

SEPARATION AND PURIFICATION OF NIOBIUM AND TANTALUM FROM SYNTHETIC AND NATURAL COMPOUNDS

by
Motlalepula Nete

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Supervisor: Prof. W. Purcell

Co-Supervisor: Dr. J. T. Nel

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DECLARATION

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LIST OF ABBREVIATIONS

Analytical equipment

FAAS	Flame atomic absorption spectroscopy
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectroscopy
MSB	Magnetic susceptibility balance
ETV	Electrothermal vaporization
NAAS	Neutron activation analysis spectrometry
NMR	Nuclear magnetic resonance
XRF	X-ray fluorescence
XRD	X-ray diffraction
UV/VIS	Ultra violet visible spectroscopy
IR	Infrared
PTFE	Polytetrafluoroethylene
GD-MS	Glow discharge mass spectrometry

Miscellaneous terms

M_xO_y	Metal oxide
EIEs	Easily Ionisable Elements
Sam A	Sample A
Sam C	Sample C
RSD	Relative standard deviation
EU	European Union
FST	Future sustainable technologies
HSLA	High strength, low alloy
CBMM	Companhia Brasileira de Metalurgia e Mineração
MCG	Mineracao Catalao de Goias
MRI	Magnetic Resonance Imagery
NORMs	Naturally Occuring Radioactive Materials

LLE	Liquid-liquid extraction
EBM	Electron beam melting
CRM	Certified Reference Materials

Ligands and solvents

MIBK	Methyl isobutyl ketone
EDTA	Ethylenediaminetetra-acetic acid
MIAC	Methyl isoamyl ketone
TPB	Tributyl phosphate
DIPK	Diisopropyl ketone
DEHPA	bis(2-ethylhexyl)phosphoric acid
DAM	Diantiprylmethane
DCE	Dichloroethane
PPDA	<i>p</i> -Phenylenediamine
MIPK	Methyl-isopropyl ketone
4-Hep	4-Heptanone
1-Oct	1-Octanol

KEY WORDS

Niobium

Tantalum

Tantalite samples

Quantitative analysis

Qualitative analysis

Beneficiation

Dissolution

Separation

Purification

Recovery

1 Background and scope of the study

1.1 Introduction

The demand for niobium and tantalum in various applications has increased steadily over the past two decades due to their importance in the production of modern industrial materials and high tech consumer products, ranging from super alloys to electronic devices such as cell phones (see **Section 1.3**).¹ Tantalum and niobium, together with metals such as tellurium, indium, silver, dysprosium, neodymium and molybdenum have recently been declared as critical metals by the European Union (EU) due to their potential use in strategic energy technologies such as nuclear, solar, wind, carbon capture and storage, their use in future sustainable technologies (FST)^{2,3} as well as the significant contribution that these metals currently make to the EU economy. Brazil, the world's largest niobium producer (see **Section 1.2**) has recently engaged in a partnership with Korean and Japanese companies with the aim of developing new processing technologies as well as expanding niobium and tantalum production and applications. It is estimated that niobium demand will grow at a rate of 5 – 7% per year going forward, due to the growth in the emerging markets and their anticipated consumption, especially in high strength, low alloy (HSLA) steel.⁴

1. Hayes, K. and Burge, R., 2003, "Coltan Mining in the Democratic Republic of Congo: How tantalum-using industries can commit to the reconstruction of the DRC." Fauna & Flora International, Cambridge, UK.

2. Moss, R.L., Tzimas, E., Kara, H., Willis, P. and Kooroshy, J., Critical Metals in Strategic Energy Technologies: Assessing Rare Metals as Supply-Chain Bottlenecks in Low-Carbon Energy Technologies [homepage on the Internet]. C2011 [cited 2012 Feb 28]. Available from: http://setis.ec.europa.eu/newsroom-items-folder/copy_of_jrc-report-on-critical-metals-in-strategic-energy-technologies

3. Lowder, S., Demand for key rare earths, niobium and ferroalloys soaring: Handwerke [homepage on the Internet]. C2012 [updated 2012 Feb 15; cited 2012 Feb 28]. Available from: <http://www.mineweb.com/mineweb/view/mineweb/en/page72102?oid=145424&sn=Detail>

4. Moreno, L., Tantalum and Niobium Primer – two critical metals [homepage on the Internet]. C2011 [updated 2011 July 19; cited 2011 Aug 01]. Available from: www.jacobsecurities.com

The two metals are extracted from a variety of minerals and concentrates. The major source of niobium and tantalum is the columbite-tantalite mineral, also called coltan, $(\text{Fe,Mn})(\text{Nb,Ta})_2\text{O}_6$ (**Figure 1.1a**) which contains (5 – 30 Ta_2O_5 , wt.% in columbite and 42 – 84 Ta_2O_5 , wt.% in tantalite) and (55 – 78 Nb_2O_5 , wt.% in columbite and 2 – 40 Nb_2O_5 , wt.% in tantalite). Another important source of niobium is pyrochlore $(\text{Ce,Ca,Y})_2(\text{Nb,Ta})_2\text{O}_6(\text{OH,F})$ (**Figure 1.1b**) with Nb_2O_5 content between 37 and 66 wt.% and Ta_2O_5 content up to 6 wt.%.

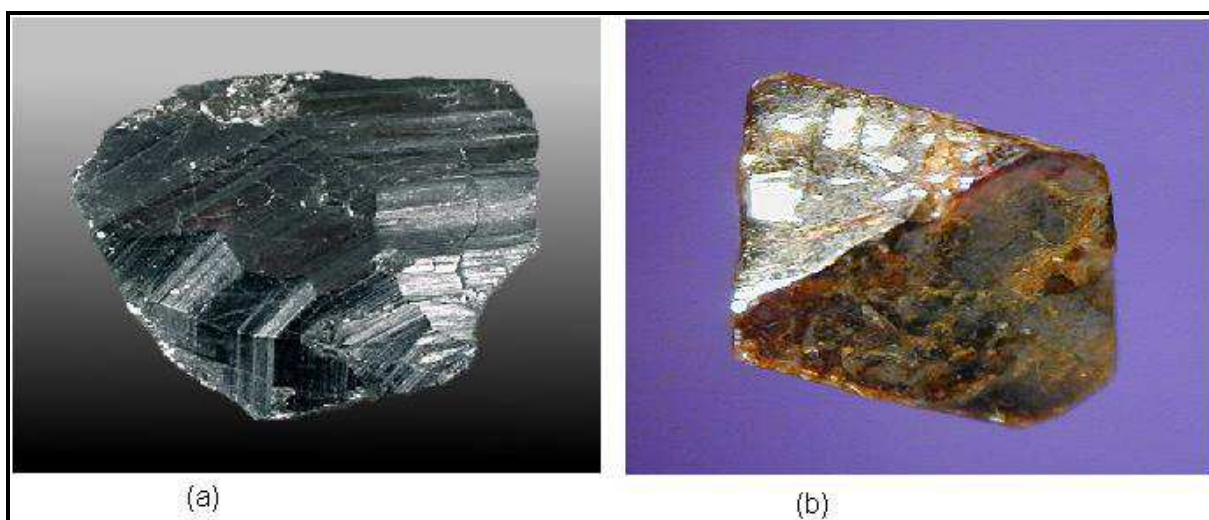


Figure 1.1: Tantalum and niobium minerals: (a) columbite-tantalite⁵ and (b) pyrochlore.⁶

Tantalum and niobium exist in other minerals (more than 150) as complex oxides and hydroxides with the exception of the borate mineral behierite $(\text{Ta,Nb})(\text{BO}_4)$ and the only known non-oxide mineral containing tantalum carbide TaC .⁷

5. Mark, N., ColTan: The Meta-Science of Columbite – Tantalit [homepage on the Internet]. C2009 [updated 2009 Feb 12; cited 2011 Nov 08]. Available from:

<http://lifestreasureskauai.com/blog/crystals/the-meta-science-of-columbite-tantalite/>

6. Glendale Community College earth science image archive [homepage on the Internet]. [cited 2011 Nov 08]. Available from: http://www.gccaz.edu/earthsci/imagearchive/pyrochlore_pictures.htm

7. Ta – Tantalum, [homepage on the Internet]. [cited 2011 Sep 22]. Available from: <http://www.gsf.fi/publ/foregsatlas/text/Ta.pdf>

1.2 Tantalum and niobium world production

Tantalum and niobium mineral deposits are widespread across the globe, (**Figure 1.2**) as published in the Roskill report^{8,9} but many of these deposits are low grade in both niobium and tantalum content. Brazil and Australia have the largest high grade niobium and tantalum resources (see **Figure 1.3**), hence they are the major world producers of these metals followed by Canada, Mozambique and Ethiopia. However, in 2008 due to the world economic crisis the production decreased substantially. Mining operations in Australia, Canada and Mozambique were mostly affected by the economic crisis which led to the closure of a number of mines in those countries. In mid-2009 Brazil, Ethiopia and China were the only reliable tantalum and niobium producers. Production in Mozambique resumed in 2010 while in Australia and Canada it was expected to resume in 2011.



Figure 1.2: The world map showing selected areas (■ symbol) of coltan distribution.¹⁰

8. Roskill Information, *The Economics of Tantalum*, 9th ed., Roskill Information Services Ltd., London, 2005.

9. Roskill Information, *The Economics of Niobium*, 10th ed., Roskill Information Services Ltd., London, 2005.

10. Ralph, J. and Chau, I., 1993-2011, *Columbite – Tantalite*, [homepage on the Internet]. [update 15th Jul 2011, cited 20 October 2011]. Available from: <http://www.mindat.org/show.php?id=10303&ld=1>

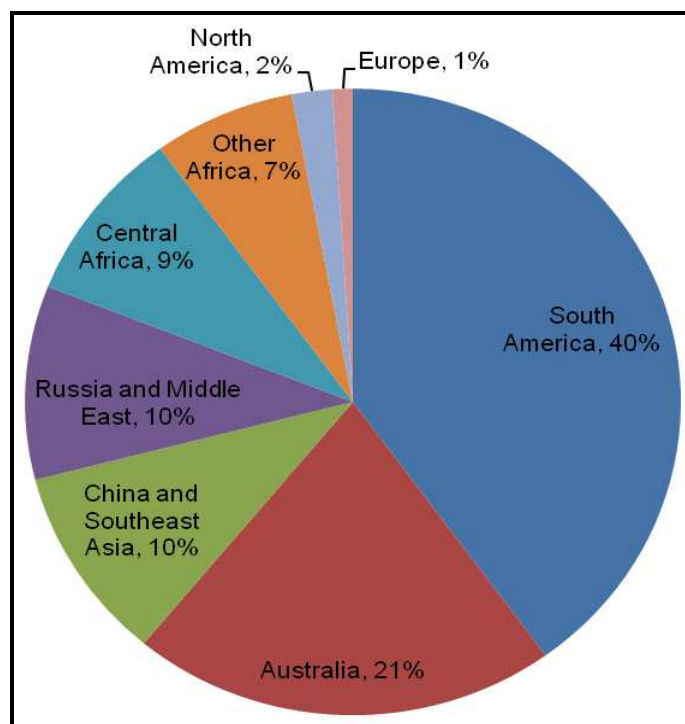


Figure 1.3: Major tantalum and niobium producers in 2010. African countries include Nigeria, Namibia, Egypt, Ethiopia, Mozambique and Zimbabwe.¹¹

Although both pyrochlore and columbite-tantalite minerals are the major niobium sources, current production is dominated by three pyrochlore mining companies namely Companhia Brasileira de Metalurgia e Mineração (CBMM), Brazil¹² Mineracao Catalao de Goias (MCG), Brazil and Niobec, Canada.¹³ The open-pit mine (**Figure 1.4**) operated by CBMM at Araxá, in the Minas Gerais State in Brazil supplies 65% to 70% of world's total niobium demand. The Catalão open pit mine in Brazil, operated by Anglo American's MCG, is the second largest pyrochlore producer followed by the Niobec mine in north-eastern Quebec, Canada which produces both pyrochlore and columbite.¹²

11. Louvain, C., Tantalum – Raw Materials and Processing [homepage on the internet]. [cited 2011 Nov 10]. Available from: <http://tanb.org/tantalum>

12. Serjak, W. A., Technical Promotion Officer Tantalum-Niobium International Study Center 40 Rue Washington, 1050 Brussels, Belgium.

13. Roskill information, The Economics of Niobium, 11th ed., Roskill Information Services Ltd., London, 2009.



Figure 1.4: CBMM open pit mine in Araxa in Brazil.¹⁴

Additional quantities of tantalum and niobium minerals are provided by a number of central African countries such as Uganda, Burundi, Democratic Republic of Congo (DRC) and Rwanda as well as Russia and Southeast Asia. In Southeast Asia, it is mainly Malaysia and Thailand that produce tantalum as a by-product of the smelting of cassiterite (SnO_2) ore concentrates in the tin industry. Struverite (Ti-Nb-Ta) concentrates obtained from northern Malaysia contains 9 – 12% Ta_2O_5 . The Lovozero syenite massif and Tomtor carbonatite deposits found in Siberia, Russia contain small amounts of niobium and tantalum in eudialyte ($\text{Na}_4(\text{Ca,Ce,Fe,Mn})_2\text{ZrSi}_6\text{O}_{17}(\text{OH,Cl})_2$), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$) and loparite ($(\text{Ce,Na,Ca})(\text{Ti,Nb})\text{O}_3$) minerals.

In Africa tantalum and niobium containing minerals have been identified in Ethiopia, Egypt, Nigeria, Namibia, Zambia, Malawi, Rwanda, Angola, Mozambique, Zimbabwe and South Africa. In 2009 it was estimated that approximately 50% of world supply of the tantalum came from the DRC and Rwanda. Mining in the DRC, Rwanda and Zimbabwe is however very risky due to the political instabilities in those countries which makes the supply from these countries highly unreliable. It is believed that the illegal mining and the subsequent selling of coltan from DRC supplies the finances to sustain the conflicts in this region that have resulted in a number of humanitarian disasters. These conflicts not only led to the decline of social structures and

14. Niobium mine, [homepage on the Internet]. [cited 2011 Nov 08]. Available from: <http://www.minerschoice.co.za/the%20worlds%20largest%20niobium.html>

economic activity in these areas but also to the destruction of the natural resources such as wildlife, endangering the continued existence of eco-sensitive species such as the African mountain gorilla. As a result the United States of America drafted a bill in September 2001 which prevented the trade of coltan from the central African countries. Tantalum technology companies such Apple Inc. (NASDAQ:AAPL), Alcatel, Compaq, Dell, Ericsson, HP, IBM, Lucent, Nokia and Siemens and Motorola Solutions Inc. were ordered to comply with this law by refraining from buying coltan (also called the blood mineral) from these countries.¹

The tantalum and niobium deposits in Angola have been identified as intrusions in the alkaline carbonatite belt in Bonga, Bailundo and Virolundo, but the main occurrences are believed to exist in Huambo and Benguela provinces. However, there is a lack of geological information on these resources for mining operations.⁸ In Egypt the main niobium-tantalum bearing mineral is euxinite (Y,Er,La,Ce,U,Th)(Nb,Ta,Ti)(O,OH) obtained from the central eastern desert of the Kab Amiri area. This mineral occurs in association with davidite (Fe,La,U,Ca)(Ti,Fe,V,Cr)(OH,O) and zircon (Zr,U,Th,Hf)SiO₄). Chemical analysis¹⁵ of the mineral mixture indicated a 7.90% Ta₂O₅ and 10.60% Nb₂O₅ content with U₃O₈ (17.5%), ThO₂ (10.0%) as major impurities. The Nigerian tantalum and niobium deposits is obtained from tantalite and columbite as major minerals and the chemical analysis¹⁶ on samples collected from different geographical locations in the country indicated the presence of 8 – 60% Ta₂O₅ and 20 – 38% Nb₂O₅ contents with MnO (0.74 – 10.1%), Fe₂O₃ (2.85 – 10.69%) and TiO₂ (up to 33.38%) as major impurities.

A number of new mines which will process lower grades in both Ta and Nb minerals and which are in their early developmental stages are given in **Table 1.1**. These include Kanyika in Malawi and Sanguenay in Canada.¹³ Recent geological surveys in the central and eastern part of Malawi (Kanyika-niobium and Salambidwe projects respectively) revealed significant deposits of Ta and Nb minerals. The compliant

15. El-Hussaini, O. M. and Mahdy, M. A., 2002, "Sulfuric acid leaching of Kab Amiri niobium–tantalum bearing minerals, Central Eastern Desert, Egypt" *Hydrometallurgy*, **64**: pp. 219–229.

