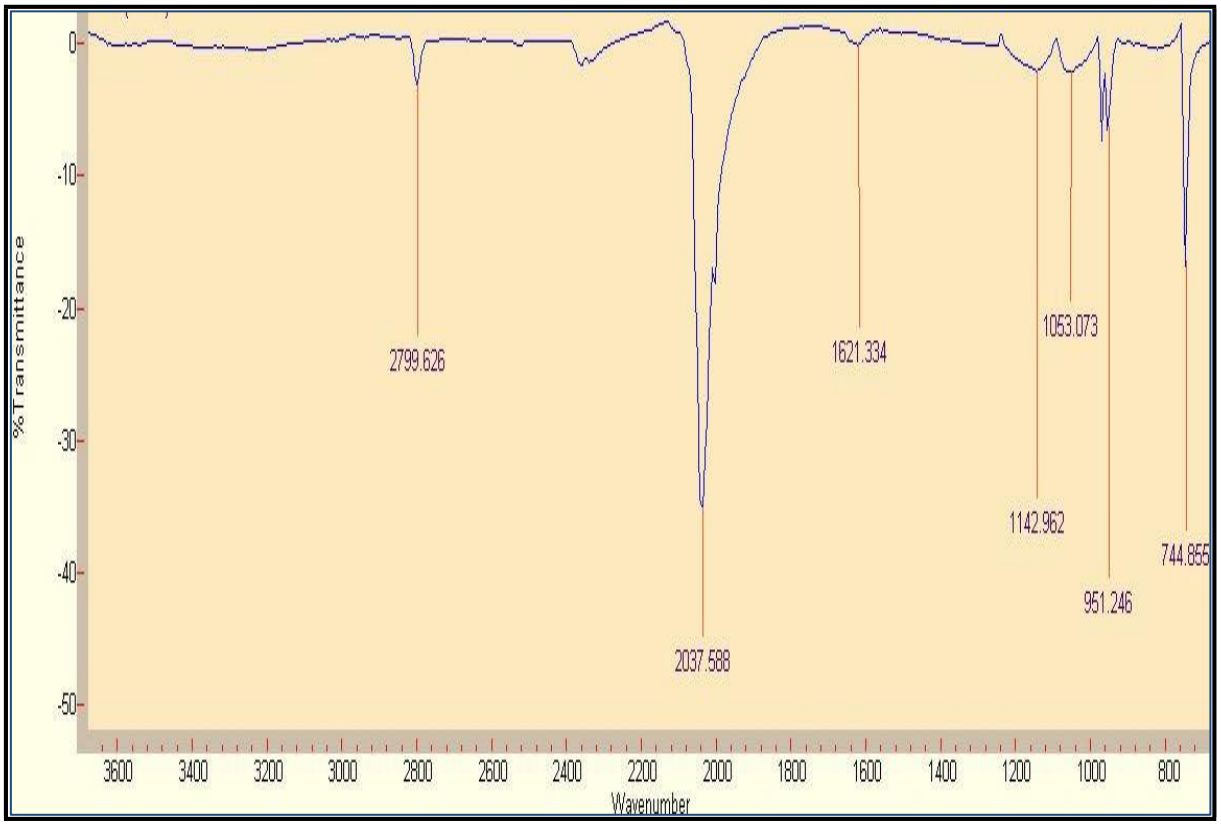

Figure 5.7: IR spectrum of hafnyl thiocynate

Table 5.12: IR stretching frequencies of hafnyl thiocyanate

IR Stretching frequencies of $HfO(SCN)_2$, cm^{-1}	
ν(CN)	2038
ν(Hf-N)	745
ν(Hf=O)	951

5.3.5.2. Open vessel digestion of hafnyl thiocyanate

A stock solution of the synthesized $HfO(SCN)_2$ was prepared by accurately weighing (0.029 – 0.030 g) and quantitatively transfer them to 100.0 mL volumetric flask with purified water. 10 mL of H_2SO_4 aliquots were added and the flask was filled to the mark with water and thoroughly shaken to homogenize it. 10.0 mL aliquots of this solution were subsequently transferred to 100.0 mL volumetric flasks and filled to the mark with purified water. These diluted solutions were analyzed for Hf concentrations using ICP-OES and the results are given in **Table 5.13**. The elemental analysis for isolated $HfO(SCN)_2$ is as follow: experimental (calculated): C 11.69 (11.65), N 13.64 (14.12), S 32.22 (26.58) %.

Table 5.13: Quantification of Hf in hafnyl thiocyanate using H_2SO_4 (λ = 277.33 nm)

Trial number	Hafnium concentration, ppm		% Hf recovery
	Expected	Found	
Replicate 1	1.259	1.218	96.72
Replicate 2	1.239	1.238	99.90
Mean			98.31
Standard deviation			2.25

5.4. DISSOLUTION OF HAFNIUM OXIDE

The final step in this study involved the possible dissolution of HfO_2. The chemically inertness of hafnium and therefore the combination of ZrO_2/HfO_2 was strongly emphasized in **Chapter 2** and **Chapter 3**. The successful dissolution of HfO_2 and the comparison/evaluation of the same procedure on ZrO_2, zircon and PDZ with identification of any differences may lead to the development of a Zr/Hf separation process. Different methods of digestion which

include open vessel, flux fusion and microwave acid-assisted digestion were investigated to evaluate HfO_2 dissolution.

5.4.1. OPEN VESSEL ACID DIGESTION OF HAFNIUM OXIDE

Three portions of approximately 0.02 g of HfO_2 (accurately weighed to 0.1 mg) were dissolved in separate beakers containing 2.5 mL of HNO_3 (65 %), HCl (32 %), *aqua regia*, H_2SO_4 (98 %), H_2SO_4 + $(NH_4)_2SO_4$ and H_2SO_4 + NH_4F respectively (see **Table 5.14**). These mixture were heated to a temperature of 70 °C for HNO_3 (65 %), HCl (32 %), *aqua regia* and 120 °C for H_2SO_4 (98 %), H_2SO_4 + $(NH_4)_2SO_4$ and H_2SO_4 + NH_4F for 3 hours. The reaction mixtures were then filtered to separate the filtrate from the undigested samples. All the filtrates were heated to almost dryness to evaporate the acids. 2.5 mL of water was added to the samples and 2.5 mL portions of the different acids were then added to these samples to ensure acid matrix matching. After cooling to room temperature, the solutions were transferred to 100.0 mL volumetric flasks and diluted to the mark with purified water for ICP-OES analysis and the results are given in **Table 5.15**.

Table 5-14: Experimental condition for the HfO_2 digestion details with wet ashing

Mass range of HfO_2, g	Reagents	Temperature, °C
0.0176 – 0.0178	HCl	70
0.0140 – 0.0143	HNO_3 (65 %),	70
0.0171 – 0.0172	*Aqua regia*	70
0.0176 – 0.0178	H_2SO_4 (98 %)	120
0.0201 – 0.0215	H_2SO_4 + $(NH_4)_2SO_4$	120
0.0178 – 0.0181	H_2SO_4 + NH_4F	120

Table 5.15: Hf recovery in HfO_2 after open vessel digestion in different acidic mediums (λ = 277.33 nm)

Reagents	Average Hf content in HfO_2, ppm		% Hf recoveries(S.D)
	Expected	Found	
HCl	15.0	0.201	0.13(1)
HNO_3 (65 %),	12.0	0.004992	0.041(5)
Aqua regia	14.56	0.1018	0.7(1)
H_2SO_4 (98 %)	15.01	0.1308	0.87(6)
$H_2SO_4 + (NH_4)_2SO_4$	15.03	0.5712	3.82(1)
$H_2SO_4 + NH_4F$	15.21	0.531	3.5(3)

5.4.2. FLUX FUSION DIGESTION OF HAFNIUM OXIDE

Three 0.2 g portions of HfO_2 (accurately weighed to 0.1 mg) were fused with different fluxes which include NaOH, $Na_2B_4O_7$ and NH_4HF_2 at different fusion conditions (see **Table 5.16**).

Table 5.16: Dissolution of HfO_2 melt from flux fusion in H_2SO_4

Flux	Fusion temperature, °C	Type of crucible	Dissolution period, min	Dissolution of the melt in H_2SO_4
NaOH	330	Nickel	30	×
			90	✓
$Na_2B_4O_7$	1020	Platinum	30	✓
			90	✓✓
NH_4HF_2	130	Platinum	90	✓✓

✓✓Complete
✓ Partially complete
× Incomplete

Visual inspection indicated the incomplete sample dissolution for NaOH as flux at different dissolution periods with constant stirring. The residues were separated from the solution by filtration. All the filtrates were heated to almost dryness to remove the excess of the different acids and 2.5 mL portions of the different acids were added to ensure matrix matching. The solutions were allowed cool to room temperature transferred to 100.0 mL volumetric flasks and diluted to the mark with purified water for ICP-OES. The results are reported in **Table 5.17**.

Table 5.17: Quantification of Hf in HfO_2 after flux fusion

Flux	Dissolution period, min	Average Hf content in HfO_2, ppm		% Hf recoveries(S.D)
		Expected	Found	
NaOH	30	20.0	7.1	35(2)
	90	16.37	9.3	58(6)
$Na_2B_4O_7$	30	0.023	0.017	72(4)
	90	15.43	15.56	100.8(7)
NH_4HF_2	30	2.306	2.581	111.9(4)
NH_4HF_2	90	1.416	1.398	99(2)

5.4.3. MICROWAVE ACID - ASSISTED DIGESTION OF HAFNIUM OXIDE

Accurately weighed hafnium oxide samples (0.0172 – 0.0238 g) were quantitatively transferred to pre – cleaned polytetrafluorethylene (PTFE) digestion vessels which were used for fluoride containing reagents and glass digestion microwave vessels for fluoride free reagents and 8.00 mL Analytical grade acids (see **Table 5.19**) were added into each reacting vessel. The vessels were placed into the ceramic jackets and placed inside the rotor of the microwave digestion system, sealed, tightened and finally transferred to the microwave digester. Different microwave programs involving time and pressure variations were evaluated to ensure the dissolution of hafnium oxide as shown in **Table 5.18**.

Table 5.18: Microwave acid-assisted digestion programs

Program	Time, min	Dissolution of HfO_2
1	~50	✓
2	~50	✓
3	~85	✓✓

✓ Partially complete
✓✓Complete

The complete dissolution of hafnium oxide as indicated by conditions Program 3 prompted the use of the same condition in the presence of other acids such as HCl, HNO_3, H_2SO_4 + $(NH_4)_2SO_4$ and H_2SO_4 + NH_4F for the rest of the study. Although Program 1 required less dissolution time at a higher pressure, hafnium oxide was only partially dissolved. The ICP-OES results for the microwave-acid assisted analysis are reported in **Table 5.19**.