16. Adetunji, A. R., Siyanbola, W. O., Funtua, I. I., Olusunle, S. O. O., Afonja, A. A. and Adewoye, O. O., 2005, "Assessment of beneficiation routes of tantalite ores from key locations in Nigeria," *J. Miner. Mater. Charact. Eng.*, **4**(2): pp. 67–73.

resources of the Kanyika-niobium project are 56-million tons containing niobium, uranium, tantalum and zircon and the mine has an estimated life span of 20 years. Projections indicate that production of niobium will start in 2013 with an initial rate of 3000 t/a.^{17,18} Columbite-tantalite mining operations at Ghurayyah in Saudi Arabia, Blue River in Canada and Abu Dabbab in Egypt were expected to begin in 2010.¹³

Table 1.1: Summary of selected new tantalum and niobium sources¹⁹

Location	Operation Name	Owner	Deposit	Resource Size, Million tonnes	Nb ₂ O ₅ (%)	Ta ₂ O ₅ (%)
Canada	Anita	Les Mineraux Crevier	Carbonatite nepheline syenite	23.75	0.186	0.019
Malawi	Kanyika	Globe Metals	Alkaline-peralkaline granite	21	0.41	0.018
Saudi Arabia	Ghurayyah	Tertiary Minerals	n.a	n.a	0.28	n.a
Egypt	Abu Dabbab	Gippsland	LCT granite	44.5	n.a	0.025
Greenland	Motzfeldt	Ram Resources	Alkaline-peralkaline granite	500	0.13 – 0.30	0.011 – 0.013
Tanzania	Panda Hill	n.a	n.a	n.a	0.33	n.a
Canada	Crevier	MDN Inc	Carbonatite nepheline syenite	25.4	0.20	0.023
Egypt	Nuweibi	Gippsland	LCT granite	98	0.0095	0.014
Mozambique	Marrupino	Noventa	LCT granite	7.4	n.a	0.023
British Columbia	Upper fir	Commerce Resources Cop.	Carbonatite nepheline syenite	36.4	0.17	0.019

n.a = not available

17. Swanepoel E. Globe regains full ownership of Malawi niobium [homepage on the Internet]. C2010 [updated 2010 June 15; cited 2011 Jan 28]. Available from:

http://www.miningweekly.com/topic/kanyika-niobium_mine

18. Commencement of FeNb Metallurgical Program – Kanyika Niobium Project [homepage on the Internet]. c2009 [updated 2009 Aug 19; cited 2011 Jan 28]. Available from:

<http://www.globemetalsandmining.com.au/>

19. Shaw, R., Goodenough, K., Gunn, G., Brown, T. and Rayner, D., Niobium – tantalum, British Geological Survey, [homepage on the Internet]. C2011 [updated 2011 April; cited 2011 Nov 10]. Available from:

<http://tanb.org/tantalum>

The tantalite-bearing ores in South Africa exist in the pegmatite belt in the western portion of the Limpopo province. The geological information has indicated that tantalum and niobium resources are of low grade and the mining of tantalite in South Africa is therefore uneconomical.²⁰ In Mozambique Ta/Nb minerals are mined in pegmatite mines namely Muiane, Morrua, Marropino and Naquissupa, in the north-west of Alto Ligonha in Zambesia province. The opening of the new Naquissupa mine and reopening of the Morrua and Marropino mines in 2004 resulted in a dramatic increase of tantalite production by 227.4%, compared to the previous year, (see **Figure 1.5**) in Mozambique.

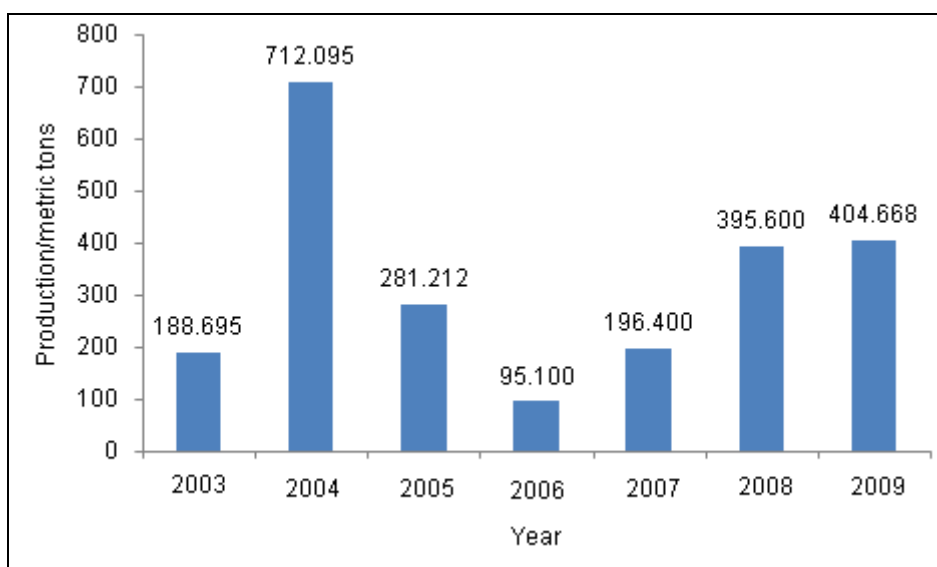


Figure 1.5: Tantalite production in Mozambique, 2003 to 2009.²¹

1.3 Market and application requirements

1.3.1 Niobium

The global niobium market has grown remarkably during the 2000's. The ferro-niobium demand in Japan forced a sharp increase in niobium prices from US\$14.50/kg to over US\$32/kg (~\$18 increase) in 2007 after a long time of price

20. Northern Cape Province – Mineral sector strategy [Internet], [cited 2012 Aug. 03]. Available from: <http://www.northern-cape.gov.za/oldsite/ncpgds/mining/sec6.pdf>

21. Mozambique niobium and tantalum production by year [homepage on the Internet]. [cited 2011 Aug 01]. Available from: <http://www.indexmundi.com/minerals/?country=mz&product=niobium&graph=production>

stability (**Figure 1.6**).¹³ In 2008 the major niobium producer, CBMM, cut down its production to adjust to lower demand levels, due to changes in the world economy, and to maintain stable niobium prices through the crisis. In February 2010 niobium price was reported at an average of US\$32.28 and exactly a year later (February 2011) the price had increased to approximately US\$39.38 – 41/kg.²²

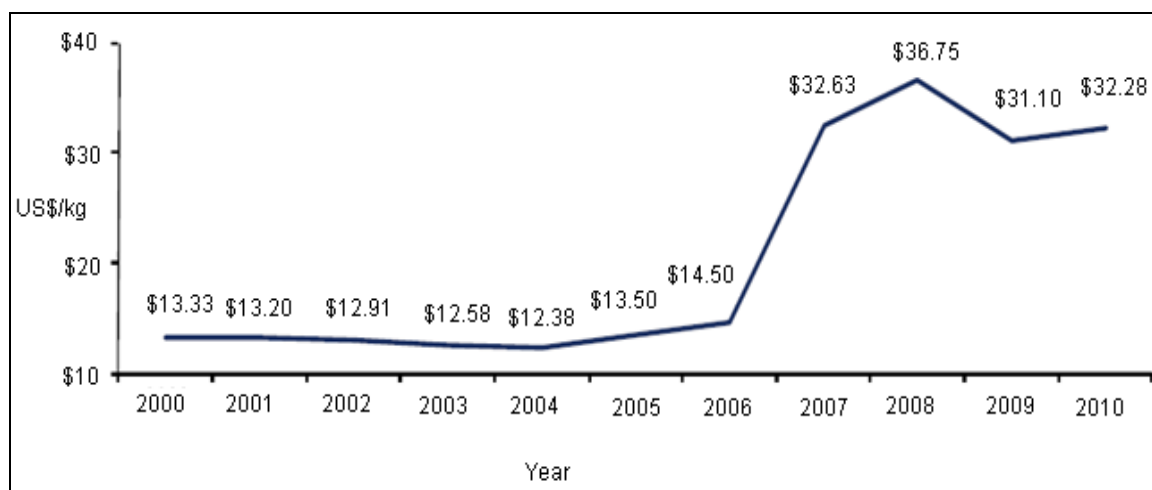


Figure 1.6: Niobium price performance in US\$/kg, 2000 – 2010.²³

All Ta and Nb applications in industry are dependent on the levels of impurities present in the final product. Other applications are affected by factors such as particle size.²⁴ **Table 1.2** contains some of the common niobium and tantalum impurities and the levels of concentration limits allowed for different applications.

22. ASX/Media Announcement, Globe Metals & Mining, Niobium Market Update [homepage on the Internet]. C2011 [updated 2011 June 07; cited 2011 Nov 08]. Available from: http://www.globemetalsandmining.com.au/uploads/files/exchange_releases/2011/Niobium%20Market%20Update%20-%20June%202011.pdf

23. Niobium 101, [homepage on the Internet]. [cited 2012 Feb 24]. Available from: http://www.iamgold.com/Theme/IAmGold/files/images/Niobec%20101/Niobium%20101%20Final%20December%202011_v001_m4s45i.pdf

24. Park, K. S., Kim, N. B., Woo, H. J., Lee, K. Y., Yoon, Y. Y. and Hong, W., 1994, "Determination of impurities in niobium metal by a radiochemical neutron activation analysis" *J. Radioanal. Nucl. Chem. Art.*, **179**(1): pp. 81–86

Niobium's high melting temperature (2443 °C) have made it an important element in the metallurgical field where about 90% of it is consumed in the production of different steel products that can be used at elevated temperatures.²⁵ About 75% of it is used in the ferro-niobium alloy by HSLA steel manufacturers. Niobium improves the strength and reduces grain boundary deformation of the HSLA steel which is used for the manufacturing of vehicle bodies, railway tracks, ship hulls and oil and gas pipelines. About 20% of total niobium is used in stainless steel production (used in pipeline construction) to increase its mechanical strength, corrosion resistance and prevent brittleness. Niobium's low thermal neutron capture cross section makes it an attractive metal for nuclear power application where it is used with zirconium to produce zirconium alloys for nuclear reactors. High purity zirconium metal has low mechanical strength at high temperatures and the addition of niobium in concentrations not exceeding 2.5% imparts high mechanical strength to the zirconium metal used for cladding and assembly components in both light and heavy water-cooled reactors. The presence of tantalum as impurity in the niobium metal that is applied in the nuclear industry must be very low due to its high thermal neutron capture cross section that is twenty times that of niobium which can reduce its effectiveness as cladding material.²⁶

25. Bayot, D. and Devillers, M., 2006, "Peroxo complexes of niobium(V) and tantalum(V)" *Coord. Chem. Rev.*, **250**: pp. 2610–2626

26. Sadoway, D. R. and Flengas, S. N., 1980, "A new process for the separation of tantalum from niobium" *Metall. Trans. B*, **11B**, pp. 57–62

Table 1.2: Specification for Ta₂O₅, Nb₂O₅ and Nb metal for various applications^{27,28,29}

Element	Nb ₂ O ₅			Nb metal		Ta ₂ O ₅	
	Ceramics Grade (%)	Optical Grade (%)	High Purity Grade (%)	FeNb Grade (%)	Reactor Grade Nb-Zr alloy (%)	Standard Grade (%)	Optical Grade (%)
Nb	>99.9	>99.9	>99.99	min. 60	-	0.30	0.008
Ta	0.02	0.02	0.002	0.50	0.1	>99.5	>99.99
Al	0.0005	0.0005	0.0003	2.00	0.002	0.015	0.001
Ca	0.001	0.0002	-	-	-	-	-
Co	0.0005	0.0002	-	-	0.002	-	-
Cr	0.0005	0.0005	0.0003	0.10	0.002	-	0.001
Cu	0.0005	0.0003	-	-	-	-	0.001
F	0.03	0.0005	-	-	-	0.15	0.015
Fe	0.0005	0.0005	0.0003	-	0.005	0.03	0.001
Mn	0.0005	0.0005	0.0003	-	-	0.005	0.0005
Hf	0.001	-	-	-	0.02	-	-
Ni	0.0005	0.0005	0.0003	-	0.005	-	0.001
Zr	-	-	-	-	0.8 to 1.2	-	-
Si	0.005	0.005	0.001	2.50	0.005	0.05	0.005
Ti	0.0005	0.0005	0.0003	0.10	-	0.03	0.0005
C	-	-	-	0.15	0.01	-	-
P	-	-	-	0.20	-	-	-
S	-	-	-	0.05	-	-	-
Mo	-	-	-	-	0.02	-	0.001
W	-	-	-	-	0.03	-	0.001
Average particle Size x20.6	0.6-1.0 μm	1.0-1.6 μm	1.0-3.0 μm	-	-	-	-

27. Okada, T., "Manufacturing of special niobium oxides for optical and ceramic applications"

Mitsui Mining & Smelting Co., Ltd. Rare Metals Division, 1-11-1 Osaki, Shinagawa-ku, Tokyo 141-8094, Japan, [Internet] (Cited 16 March 16, 2012), Available from:

<http://www.cbmm.com.br/portug/sources/techlib/science techno/table content/sub 2/images/pdfs/012.pdf>

28. Sattelberger, S. and Löber, G., "Production of High Purity Niobium Masteralloys" GfE Gesellschaft für Elektrometallurgie mbH, Höfenerstraße 45, D-90431 Nuremberg, Germany [homepage on the Internet]. [cited 2011 Nov 03]. Available from:

http://www.gfe.com/userfiles/file/pdfs/Veroeffentlichungen/Master%20Alloys_HP Nb Masteralloys.pdf

29. Treibacher Industrie AG, Auer von Welsbach Strasse 1, A9330 Althofen, Austria. [homepage on the Internet]. [cited 2011 Nov 09]. Available from:

<http://www.treibacher.com/downloads/TantalumOxide.pdf>

Niobium also has several medical applications due to its non-toxicity and physiological inertness.²⁴ For example, niobium metal is used in medical implants to aid a quicker osseointegration (the bone tissue adherence to metal) and is also used in manufacturing of medical devices such as pacemakers. A niobium-titanium alloy is furthermore used for construction of the superconducting magnetic coils for magnetic resonance imagery (**Figure 1.7**) which is used for detection of anomalies in soft tissue. Niobium has recently been found to be also a useful catalyst for conversion of palm oil into biodiesel fuel.¹²

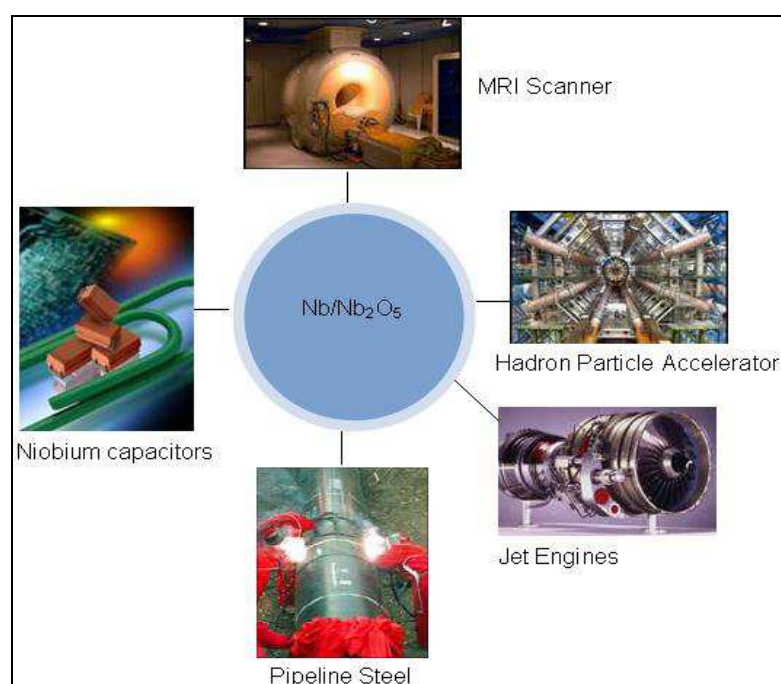
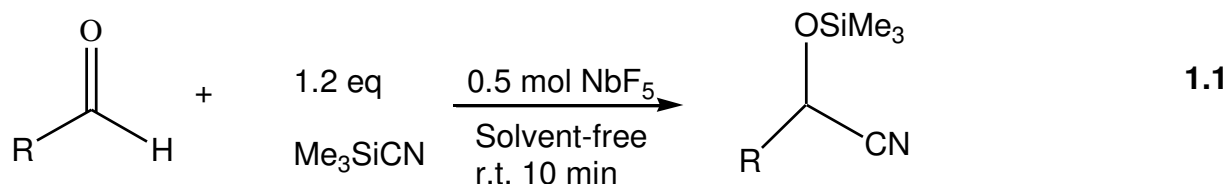


Figure 1.7: Some modern industrial equipment made of niobium or niobium compounds.

1.3.2 Niobium compounds

Niobium oxide is used in the production of high refractive index lenses, high dielectric, multilayer ceramic capacitors and in the manufacture of lithium niobate for surface acoustic wave filters which is mainly used in cell phones. Niobium oxide is currently consumed at an annual rate of 20% of total production in the manufacturing of lenses for digital photography and other electronic applications. Niobium carbide on the other hand is used in the manufacture of cutting tools and niobium

pentafluoride is used as a catalyst in the production of cyanohydrins from trimethylsilylcyanide and aldehydes as indicated in **Equation 1.1**.³⁰



1.3.3 Tantalum

Tantalite mineral prices used to be stable until 1978 when the first tantalum price increase was observed. This was due to a strong global demand and ungrounded fears of a future shortage of tantalum resources. Two decades that followed saw small tantalite price fluctuations with more price stability in 1990 to early 2000. The high demand for tantalum capacitors from mobile phone (35%) and computer makers has resulted in 60% tantalum price increase due to booming sales of cell-phones.^{31,8} At the beginning of 2000 tantalum was sold in the range US\$40 – 50/lb (US\$88 – 110/kg), but by December 2000 capacitor grade tantalum was selling at an all time high price of US\$300/lb (US\$660/kg) (**Figure 1.8**).

30. Kim, S. S. and Rajagopal, G., 2007, "Niobium Fluoride (NbF₅): A Highly Efficient Catalyst for Solvent-Free Cyanosilylation of Aldehydes" *Synthesis*, pp. 215–218

31. Primary Information Services, Tantalum. [homepage on the Internet]. [cited 2011 Sep 22]. Available from: <http://www.primaryinfo.com/industry/tantalum.htm>

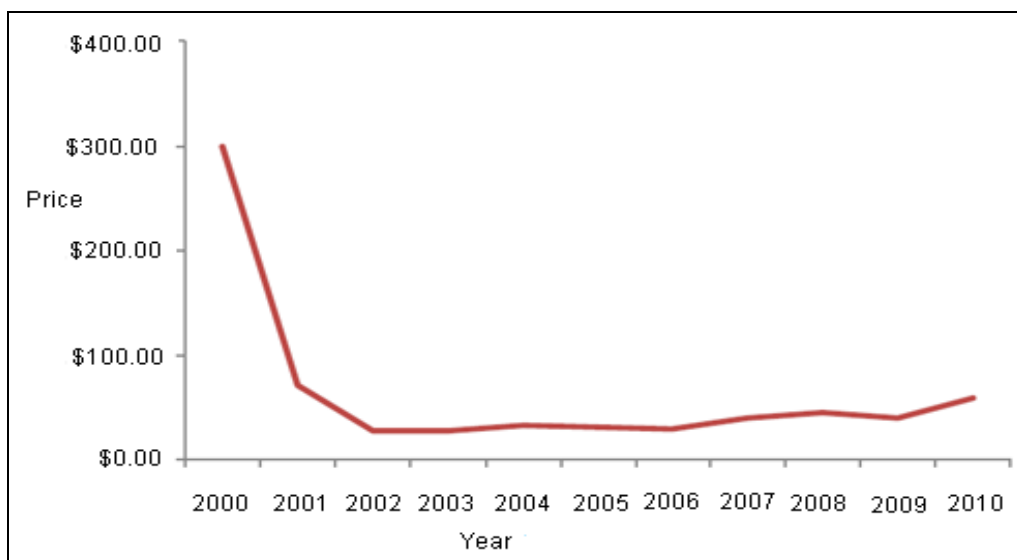


Figure 1.8: Tantalum price performance over 10 years (US\$/lb), 2000 – 2010.³²

The high tantalum prices and resources' shortages threats that continued until 2001 pushed capacitor manufacturers into entering into long-term, fixed price contracts and seeking cheaper and readily available substitutes for tantalum. These buying strategies did not only negatively affect the tantalum suppliers, but also the end users such as mobile phone and aerospace industries. Tantalum prices fell sharply and stayed below US\$100/lb (US\$220/kg) for the following nine years. It was these low tantalum prices which led to the suspension of some tantalum mines such as Wodgina mine in Australia. Tantalum consumption in 2009 was estimated at a value of about US\$127 million and was expected to increase to about US\$170 million in 2010. In U.S. tantalum consumption was estimated to increase by about 150% in 2010 from that of 2009.³³

The biocompatibility of tantalum, as illustrated by its inertness towards body fluids, made it ideal to be used in different medical applications such as hip and knee replacements, as material that supports quick bone growth, as well as in the

32. Admin, Tantalum Prices About to Go Through The Roof? [homepage on the Internet]. C2011 [updated 2011 Jan 20; cited 2011 Nov 08]. Available from: <http://agmetalminer.com/2011/01/20/tantalum-prices-about-to-go-through-the-roof/>

33. U.S. Geological Survey, Mineral Commodity Summaries, January 2011

production of surgical clips, metal plate screws and wire for repairing fractured bones.¹²

1.3.4 Tantalum compounds

Tantalum metal and Ta₂O₅ also play an important role in the production of modern industrial materials (**Figure 1.9**) in which relatively small amounts of the metal or its compounds are consumed such as in the manufacturing of cell phones' capacitors.⁸ Tantalum capacitors offer high capacitance density needed in smallest possible size. As such the use of tantalum capacitors allows for production of small size electronic equipment such as cell phones and laptops. High-purity Ta₂O₅ is also used in the preparation of tantalate X-ray phosphors for X-ray intensifier screens.⁴ Tantalum production is highly dependent on its demand in electronic industry for the manufacturing of capacitors, rectifiers, amplifiers, oscillators, surface acoustic wave filters, pyroelectric infrared sensors, and optoelectronic devices, control signal devices, alarm systems and timing devices which account for over 60% of the total global tantalum consumption. Purities of 99.999 or 99.9999% are required for tantalum or tantalum compounds to be used in electronic applications while 99.99% purity is required for electro-optical components and acoustic uses.³⁴

34. Conte, R.A., Mermet, J.M., Rodrigues, J.D.A. and Martino, J.L., 1997, "Analysis of Tantalum Products by Inductively Coupled Plasma Atomic Emission Spectrometry" *J. Anal. At. Spectrom.*, **12**: pp. 1215–1220

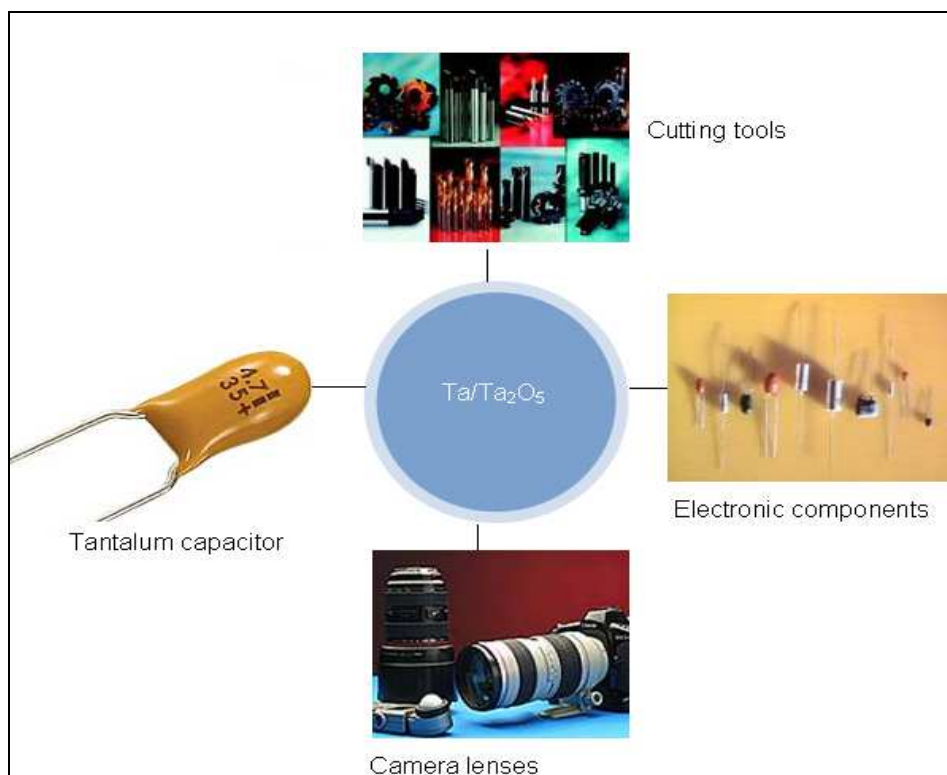


Figure 1.9: Modern industrial equipment made of tantalum or tantalum compounds.

1.4 Chemistry of niobium and tantalum

The elements tantalum and niobium are members of group 5b on the periodic table with average crustal abundances of $1.7 \text{ mg}\cdot\text{kg}^{-1}$ and $20 \text{ mg}\cdot\text{kg}^{-1}$ respectively. In nature, tantalum and niobium exist primarily as refractory oxides (Ta_2O_5 and Nb_2O_5) and no free metal deposits are known. Both niobium and tantalum form complexes with a variety of oxidation states namely +2, +3, +4 and +5 but the +5 oxidation state is the most stable possibly due to the loss of the valence s and d electrons. The electron configuration of niobium and tantalum as elements are as follows (Nb [Kr] $4d^4 5s^1$ and Ta: [Xe] $4f^{14} 5d^3 6s^2$) which changes to [Kr] $4d^0 5s^0$ and [Xe] $4f^{14} 5d^0 6s^0$ for the respective metals in the +5 oxidation state. Although these elements have metallic properties, they also possess chemistries similar to those of typical non-metals mainly in their +5 oxidation state, especially tantalum. These elements are also known to form many anionic complexes with coordination numbers of seven and eight and almost no cationic complexes.³⁵ The pentoxides (Nb_2O_5 and Ta_2O_5) are by

35. Cotton, F. A., Wilkinson, G. and Gaus, P. L., *Basic Inorganic Chemistry*, John Wiley & Sons, New York, 1987, p. 519

far the most important compounds since they are the final products in many separation and isolation processes and starting material for the production of other niobium and tantalum compounds. Both of the tantalum and niobium pentoxides, are built of MO_6 octahedral sharing edges and corners³⁶ (see **Figure 1.10**). In the production of other compounds the pentoxides are first dissolved in HF, fluoride containing acid solutions or potassium hydroxide solutions.

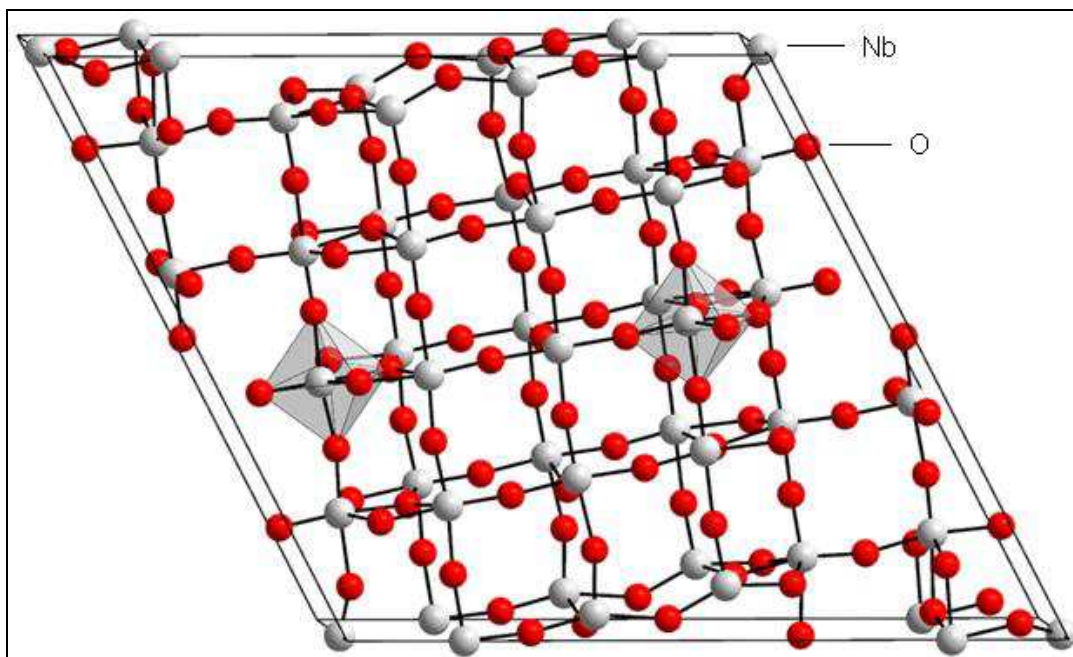


Figure 1.10: The structure of the niobium pentoxide showing an octahedral orientation.

Tantalum and niobium share quite a number of physical and chemical properties. Both the metals are very ductile which allows them to be drawn into sheets and are also very corrosion resistant due to formation of passive oxide films on the surface of the metal. Other important properties of the two metals are summarized in **Table 1.3**. It is properties such as the high melting point and thermal conductivity that make them extremely attractive to be used in defensive weaponry, new generation helicopters and in the electric industry.

36. Cotton, A.F., and Wilkinson, G., *Advanced Inorganic Chemistry*, 5th edition, John Wiley & Sons, New York, 1988, pp. 787–788

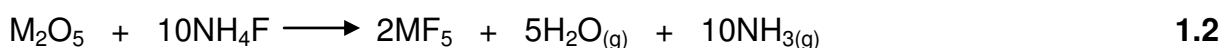
Table 1.3: Selected physiochemical and mechanical properties of tantalum and niobium

Property	Ta	Nb
Lattice type	Body centered cubic	Body centered cubic
Atomic volume, cm ³ /mol	10.90	10.87
Atomic radius, pm	147	146
Density, g·cm ⁻³ (at 20 °C)	16.62	8.57
Melting Point, °C	2996	2477
Boiling point, °C	5560	4744
Specific heat capacity, J g ⁻¹ K ⁻¹	0.15	0.26
Thermal conductivity, W m ⁻¹ K ⁻¹ (at 20 °C)	54.4	53.7
Electrical conductivity, S m ⁻¹	8.1 x 10 ⁶	6.6 x 10 ⁶
Hardness, mohs	6.5	6.0
Electronegativity (Pauling Scale)	1.50	1.60
Thermal Neutron Absorption Cross Section, Barns/Atom	21.3	1.1
Electron configuration	[Xe] 4f ¹⁴ 5d ³ 6s ²	[Kr] 4d ⁴ 5s ¹
Ionization energies (kJ·mol ⁻¹):	1 st	652.1
	2 nd	1381.7
	3 rd	2416.0

It is clear from **Table 1.3**, that the similarity between tantalum and niobium does not extend to all their properties. The most obvious differences are in their thermal neutron absorption cross section and the densities. Tantalum has a thermal neutron absorption cross section that is almost 20 times higher than that of niobium and has a density which is almost twice that of niobium. Although there is some overlap in the industrial application of these metals due to the similarities in properties such as the use in alloys for building heat resistant equipment in some cases the applications are different due to these difference in properties. For example, the low thermal neutron absorption cross section for niobium makes this metal relevant for nuclear applications such as the use in the (see **Section 1.3.1**) cladding of nuclear fuel and tantalum's presence is a nuisance for this purpose. However, tantalum's ability to absorb neutrons, high mechanical strength and high corrosion resistance make it ideal for use in the production of the control rods in the nuclear reactor. The difference in densities of tantalum and niobium on the other hand can be utilised to separate these elements by gravimetric methods.

1.4.1 Niobium(V) and tantalum(V) oxides (Nb₂O₅ and Ta₂O₅)

The metal oxides, M₂O₅, are dense white powders, commonly made by the ignition of other Nb or Ta compounds in air. Addition of OH⁻ to halide solutions gives the gelatinous hydrous oxides with general chemical formula M₂O₅·nH₂O. The oxides are scarcely attacked by acids other than HF, but are dissolved by fusion with borate, sulphate, fluoride (**Equation 1.2**) and hydroxide fluxes. Alkali fusion^{37,38} of the pentoxides gives oxo anions that are stable in aqueous solution only at high pH.³⁵ The fluoride dissolution of the metal and the pentoxides gives fluoro complexes such as [NbOF₅]²⁻, [NbF₆]⁻, and [TaF₆]⁻ plus [TaF₇]²⁻. Other niobium and tantalum fluoride salts of different stoichiometry, [NbOF₆]³⁻, [NbF₇]²⁻ and [TaF₈]³⁻, can be obtained by changing some of the experimental conditions such as the fluoride concentration.