Table 5.19: Hf recovery in HfO_2 after microwave acid-assisted digestion in different acidic mediums (λ = 277.33 nm)

Reagents used	Average Hf content in HfO_2, ppm		% Hf recoveries(S.D)
	Expected	Found	
Program 1			
H_2SO_4	16.22	12.15	74.9(4)
Program 2			
H_2SO_4	18.84	16.20	86(5)
Program 3			
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)

5.5. RESULTS AND DISCUSSION

The decomposition of the different hafnium samples were carried out in open vessel (wet ashing), flux fusion and microwave-acid assisted digestion with different reagents in order to identify the most suitable for this purpose. The evaluation of the successful dissolution procedure was based on the % recovery of Hf (as compared to its theoretical value) and recoveries of ~100 % were regarded as successful. Experimental parameters which were investigated include acids and bases, type of fluxes as well as time and temperature of reaction. ICP-OES was used to quantify the hafnium content in the different hafnium compounds. The developed methods were also validated using different statistical parameters such as limit of detection (LOD), limit of quantification (LOQ), accuracy and precision to ensure the accuracy and reliability of the methods that were developed.

5.5.1. QUANTIFICATION OF HAFNIUM IN HAFNIUM COMPOUNDS

5.5.1.1. LOD AND LOQ

The first step in developing the analytical method for the accurate analysis of Hf in this study was the determination of the limit of detection (LOD) and limit of quantification (LOQ) in different acid matrices using the ICP-OES. The parameters were quantified to ensure that reliable Hf quantities were obtained and reported. The LOD and LOQs were determined only for the wavelength of 277.33 nm. The LOD and LOQ were measured in HNO_3, HCl, *aqua regia* and H_2SO_4 and were calculated as 0.006 and 0.062, 0.034 and 0.342, 0.0985 and 0.985, 0.087 and 0.873 ppm for the different acids respectively. The LOD and LOQ values obtained in this study confirm that these levels were well below the Hf content that were investigated in this study and which enabled/confirmed the accurate determinations of Hf in the different samples. The LODs and LOQs obtained for HNO_3 were at least a factor lower than those obtained for the other acids followed by HCl, H_2SO_4 and *aqua regia*.

Table 5.20: LOD for hafnium in different studies.

Acid Medium	Limit of detection (wavelength), ppm			
	This study (277.336 nm)	**Zircon, PDZ and other relevant Zr products (277.336)**[67]	**Nuclear grade zirconium (282.023 nm)**[68]	**Zircon (264.141 nm)**[115]
HCl	0.0985	-	-	-
HNO_3	0.0322	0.00578	0.01825	0.18
Aqua regia	0.0649	-	-	-
H_2SO_4	0.0051	0.002	-	-

The ICP-OES detection limits of this study compared favorably with the detection limits obtained for various samples (see **Table 5.20**) in previous studies.[67, 68, 115.]Differences such as wavelengths and matrix clearly affects the hafnium emission intensities and lead to differences in the detection limits as indicated in this study, but also the results reported in **Table 5.5**.

5.5.1.2. Quantification of hafnium tetrachloride

The dissolution of pure hafnium tetrachloride was initially accomplished using HNO_3 and a good average recovery of 97.8(4) % was obtained. However, this dissolution procedure also produced an unacceptable standard deviation of 2.8 %. This prompted the use of a different acid and H_2SO_4 was used. Dissolution by H_2SO_4 was successful with an excellent average recovery of 99.9(4) % (see **Table 5.5, Section 5.3.2**) and relative standard deviation of 0.1 %.

5.5.1.3. Quantification of hafnium tetrafluoride

The wet ashing of hafnium tetrafluoride using H_2SO_4 as acid showed the complete dissolution and yielded an excellent average recovery of 99.7(1) % (see **Table 5.5, Section 5.3.2**). The method was found to be accurate and precise with the standard deviation of 0.43 %.

[115] C. Sarbajna, S. Durani, V Rajagopalan, K Satyanarayana, K Shivkumar, ***The Indian Mineralogist***, 45, p. 217 (2011)

The qualitative analyses of the sample did not show the presence of any other elemental impurities and was therefore used as the starting material for the synthesis of a number of different hexafluorohafnate complexes (in-house reference materials).

5.5.2. THE PREPARATION OF DIFFERENT HEXAFLUOROHAFNATE COMPLEXES

In the absence of other Hf reference materials, it was decided to synthesize a number of hexafluoro complexes which may be highly water soluble, easy to prepare, have a well-known empirical formula with a high degree of purity which can be used as a RM for hafnium in simple matrices. The previously analysed hafnium tetrafluoride was used as the starting material for the syntheses of most of the different hexafluorohafnate complexes according to **Equation 5.7**.

$$2MF + HfF_4 \xrightarrow{HF} M_2HfF_6 \qquad (\mathbf{5.7})$$

where, M = Na^+, K^+, Rb^+, Cs^+, PPh_4^+

Both the alkali fluoride salts and the HfF_4 completely dissolved in 98 % H_2SO_4. HF was added to the reaction mixture to create an acidic environment and to act as extra source of the fluoride ions to ensure the formation of highly soluble HfF_6^{2-} anion. The synthesized complexes were quantified for hafnium content with ICP-OES and characterised by IR and X-ray crystallography.

A different method was used for the synthesis of ammonium hexafluorohafnate complex using hafnium tetrachloride as the starting material (see **Section 5.3.4.2**). The complex completely dissolved in 98 % H_2SO_4. Ammonium bifluoride was used as the source of fluoride ions to ensure the formation of highly soluble HfF_6^{2-} anions.

5.5.3. CHARACTERISATION OF HAFNIUM HEXAFLUOROHAFNATE COMPLEXES

5.5.3.1. Characterisation with Infrared spectroscopy

The vibration frequencies of metal-fluoride bonds have been reported to be in the region of 500-750 cm^{-1}.[116] The fingerprint region between 1800 and 688 of hafnium tetrafluoride spectrum is similar to that of hexafluorohafnate complexes. The stretching frequency peaks of ν(Hf-F) observed at 688 and 645 cm^{-1} have shifted significantly in potassium hexafluorohafnate spectrum to frequencies (ν(Hf-F)) at 738 and 682 cm^{-1} and this suggest the formation of a new product which is different from the starting material (HfF_4).

Vibration frequencies for all the other complexes were also observed within the region of 668 – 746 cm^{-1} for M_2HfF_6 (M = Na^+, K^+, Rb^+, Cs^+, NH_4^+, $N(CH_3)_4^+$, PPh_4^+) and the stretching frequencies of N-H bonds in ammonium groups of $[N(CH_3)_4]HfF_5.H_2O$ and $(NH_4)_2HfF_6$ were observed in the 3000 – 3209 cm^{-1} region and the broad water peak was observed at 3286 cm^{-1} (see **Figure 5.5** and **Figure 5.6**). Literature[85] has indicated that the N-H bonds in ammonium groups of hafnium fluoro complexes $(NH_4)_6MHfF_{23}$ (M= K, Rb, Cs) has the stretching frequencies in the region of 3000 – 3330 cm^{-1}. Nakamoto[116] has shown that N-H bonds in ammonium groups have the stretching frequencies appearing between 3000 and 3400 cm^{-1}.

5.5.3.2. X-ray crystal structure determinations of the synthesized hexafluorohafnate complexes

5.5.3.2.1. Crystal structure of K_2HfF_6

K_2HfF_6 is orthorhombic and crystalizes in the Cm space group with 4 molecules per unit cell. The complex forms long polymeric chains with bridged Hf-F bonds. The complex was synthesized according to the proposed method in **Section 5.3.4.1**. The most important bond distances and angles of K_2HfF_6 are listed in **Table 5.21** and **Table 5.22** and the polymeric structure is presented in **Figure 5.8**. There are two types of Hf-F bonds, namely bridged and terminal bonds with the bridging fluorine atoms connecting alternating hafnium atoms. The Hf-F bond distances in crystals of K_2HfF_6 range between 2.031(9) – 2.108(9) Å while K--F contact distances are between 2.708(8) and 3.351(2) Å. The average bridged Hf-F bond distance of is 2.108 Å, while the average non - bridged Hf-F bond distance is significantly shorter with

[116]K Nakamoto, Infrared spectra of Inorganic and Coordination Compounds, 2nd Edition, pp. 151 - 214 (1970)

the bond distance of 2.044 Å. The *cis* - F-Hf-F bond angles varied between 66.0(4) and 79.9(5)° and *trans* bond angles between 139.7(6) and 146.7(4)°. The results clearly shows the difference between the monodentate and the bridging bond angles angle ranging between 66.0(4) and 145.9(3)° and ranging between 73.2 and 146.7° respectively. These results are comparable to those obtained by Lötter[117] for the structure of K_2ZrF_6, with the Zr-F bond distances ranging from 2.030(4) – 2.079(4) Å for the monodentate bonds and Zr-F bond distances ranging from 2.140(4) and 2.194 (4) Å for bridged bonds while K-F bond distances varied between 2.623(4) and 3.002(2) Å.

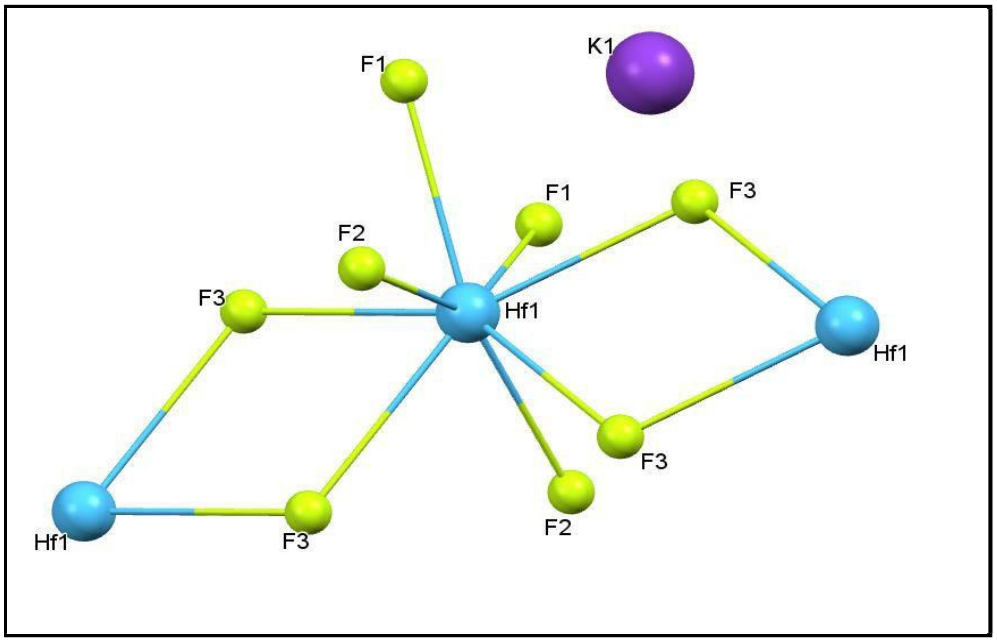

Figure 5.8: Polymeric crystal structure of K_2HfF_6

Table 5.21: Selected bond distances for K_2HfF_6 complex

Bond	Distance, Å	Bond	Distance, Å
Hf1 - F2	2.031(10)	F2 --- K1	2.725(8)
Hf1 - F1	2.058(9)	F2 --- K1	2.928(8)
Hf1 - F3	2.108(9)	F3 --- K1	2.802(9)
F1 --- K1	2.708(8)	F3 --- K1	3.351(2)
F1 --- K1	2.710(8)	F2 --- K1	2.725(8)