Although, tantalum and niobium are so similar in their chemistry, it has been found³⁹ that there are some differences in the reactions of their oxides in the +5 oxidation state. A recent study was carried out to investigate the differences in the oxides of tantalum and niobium in terms of their behaviour in acidic and basic solutions. The results obtained indicated that Ta₂O₅ is more soluble and stable in basic media (solvents and fluxes) than in acidic media which points to its acidic property. On the contrary, Nb₂O₅ is relatively more soluble in acids and acidic fluxes suggesting a more basic character for the Nb₂O₅.⁴⁰ In general, this difference can be explained in terms of the acid/base properties of the metal oxygen bond character of the oxides, with acidic oxides having relatively stronger metal oxygen bonding. The tantalum–oxygen bond (in Ta₂O₅) is more covalent compared to the more ionic nature of the niobium compound counterpart. This increased metal oxygen bond covalent

37. Mackay, K.M., Mackay, R. A., and Henderson, W., *Introduction to Modern Inorganic Chemistry*. 5th ed., Stanley Thornes (Publishers) Ltd., Cheltenham, 1996, p. 261

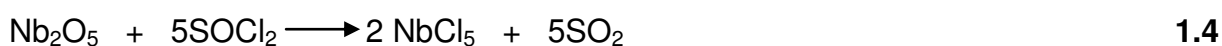
38. Tikhomirova, E. L., Makarov, D.V. and Kalinnikov, V.T., 2008, "Reaction of Niobium Pentoxide with Ammonium Hydrodifluoride" *Russ. J. Inorg. Chem.*, **53**(7): pp. 988–992

39. Theron, T.A., Nete, M., Venter, J.A., Purcell, W. and Nel, J.T., 2011, "Dissolution and quantification of tantalum containing compounds: Comparison with niobium" *S. Afr. J. Chem.*, **64**: pp. 173–178

40. Nete, M., Purcell, W., Snyders E. and Nel, J.T., 2010, "Alternative dissolution methods for analysis of niobium containing samples" *S. Afr. J. Chem.*, **63**: pp. 130–134

character results in less oxygen electron density available for hydrogen bonding and therefore decreases the possible interaction with acids.³⁷

Tantalum pentoxide reacts with carbon tetrachloride under high pressure and temperature in a sealed glass tube to produce TaCl₅ (see **Equation 1.3**). Under the same conditions Nb₂O₅ reacts with carbon tetrachloride to give niobium oxychloride, NbOCl₃. A complete conversion of Nb₂O₅ to NbCl₅ is achieved by reaction with thionyl chloride, SOCl₂, (**Equation 1.4**).



The production of tantalum and niobium metals is normally achieved by the reduction of their oxides in the presence of a reductant such as Al as indicated in the following **Equations 1.5** and **1.6**:



The reduction process occurs at temperatures in excess of 1000 °C and the metal is obtained in the form of an ingot. The metallic Ca or CaO is added to the reaction mixture to the slag melting point and enable the vapourization of the slag phase. Addition of Ca or CaO also promotes the phase separation between the reduced metal and the slag by reducing the viscosity and surface tension of the slag. A control of vaporization of is extremely important to prevent the vapour pressure interference in the separation of metal and slag phases, coagulation and settling of metal particles as well as formation of ingot.^{28,41}

41. Munter, R., Parshin, A., Yamshchikov, L., Plotnikov, V., Gorkunov, V. and Kober, V, 2010, "Reduction of tantalum pentoxide with aluminium and calcium: thermodynamic modelling and scale skilled tests", *Proceedings of the Estonian Academy of Sciences*, **59**(3): pp. 243–252

1.4.2 Niobium and tantalum fluorides

A large number of halogen compounds of tantalum and niobium has been synthesised and characterised successfully. The examples of some of the known tantalum and niobium halides and oxohalides are presented in **Table 1.4**.⁴² The halogen compounds (mainly chlorides and fluorides) of tantalum and niobium are the most important group of compounds for these metals since they have physical and chemical properties which enable successful separation of these metals (see **Chapter 2, Sections 2.3.2 and 2.3.3**). The oxides, in the mineral concentrate, are converted to chlorides at high temperatures (250 to 350 °C). The chlorides, NbCl₅ and TaCl₅ are separated by fractional distillation.

Table 1.4: Examples of tantalum and niobium halides and oxohalides

Metal	Chlorides	Fluorides	Bromides	Iodides
Tantalum	TaCl ₃ , TaCl ₅ , TaCl ₅ OEt ₂ , TaOCl ₃ , Ta ₃ O ₇ Cl	TaF ₅ , TaOF ₃ , K ₂ TaOF ₅ , KTaF ₆ , K ₂ TaF ₇ , K ₃ TaF ₈ , (NH ₄) ₃ TaF ₈ , (NH ₄) ₃ TaOF ₆	TaOBr ₃ , TaBr ₃ , TaBr ₄ , TaBr ₅	TaOI ₃ , TaI ₃ , TaI ₄ , TaI ₅
Niobium	NbCl ₅ , [NbOCl ₅] ²⁻ , NbCl ₃ , NbCl ₄ , Nb ₅ O ₁₁ Cl ₃ , Nb ₃ O ₇ Cl	NbF ₅ , K ₂ NbF ₇ , K ₂ NbOF ₅ , KNbF ₆ , (NH ₄) ₃ NbF ₈ , NH ₄ NbOF ₄ , (NH ₄) ₂ NbOF ₅ , (NH ₄) ₃ NbOF ₆ , (NH ₄) ₅ Nb ₃ O ₃ F ₁₄	NbBr ₃ , NbBr ₄ , NbBr ₅	NbI ₃ , NbI ₄ , NbI ₅

The fluoride compounds of Nb and Ta on the other hand are important for the successful separation by solvent extraction. The simplicity of their syntheses is due to low dissociation energy of the fluorine molecule, relatively high energies of bond formation found in fluoride compounds, fluorine's high electronegativity and strong oxidising properties leading, sometimes, to spontaneous fluorination. The fluorine atom/molecule's relatively high electronegativity is responsible for the ionic character of the bonds in the fluoride compounds. More over, fluoride compounds of Ta and Nb have relatively low thermal stability and tendency to undergo hydrolysis and pyrolysis. Their synthesis therefore requires special conditions such as a dry

42. Angulyansky, A., *The Chemistry of Tantalum and Niobium Fluoride Compounds*. 2004, Elsevier B.V., Amsterdam, pp. 257

atmosphere for their successful isolation. The high corrosivity of fluorides necessitates the use of special installations and containers made of teflon, platinum, gold and glassy carbon for their synthesis.⁴²

Methods for Ta/Nb fluoride compounds' preparation from the metals and/or oxides, include the use of anhydrous hydrogen fluoride, hydrofluoric acid, and to a lesser extend alkali metal fluorides and ammonium fluoride salts.⁴² The dissolution of Nb and Ta metals in HF at low temperatures is a relatively slow and moderately exothermic reaction (See **Equations 1.7** and **1.8**).



Concentrated H₂SO₄ has to be added at a temperature of about 70 – 90 °C to niobium and tantalum oxides in HF to increase the rate of dissolution. However, conversion of the oxides to hydroxides (Ta₂O₅·nH₂O and Nb₂O₅·nH₂O) makes them more soluble even in dilute HF.

Crystallisation of fluorotantalates and fluoroniobates such as heptafluorotantalate and hexafluorotantalate as potassium salts has indicated that the isolation of the final product depends heavily on the HF concentration during the reaction and the different inorganic compounds such as the monooxyfluoroniobate, heptafluoroniobate and hexafluoroniobate is highly dependent on the HF concentration as indicated in **Figures 1.11** and **1.12**. At higher HF concentrations the hexafluorometalate is converted to heptafluorometalate with the release of a bifluoride ion, HF₂⁻ which is recycled into the system to react with the starting material again (see **Equation 1.9**).⁴²

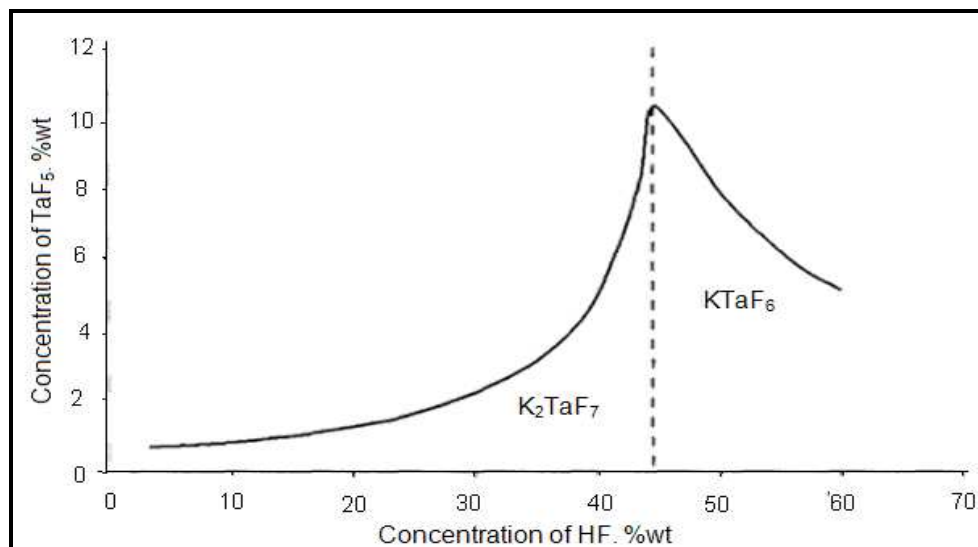


Figure 1.11: Crystallisation of fluorotantalates in HF solutions at 25 °C.

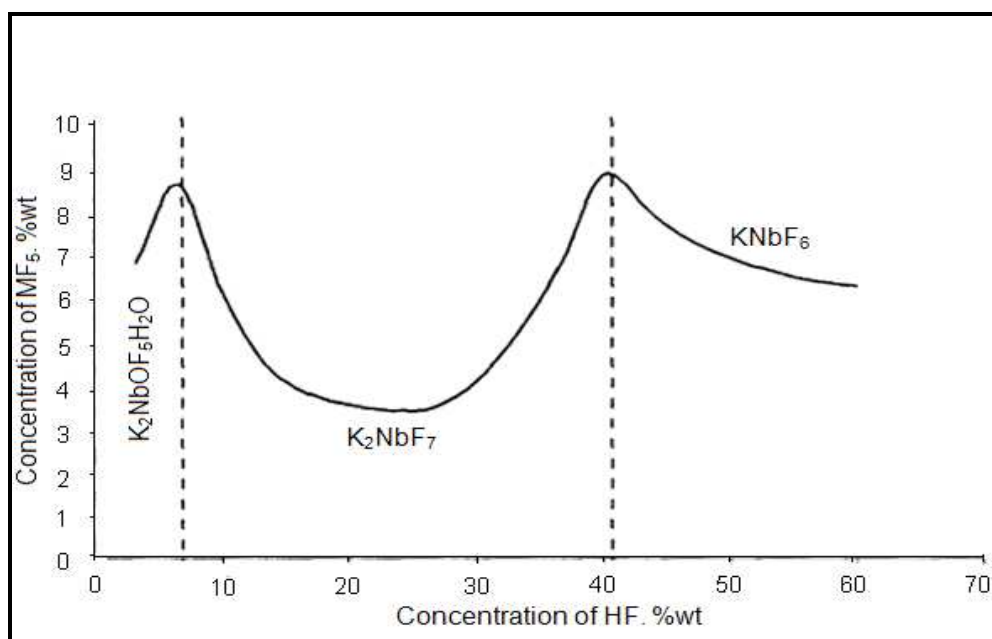
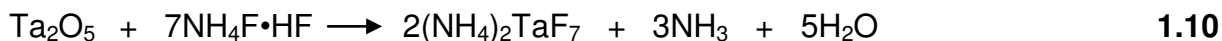


Figure 1.12: Crystallisation of fluoroniobates in HF solutions at 25 °C.



From the oxides (Nb_2O_5 and Ta_2O_5) the fluorides may be prepared by dissolving Nb_2O_5 or Ta_2O_5 in liquid ammonium bifluoride, $\text{NH}_4\text{F}\cdot\text{HF}$. The reaction between Ta_2O_5 and $\text{NH}_4\text{F}\cdot\text{HF}$ occurs at a temperature of 156 – 190 °C yielding ammonium heptafluorotantalate (see **Equation 1.10**). The obtained $(\text{NH}_4)_2\text{TaF}_7$ decomposes to

ammonium hexafluorotantalate at the temperature of 260 – 300 °C as indicated in **Equation 1.11**:



On the other hand the fluorination of Nb_2O_5 with $\text{NH}_4\text{F}\cdot\text{HF}$, forms only ammonium oxofluoroniobates,⁴³ $(\text{NH}_4)_3\text{NbOF}_6\cdot 1.5\text{H}_2\text{O}$ or $(\text{NH}_4)_3\text{NbOF}_6$ at 100-130 °C.⁴² Differential thermal analysis for the decomposition of $(\text{NH}_4)_3\text{NbOF}_6$ indicated that this compound gives $(\text{NH}_4)_2\text{NbOF}_5$, NH_4NbOF_4 and NbO_2F at 255, 320, and 420 °C respectively.⁴³ The same fluorination product for tantalum ($(\text{NH}_4)_3\text{TaOF}_6$) was found to undergo thermal decomposition at 175, 290 and 320 °C to successively produce $(\text{NH}_4)_2\text{TaOF}_5$, NH_4TaOF_4 and TaO_2F . The third decomposition step (NH_4MOF_4 to MO_2F) for both elements is believed to produce MOF_3 which then decomposes to produce gaseous TaF_5 , NbF_5 as indicated by **Equation 1.12**:^{43,42,44}



Tantalum and niobium pentafluorides can also be synthesised by reacting the pure metals with fluorine gas or the pentoxides with anhydrous hydrogen fluoride, HF ⁴² or fluoride compounds at elevated temperature as indicated in the following chemical **Equations 1.13** and **1.14**:



where M = Ta or Nb

43. Rakov, E.G. and Mel'nichenko, E.I., 1984, "The Properties and Reactions of Ammonium Fluorides" *Russ. Chem. Rev.*, **53**(9): pp. 851–869

44. Buslaev, Y. A., Ii'in, E.G., Kopanev, V.D. and Gavrish, O.G., 1971, "Synthesis and properties of complex ammonium fluorides of niobium and tantalum" *Inorg. Anal. Chem.*, **6**: pp. 1055–1059

Some physiochemical properties of tantalum and niobium pentafluorides are presented in **Table 1.5**. The pentafluorides are the easiest to work with since they dissolve in a variety of solvents (simple matrix and simple sample preparation) which include some organic solvents. This enables an investigation of various separation methods from different solvent systems.

Table 1.5: Physiochemical properties of TaF₅ and NbF₅⁴²

Properties	NbF ₅	TaF ₅
*Density, g·cm ⁻³	3.3	4.98
Melting point, °C	79.5	96
Dissolves in	HCl; HNO ₃ ; Conc. H ₂ SO ₄ ; Ethanol; Chloroform; CCl ₄ ; CH ₃ COOH	Conc. HCl; Conc. HNO ₃ ; Hot H ₂ SO ₄ ; Chloroform; CCl ₄ ; CS ₂

(standard conditions)

1.5 Motivation of the study

1.5.1 Mineral processing

The ideal mineral processing method such as hydrometallurgy and froth flotation calls for the easy scalability from laboratory to an industrial scale to give high value, high purity products with only a few separations steps. The ideal process also calls for low amounts of energy with low pollution and by-product levels. Very few industrial beneficiation processes however adhere to all of these principles, but they always remain extremely important with the development and acceptance of any new process.

The mineral beneficiation processes which are used on complex mineral matrices such as ores are normally dictated by criteria such as its elemental composition, physical and chemical properties of the impurities as well as those of the target analyte(s). For example, a number of technical, economical and environmental issues need to be considered with the development of an industrially acceptable hydrometallurgical technique which allow for the successful separation, isolation and purification of elements from their mineral ores. These issues include the following:

- Technical – scalability of method, specification of type and amount of impurity, number of separation steps
- Economical – cost of beneficiation and profit, energy needed and market

- Environmental – pollution, storage and handling of by-products, waste products and following environment, ISO 14001 guidelines
- Safety – processing facility requirements in terms of employer safety and by-product handling and storage (e.g. NORMs) and maintaining safety and health, OHSAS 18001 standards
- Quality – implementation and maintenance of a quality management system which is compatible with the ISO 9001 and ISO 17025 standards.

Another important principle to remember with the development of a new hydrometallurgical process is that the dissolution method dictates the identity or the chemical composition of the initial chemical species in solution. By definition these chemical compounds then also dictate the type of separation and isolation techniques that can successfully be employed to achieve beneficiation. Dissolution for example with HF will mainly produce fluoride complexes in solution and any separation and isolation method will need to utilize the chemical properties of the different metal fluoride complexes (most probably anion chemistry) or species present in solution. Dissolution with acids or fluxes containing cations or anions with low/weak coordination ability such as H_2SO_4 , LiBO_4 or Na_2O_2 will most likely produce hydrated metal ions in solution and the successful separation and isolation of the different elements need to utilize the cationic chemistry/properties of the metals.

Hydrometallurgical beneficiation of minerals such as tantalite involves the complete dissolution of the complex mineral ore with the subsequent stepwise enrichment and isolation of some of the impurities (unwanted chemical compounds) or the elements of interest. Sometimes the first steps in the beneficiation process involve the isolation and the subsequent removal of an impurity from the rest of the solution matrix which simplify the down-stream isolation and purification process while the isolation of the main elements are sometimes achievable in the initial steps of the separation process. The technical success of any beneficiation process is measured in terms of amount of recovery of the original amount of the main element/s in the sample with the least amount of impurities in the smallest number of separation or isolation steps.

1.5.1.1 Properties and mining of tantalite ore

Columbite and tantalite are the most widespread niobium and tantalum minerals. The major difference between the two minerals is the greater specific gravity of tantalite, $8.0 <$ compared to columbite's 5.2. Other slight variations are found in their colour, transparency and streak. Tantalite has an orthorhombic crystal structure and is a dimorph to tapiolite $((\text{Fe,Mn})(\text{Ta,Nb})_2\text{O}_6)$ which has tetragonal structure.⁴⁵ The method of mining the minerals is dictated by several factors such as the tonnage and grade, rock type and depth of ore body. Mining is done by conventional techniques such as blasting and crushing. The minerals are mined mostly from open-pit mines with a few underground mines such as TANCO, in Canada and Greenbushes, in Australia. A significant amount is obtained by artisanal and small scale mining.

1.5.1.2 Physical processing of tantalite ore

After the ore has been mined by any of the above mentioned methods there follows a disintegration step of the ore which converts it into a form that is ready to be used in the subsequent beneficiation processes to obtain purer elements of compounds for different applications. The sample ore is firstly crushed and milled to reduce the particle size and increase the surface area thus exposing the tantalite mineral for efficient processing. Sometimes an advantage of the physical properties, such as magnetism, of the mineral is used to separate impurities from tantalum and niobium. For example, the coltan which is mined illegally in the DRC is first freed of the iron particles by magnetic separation using magnetic tweezers before the sample is washed and analysed for tantalum content.⁴⁶ At the Greenbushes plant in Australia ilmenite is separated from tantalite using magnetic separation prior to dissolution by HF and subsequent steps.⁸ In a recent study 97% iron and 86% titanium (in ilmenite mineral) were successfully removed from the tantalite mineral by magnetic separation.⁴⁷

45. Amethyst Galleries [homepage on the Internet]. [cited 2011 Aug 15]. Available from; <http://www.galleries.com/minerals/oxides/tantalit/tantalit.htm>

46. Vesperini, H, 2001, 'Congo's coltan rush' bbc online news, 1 August, 2001 [cited 2011 Nov. 29]. Available from: <http://news.bbc.co.uk/2/hi/africa/1468772.stm>>

47. Theron, A. T., 2010, Quantification of tantalum in series of tantalum-containing compounds, [MSc thesis]. Bloemfontein: University of the Free State; 2010 [cited 2012 March 13]. Available from: University of the Free State Library.

1.5.1.3 Chemical processing of tantalite mineral

Generally the chemical separation or purification of Ta and Nb to their metallic component is a complex process. This could be partly due to the similarity in their chemical properties, resistance to chemical attack and the ease with which their compounds are hydrolysed in aqueous solutions.⁴⁸ Separation of metals generally involves three steps: (i) conversion of the original sample into a form suitable for separation techniques to be explored, (ii) finding a separation procedure that is cost effective and promotes green chemistry and (iii) measurement of the amount or concentration of the final product as well as the levels of impurities.

(i) Sample dissolution/conversion

For tantalum and niobium production, the most common and frequently used production process is related to the well known Marignac's process.⁸ In this process the metal oxides of the two elements are converted to fluorinated substances. The raw material is digested at elevated temperatures using a mixture of highly concentrated hydrofluoric acid, HF, and other mineral acids such as H₂SO₄. This process dissolves the tantalum and niobium and all the other metal impurities within the ore as fluoride salts.

(ii) Separation and purification processes

a) Solvent extraction

Solvent extraction is known as one of the oldest and most diversified techniques for concentration, separation and purification of the Ta/Nb compounds that occur in different matrices.⁴⁹ A literature study has indicated that fluoride derivatives have become the backbone for the success of this technique. In general the sample conversion into fluoride complexes is achieved by reaction of the Ta/Nb samples with HF, a mixture of mineral acids containing HF or fluoride containing salts at elevated temperatures. The basic outline of the hydrometallurgical process which includes a

48. Morrison, G. H. and Freiser, H., Solvent Extraction in Analytical Chemistry, New York, John Wiley & Sons, Inc., 1962, p. 3

49. Gherman, G.D., 2010, Organothiophosphoric ligands – Agents for metal ions separation, [PhD thesis]. Cluj-Napoca: "Babeş-Bolyai" University; 2010 [cited 2011 Oct 27]. Available from: http://doctorat.ubbcluj.ro/sustinerea_publica/rezumat/2010/chimie/Gherman_Georgeta_Diana_EN.pdf

solvent extraction step is given in a flow chart in **Figure 1.13**. There may be some modifications to this basic beneficiation process based on factors such the sample background i.e. type of rock and associated minerals.

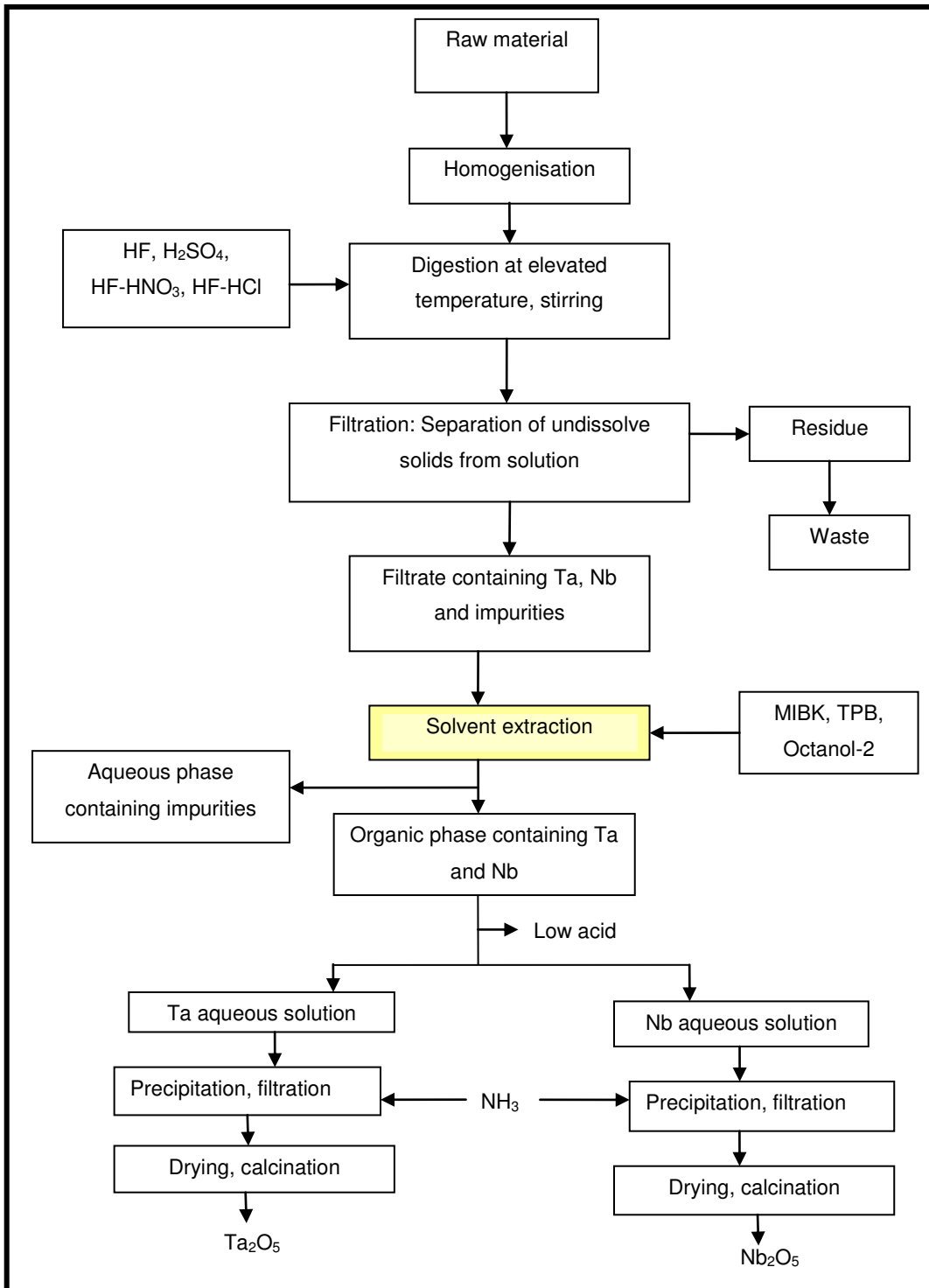


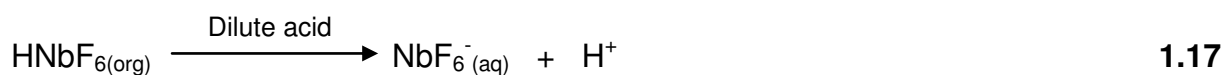
Figure 1.13: A generalised process flow diagram of the tantalum and niobium raw material decomposition process.⁸

The tantalum and niobium fluoride solution's acidity is next adjusted by the addition of H_2SO_4 and then processed using liquid-liquid extraction (LLE) which was developed by the Ames Laboratory together with the US Bureau of Mines in 1957.⁴² Both tantalum and niobium are extracted into the organic phase, usually methyl isobutyl ketone (MIBK) at higher acidity levels (see **Section 2.3.3**) leaving most of the impurities in the aqueous solution. Tantalum and niobium are separated during the re-extraction from the organic phase into the aqueous phase at different acid concentrations due to their different acid dissociation constants (see **Equations 1.15** to **1.18**)

Extraction from aqueous to organic at high acidity



Extraction from organic to aqueous at, after removal of impurities, at low acidity



The two metals' fluoride complexes in the now separate aqueous solutions are precipitated as hydroxides using ammonia solution. The precipitates are then calcined to oxides in which the pure metals are obtained by sodium (**Figure 1.14**), electrochemical (**Figure 1.15**) or by magnesium vapour reduction step.⁴²

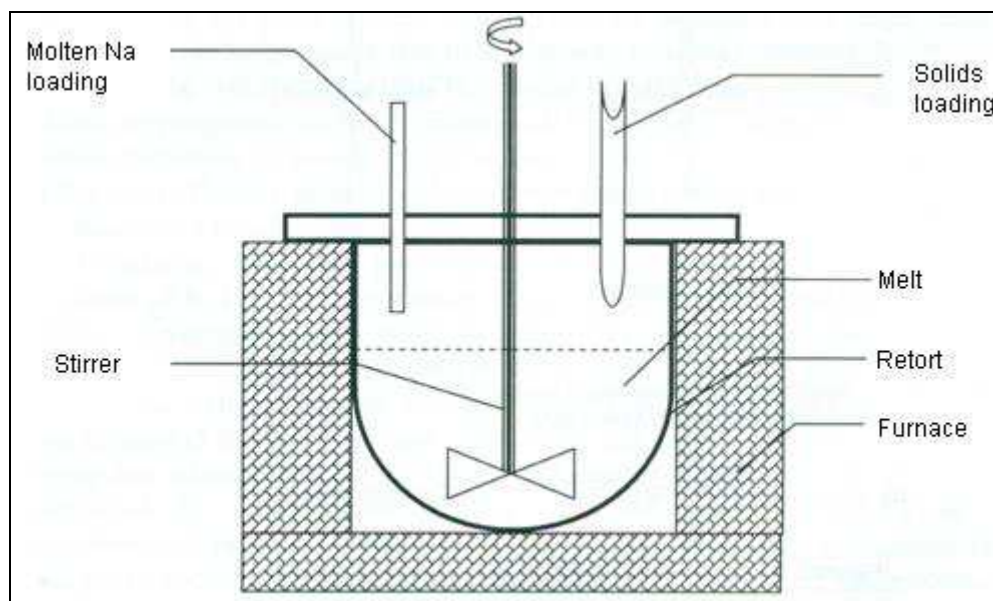


Figure 1.14: Schematic structure of reactor for K_2TaF_7 reduction to tantalum by molten sodium.

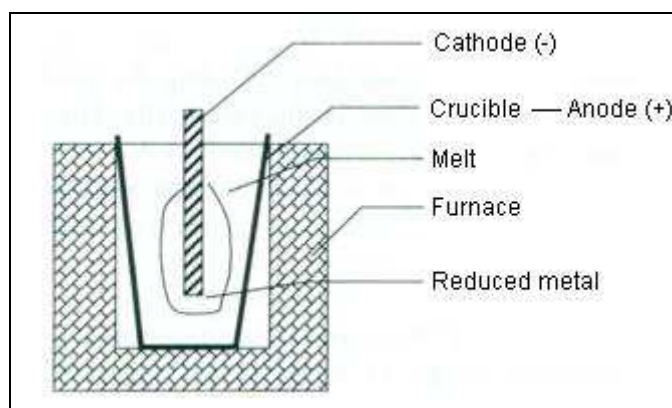


Figure 1.15: Electrolytic bath for reduction Ta in K_2TaF_7 to tantalum metal.

Alternative to the use of HF and H_2SO_4 for the dissolution of tantalite, as a step towards “green chemistry” is the use of $NH_4F \cdot HF$ as fluoride source. $NH_4F \cdot HF$ is about 70% less expensive, much safer, easier to handle and store than HF.^{42,50} Another important advantage of this fluorination method is that quantitative amounts of niobium and tantalum fluoride compounds can be leached with water from

50. Gaur, R. P. S. and Mendenhall, R. G., 2007, Inventors; Osram Sylvania Inc., assignee. Tantalum concentrates dissolution and purification method. United States Patent US 7182925 B2. 2007 Feb 27.

fluorinated material. This means that the tantalum and solution prepared in this procedure has low overall acidity which makes them safer to handle for further processing.⁴² The $\text{NH}_4\text{F}\cdot\text{HF}$ sample preparation procedure is simple but it has been found⁵⁰ to be effective for purification of Ta only and Nb remains in the aqueous solution with all other impurities after the LLE of Ta using MIBK, which means that another method is required for recovery of Nb in the presence of the rest of the impurities.

b) Heat treatment process

At the CBMM plant in Brazil niobium is purified from mainly pyrochlore by the electron beam melting (EBM) process (see **Section 2.3.2**). The raw material is chlorinated at elevated temperatures and tantalum and niobium are separated as pentachlorides. Some impurities, such as tungsten, which co-exist together with Ta/Nb in natural ore are difficult to remove from either Ta or Nb, for example, by melting treatment such as EBM or similar processes.⁵¹ This means that the low vapour pressure impurities should be removed by other separation techniques such as solvent extraction.

(iii) **Concentration determinations**

The third step in the beneficiation process of metals involves the quantitation of the main elements as well as possible impurities which have been carried over. Products of wet separation processes have been quantified using spectrometric methods such as neutron activation analysis spectrometry (NAAS), inductively coupled plasma optical emission and mass spectrometry (ICP-OES, ICP-MS), and flame or graphite furnace atomic absorption spectrometry (FAAS or GFAAS). Other techniques such as X-ray fluorescence spectrometry (XRF) and electrothermal vaporization (ETV) coupled to ICP-OES/MS have successfully been used on solid samples. These techniques have in common very low detection limits (MS – 1-10 parts per trillion (ppt) or lower, OES – 1-10 parts per billion (ppb)), for the different elements.

51. Koethe, A. and Moench, J. I., 2000 "Preparation of Ultra High Purity Niobium" *Mat. Trans. JIM*, **41**(1), pp. 7–16

1.5.2 Sample background

Work previously done in this laboratory reported^{39,40,52} the successful dissolution and accurate determination of pure niobium metal, niobium pentoxide, niobium pentafluoride and pure tantalum metal, tantalum pentoxide and tantalum pentafluoride, tantalum pentachloride, TAN-1 CRM (contains 0.2886% Ta₂O₅)⁴⁷ as well as tantalite minerals. The samples were dissolved using flux fusion as well as microwave assisted acid digestion methods. The microwave assisted acid digestion proved successful in dissolving Nb metal, Nb₂O₅, NbF₅, TaF₅ and TaCl₅ with recoveries in 98.8 – 101% range but very low recoveries were obtained to Ta metal (4.1%) and Ta₂O₅ (9.7%). Recoveries in the range of 90 – 95% Ta and 90 – 103% Nb were obtained for TAN-1 CRM, Ta₂O₅, Nb₂O₅ and the tantalite mineral samples using Li₂B₄O₇ as fluxing agent when excess boric acid was removed prior to analysis by ICP-OES. The present work deals with the separation and purification of niobium and tantalum from the tantalite mineral.