[117]S.J Lötter., Analysis of Zirconium-containing materials using multiple digestion and spectrometric techniques, PhD. Dissertation at the Department of Chemistry, University of the Free State, RSA (2014)

Table 5.22: Selected bond angles for K_2HfF_6 complex

Bond	Angle, °	Bond	Angle, °
F2 - Hf1 - F1	146.7(4)	F1 - Hf1 - F3	77.2(2)
F2 - Hf1 - F1	73.5(4)	F2 - Hf1 - F3	74.7(2)
F2 - Hf1 - F2	139.7(6)	F1 - Hf1 - F3	128.0(2)
F1 - Hf1 - F1	73.2(5)	F3 - Hf1 - F3	145.9(3)
F2 - Hf1 - F3	95.44(11)	F3 - Hf1 - F3	66.0(4)
		F3 - Hf1 - F3	79.9(5)
		F2 - Hf1 - Hf1	84.00(8)
		Hf1 - F3 - Hf1	114.0(2)

5.5.3.2.2. Crystal structure of Rb_2HfF_6

Rb_2HfF_6 crystalized in a monoclinic space group C2/c with 4 molecules per unit cell. The most important bond distances and angles of Rb_2HfF_6 are listed in **Table 5.23** and **Table 5.24** and the polymeric structure is presented in **Figure 5.9**. The complex was synthesized according to the proposed method in **Section 5.3.4.1**. The Hf-F bond distances in crystals of Rb_2HfF_6 varied between 1.89(5) – 2.10(5) Å while Rb-F bond distances varied between 4.017(12) and 4.043(10) Å. The average bridged Hf-F bond distance is 2.10 Å, while the average non - bridged Hf-F bond distance is 2.094 Å. The non-bridging bonds are approximately 0.01 Å longer than the bridging fluorine bond length. The *cis* - F-Hf-F bond angles varied between 70.3(14)° and 144.9(13)° and *trans* bond angles between 126.9(15) and 142.5(18) Å. The distance between fluoride and hafnium of 3.16(8) Å, was found to be close enough to allow interaction between the cation and the metal anion.

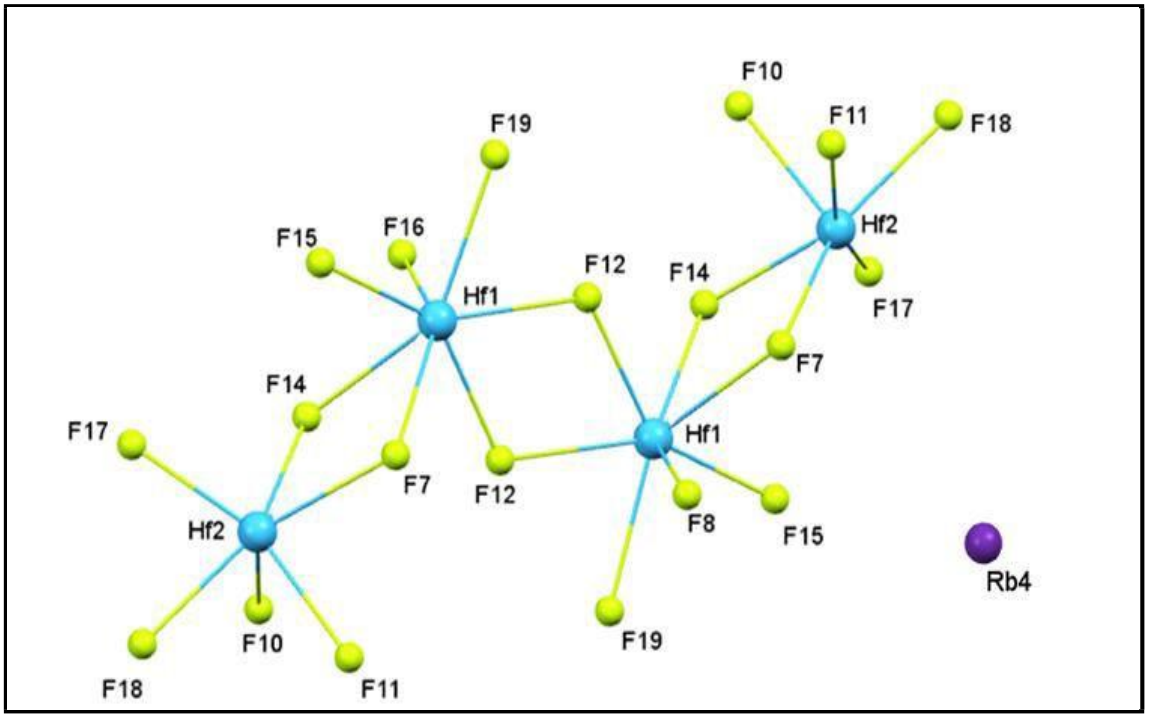

Figure 5.9: Crystal structure of Rb_2HfF_6

Table 5.23: Selected bond distances for Rb_2HfF_6 complex

Bond	Distance, Å	Bond	Distance, Å
Hf1 - F16	1.89(5)	Hf1 --- Rb4	4.30(8)
Hf1 - F15	1.97(3)	F15 --- Rb4	3.27(3)
Hf1 - F14	2.20(3)	F19 --- Rb4	3.16(8)
Hf1 - F12	2.03(4)		
Hf1 - F19	2.22(4)		
Hf1 - F7	2.19(3)		

Table 5.24: Selected bond angles for Rb_2HfF_6 complex

Bond	Angle, °	Bond	Angle, °
F16 - Hf1 - F15	96(2)	F15 - Hf1 - F12	144.9(13)
F16 - Hf1 - F12	95(2)	F16 - Hf1 - F7	142.5(18)
F12 - Hf1 - F19	134(2)	F15 - Hf1 - F7	77.0(14)
F12 - Hf1 - F14	73.3(15)	F14 - Hf1 - F19	145(2)
F12 - Hf1 - F14	126.9(15)	Hf1 - F12 - Hf1	115.2(15)
F14 - Hf1 - F15	77.3(15)	Hf1 - F15 - Rb4	116.1(12)
F12 - Hf1 - F7	73.9(16)	F8 - Hf1 - F14	136.1
F8 - Hf1 - F19	74(2)	F8 - Hf1 - F7	70.3(14)

5.5.3.2.3. Crystal structure of Cs_2HfF_6

Cs_2HfF_6 crystalized in a trigonal space group P3m1 with one molecule per unit cell. The Hf atom lies on a special position and the symmetry around the Hf necessitate the placement of any one of F-atom and the rest is generated by symmetry operators. The most important bond distances and lengths of Cs_2HfF_6 are listed in **Table 5.25** and **Table 5.26** and compound structure is presented in **Figure 5.10**. The complex was synthesized according to the proposed method in **Section 5.3.4.1.** The Hf is octahedrally surrounded by 6 fluoride ions with the Hf – F bond distance of 1.995(6) Å. The Cs-F contact distances varies between 3.079(6) and 3.351(2) Å. Interestingly the *cis* - F-Hf-F bond angles varied between 87.5(3) and 92.5(3) Å. These results are comparable to those obtained by Lotter[117] for the structure of Cs_2ZrF_6 with Zr – F bond distance of 2.007(6) Å and all *cis* - F-Hf-F bond angles were in the range of 87.4(2) – 92.5(2)° and the cation/anion interaction between Cs and F ranging between 3.091(1) and 3.322(1) Å.

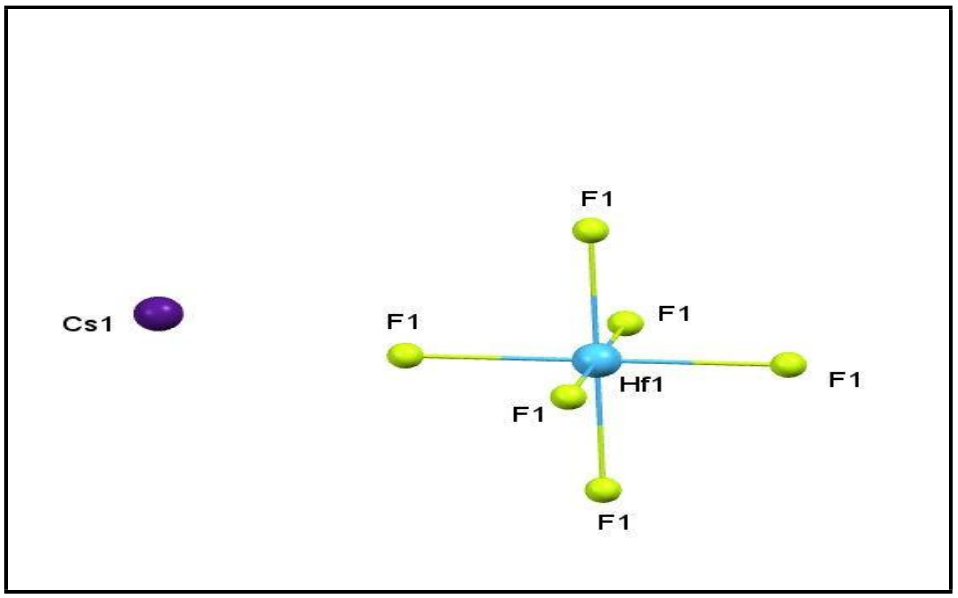

Figure 5.10: Crystal structure of Cs_2HfF_6

Table 5.25: Selected bond distances for Cs_2HfF_6 complex

Bond	Distance, Å	Bond	Distance, Å
Hf1 - F1	1.995(6)	F1 --- Cs1	3.208(10)
F1 --- Cs1	3.079(6)	F1 --- Cs1	3.312(7)
		Hf1 --- Cs1	3.975(10)

Table 5.26: Selected bond angles for Cs_2HfF_6 complex

Bond	Angle, °	Bond	Angle, °
F1 - Hf1 - F1	87.5(3)	Hf1 - F1 - Cs1	164.0(3)
F1 - Hf1 - F1	180.0(3)	Hf1 - F1 - Cs1	96.84(11)
F1 - Hf1 - F1	92.5(3)	Hf1 - F1 - Cs1	93.7(2)

5.5.3.2.4. Crystal structure of $(PPh_4)_2HfF_6.2H_2O$

$(PPh_4)_2HfF_6.2H_2O$ crystallize in the triclinic space group $P\bar{}$ and has 2 molecules per unit cell. The most important bond distances and lengths of $(PPh_4)_2HfF_6.2H_2O$ are listed in **Table 5.27** and **Table 5.28** and the structure is presented in **Figure 5.11**. The complex was synthesized according to the proposed method in **Section 5.3.4.1.** The Hf – F bond distance ranged between 1.9824(9) and 2.0155(9) Å. The interaction between tetraphosphenyl cation and $HfF6^-$ is through hydrogen bond contact with fluorine atoms. The C-C bond length of the cation ranged from 1.388(2) to 1.399(2) Å and bond angle of C-P-C ranged from 106(7) to 119.80(12)°.

Similarly to the Cs_2HfF_6 complex, the Hf-F average bond distance in $(PPh_4)_2HfF_6.2H_2O$ is 1.995 Å with the *cis* - F-Hf-F bond angles in the range of 88.75(4) and 91.73(4)°.