The main aim of this study was to develop alternative separation and purification steps for tantalum and niobium from tantalite which are safe, economically viable and has reduced number of steps compared to the currently used procedure outlined in **Figure 1.15** above. The different purification and separation procedures were investigated using pure samples with known compositions. The pure compounds selected for this purpose were tantalum pentoxide and niobium pentoxide together with tantalum pentafluoride and niobium pentafluoride. The pentoxides were chosen on the basis that they have similar properties (such as the difficulty to dissolve) to the tantalite mineral. The pentafluorides on the other hand were selected on the basis of their ease to dissolve even in some organic solvents which would enable an investigation of a variety of separation techniques. The procedures investigated in the study include flux fusion dissolution using NH₄F•HF as fluoride source, precipitation, solvent extraction and ion exchange separation techniques. The knowledge obtained from studying these techniques on pure compounds was to be applied on the mineral samples with complex matrices.

52. Nete, M., Purcell, W., Snyders, E., Nel, J. T., and Beukes, G., 2011, "Characterization and alternative dissolution of tantalite mineral samples from Mozambique", *J. S. Afr. Inst. Min. Metall.*, **112**: pp. 1079–1086

The mineral samples, **Figure 1.16**, used in this study were obtained from Mozambique's Naquissupa mine. X-ray diffraction (XRD) analysis⁵³ of these minerals indicated that the major component in Samples A and B is maganotantalite and in Sample C is ferrotantalite. Other minor mineral components identified by XRD, microscopy, scintillation and magnetic determinations included microlite ((Na,Ca)₂Ta₂O₆(O,OH,F)), quartz (SiO₂), muscovite (mica) (KAl₂(Si₃Al)O₁₀(OH,F)₂), garnet ((Mg,Fe,Ca)₃-(Al,Fe³⁺,Cr)₂(SiO₄)₃), euxenite ((Y,Ca,Ce,U,Th)(Nb,Ta,Ti)₂O₆) tourmaline ((Na,Ca)(Mg,Li,Al,Fe²⁺)₃Al₆(BO₃)₃Si₆O₁₈(OH)₄), and ilmenite (FeTiO₃).⁵²

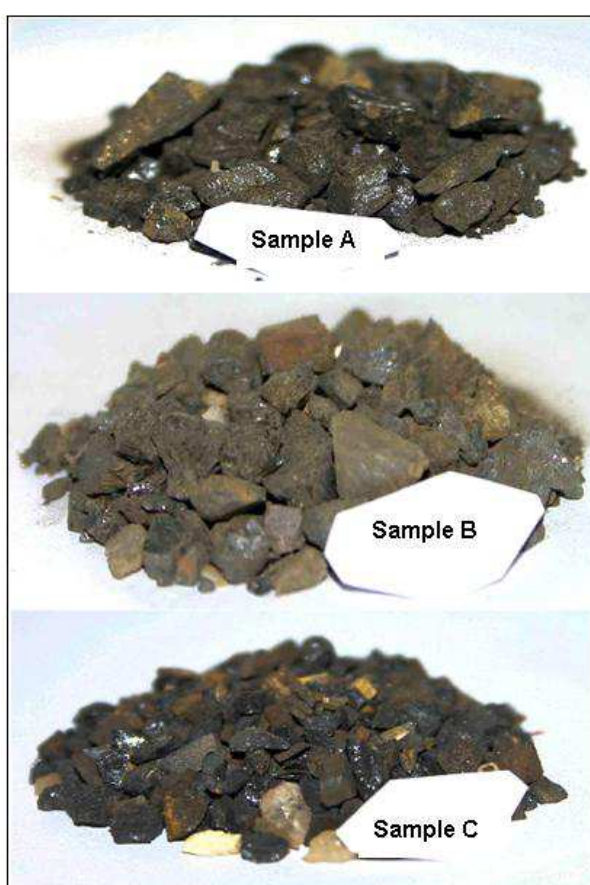


Figure 1.16: Crushed tantalite ore samples from Mozambiquecan mines.

The elemental compositions and quantities of these samples that were determined by ICP-OES and XRF are presented in **Table 1.6**

53. Nete, M., 2009, Dissolution and analytical characterization of tantalite ore, niobium metal and other niobium compounds, [MSc thesis]. Bloemfontein: University of the Free State; 2009 [cited 2011 Sep 23]. Available from: University of the Free State Library.

Table 1.6: Chemical composition of tantalite minerals from Mozambique mines

Analyte	Average concentration (%)		
	Sample A	Sample B	Sample C
Ta ₂ O ₅	27.8(3)	32.88(6)	33.0(2)
Nb ₂ O ₅	27.0(2)	17.47(8)	13.7(2)
ThO ₂	0.54(2)	0.41(1)	0.29(1)
U ₃ O ₈	2.81(2)	1.20(1)	0.14(1)
Al ₂ O ₃	2.04(6)	2.85(4)	1.47(1)
SiO ₂	3.5(1)	10.99(6)	2.51(4)
WO ₃	1.18(2)	0.84(1)	0.16(1)
TiO ₂	2.77(2)	6.50(6)	8.19(1)
Mn ₃ O ₄	8.91(7)	7.6(1)	3.13(1)
Fe ₂ O ₃	8.3(2)	7.01(5)	18.71(6)
SnO ₂	1.64(3)	2.91(3)	0.15(1)
Y ₂ O ₃	-	-	0.24(1)
CaO	-	-	0.52(4)

1.5.3 Specific objectives of this study

The overall objective of this study was to investigate the possibility of the separation and purification of Ta and Nb from the tantalite mineral using new or alternative methods to that already known. The specific objectives include:

- ❖ Development of a sample preparation method that is safe for the environment and allows further processing of Ta/Nb concentrates to pure Ta and Nb compounds.
- ❖ Use of inorganic and organic ligands as complexing agents for selective precipitation of Ta or Nb using synthetic mixtures of commercial and complex mineral samples.
- ❖ Use of solvent extraction procedures from a non HF solution and the study of other organic solvents for extraction utilising properties such as solubility in aqueous solution, flammability and immiscibility.

- ❖ Utilisation of magnetic properties of the mineral samples to explore a possibility of a purification process.
- ❖ Utilisation of purification methods, such as acid leaching from studies conducted by other researchers in our lab, for removal of the more soluble impurities as well as the use of ion exchange methods to purify the metals of interest and
- ❖ Characterisation and quantification of the products as monitoring steps to assess the success of the purification and separation methods that were studied.

2 History of tantalum and niobium separation: Literature review

2.1 Introduction

Most elements exist in mineral ores as compounds such as oxides and silicates that are normally difficult to separate from one another or to concentrate them by conventional separation and/or enrichment techniques. It is especially difficult to process ores such as tantalite in which the most valued elements tantalum and niobium have very similar chemical properties, such as their unreactivity towards acids and alkalis. From 1866, the commercial separation of tantalum and niobium was accomplished by a process that was developed by Jean Charles Galissard de Marignac⁵⁴ which made use of the fractional crystallization to separate tantalum and niobium as potassium heptafluorotantalate and potassium oxypentafluoroniobate. This popular separation method was replaced in the middle of the 20th century by liquid-liquid extraction (LLE) which utilises the differences in the solubility of the fluoride ions of the two elements in different organic solvents. Even after the development of the LLE method for element separation, a large number of new or alternative processing procedures were developed which included the dissolution of the mineral to effect the selective or stepwise separation of tantalum and niobium from the same reaction mixture for various economic, energy as well as environmental reasons.

The aim of this chapter is to highlight some of the research work that was done up to now on the physical and chemical processes for the beneficiation of tantalum and niobium from their mineral ores. The discussions in this chapter include the major production methods, dating back to early 1820s to the most recent work, the findings and conclusions made thereof.

54. Mellor, J.W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green & Co. LTD, London, 1947, **IX**: pp. 843–845

2.2 Dissolution and analysis of tantalum and niobium mineral sources

The challenge for tantalum and niobium separation⁵⁵ starts with the dissolution of the primary tantalum and niobium sources due to their resistance to acid attack at moderate conditions. The only step as part of the purification of the elements that does not require complete solubilisation of the primary material⁸ is the removal of iron and titanium (ilmenite) by magnetism prior to dissolution. The primary reason for the inertness of the tantalum/niobium containing ores to acid dissolution is the presence of the metals as oxides within these minerals. It is the same oxides that induce the unique corrosion resistance properties to the pure metals.

The importance of the decomposition step in extracting tantalum and niobium from their ore has encouraged several studies which investigated the development of the successful dissolution of tantalum/niobium sources. These included fusion digestion as well as acid leaching techniques. Different fluxes have been tested for the fusion dissolution of tantalum and niobium minerals namely (i) potassium hydrogen sulphate and the subsequent melt digestion with H₂SO₄ and HF,⁵⁶ (ii) sodium pyrosulphate in which the melt was dissolved in H₂SO₄ and HF,⁵⁷ (iii) potassium hydrogen fluoride and the melt was dissolve in HF,⁵⁸ (iv) potassium pyrosulphate followed by the melt dissolution in tartaric and oxalic acids,⁵⁹ (v) sodium carbonate and sugar charcoal and the melt dissolution with boiling HCl,⁶⁰ (vi) borax,⁶¹ (vii) alkali hydroxides and the

55. Cockbill, M. H., 1962, The Determination of Tantalum and Niobium, A review, [Internet]. [cited 2011 Nov 22]. Available from: <http://pubs.rsc.org/doi:10.1039/AN9628700611>

56. Kock, W. and Paschen, P., 1989, "Tantalum-Processing, Properties and Applications", *JOM*, pp. 33–39

57. Sears, G. W. and Quill, L., 1925, "Fusion of Rare-metal Ores: Pyrosulphate Fusion of Titanium Ores" *J. Amer. Chem. Soc.*, 47, pp. 922–929

58. Gibbs, O.W., 1864, *Amer. J. Science*, 37(2): p. 355

59. Uria, J.E.S., Ortiz, C.G., Garcia, A.M., and Sanz-Medel, A., 1987, "Determination of niobium and tantalum in some ores and special alloys by inductively coupled plasma atomic emission spectrometry.", *Mikrochim. Acta [Wien]*. 2: pp. 195–202

60. Joly, A., 1877, *Ann. Ecole. Norm.*, 6(2): p. 738

61. Pennington, M.E., 1896, "Derivatives of columbium and tantalum", *J. Am. Chem. Soc.*, 18(1): pp. 38–67

dissolution of the melt in dilute HCl,⁶² (viii) a mixture of disodium hydrogen phosphate and sodium dihydrogen phosphate monohydrate followed by melt dissolution in water,⁶³ (ix) lithium metaborate/tetraborate and the subsequent melt digestion with HF and (x) lithium tetraborate followed by the melt dissolution in H₂SO₄/methanol^{39,53} or H₃PO₄/methanol.⁵²

It is only the latter three fusion methods that proved to be very successful achieving 100% dissolution of tantalum-niobium minerals. Even these successful fusion dissolution procedures proved not to be useful for the immediate separation and isolation of tantalum and niobium since they did not convert the two metals into compounds which allowed for the subsequent separation step with well known techniques such as LLE. Other fluxes such as potassium pyrosulphate have only been found to be successful for the complete dissolution of pure metal oxides, but only partial dissolution was obtained with the minerals.

The acid digestion methods that have been investigated include (i) direct leaching of the tantalite ore with H₂SO₄ alone^{15,64} and a mixture of H₂SO₄ and HNO₃ at elevated temperature¹⁵ (ii) leaching with HNO₃⁶⁵ (iii) microwave assisted leaching of tantalite ore with HNO₃, H₃PO₄, HCl and H₂SO₄⁵¹ (iv) HF alone, HF-HCl, NH₄F-HCl, HF-H₂SO₄, and NH₄F-H₂SO₄ mixtures for the leaching of columbite and tantalite⁶⁶ and (iv) HF/H₂SO₄ leaching.⁶⁷ Sulphuric acid alone has been found to be successful for

62. Wang, X., Zheng, S., Xu, H. and Zhang, Y., 2009, "Leaching of niobium and tantalum from a low-grade ore using a KOH roast-water", *Hydrometallurgy*, **98**: pp. 219–223

63. Mahanta, P. L., Hanuman, V. V., Radhamani, R. and Srivastava, P. K., 2008, "ICP-OES Determination of Nb, Ta, Ti, Fe, Mn, W, and Sn in Columbite and Tantalite Minerals After Decomposition and Dissolution With a Novel Flux and Complexing Agent", *At. Spectrosc.*, **29**(5): pp. 172–179

64. Spence, W. C. and Svendsen, P. V. H., 1963, Inventors; Dominion Gulf Company, "Sulphuric acid leaching of niobium ores", United States Patent US 3087809. 1963, April 30

65. Baba, A. A., Adekola, F. A., Dele-Ige, O. I. and Bale, R. B., 2007, "Investigation of Dissolution Kinetics of A Nigerian Tantalite Ore in Nitric Acid", *J. Min. Mater. Charact. Eng.*, **7**(1): pp. 83–95

66. Majima, H., Awakura, Y., Mashima, M. and Hirato, T., 1988, "Dissolution of Columbite and Tantalite in Acidic Fluoride Media" *Metall. Trans. B*, **19B**: pp. 355–363

67. Htwe, H. H. and Lwin, K. T., 2008, "Study on Extraction of Niobium Oxide from Columbite-Tantalite Concentrate", *World Academy of Science, Engineering and Technology*, **46**: pp. 133–135

leaching of mainly niobium oxide^{15,51} and in mixtures with HNO₃ both niobium oxide and tantalum oxide were leached to more than 90%.¹⁵ The microwave assisted H₂SO₄ results, in which only partial dissolution of all the material was achieved, also indicated the possible use of this technique to selectively separate niobium from the tantalite mineral thereby separating it from tantalum.⁵¹ At present however, HF, HF mixtures as well as the fluoride/acid digestion are the most commonly,^{68,69,70} used methods for the decomposition of tantalum-niobium ores which allow for the immediate separation and the subsequent isolation of these elements as fluoride compounds.

2.3 Purification and separation of tantalum and niobium

The separation and purification of elements with very similar physical and chemical properties such as tantalum and niobium is always a big challenge in the hydrometallurgical field or extractive metallurgy. Literature indicates that the first tantalum metal which was heavily contaminated with niobium due to difficulty in separating the two metals was obtained from tantalite ore by Berzelius in 1824.⁵⁶ The first effective separation procedure for tantalum and niobium (which led to the production of a purer tantalum metal) was developed in 1866 by J.C.G. de Marignac. Marignac's procedure became the dominant industrial production method for the separation and isolation of a pure tantalum from its ore but was less successful in the production of pure niobium (see **Section 2.3.1**). In addition to not being able to produce pure niobium, the Marignac's method had the disadvantage of producing low tantalum recoveries (~70%).⁷¹ This method of tantalum production was replaced in by

68. Grebneva, O.N., Kubrakova, I.V., Kudinova, T.F., and Kuz'min, N.M., 1997, "Direct determination of trace elements in niobium, tantalum and their oxides by inductively coupled plasma atomic emission spectrometry after microwave dissolution", *Spectrochimica Acta Part B*, **52**: pp. 1151–1159

69. Hall, G. E. M., and Pelchat, J. C., 1990, "Determination of Zirconium, Niobium, Hafnium and Tantalum at Low Levels in Geological Materials by Inductively Coupled Plasma Mass Spectrometry", *J. Anal. At. Spectrom.*, **5**: pp. 339–349

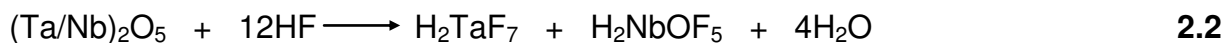
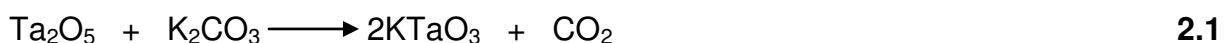
70. Uria, J.E.S., Ortiz, C.G., Garcia, A.M., and Sanz-Medel, A., 1987, "Determination of niobium and tantalum in some ores and special alloys by inductively coupled plasma atomic emission spectrometry", *Mikrochim. Acta [Wien]*, **2**: pp. 195–202

71. Alexander, G. B., 1969, "Tantalum Recovery by Liquid-Liquid Extraction", *J. Chem. Educ.*, **46**(3): pp. 157–159

the LLE method which was implemented in 1957.⁴⁰ Although, the LLE method has solved most of the problems which previous researchers encountered for the purification of mainly niobium, it has never been free from criticism which prompted more research for better processes. The separation processes that have been investigated so far can be divided into precipitation, distillation, solvent extraction, ion exchange chromatography and the less common membrane separation technique.