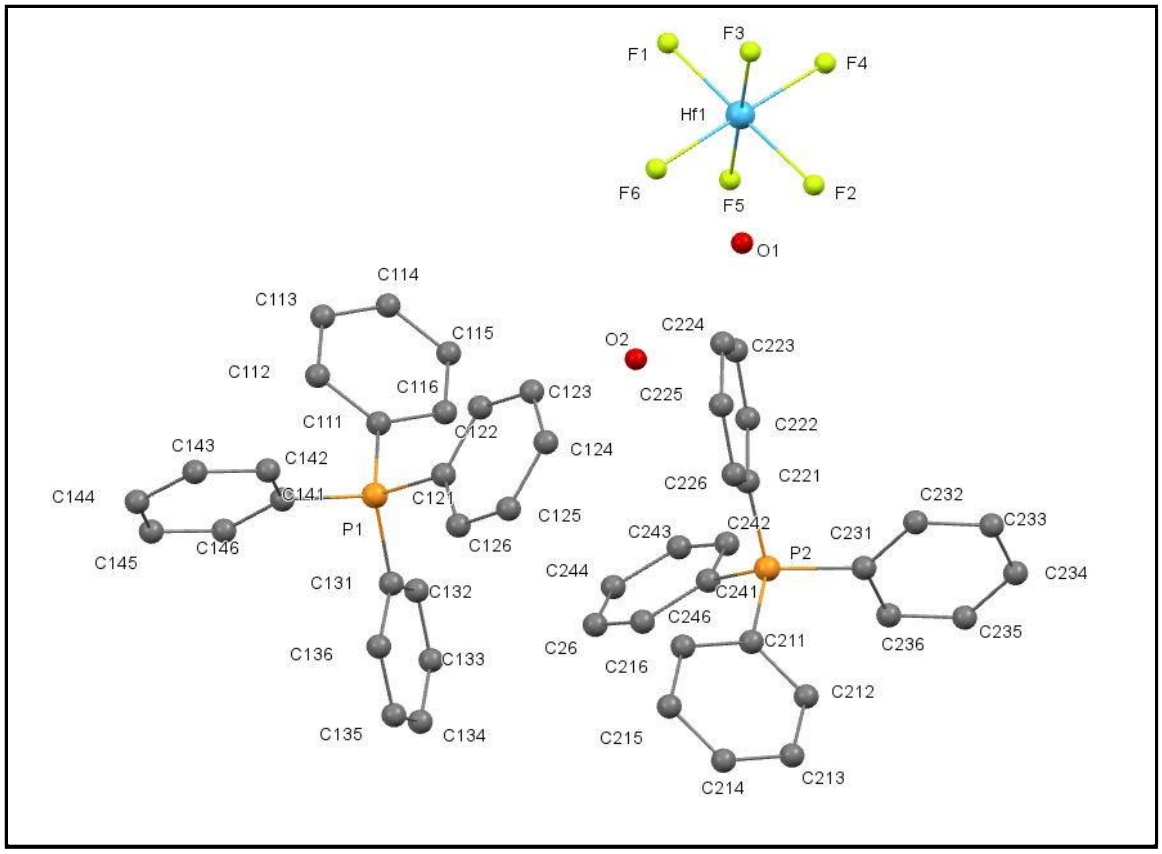

Figure 5.11: Crystal structure of $(PPh_4)_2HfF_6.2H_2O$

Table 5.27: Selected bond distances for $(PPh_4)_2HfF_6.2H_2O$ complex

Bond	Distance, Å	Bond	Distance, Å
Hf1 - F1	1.9824(9)	O1 - H12	0.786(19)
Hf1 - F4	1.9869(9)	O1 - H11	0.784(19)
Hf1 - F6	1.9866(10)	P1 - C131	1.7936(15)
Hf1 - F2	1.9938(9)	P1 - C111	1.7933(15)
Hf1 - F5	2.0036(9)	P1 - C141	1.7956(16)
Hf1 – F3	2.0155(9)		

Table 5.28: Selected bond angles for $(PPh_4)_2HfF_6.2H_2O$ complex

Bond	Angle, °	Bond	Angle, °
F1 - Hf1 - F4	90.23(4)	F4 - Hf1 - F5	89.23(4)
F1 - Hf1 - F6	90.59(4)	F6 - Hf1 - F5	89.85(5)
F4 - Hf1 - F6	178.78(4)	F2 - Hf1 - F5	90.51(4)
F1 - Hf1 - F2	178.08(4)	F1 - Hf1 - F3	89.34(4)
F4 - Hf1 - F2	89.63(4)	F4 - Hf1 - F3	91.73(4)
F6 - Hf1 - F2	89.59(4)	F6 - Hf1 - F3	89.19(5)
F1 - Hf1 - F5	91.41(4)	F2 - Hf1 - F3	88.75(4)
		F5 - Hf1 - F3	178.79(4)

5.5.4. QUANTIFICATION OF HAFNIUM IN HEXAFLUOROHAFNATE COMPLEXES

The quantitative analysis of the Hf in K_2HfF_6 by ICP-OES yielded percentage recovery of 99.7(1) % (see **Table 5.8**, **Section 5.3.4.3**) while the hexafluorohafnate complexes of Rb^+, Cs^+, NH_4^+, PPh_4^+ gave good recoveries of 98 – 103 %. The formula weight determined by X-ray crystallography corresponds to the theoretical formula weight hence the desired compound was obtained. The Hf percentage recoveries in Na_2HfF_6 and $[N(CH_3)_4]_2HfF_6$, were however disappointing with recoveries of 92(2) and 79(6) % respectively. These low recoveries may be due to a number of reasons. The isolation of impure products (contaminated with starting material), the incorrect empirical/molecular formula and the isolation of a different (unexpected) product may be reasons for these poor recoveries. The presence of crystal waters, additions of different cations:Hf ratios may lead to inaccurate empirical formulas. A good example is that obtained by Lötter during the isolation of different Z-F complexes, the isolated product using $[N(C_2H_5)_2]^+$ as cation yielded the $[N(C_2H_5)_4]ZrF_5$ product with a 1:1 cation:Zr ratio compared to 2:1 cation:Zr ratio for all other cations (Rb^+, Cs^+, PPh_4^+). Crystals suitable for the X-ray characterisation of Na^+ and NH_4^+ in the current study were however unsuccessful. Low recoveries of Na_2HfF_6 could be attributed to high emission intensity of Na (which strongly emits the yellowing flame in the visible spectrum).[73]

Due to the ineffectiveness of the proposed method (see **Section 5.3.4.1**) to form crystalline $(NH_4)_2HfF_6$, a different synthetic route (see **Section 5.3.4.3**) was followed. The colourless crystalline product of $(NH_4)_2HfF_6$ completely dissolved in H_2SO_4 and yielded Hf recovery of 103(3) %

5.5.5. QUANTIFICATION OF HAFNIUM IN HAFNYL THIOCYANATE

One of the earliest and most successful Zr/Hf separation processes involved the use of thiocyanate as ligand. The process involved the reaction of dissolved zircon (98 % Zr, 2 % Hf) with NCS^- and their subsequent separation with ion-exchange to produce an enriched Zr product (deficient in Hf). This process is then repeated numerously to eventually produce nuclear grade Zr.

The ability of NCS^- to discriminate between the two elements (even to a very small degree) prompted the interest in the isolation of the thiocyanate product. The ability at NCS^- to bond either via nitrogen (thio) or sulphur (iso-thiocyanate) may be the reason for the difference in the chemistry of the two cyanate complexes. The hafnyl thiocyanate was synthesized according to **Section 5.3.5** and the isolated complex dissolved completely in H_2SO_4 at 120 °C. The Hf determination in the hafnyl thiocyanate complex yielded good recovery of 98(2) % at 277.336 nm (see **Table 5.13**). The prepared hafnyl thiocyanate complex was characterized by IR spectrometry. Numerous efforts to grow crystals suitable for X-ray analysis on this compound were unsuccessful due to the rapid decomposition of crystals with time. However, the process will be revisited in future.

IR characterisation of the hafnyl thiocyanate complexes

The IR spectrum of hafnyl thiocyanate is reported in **Section 5.3.5.1** (see **Figure 5.7**). The stretching frequency of the Hf-O bond was identified at 951 cm^{-1}. The absorption frequency at 745 cm^{-1} is assigned to Hf-N bond. A strong peak at 2038 cm^{-1} (CN stretching) suggests the presence of thiocyanate within the complex reacted.[116] According to literature[86] if the thiocyanate group bonds to the central atom of the complex through a nitrogen atom, the absorption frequencies of S-C bonds lie in the region 694-748 cm^{-1}. The ν(CN) at 2038 cm^{-1} is substantially lower than a normal cyano ligand stretching frequency which is normally in the 2100 cm^{-1} area. This suggests the presence of substantially π-back bonding between the metal and the nitrogen resulting in weaker carbon-nitrogen triple bond character and hence the lower ν(CN) stretching frequency. Research also reported much higher ν(CN) for sulphur bond thiocyanate ligands due to less π-back bonding and hence a larger degree of carbon nitrogen triple bond character. The Hf determination in hafnyl thiocyanate complex yielded recovery of 98(2) %. If the thiocyanate group bonds to the central atom of the complex through a sulphur atom, the absorption frequencies of N-C bonds lie in the region 690 – 720 cm^{-1}. The nitrogen bonded complex is either linear ($M-N=C-S^-$) or bent (M=N=C-S).[116]

A decrease in the Hf-N π-bonding may decrease the stretching frequencies of Hf-N which increases the terminal C≡N stretching frequencies due to the conjugation of electrons. The N bonded synthesized complex absorbs at ν(CN) of 2038 cm^{-1}.

5.6. METHOD DEVELOPEMENT FOR THE DIGESTION AND QUANTIFICATION OF HAFNIUM OXIDE

5.6.1. DISSOLUTION AND QUANTIFICATION OF HAFNIUM OXIDE

The importance of the successful dissolution of HfO_2 was previously emphasized. Any method that discriminate between Zr and Hf has enormous potential as hydrometallurgical separation process, especially in the manufacturing of the nuclear grade Zr metal but also in the development and expansion of Hf chemistry. The hafnium oxide solutions obtained from the different digestions techniques were analysed for Hf content. HfO_2 is highly refractory and therefore difficult to dissolve (see **Chapter 2, Section 2.7.1**).

5.6.1.1. Open vessel acid digestion

Different single and combination of reagents were used in wet ashing digestion of hafnium oxide. The use of different reagents namely; 32 % HCl, 65 % HNO_3, *aqua regia*, 98 % H_2SO_4 and a mixture of H_2SO_4 + $(NH_4)_2SO_4$ and 98 % H_2SO_4 + NH_4F were studied to identify an effective reagent for the dissolution of the Hf oxides. After the digestion period of 3 hours, hafnium oxide remained undissolved in all the reagents studied and therefore from visual inspection these different reagents were ineffective in the total dissolution of HfO_2 sample under open vessel. The undissolved solid was removed by filtration which was transferred to 100.0 mL volumetric flasks. The flasks were then filled to the mark with purified water. The ICP-OES measurements were performed to determine the quantitative amount of hafnium recovered (see **Table 5.15**). Results in this study confirmed the incomplete dissolution of HfO_2 within the technique. The Hf recovery was exceptionally poor with only 3.82(1) % using H_2SO_4 + $(NH_4)_2SO_4$, 3.5(3) % for H_2SO_4 + NH_4F, 0.87(6) % recovered in H_2SO_4 while only 0.041(5) % was recovered in HNO_3 (see **Table 5.15)**. These results confirmed the extreme resistance of Hf (and Zr) oxides to acid attack under mild experimental conditions.

5.6.2. FLUX FUSION DIGESTION

The poor recoveries of HfO_2 using conventional bench top digestion (wet ashing) (see **Section 5.4.2**) led to a change in the dissolution procedure. NaOH, $Na_2B_4O_7$ and NH_4HF_2 were investigated in a flux fusion salts. Results obtained using this technique are presented in **Table 5.17**. Total Hf recovery was obtained with $Na_2B_4O_7$ as flux while 35(2) to 58(6) % were recovered using NaOH as flux and it depends on the reaction time with an increase in dissolution with an increase in time. The low Hf recoveries in NaOH digestion may be explained in terms of acid-base properties of the HfO_2. Relatively higher Hf recoveries were obtained in more acidic type fluxes than the less acidic (or more basic) fluxes. The more reactivity of the HfO_2 towards acidic fluxes suggesting more basic character of HfO_2 complex. The Hf recovery of 111.9(4) % using NH_4HF_2 as flux was exceptionally high. A literature study[118] has indicated that the high Hf recoveries (in excess of 100 %) could be due to emission line intensity interence by the large excess of F^- ions in solution. Another study[119] also indicated that the ICP-OES results may be negatively affected by an excess amount of fluoride ions (from NH_4HF_2 flux) in solution. The fluoride concentration was corrected by 100 fold dilution of the original solution prior to analysis which brought the HF recovery within an acceptable range and good recoveries were obtained. Literature[11] has shown that the excess fluoride can easily be removed by the addition of concentrated H_2SO_4 and heating the subsequent solution to dryness. Improved dissolution was visually observed as the dissolution time increased and hence an increase in dissolution time also increased the recovery of hafnium in hafnium oxide (see **Table 5.16** and **Table 5.17**).

[118]C.C. Chan, H. Lam, Y.C. Lee, X. Zhang, Analytical method validation and instrument performance verification, p. 18 (2004)

[119]M. Nete, W. Purcell, J.T. Nel, Comparative study of tantalite dissolution using different fluoride salts as fluxes, ***Journal of the Chemical Society***, 165, pp. 20 - 26 (2014)

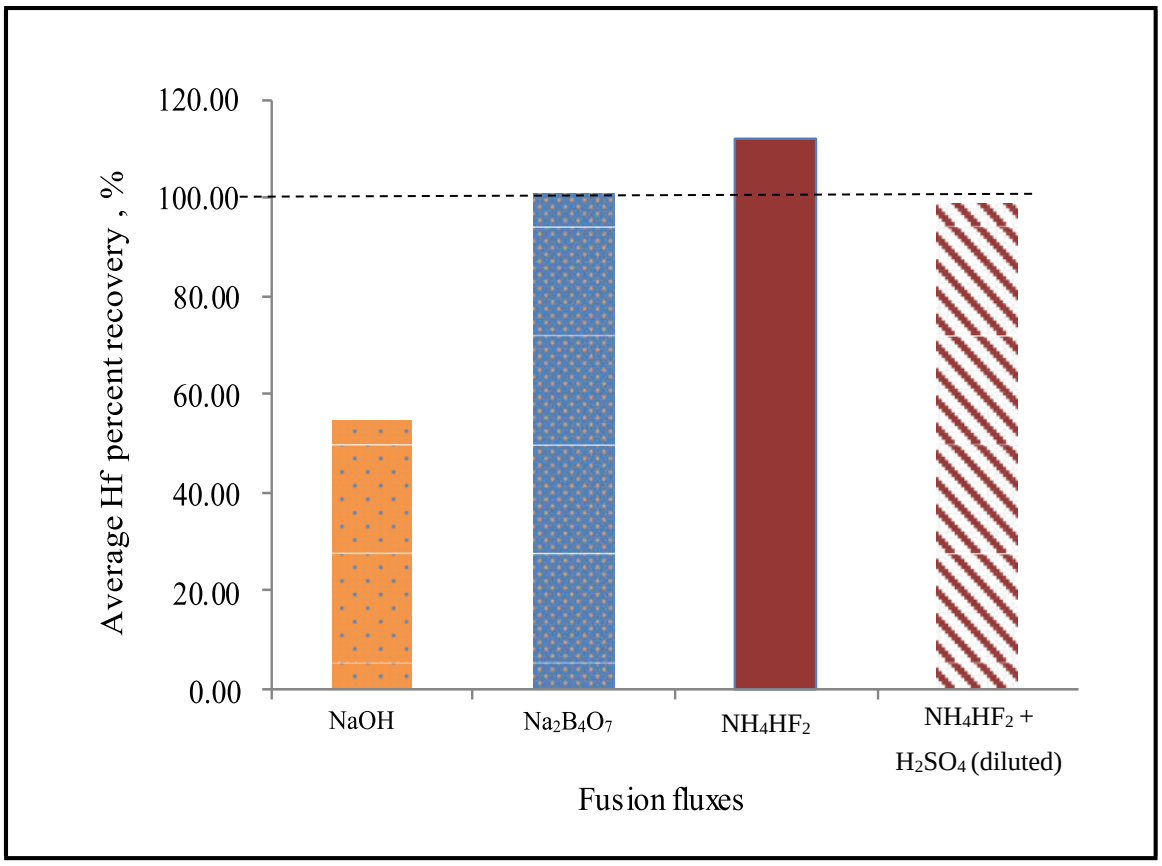

Figure 5.12: Hf recovery from HfO_2 using different fusion fluxes at 90 min

5.6.3. MICROWAVE ACID ASSISTED DIGESTION

The use of microwave acid-assisted digestion for HfO_2 dissolution was also investigated. Different reagents were used during the digestion process to determine the most effective digestion medium. In this part of the study more attention was given to H_2SO_4 mainly due to the fact that it showed a lot of promising (although poor in terms of recovery) results with the open digestion procedure. Three different microwave programmes were used to investigate HfO_2 dissolution and the ICP-OES results are given in **Table 5.19**.

Visual inspection of all the triplicate solutions indicated incomplete dissolution in all the reagents which did not entail the use of H_2SO_4. Complete dissolutions were obtained for all the H_2SO_4 solutions and the experimental conditions of Program 3 was followed (see **Table 5.18**). A prevailed literature study suggested that mixing H_2SO_4 with salts such as $(NH_4)_2SO_4$ enhances its boiling point and thereby increasing its reactivity and is therefore more effective as a dissolution reagent. However, from the results in **Table 5.19** it is clear that H_2SO_4 alone is effective in dissolving HfO_2 under microwave conditions. The average recoveries of Hf are graphically presented in **Figure 5.14.** Better dissolution was visually observed as the dissolution time increased and hence an increase in dissolution time

increased the recovery of hafnium in hafnium oxide. Improved Hf recovery was obtained with a maximum digestion period of approximetly 85 min (see **Table 5.18** and **Table 5.19**).

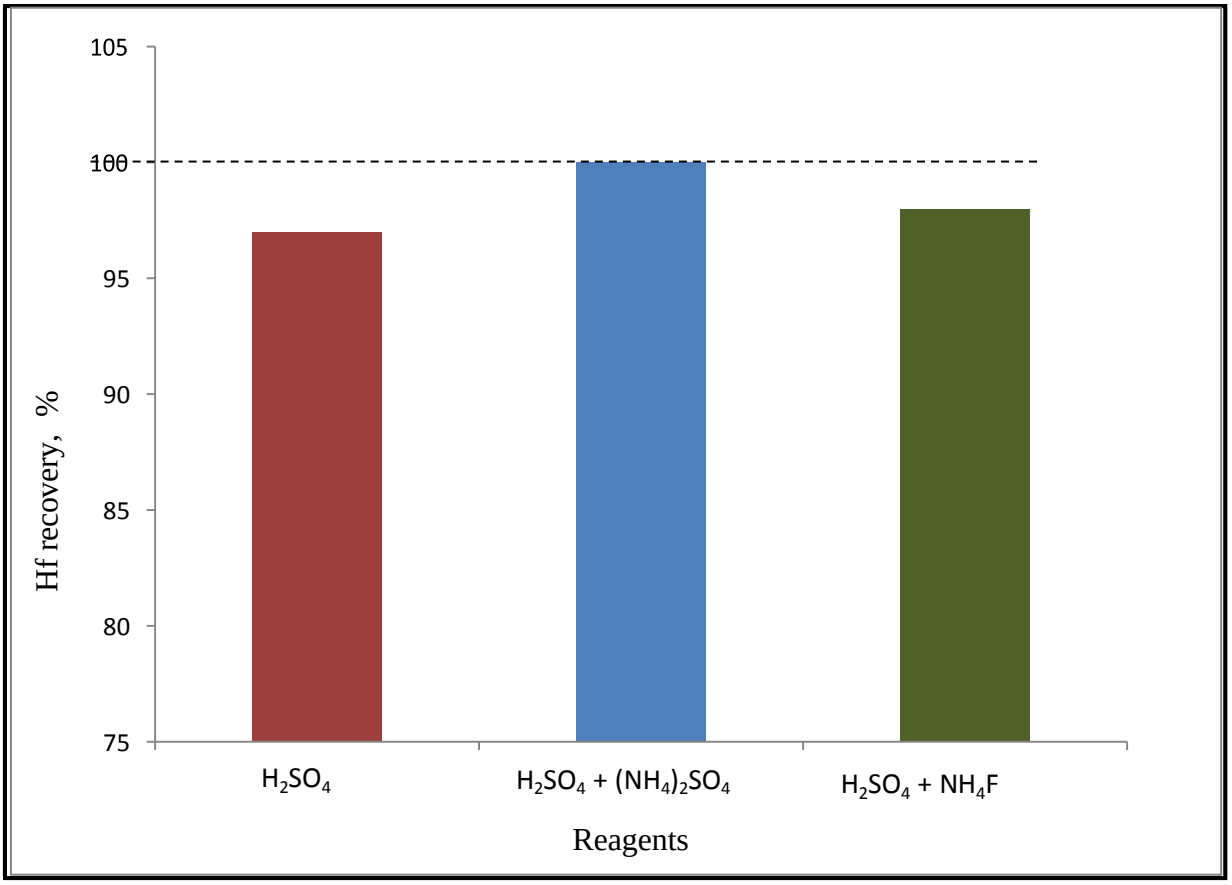

Figure 5.13: Hf recovery from HfO_2 using microwave system – program 3

The graphical comparison of open vessel and microwave digestion of hafnium oxide using different reagents is given in **Figure 5.14**.