2.3.1 Precipitation methods

The well known Marignac's procedure was based on the difference in solubility of tantalum and niobium fluoride salts.⁷² It involved the fusion of the mineral sample with potassium carbonate in a 1:8 mass ratio (see **Equation 2.1** for the chemical reaction involved, using Ta₂O₅ as an example). The melt from this fusion was dissolved in water and any remains of the starting solid material was filtered, ignited and fused again with K₂CO₃. The solution was boiled with dilute HCl to precipitate niobic and tantallic acids, (Ta/Nb)₂O₅·nH₂O.⁴⁰ Hot water was added to the precipitate and followed by addition of dilute HF (see **Equation 2.2**).⁷³ Potassium fluoride was then added slowly with constant stirring to the solution which allowed for the precipitation of tantalum as K₂TaF₇ which was then isolated by filtration, leaving the more soluble potassium oxyfluoronioate (K₂NbOF₅·H₂O) salt in solution (see **Equation 2.3**), K_{sp} (K₂TaF₇) << K_{sp} (K₂NbOF₅·H₂O).

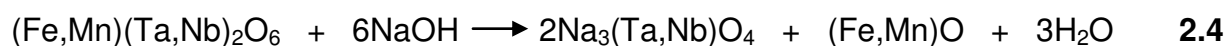


72. Zelikman, A.N., Krein, O.E. and Samsonov, G.V., 1966, *Metallurgy of Rare Metals*, ed. L.V. Belyaevskaya (Jerusalem, 1966), ch. II; available from the U.S. Department of Commerce, Clearinghouse for Federal Scientific and Technical Information, Springfield, VA 22151

73. Singh, R. P., 2001, "Processing of Ta₂O₅ Powders for Electronic Applications" *J. Electron. Mater.*, **30**(12): pp. 1584–1594

Results from this study indicated that $Ta_2O_5 \cdot nH_2O$ and $Nb_2O_5 \cdot nH_2O$ dissolved in dilute HF but several steps of fusion with K_2CO_3 and K_2TaF_7 crystallisation with KF was needed to ensure the complete separation of these elements which made this process tedious. Simpson and co-workers⁷⁴ described a modified procedure of the Marignac method for the separation of tantalum and niobium from the columbite mineral. The modification that they introduced involved the washing of the moist metallic acids ($(Ta/Nb)_2O_5 \cdot nH_2O$) with dilute H_2SO_4 followed by the dissolution with concentrated HF. The reaction mixture was then filtered to separate the undigested mineral and potassium silicofluoride from the filtrate. Potassium hydroxide was then added to the filtrate to precipitated most of the potassium tantalum fluoride and was again removed from the solution by filtration. This modification reduced the number of repetitions especially in the dissolution step.

However, not even the modified version of Simpson was able to solve the problem of niobium pentoxide contamination by impurities such as Ti(up to 100 mg/L), Si(up to 3000 mg/L), and Fe(up to 2000 mg/L) which were difficult to remove. Rose⁷⁵ digested the tantalum and niobium ore by NaOH fusion and dissolved the resulting melt in water (see **Equation 2.4** and **2.5**). A stream of CO_2 gas was then passed through the solution which resulted in precipitation of tantalum and niobium oxides. The precipitate was then boiled with soda-lye (NaOH) and then with dilute sodium carbonate. During this process the niobium dissolved while tantalum formed an insoluble sodium compound. Dilute sulphuric acid was then added to the filtrate to test the completeness of the precipitation reaction and the boiling was stopped when opalescence could no longer be observed in the filtrate.



74. Simpson, E. S., 1906, *Bull. West Australia Geol. Sur.*, **23**: p. 72

75. Rose, H., 1861, *ib*, **113**: p. 301

In later studies the Rose method was re-evaluated by Giles⁷⁶ and Blomstrand.⁷⁷ Giles obtained a satisfactory separation of these two metals using Rose alternative method, while Blomstrand's results were unsatisfactory suggesting poor reproducibility of the separation using this procedure. In turn this allowed Hermann,⁷⁸ Oesten⁷⁹ and Blomstrand⁷⁷ to modify the procedure to ensure reproducibility.

Gillis and co-workers⁸⁰ separated the tantalum from niobium by repeating the precipitation step with ferroin (o-phenanthroline – ferrous sulfate complex) from a hydrofluoric acid solution. This method however required the subsequent removal of the iron from the tantalum precipitate. A method developed by Weiss and Landecker^{81,82} obtained good separation from the fusion of the tantalum and niobium mineral with sodium carbonate and sodium nitrate. The obtained melt from this fusion step was cooled and then dissolved in warm water and the tantalum was precipitated by passing stream of CO₂ gas through the cold solution. However, the Weiss and Landecker method lacked robustness and slight variations in experimental conditions such as acidity of the solution seriously affected the effectiveness of the separation. Powell and Schoeller on the other hand advocated the separation of tantalum and niobium by the fractional hydrolysis of their oxalates in the presence of tannin and a weakly acidic solution.^{55,83}

76. Giles, W. B., 1909, *Chem. News*, **99**: p. 1

77. Blomstrand, C. W., 1866, *Journ. prakt. Chem.*, **99**(1): pp. 40

78. Hermann, R., 1856, *Journ. Prakt. Chem.*, **66**(1): p. 65

79. Oesten, F., 1856, *ib*, **99**: p. 617

80. Gillis, J., Eeckhout, J., and Poma, K., 1944, *Ver. Kon. Vlaam. Acad. Wetenschap. Belg.*, **6**: p. 5

81. Weiss, L. and Landecker, M., 1909, "Separation of Tantalum and Niobium from other Metals and from One Another", *Zeits. anorg. Chem.*, **64**: pp. 65–103

82. Schoeller, W. R. and Deering, E. C., 1927, *Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates*, [Internet]. [cited 2012 April 17]. Available from: <http://pubs.rsc.org/en/content/articlepdf/1927/an/an9275200625>

83. Powell, A. R. and Schoeller, W. R., 1921, "Tantalum, Columbium, and their Mineral Associates: I. Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates: II. Separation of Zirconium from Tantalum and from Columbium", *J. Chem. Soc.*, **120**: pp. 1927–1935

In another study⁸⁴ niobium and tantalum were separated from other metals in a mineral solution by their precipitation with tannic acid and ammonium hydroxide from oxalate solutions in the presence of glycerine (in the case of ammonium hydroxide) and disodium salt of ethylenediaminetetra-acetic acid (EDTA) which was used as masking agent for other cations in the solution. Titanium co-precipitation was found to interfere heavily with this purification process.

Fucke and Daublander⁸⁵ studied the separation of tantalum from niobium by the selective precipitation of tantalum with phenylarsonic acid in a sulfuric acid-hydrogen peroxide solution. This separation was however not quantitative and the precipitate was contaminated with arsenic due to phenylarsonic acid dissociation. Dupraw⁵⁵ successfully separated tantalum from niobium, titanium, and tungsten using n-propylarsonic acid with the precipitation of tantalum in an oxalic acid-sulfuric acid solution. This separation was less successful due to the co-precipitation of titanium and zirconium. Moshier and Schwarberg⁸⁶ achieved a quantitative separation of tantalum from niobium, titanium, and zirconium containing solution by the precipitation of tantalum with N-benzoyl-N-phenylhydroxylamine from a hydrofluoric acid solution at pH 1. Niobium in any amount greater than 20% in solution was found to be co-precipitating with tantalum while titanium and zirconium did not interfere at all.

The precipitation methods reviewed in the above paragraphs seem to have one common disadvantage in that they all proved to be unsuccessful or non-selective to produce pure Nb or Ta in quantitative amounts due to the co-precipitation of one another or from other cations that may have been present in solution. In addition, the sample preparation for dissolution either used an energy intensive fusion method or the potentially toxic HF to obtain solution from which tantalum or niobium was

84. Athavale, V. T., Menon, V. P. M. AND Venkateswarlu, C. H., 1960, "Separation of Niobium and Tantalum together from Titanium" [homepage on the Internet]. [cited 2011 Aug. 09]. Available from: <http://pubs.rsc.org/en/content/articlepdf/1960/an/an9608500208>

85. Fucke, H., Daublander, J., 1939, J., *Tech. Mitt. Krupp. Forsch.*, **14**: p. 174

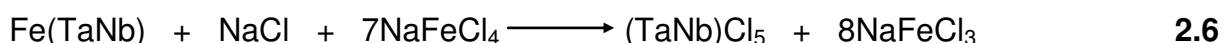
86. Moshier, R. W. and Schwarberg, J. E., 1957, "Tantalum Determination in Presence of Niobium by Precipitation with N- Benzoyl -N- p henyhydroxylamine" *Anal. Chem.*, **29**(6): pp. 947–951

precipitated. Other factors affecting precipitation as a separation method are discussed in details in **Chapter 3, Section 3.2.**

2.3.2 Fractional distillation separation procedures

Separation of tantalum and niobium from ores or concentrates by distillation has been achieved after the chlorination of the primary source.⁸⁷ The chlorination process for both the dissolution and the purification of the elements from the ores and concentrates has been made easy by important chemical features such as the high reactivity of the chlorine molecule towards tantalum and niobium, relative ease in gasifying many of the constituents of the concentrates at moderate temperatures to produce volatile chlorinated compounds as well as the water solubility of most of the chlorides.

The chlorination reactions were accomplished in a temperature range of 400 – 1000 °C using special apparatus such as a sealed high-pressure chlorination system (especially if carbon tetrachloride was used as the chlorinating agent).⁵⁵ NbCl₅, TaCl₅ and WOCl₄ are separated by fractional distillation at their boiling temperatures between 228 °C and 248 °C. The resulting product, NbCl₅, contained less than 5 mg/L tantalum and 1 to 2 mg/L of other metallic impurities by the chlorination of the ferro-niobium alloy (or niobium scrap), (see **Equation 2.6**). The NbCl₅ is then converted into high purity Nb₂O₅ by a hydrolysis step using steam. The chlorination process which is energy intensive has been largely replaced by a much simpler and more economical solvent extraction process. In fact, the fractional distillation process has been found to be more suitable for the elimination of impurities such as Si, Ti, Sn, Al, Fe, Sb, Bi and Mo than for successful separation of niobium and tantalum from the ore.²⁵



In another procedure, niobium and tantalum were separated by reacting the mixed NbCl₅ and TaCl₅ vapours with an alkali-metal chloride powder as indicated in

87. Ayanda, S. O. and Adekola, A. F., 2011, "A Review of Niobium-Tantalum Separation in Hydrometallurgy" *J. Min. Mater. Charact. Eng.*, **10**(3): pp. 245–256

Equation 2.7, where A is an alkali metal (Na, K, Rb, or Cs), and M is Nb or Ta. The tantalum complex (ATaCl₆) is isolated in the condensed phase, while the ANbCl₆ remains in the vapour phase.²⁵



In another method described in a US patent⁸⁸ it was reported that the experimental conditions were controlled in such a manner that niobium and tantalum oxides are chlorinated to form niobium oxychloride and tantalum pentachloride respectively which were then condensed in an air cooled chamber. The condensed phase was then extracted with an inert solvent such as carbon tetrachloride while chloroethane, silicon tetrachloride and sulphur dioxide also proved to be successful as extractants. The results obtained from this separation method indicated 13.0% Nb₂O₅ and 87.0% Ta₂O₅ in the condensed phase while 90.9% Nb₂O₅ and 9.1% Ta₂O₅ remained in the vapour phase. Impurities such as titanium, silicon and manganese were separated from the tantalum and niobium on the basis of their boiling and volatilizing points by adjusting the temperature in the chlorination vessel as well as in the condenser.

Choi *et al.* reported⁸⁹ the purification of commercial grade (~99.9%) niobium to 99.99% using multiple electron beam melting (EBM). The quantification of the supposedly purified niobium and of about 60 impurity elements (such as aluminum, iron, molybdenum and zirconium) in niobium was carried out by glow discharge mass spectrometry (GD-MS). At Companhia Brasileira de Metalurgia e Mineração (CBMM) contaminants are removed from niobium by the EBM technique based on their vapour pressures. Elements such as aluminum, iron, titanium, manganese, barium, potassium and silicon whose vapor pressures are considerably higher than that of niobium (at its melting point) are easily eliminated from the niobium sample by volatilization. Niobium loss due to evaporation during this separation process was in the range of 1 to 3%. On the other hand, elements with lower vapour pressure than

88. Arlesheim, W.S. and Benningen, F. K., 1958, Assignors: Ciba limited, Basel, Switzerland. Process for separating niobium and tantalum from materials containing these metals. United States Patent US 2842424. 1958 July 8

89. Choi, G., Lim, J., Munirathnam, N. R. and Kim, I., 2009, "Purification of Niobium by Multiple Electron Beam Melting for Superconducting RF Cavities", *Met. Mater. Int.*, **15**(3) pp. 385–390

niobium, such as tantalum, tungsten and molybdenum cannot be removed by this method.⁹⁰

The heat treatment procedures discussed in this section produce good separations with cleaner products. This method of separation however, may require sophisticated equipment to avoid loss of volatile compounds of interest. The method of purification is again more suitable for synthetic concentrates with high niobium purity since complex matrix such as in minerals, can complicate the purification process through boiling points' interferences and the fact that these processes generate relatively few volatile inorganic compounds.

2.3.3 Solvent extraction methods

Solvent extraction as separation method has a number of important advantages such as the reduction of the number of production steps and cleaner tantalum and niobium products.²⁶ The first step in LLE procedure which was employed for tantalum and niobium separation from their raw material involved its digestion by a mixture of HF/H₂SO₄ or HF/NH₄F. Inorganic studies indicated that at least four different metal complexes of tantalum and niobium exist in fluoride solutions namely TaF₇²⁻ and TaF₆⁻ and NbOF₅²⁻ and NbF₆⁻ (see **Figures 1.11** and **1.12, Section 1.4.2**).

In this separation process the impurities such as Fe, Ti, Mn and Si are first removed by the extraction of tantalum and niobium complexes into the organic solvent which leaves the impurities dissolved in the aqueous solution.⁹¹ Successful extractions of both Ta and Nb have been obtained from the mixture of HF and H₂SO₄ and it has been found that at fixed fluoride concentration, the extractability of Ta and Nb into an organic solvent is largely dependent on the concentration of H₂SO₄ as indicated in

90. Moura, H. R. S., Melting and purification of niobium, [Internet]. [Cited 2012 March 16], Available from:<http://www.cbmm.com.br/portug/sources/techlib/science techno/table content/sub 2/images/pdfs/010.pdf>

91. Varga, L. P., Wakley, W. D., Nicolson, L. S., Madden, M. L. and Patterson, J., 1965, "Solvent Extraction Studies of Tantalum Fluoride Complexes with N-Benzoylphenylhydroxylamine, Tri-n octylphosphine Oxide, and Methyl isobutyl Ketone Using Computer Techniques", *Anal. Chem.*, **37**(8): pp. 1003–1009

Figure 2.1.^{26,92} From this results it is clear that tantalum and niobium can collectively be extracted into organic phase from aqueous solution at higher acidity levels. The subsequent separation of the niobium from the tantalum in the organic phase can be achieved by the lowering of the HF concentration or increase in pH. Alternatively, separation can be achieved by the selective extraction of tantalum at low acid concentration, followed by the niobium extraction at increased acidity levels for the same solution.⁹³ The role of H₂SO₄ in this extraction was investigated by Zhu and Cheng⁹⁴ and the results suggested it was only to increase the solubility of the tantalum/niobium fluoride in the organic solvent through a common ion effect.