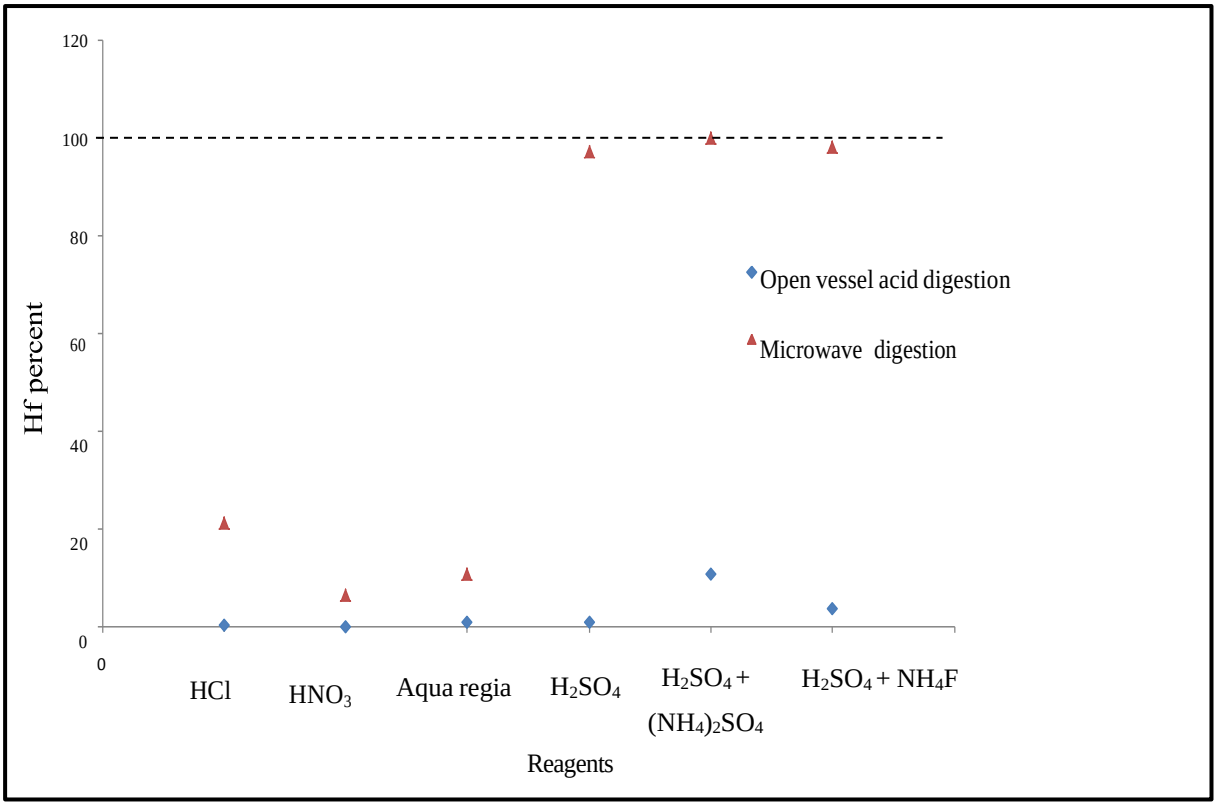

Figure 5.14: Comparison of open vessel and microwave digestion of HfO_2 in various reagents

5.7. METHOD VALIDATION OF RESULTS

All the analytical methods were validated in this study to ensure the accuracy and reliability of the obtained results. Several factors such as sensitivity of the instrument or the stability of solution can affect the analytical results and therefore should be considered during the analysis of samples. The validation parameters (see **Table 5.29**) which were investigated include range, accuracy, precision, selectivity and specificity, linearity, robustness, limit of detection (LOD) and quantification (LOQ). All the validation parameters were evaluated using ICP- OES for hafnium analysis in various samples using different acids (see **Tables 5.33** to **5.43)**.

Table 5.29: General validation parameters used for the validation for the different Hf quantification methods.[120]

Validation Parameters		Impurities		Assay(Dissolution, Potency, Content uniformity)
		Quantitation	Limit	
Accuracy		✓		✓
Precision	Repeatability	✓		✓
	Intermediate	✓		✓
Specificity		✓	✓	✓
Limit of Detection			✓	
Limit of Quantification		✓		
Linearity		✓		✓
Range		✓		✓
Robustness		✓	✓	✓

The acceptability criteria for accuracy (expressed as recovery) and precision of the analytical results are shown in **Table 5.30**.

[120]Method validation steps, [Accessed 10-10-2015]. Available from: http://www.solartechlab.com/images/valid1.gif

Table 5.30: Criteria for the acceptable accuracy and precision values.[121]

Impurity content, %	The range of acceptable criteria	
	Recovery, %	Precision, %
≤ 0.1	98 – 102	≤ 2
0.1 - 1	90 – 110	≤ 5
≥ 1	80 – 120	≤ 10
≥ 10	75 – 125	≤ 20

[121] Guidelines for the validation of analytical methods for active constituent, agricultural and veterinary chemical products, [Accessed 21-11-2015]. Available from:http://apvma.gov.au/sites/default/files/docs/guideline-69-analytical-methods.pdf.

Table 5.31: Validation of ICP-OES analyses for Hf in $HfCl_4$ using open vessel acid digestion

Validation Criteria	Parameter	HNO_3	H_2SO_4
Recovery	Mean (SD), %	97.8(4)	99.9(4)
Precision	RSD, %	0.4498	0.4302
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9977	0.9978
Sensitivity	Slope	0.0085	0.0101
Selectivity	S_m	0.0002	0.0021
Error of the slope	Y-intercept	-0.0022	-0.001
Specificity	Sc	0.0008	0.0010
Average concentration ($\bar{x}$), ppm		7.745	6.483
Theoretical average concentration (μ), ppm		7.916	6.486
Standard deviation of the concentration		0.5199	0.0197
t-crit at 95 % confidence interval		4.3	
t-test		0.5708	0.0120
Decision		Accepted	Accepted

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.32: Validation of ICP-OES analyses for hafnium in hafnium tetrafluoride

Validation Criteria	Parameter	H_2SO_4
Recovery	Mean (SD), %	99.7(1)
Precision	RSD, %	0.4327
Working range	Calibration curve	0.4 – 10 ppm
Linearity	r^2	0.9998
Sensitivity	Slope	0.1197
Selectivity	S_m	0.0010
Error of the slope	Y-intercept	0.004
Specificity	Sc	0.0036
Average concentration ($\bar{x}$), ppm		6.483
Theoretical average concentration (μ), ppm		6.486
Standard deviation of the concentration		0.2350
t-test		0.01965
t-crit at 95 % confidence interval		4.3
Decision		Accepted

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.33: Validation of ICP-OES analyses for hafnium in different hexafluorohafnate complexes

Validation Criteria	Parameter	Na_2HfF_6	K_2HfF_6	Rb_2HfF_6	Cs_2HfF_6
Recovery	Mean (SD), %	92(2)	99.7(4)	98(3)	102(2)
Precision	RSD, %	2.174	0.4316	3.061	1.960
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9998	0.9998	0.9998	0.9998
Sensitivity	Slope	0.0919	0.0919	0.0919	0.0919
Selectivity	S_m	0.0010	0.0010	0.0010	0.0010
Error of the slope	Y-intercept	-0.0056	-0.0056	-0.0056	-0.0056
Specificity	Sc	0.0037	0.0037	0.0037	0.0037
Average concentration ($\bar{x}$), ppm		7.463	3.847	2.738	5.338
Theoretical average concentration (μ), ppm		8.131	3.859	2.637	5.221
Standard deviation of the concentration		0.217	0.01315	0.8688	0.1505
t-crit at 95 % confidence interval		4.3			
t-test		4.870	1.599	0.236	-1.041
Decision		Rejected	Accepted	Accepted	Accepted

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.34: Validation of ICP-OES analyses for hafnium in different hexafluorohafnate complexes

Validation	Parameter	$(PPh_4)_2HfF_6.2H_2O$	$(NH_4)_2HfF_6$	$[N(CH_3)_4]HfF_5.H_2O$
Recovery	Mean (SD), %	102(3)	103(3)	79(8)
Precision	RSD, %	2.94	2.91	7.59
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9998	0.9998	0.9998
Sensitivity	Slope	0.0919	0.0919	0.0919
Selectivity	S_m	0.0010	0.0010	0.0010
Error of the	Y-intercept	-0.0056	-0.0056	-0.0056
Specificity	S_c	0.0037	0.0037	0.0037
Average concentration ($\bar{x}$), ppm		2.738	7.463	3.737
Theoretical average concentration (μ),		2.637	8.131	4.474
Standard deviation of the concentration		0.2652	0.002927	0.09339
t-crit at 95 % confidence		4.3		
t-test		-0.3001	-916.199	14.016
Decision		Accepted	Rejected	Rejected

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.35: Validation of ICP-OES analyses for hafnium in $HfO(SCN)_2$

Validation Criteria	Parameter	H_2SO_4
Recovery	Mean (SD), %	98(2)
Precision	RSD, %	2.286
Working range	Calibration curve	0.4 – 10 ppm
Linearity	r^2	0.9998
Sensitivity	Slope	0.1197
Selectivity	S_m	0.0004
Error of the slope	Y-intercept	0.004
Specificity	Sc	0.0015
Average concentration ($\bar{x}$), ppm		1.228
Theoretical average concentration (μ), ppm		1.249
Standard deviation of the concentration		2.085
t-crit at 95 % confidence interval		4.3
t-test		2.100
Decision		Accepted

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.36: Validation of ICP-OES analyses for Hf in HfO_2 using open vessel acid digestion

Validation Criteria	Parameter	HCl	HNO_3	*Aqua regia*
Recovery	Mean (SD), %	0.13(1)	0.042(6)	0.7(1)
Precision	RSD, %	8.639	1.364	15.15
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9999	0.9996	1
Sensitivity	Slope	0.1305	0.1611	0.1331
Selectivity	S_m	0.0009	0.0018	0.0002
Error of the slope	Y-intercept	0.001	0.0029	-0.0011
Specificity	Sc	0.0032	0.0065	0.0008
Average concentration ($\bar{x}$), ppm		0.201	0.04992	1.0182
Theoretical average concentration (μ), ppm		15.00	12.00	14.56
Standard deviation of the concentration		0.01659	0.000927	0.1509
t-test		1545.8	22397.8	155.38
t-crit at 95 % confidence interval		4.3		
Decision		Rejected	Rejected	Rejected

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.37: Validation of ICP-OES analyses for Hf in HfO_2 using open vessel acid digestion

Validation Criteria	Parameter	H_2SO_4	H_2SO_4 + NH_4F	H_2SO_4 + $(NH_4)_2SO_4$
Recovery	Mean (SD), %	0.87(6)	3.5(3)	3.82(3)
Precision	RSD, %	6.765	9.863	2.62
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9999	0.9999	0.9998
Sensitivity	Slope	0.1213	0.117	0.0919
Selectivity	S_m	0.0008	0.0006	0.0010
Error of the slope	Y-intercept	0.0084	0.0005	-0.0056
Specificity	S_c	0.0028	0.0023	0.0037
Average concentration ($\bar{x}$), ppm		0.1308	0.5712	0.531
Theoretical average concentration (μ), ppm		15.01	15.03	15.21
Standard deviation of the concentration		0.009014	0.5664	0.03638
t-test		2859	30.24	369.06
t-crit at 95 % confidence interval		4.3		
Decision		Rejected	Rejected	Rejected

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.38: Validation of ICP-OES analyses for Hf in HfO_2 using flux fusion with NaOH

Validation Criteria	Parameter	H_2SO_4
Recovery	Mean (SD), %	58(6)
Precision	RSD, %	13.89
Working range	Calibration curve	0.4 – 10 ppm
Linearity	r^2	0.9968
Sensitivity	Slope	0.1027
Selectivity	S_m	0.0030
Error of the slope	Y-intercept	-0.0129
Specificity	Sc	0.0109
Average concentration ($\bar{x}$), ppm		9.3
Theoretical average concentration (μ), ppm		16.37
Standard deviation of the concentration		1.056
t-test		10.55
t-crit at 95 % confidence interval		4.3
Decision		Rejected

S_m = Standard deviation of the slope

S_c = Standard deviation of the intercept

Table 5.39: Validation of ICP-OES analyses for Hf in HfO_2 using flux fusion with NH_4HF_2

Validation Criteria	Parameter	H_2SO_4
Recovery	Mean (SD), %	111.9(4)
Precision	RSD, %	0.3688
Working range	Calibration curve	0.4 – 10 ppm
Linearity	r^2	0.9999
Sensitivity	Slope	0.0976
Selectivity	S_m	0.0006
Error of the slope	Y-intercept	0.0008
Specificity	S_c	0.0023
Average concentration ($\bar{x}$), ppm		2.581
Theoretical average concentration (μ), ppm		2.306
Standard deviation of the concentration		0.007967
t-test		-598.76
t-crit at 95 % confidence interval		4.3
Decision		Rejected

S_m = Standard deviation of the slope

S_c = Standard deviation of the intercept

Table 5.40: Validation of ICP-OES analyses for Hf in HfO_2 using flux fusion with NH_4HF_2

Validation Criteria	Parameter	H_2SO_4
Recovery	Mean (SD), %	99(2)
Precision	RSD, %	0.3688
Working range	Calibration curve	0.4 – 10 ppm
Linearity	r^2	0.9999
Sensitivity	Slope	0.0976
Selectivity	S_m	0.0006
Error of the slope	Y-intercept	0.0008
Specificity	S_c	0.0023
Average concentration ($\bar{x}$), ppm		1.398
Theoretical average concentration (μ), ppm		1.416
Standard deviation of the concentration		0.3758
t-test		0.02890
t-crit at 95 % confidence interval		4.3
Decision		Accepted

Table 5.41: Validation of ICP-OES analyses for Hf in HfO_2 using flux fusion with $Na_2B_4O_7$

Validation Criteria	Parameter	H_2SO_4
Recovery	Mean (SD), %	100.8(7)
Precision	RSD, %	0.6553
Working range	Calibration curve	0.4 – 10 ppm
Linearity	r^2	0.9999
Sensitivity	Slope	0.1037
Selectivity	S_m	0.0003
Error of the slope	Y-intercept	-0.0045
Specificity	Sc	0.0012
Average concentration ($\bar{x}$), ppm		15.56
Theoretical average concentration (μ), ppm		15.43
Standard deviation of the concentration		0.0421
t-test		-4.1
t-crit at 95 % confidence interval		4.3
Decision		Accepted

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

Table 5.42: Validation of ICP-OES analyses for Hf in HfO_2 using microwave acid-assisted digestion

Validation Criteria	Parameter	HCl	HNO_3	*Aqua regia*
Recovery	Mean (SD), %	21.7(4)	6.09(4)	10.8(1)
Precision	RSD, %	2.249	0.6687	1.197
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9999	0.9996	1
Sensitivity	Slope	0.1277	0.1588	0.1331
Selectivity	S_m	0.0008	0.0015	-0.0016
Error of the slope	Y-intercept	0.0001	0.0027	0.0002
Specificity	Sc	0.0029	0.0053	0.0006
Average concentration ($\bar{x}$), ppm		0.201	0.004992	0.1018
Theoretical average concentration (μ), ppm		15.00	12.00	14.56
Standard deviation of the concentration		0.07588	0.00681	0.02440
t-test		290.01	3510	941.44
t-crit at 95 % confidence interval		4.3		
Decision		Rejected	Rejected	Rejected

S_m = Standard deviation of the slope

S_c = Standard deviation of the intercept

Table 5.43: Validation of ICP-OES analyses for Hf in HfO_2 using microwave acid-assisted digestion at 240 °C, 90 min and 600 W

Validation Criteria	Parameter	H_2SO_4	H_2SO_4 + NH_4F	H_2SO_4 + $(NH_4)_2SO_4$
Recovery	Mean (SD), %	97(2)	98(2)	100(3)
Precision	RSD, %	2.455	2.083	2.596
Working range	Calibration curve	0.4 – 10 ppm	0.4 – 10 ppm	0.4 – 10 ppm
Linearity	r^2	0.9999	0.9999	0.9998
Sensitivity	Slope	0.1213	0.117	0.0919
Selectivity	S_m	0.0008	0.0006	0.0010
Error of the slope	Y-intercept	0.0084	0.0005	-0.0056
Specificity	S_c	0.0028	0.0023	0.0037
Average concentration ($\bar{x}$), ppm		16.26	14.36	17.53
Theoretical average concentration (μ), ppm		16.87	15.29	17.48
Standard deviation of the concentration		0.4440	0.3581	0.0012
t-test		2.07	1.2202	-0.0816
t-crit at 95 % confidence interval		4.3		
Decision		Accepted	Accepted	Accepted

Sm = Standard deviation of the slope

Sc = Standard deviation of the intercept

5.8. CONCLUSION

The results obtained from this study indicated that hafnium recoveries of 99.8(1) % in hafnium tetrafluoride (HfF_4) in H_2SO_4 were obtained. HfF_4 was then used as the starting material for the synthesis of different hexafluorohafnate complexes. All the synthetic compounds easily dissolved in sulphuric acid and good Hf recoveries of 99.7(1), 98(3), 102(2), 103(3) and 102(3) % were obtained for K_2HfF_6, Rb_2HfF_6,Cs_2HfF_6, $(NH_4)_2HfF_6$ and $(PPh_4)_2HfF_6.2H_2O$ respectively. Poor recoveries were obtained for $[N(CH_3)_4]HfF_5.H_2O$ and Na_2HfF_6 and this could be due to different factors such as that the predicted empirical formula is incorrect or the isolation of more than one product and thereby leading to incorrect or poor recoveries. The newly synthesized hafnyl thiocyanate complex completely dissolved in sulphuric acid and yielded an excellent recovery of 98(2) %. Some of the synthesised products namely K_2HfF_6, Rb_2HfF_6, Cs_2HfF_6, $(PPh_4)_2HfF_6.2H_2O$ were characterized by IR and X - ray crystallography.

The main focus of this study was to develop a digestion method for hafnium oxide which is chemically inert and hence resistant to attack by many mineral acids. Prior to the digestion of hafnium oxide, pure hafnium chloride with a known Hf content was used as a simple matrix to develop a method for Hf quantification. The sample completely dissolved in 98 % H_2SO_4 and gave excellent Hf recovery of 99.9(4) %.

Different dissolution techniques namely open vessel (wet ashing), flux fusion and microwave acid-assisted digestion were investigated by applying different experimental conditions for the dissolution of hafnium oxide. Open vessel digestion technique with different reagents was highly unsuccessful in dissolving HfO_2 and poor Hf recoveries ranging from 0.041(6) % to 3.82(1) % were obtained.

HfO_2 was successfully dissolved by fusion using $Na_2B_4O_7$ followed by its dissolution with 98 % H_2SO_4. This procedure has an advantage of a shorter dissolution time of 30 min with complete Hf recovery of 101.73(3) %. However, improved results of 100.8(7) % were obtained with a longer dissolution time of 90 min. The other fluxes such as NaOH and NH_4HF_2 which were investigated gave (relatively) poor recoveries of 58(6) % and 111.9(4) % which could be attributed to the sample matrices. The results obtained for fusion with

NH_4HF_2 was improved through boiling with H_2SO_4 to evaporate HF thereore reducing the influence of excess fluoride in solution.

Microwave acid- assisted digestion using different acids at different microwave conditions were investigated. Improved Hf recoveries (compared with open vessel) in the range of 6.5(6) –21(1) % were obtained for HCl, HNO_3, *aqua regia*, H_2SO_4, H_2SO_4 + $(NH_4)_2SO_4$, H_2SO_4 + NH_4F using microwave program 3 (temperature = 240 °C, dissolution time = 90 min and power = 600 W). Digestion with H_2SO_4 on its own or in combination with different salts namely, $(NH_4)_2SO_4$ and NH_4F showed the complete dissolution of hafnium by visual inspection and recoveries in the range of 97(2) – 100(3) % were obtained under these experimental condition. Results indicated that microwave-acid assisted digestion using only H_2SO_4 recovered Hf of 97(2) % in solution/filtrate.

The results obtained for hafnium in different hafnium containing compounds were validated at 95 % confidence interval. Using hypothesis testing most of the results with low Hf recoveries recorded a rejection outcome. A summary of the accepted and rejected results is presented in **Table 5.46**. Using different validation parameters which include accuracy and precision, dissolution by microwave acid-assisted system and fusion using NH_4HF_2 and $Na_2B_4O_7$ were found to be the most successful methods for digestion and dissolution of pure hafnium oxide.

Table 5.44: A summary of the accepted and rejected using hypothesis testing

Material	Digestion technique	Acid medium	Successful	Unsuccessful
$HfCl_4$	Open vessel	HNO_3	✓	
	Open vessel	H_2SO_4	✓	
M_2HfF_6, M = K^+, Rb^+, Cs^+ or PPh_4^+	Open vessel	H_2SO_4	✓	
M_2HfF_6, M = Na^+, NH_4^+, or $N(CH_3)_4^+$	Open vessel	H_2SO_4		✓
Hafnyl thiocynate	Open vessel	H_2SO_4	✓	
HfO_2	Open vessel	HNO_3		✓
	Open vessel	HCl		✓
	Open vessel	H_2SO_4		✓
	Open vessel	H_2SO_4 + $(NH_4)_2SO_4$		✓
	Open vessel	H_2SO_4 + NH_4F		✓
HfO_2	Microwave acid assisted	HNO_3		✓
	Microwave acid assisted	HCl		✓
	Microwave acid assisted	H_2SO_4	✓	
	Microwave acid assisted	H_2SO_4 + $(NH_4)_2SO_4$	✓	
	Microwave acid assisted	H_2SO_4 + NH_4F	✓	

6 Evaluation of the study and future research

6.1. INTRODUCTION

This chapter gives an evaluation of the success of this study relative to the objectives indicated in **Chapter 1, Section 1.3** as well as the identification of the future studies that may supplement the current study.

6.2. EVALUATION OF THE STUDY

The objectives of the study as outlined in **Chapter 1, Section 1.3** were as follow;

- Perform an in depth literature study on the dissolution and analytical techniques for the dissolution and analysis of hafnium compounds.
- Establish measurement traceability in synthesized and analysing hafnium reference materials.
- Develop digestion method for hafnium oxide using different digestion methods such as open beaker, fusion and acid-assisted microwave digestion.
- Investigate the ability of the different analytical techniques such as ICP-OES and CHNS-microanalyser for the analysis of hafnium.
- Optimize analytical technique's operating conditions for the determination of hafnium at trace levels.
- Carry out method validation by performing the statistical calculations on the analytical data.

The study is been regarded as successful in achieving the set objectives outlined in **Chapter 1, Section 1.3**, which correlates with the results obtained in **Chapter 5**. Different hafnium containing compounds were dissolved using different digestion techniques and quantified by

ICP-OES at a wavelength of 277.33 nm to determine the efficiency of each dissolution technique. Firstly, the digestion of hafnium fluoride as the starting material for the synthesis of hafnium fluoride complexes was successfully accomplished with H_2SO_4 in an open vessel. The newly synthesised hafnium fluoride complexes completely dissolved in H_2SO_4 and good recoveries were obtained. Successful hafnium fluoride complex were characterised by X-ray crystallography to confirm the desired product as well characterisation by IR.

Prior to the digestion of HfO_2, pure hafnium chloride salt was used as reference material and a complete dissolution of the salt (by visual inspected) using H_2SO_4 in an open vessel at temperature of 70 °C for HNO_3 and 120 °C for H_2SO_4, excellent recoveries were obtained using H_2SO_4. However, low hafnium recoveries were obtained in different acids which include HNO_3 and H_2SO_4 in an open vessel. Flux fusion was used with the purpose of improving the results obtained using open vessel digestion. Different fluxes namely NaOH, $Na_2B_4O_7$ and NH_4HF_2 were investigated at different time and temperature. Fusion with $Na_2B_4O_7$ at 1020 **°C** and NH_4HF_2 (with removed excess fluoride through heating with sulphuric acid) at 130 °C gave good Hf recoveries. Another technique that was used which is more advantageous due to its high pressure and temperature in closed system is microwave acid assisted. It yielded improved hafnium recoveries, even good recoveries in H_2SO_4, a mixture of NH_4SO_4 and H_2SO_4 as well as NH_4F and H_2SO_4 under pressure of 600 W, 240 °C temperature and dissolution time of 90 min.

The developed methods for synthesis, dissolution and quantification of hafnium containing compounds were validated at 95 % confidence interval using different validation parameters such as accuracy, precision, limit of detection, limit of quantification and linearity. Most results from HfF_4, $HfCl_4$ reference material and new synthesised hafnium fluoride complexes by open vessel digestion were accepted (within the acceptable range of the hypothesis test). Results with low Hf recoveries such as results obtained for open vessel dissolution of HfO_2 using different reagents were rejected. Microwave digestion of HfO_2 in HNO_3, HCl and aqua regia produced poor recoveries and hence the results were rejected. However, good recoveries using microwave were obtained for H_2SO_4, $NH_4F + H_2SO_4$ and $NH_4SO_4 + H_2SO_4$ within the acceptable range of the hypothesis test at 95 % confidence level. Hence this study was considered successful in achieving all the outlined objectives.

6.3. FUTURE RESEARCH

From this study, a possible future study may be addressed to gain more knowledge on the chemistry of hafnium and its quantification. Hence, the following possible projects may be further investigated.

- The quantification of cations in the hafnium fluoride complexes by using Atomic Absorption spectrometry to determine the number of cation coordinated in the synthesised hafnium- fluoride complexes with Hf recoveries that are not within the acceptable accuracy and precision criterion.
- Potentiometrically determination of Fluorine atoms of the prepared hexafluorohafnate complexes.
- The digestion of hafnium oxide by fusion method using other fluxes such as NH_3F and $Na_2S_2O_7$ and dissolution of the melt in different acid medium.
- A comparative study on the use of different analytical technique such as ICP-MS for the quantification of hafnium containing compounds.
- The separation of zirconium from hafnium for nuclear purposes, since hafnium is used in the control rods for nuclear reactor it has to be of high purity, free from zirconium and other easily ionized elements such as calcium, sulphur, chromium, etc. Different method of separation to be employed includes ion exchange, gas chromatography and solvent extraction as well as separation by ammonium thiocyanate.

Summary

The aim of this study was to develop a method for the dissolution and quantification of hafnium in hafnium containing compounds (which include the metal oxide, different inorganic compounds as well as a number of organometallic complexes). Various digestion techniques such as open vessel, flux fusion and microwave acid-assisted system were evaluated. The same time different reagents which include HNO_3, HCl, H_2SO_4 alone and in combination with salts, e.g. $(NH_4)_2SO_4$ + H_2SO_4 were evaluated while experimental conditions such as time and temperature were varied.

Different analytical techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES), infrared spectroscopy (IR), CHNS-micro analyses and X-ray crystallography were used for the quantification and characterisation of the synthesized hafnium compounds. The criteria used to select the Hf emission wavelength for ICP-OES analysis was its sensitivity and the absence of spectral interferences from the acids used or the other elements present in solution. The experimental ICP-OES results obtained for the quantification of hafnium were also validated using different validation parameters which include accuracy, precision and the hypothesis test at a 95 % confidence interval to evaluate the validity of the most suitable digestion methods that were developed.

Open vessels digestion of HfF_4 using 98 % H_2SO_4 or 65 % HNO_3 resulted in good hafnium recoveries which ranged from 97.8 – 99.9 % with relative standard deviation (RSD) within the range of 0.4302 – 0.4327 %. The hafnium content was also quantified in a number of newly synthesized hexafluorohafnate complexes as well as a thiocyanate complex. Hafnium recoveries ranged from 79(6) to 103(3) % for the sodium, potassium, rubidium, cesium, ammonium, methyl ammonium and tetraphenyl phosphine hexafluorohafnate complexes as well for the hafnyl thiocyanate complex. All the synthesised products were characterized with IR while the crystal structures of K_2HfF_6, Rb_2HfF_6, Cs_2HfF_6 and $(PPh_4)_2HfF_6.2H_2O$ were successfully done with X-ray crystallography.

Various digestion techniques such as open vessel, flux fusion and microwave acid-assisted system with different mineral reagents which include HCl, 65 % HNO_3 and aqua regia, 98 % H_2SO_4, a mixture of $(NH_4)_2SO_4$ in 98 % H_2SO_4 and a mixture of NH_4F and 98 % H_2SO_4 were investigated for the dissolution of hafnium oxide. Digestion by wet ashing yielded poor hafnium recoveries and ranged between 0.041(6) % and 3.82(1) %. Hafnium oxide was however successfully dissolved with flux fusion using $Na_2B_4O_7$ followed by its dissolution with 98 % H_2SO_4. Hafnium recoveries improved from 72(4) to 100.8(7) %. Relatively poor hafnium recoveries ranging between 35(2) and 58(6) % (with time variation) were obtained using NaOH as flux and hafnium recoveries of 99(2) % were obtained using NH_4HF_2 as flux. Microwave acid-assisted digestion was also employed which improved the Hf recovery from 74.9(4) to 100(3) % with time and pressure as experimental variations.

The method validation of the experimental results obtained for the quantification of hafnium using the hypothesis testing of at a 95 % confidence level was considered satisfactory. The experimentally obtained LOD values ranged from 0.0051 to 0.0985 and LOQs ranged between 0.051 to 0.9846 ppm in the different mineral acid used in this study. Other statistic parameters such as linearity and sensitivity were also investigated and gave satisfactory results.

Opsomming

Die doel van hierdie studie was om ‘n metode vir die susksesvolle vertering en kwantifisering van hafnium in hverskillende afnium bevattende verbindings (onder andere die metaaloksied, verskillende anorganiese verbindings asook organometaalkomplekse) te ontwikkel. Verskeie verteringstegnieke naamlik oophouer-, gesmelte-sout- en mikrogolfvertering is ondersoek. Tydens die studie van bogenoemde tegnieke is verskillende reagense soos HNO_3, HCl, H_2SO_4 en mengsel van soute en sure soos byvoorbeeld $(NH_4)_2SO_4 + H_2SO_4$ gebruik, terwyl die invloed van eksperimentele kondisies soos reaksietyd en temperatuur ook ondersoek is.

Verskillende analitiese tegnieke wat insluit induktief-gekoppelde-optiese-plasma-emissie spektometrie (IGP-OES), infrarooi spektroskopie (IR), CHNS- mikro-element analises en X-straalkristallografie is vir die kwantifisering en karakterisering van die verskillende hafnium bevattende verbindings gebruik. Die eksperimentele IGP-OES resultate wat vir die kwantifisering van hafnium verkry is, is ook met behulp van verskillende statistiese toeetse geëvalueer en die toets het onder andere akkuraatheid, presisie en die hipotese toets by ‘n 95 % betroubaarheidsgrens ingesluit.

Hafniumherwinnings in $HfCl_4$ en HfF_4 wat strek tussen 97.8 – 99.9 % met ‘n standaardafwyling tussen 0.4302 – 0.4327 % in 98 % H_2SO_4 of 65 % HNO_3 met behulp van oophouer-vertering is verkry. Die hafniuminhoud in ‘n aantal nuut-gesintetiseerde heksafluoro- en tiosianaathafnaat-komplekse (natrium, kalium, rubidium, sesium, ammonium, metielammonium en tetrafenielfosfonium) het tussen 79(6) en 103(3) % gewissel. Al die nuut-bereide produkte heksafluorokomplekse is met behulp van IR gekaraktiseer, terwyl kristalstrukture van K_2HfF_6, Rb_2HfF_6, Cs_2HfF_6 en $(PPh_4)_2HfF_6$ susksesvol met behulp van X-straal kristallografie uitgevoer is..

Verskillende vereteringstegnieke wat insluit oophouer-, gesmelte-sout- en mikrogolfvertering is vir die vertering van hafniumokied geëvalueer. Bogenoemde tegnieke is in die teenwoordigheid van HCl, 65% HNO_3 en aqua regia 98 % H_2SO_4, asook mengesels van NH_4SO_4 en 98 % H_2SO_4 en NH_4F met 98 % H_2SO_4 bestudeer. Die ontbinding van HfO_2 met

die oophouververtering het swak herwinning opgelewer en het tussen 0.041(6) % en 3.82(1) % gestrek. Hafniumoksied is egter volledig met behulp van $Na_2B_4O_7$ gesmelte-sout vertering (gevolg deur 98 % H_2SO_4 byvoeging) opgelos. Hf-herwinnings wat tussen 72(4) % en 100.8(7) % wissel is vir die verskillende gesmelte soute verkry. Relatiewe swak hafniumherwinning wat tussen 35(5) en 58(6) % strek (wisseling van reaksietyd), is vir NaOH as gesmelte sout gekry. Goeie hafniumherwinning van 99(2) % is verkry wanneer NH_4HF_2 as gesmelte soutmedium gebruik is. Mikrogolfvertering, in die teenwoordigheid van H_2SO_4, het hafniumherwinnings tussen 74.9(4) tot 100(3) % gelewer.

Die validering van die eksperimentele resultate vir die vertering en kwantifisering van Hf is met behulp van die hipotese-toets (t-statistiese toets) by ‘n 95 % betroubaarheidsvlak uitgevoer. Die laagste vlakke waar Hf met sekerheid waargeneem is (LOD) het van 0.0051 tot 0.0985 gestrek terwyl die laagste vlakke waar Hf susksesvol gekwantifisser kan word (LOQ) het vanaf 0.051 tot 0.9846 dpm in verskillende mineraal-sure gestrek. Statistiese parameters soos lineariteit en sensitiwiteit is ook ondersoek en het bevredigende resultate gelewer.