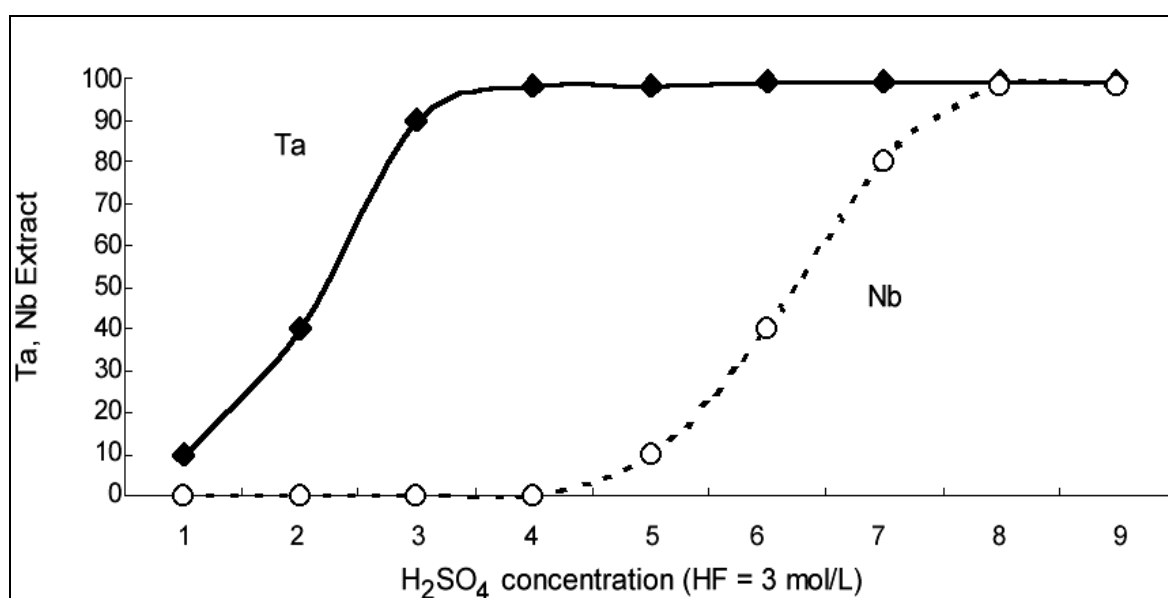


Figure 2.1: Dependence of Ta and Nb extraction on the acidity of the aqueous solution.

Challenges such as chemical waste management, pollution and economic feasibility let to a number of modifications to this basic metallurgical process which included the whole beneficiation process from the dissolution to the extraction steps. One of these

92. Konghak, H., 1991, "Solvent Extraction of Tantalum and Niobium Using Mixer-Settler", *Korea Inst. Chem. Eng.*, **29**: pp. 305–343

93. Werning, J. R. and Higbie, K. B., "Tantalum and niobium separation by liquid-liquid extraction hydrochloric acid extraction from mixed ketones", *U. S. Bureau of Mines, Albany, Ore.*

94. Zhu, Z. and Cheng, C. Y., 2011, "Solvent extraction technology for the separation and purification of niobium and tantalum: A review", *Hydrometallurgy*, **107**: pp 1–12

modifications included the use of $\text{NH}_4\text{F}\cdot\text{HF}$ ⁴⁷ as fluoride source which is cheaper (~70%) and safer than HF during the digestion of synthetic tantalum and niobium concentrate (**Table 2.1**) prior to separation of tantalum and niobium from the rest of the impurities. The synthetic concentrate was dissolved by firstly stirring it in a concentrated H_2SO_4 solution for a few minutes which was then followed by the addition of $\text{NH}_4\text{F}\cdot\text{HF}$ and water. The remaining solids were separated from the solution by decantation and an X-ray fluorescence spectroscopy (XRF) analysis of the solid indicated that more than 97% of the original concentrate was successfully dissolved. In the next step the filtrate was extracted with methyl isobutyl ketone (MIBK) and quantitative analysed. These results indicated that about 60% Ta has been extracted into the organic layer while Nb, Fe, Ti and Co remained in the aqueous layer (**Table 2.1**).⁴⁷

Table 2.1: Analytical results for extraction of tantalum from $\text{NH}_4\text{F}\cdot\text{HF}$ and H_2SO_4 solution

Element	Concentration (g/L) before extraction	Concentration (g/L) after extraction	Extracted	% Extracted
Nb	4.9	4.9	0	0
Ta	21	8.6	12.4	59.05
Fe	2.2	2.2	0	0
Ti	20	21	-1	-
Co	1.7	1.8	-0.1	-

The literature study also indicated that several other extraction systems have also been studied and some of them have proved to be highly successful to the extent that they have already been adopted for industrial productions. The studied extractants include MIBK,^{95,96} tributyl phosphate (TBP),^{92,97} octanol,^{98,99}

95. Htet, H. H. and Kay, T. L., 2008, "Study on Extraction of Niobium Oxide from Columbite–Tantalite Concentrate", World Academy of Science, Engineering and Technology, **46**: pp. 133–135

96. Blutssus, W. and Eckert, J., 1993, Inventors; Hermann C. Staack GmbH & Co. KG, "Process for the recovery and separation of tantalum and niobium", United States Patent 5209910 [cited 2012 March 16]. Available from <http://www.freepatentsonline.com/5209910.html>

97. Damodaran, A. D., Deshpande, S. G., Majmudar, A. A. and Sastri, M. S., 1969, "Extraction and Utilization of Pure Niobium and Tantalum from Indian Ores", Bhabha Atomic Research Center, Trombay, Bombay, **36**(5): pp. 306–318

cyclohexanone,¹⁰⁰ bis(2-ethylhexyl)phosphoric acid (DEHPA),¹⁰¹ diisopropyl ketone (DIPK),¹⁰² Alamine 336,¹⁰³ from HF solutions and methyl isobutyl ketone/diisobutyl ketone (MIBK/DIBK = 0.4) from a 12 M HCl solution.⁹³ Comparisons that were made between these solvents in terms of their density, water solubilities (and immiscibility), flash points (for potential fire accidents), viscosities and extractability of Ta and Nb indicated octanol to be the best extractant for the separation of Ta and Nb.^{73,98,99}

Research⁴² indicated that HTaF₆ and HNbF₆ are the main products that are found at high HF concentration as shown in **Figures 1.11** and **1.12, Section 1.4.2**. These complexes are easily extracted into the organic phase and the complexes are stripped back into aqueous media as TaF₆⁻ or NbF₆⁻ by reducing the acidity as part of the manipulation of the equilibrium constant and acid dissociation constant for the two complexes (see **Equation 1.15** to **1.18, Section 1.5.1.3**).

There is no doubt that solvent extraction is by far the most commonly used method for the separation and purification of niobium and tantalum. This is partly due to its simplicity, selectivity, speed and efficiency. The experimental procedures discussed in this section have indicated that conversion of niobium and tantalum (in ores or concentrates) to fluorides is inevitable for the successful extraction and separation of niobium and tantalum by solvent extraction. Fluorination is commonly accomplished by digestion of the primary source using HF at elevated temperatures. It is this use of HF which contribute heavily to the cost of this method since it requires specialised fluoride resistant equipment for the whole process from sample preparation (digestion

98. Agulyansky, A., Agulyansky, L., and Travkin, V. F., 2004, "Liquid-liquid extraction of tantalum with 2-octanol", *Chem. Eng. Process.*, **43**: pp. 1231–1237

99. Maiorov, V. G., Nikolaev, A. I. and Kopkov, V. K., 2002, "Extraction of Tantalum(V) Impurities from Niobium(V) Fluoride Solutions with Octanol", *Russ. J. Appl. Chem.*, **75**(9): pp. 1389–1393

100. Thakur, N., 2009, Niobium and Tantalum, [homepage on the Internet]. [cited 2009 Sep 23]. Available from: (<http://knol.google.com/k/narayan-thakur/niobiumandtantalum/2kwb871ek26nr/66>)

101. Vin, Y. Y. and Khopkar, S. M., 1991, "Separation of niobium and tantalum by extraction chromatography with bis(2-ethylhexyl)phosphoric acid", *Talanta*, **38**(9), pp. 971–975

102. Stevenson, P. C. and Hicks, H. G., 1953, "Separation of Tantalum and Niobium by Solvent Extraction", *Anal. Chem.*, **25**(10): pp. 1517–1519

103. El hussaini, O. M. and Rice, N. M., 2004, "Liquid-liquid extraction of niobium and tantalum from aqueous sulphate/fluoride solutions by a tertiary amine", *Hydrometallurgy*, **72**: pp. 259–267

vessels such as platinum crucible) including the separation steps (separatory funnels) to the final quantification of the element (e.g. by ICP).

2.3.4 Tantalum and Nb separation by ion exchange

The separation of tantalum and niobium using anion exchange as method has been investigated by several researchers and the separation process was mainly successful due to the fact that both elements form complex anions with fluorides. Niobium and tantalum separation has also been investigated¹⁰⁴ on three polyurethane foam columns which were pretreated with diantipyrylmethane (DAM) in dichloroethane (DCE), TBP and MIBK. The mixture of the two elements was loaded on to the column and eluted with dilute HF/HF + H₂SO₄, 1 M HNO₃ + 0.3% H₂O₂ and 1 M NH₄F. The results (**Table 2.2**) indicate that niobium is eluted by 1 – 2 M HF (with or without H₂SO₄) while tantalum is best eluted by 1M NH₄F and 1 M HNO₃ + 0.3% H₂O₂ mixture.

Table 2.2: Results obtained for the separation of niobium and tantalum under varying experimental conditions

Extractant	Eluent	Nb (%)	Ta (%)
0.01 M DAM/DCE	2 M HF	98	0.1
	1 M HNO ₃ + 0.3% H ₂ O ₂	0.3	96 - 98
	1 M NH ₄ F	0.3	95 - 97
TBP	1 M HF	99	0.03
	1 M HNO ₃ + 0.3% H ₂ O ₂	0.3	95.5
	1 M NH ₄ F	0.3	93.1
MIBK	1 M HF + 0.5 M H ₂ SO ₄	99	0.012
	1 M HNO ₃ + 0.3% H ₂ O ₂	0.3	97.8

Fritz and Dahmer separated niobium(V), tantalum(V), molybdenum(VI) and tungsten(VI) on a Teflon-6 support column which was impregnated with methyl isobutyl ketone. Sequential elution of the analytes was performed with eluents of

104. Caletka, R., and Krivan, V., 1985, "Separation of Niobium and Tantalum on Polyurethane Foam Pretreated with Diantipyrylmethane, TBP or MIBK", *Fresenius Z. Anal. Chem*, **321**: pp. 61–64

different HF and HCl ratios.¹⁰⁵ This group also investigated the volume effect on the element separation and found that elution of Nb is completed with 50 mL of 3 M HCl + 1 M HF, while Ta is eluted with 100 mL of 15% H₂O₂. In another study¹⁰⁶ a synthetic mixture of pure Nb₂O₅, Ta₂O₅, WO₃, FeCl₃ and MnCl₂ was digested in HF. Niobium and tantalum were separated from each other and from the other elements using macroporous polyacrylate polymer beads (Amberlite XAD-7) as an adsorbent and mixtures of HF/HCl as eluent. The effect of each acid concentration on adsorption of niobium and tantalum was also investigated and it was found that niobium is less adsorbed on to the polymer beads under the experimental conditions investigated than tantalum, which enable the required separation of the two metals.

In another study¹⁰⁷ the amberlite XAD-7 resin was impregnated with *p*-tert-butylsulfanylcalix[4]arene for the separation of tantalum and niobium. Solutions of known tantalum and niobium concentrations, prepared from the 1000 mg/L standards of each metal were mixed and then added to the sorbent material. The solutions were allowed stay in contact with the resin for time durations up to 24 h. The results indicated that niobium sorptions of greater than 90% were obtained at a 15 h contact time, while tantalum percentage sorption remained under 8% even after 24 h. The separation of the two elements was achieved by removing the supernatant liquid containing the majority of the Ta by decantation and desorbing the Nb with 9 M H₂SO₄.

Tantalum and niobium were successfully separated from each other and from vanadium in a mineral sample GSD-2¹⁰⁸ and in steel,¹⁰⁹ using reversed-phase liquid

105. Fritz, J.S., and Dahmer, L.H., 1968, "Column Chromatographic Separation of Niobium, Tantalum, Molybdenum and Tungsten", *Anal. Chem.*, **40**(1): pp. 20–23

106. Wakui, Y., Matsunaga, H., and Itabashi, U., 1995, "Chromatographic Separation of Niobium and Tantalum in a Hydrofluoric Acid-Hydrochloric Acid System with Macroporous Polyacrylate Resin Beads", *Anal. Sci.*, **11**: pp. 23–27

107. Matsumiya, H, Yasuno, S, Iki, N. and Miyano, S., 2005, "Sulfanylcalix[4]arene-impregnated Amberlite XAD-7 resin for the separation of niobium(V) from tantalum(V)", *J. Chromatogr. A*, **1090**: pp. 197–200

108. Wang, H., Zhang, H.S. and Cheng, J.K., 1995, "Determination of V (V), Nb (V) and Ta (V) as their 2-(5-nitro-2-pyridylazo)-5-diethylaminophenol complexes by reversed-phase high performance liquid chromatography", *Fresenius J. Anal. Chem.*, **351**: pp. 683–685

chromatography. The mineral sample was dissolved in the mixture of HF and HClO₄ (5:1, v/v) while 2-(5-nitro-2-pyridylazo)-5 diethylaminophenol was added to the reaction mixture for colour development. The steel sample was dissolved in nitric acid and HF (1:2, v/v) and 1% EDTA and 2-(5-Bromo-2-pyridylazo)-5-diethylamino phenol (5-Br-PADAP) was used to convert the metals to coloured complexes. In both studies Ta and Nb were separated on an ODS column using a methanol-water mixture (54:46, v/v) containing a 10 mmol/L acetate buffer (pH 3.0 and 3.5) as the mobile phase and the elements were quantitatively determined by a UV/Vis spectroscopy. Quantification of the elutions within 9 minutes indicated recoveries of 98.3 – 100.8% Nb and 98.9 – 101.4% Ta.^{108,109}

2.3.5 Liquid membrane separation

A mixture of tantalum and niobium was separated in fluoride¹¹⁰ and chloride¹¹¹ media using a liquid supported membrane. A quaternary ammonium salt (Aliquat 336) which was diluted in kerosene and tributyl phosphate were used as the carriers in the presence of fluoride and chloride solutions respectively. The high fiber supported membrane extracted 78% Ta from the mixture solution using 0.3% Aliquat 336 carrier and niobium was not extracted under these conditions. The extracted tantalum was then stripped from the membrane using 0.2 M NaClO₄ solution.

The maximum recovery of niobium in the chloride medium was achieved using TPB as carrier at HCl concentrations between 6 and 9 M. Tantalum transport however under these conditions was small thereby achieving good separation. Campderrós and Marchese¹¹² studied niobium transport across a supported liquid membrane

109. Dongling, L., Xiaoyan, H. and Haizhou, W., 2004, "Separation and simultaneous determination of niobium and tantalum in steel by reversed-phase high-performance liquid chromatography using 2-(2-pyridylazo)-5-diethylamino phenol as a pre-column derivatizing reagent" *Talanta*, **63**: pp. 233–237

110. Buachuang, D., Ramakulb, P., Leepipatpiboon, N. and Pancharoen, U., 2011, "Mass transfer modeling on the separation of tantalum and niobium from dilute hydrofluoric media through a hollow fiber supported liquid membrane", *J. Alloys Compd.*, **509**: pp. 9549–9557

111. Campderrós, M. E. and Marchese, J., 2000, "Facilitated transport of niobium(V) and tantalum (V) with supported liquid membrane using TBP as carrier", *J. Membr. Sci.*, **164**: pp. 205–210

112. Campderrós, M. E. and Marchese, J., 2001, "Transport of niobium(V) through a TBP–Alamine 336 supported liquid membrane from chloride solutions", *Hydrometallurgy*, **61**: pp. 89–95

using a synergistic mixture of TBP and Alamine 336 as carriers and their results (obtained by UV spectrophotometer measurements) indicated that niobium was recovered in excess of 71.2% with 10% (v/v) of Alamine 336 in TBP at HCl concentration between 6 and 7 M.

2.4 Conclusions

The different separation techniques that were discussed in this chapter indicate that both distillation and solvent extraction methods are the most successful procedures in terms of producing purer Nb and Ta samples. Other simple techniques such as magnetic, electrostatic and gravity separations may be coupled with most of the above mentioned processes to enhance the separation and purification of these two elements. However, this coupling of techniques requires continued studying and the understanding of the physical and chemical properties of the primary samples. Part of this study is to utilise some of the properties of the mineral samples as part of purification and separation of niobium and tantalum.

It is clear from the above discussions that solvent extraction is by far the most used method for the separation of tantalum and niobium. The solvent extraction of tantalum and niobium commonly using MIBK is carried out from hydrofluoric acid solutions which is the main acid used to dissolve the primary concentrates of these two elements. The role of HF in the digestion procedure is to convert Ta and Nb into fluoride complexes which are soluble in the organic solvent in acidic medium.

Although several conversion methods have been investigated by previous researchers, most of the available methods are either energy intensive and/or potentially harmful to the environment. The current study is aimed at the investigation of some simple, environmentally and economically feasible ways of transforming niobium and tantalum primary source into compounds which enable the successful separation and purification of the two elements.

3 Separation and quantification methods used for tantalum and niobium in tantalite

3.1 Introduction

As indicated in **Chapters 1** and **2** the elements of interest, namely niobium and tantalum occur in nature in a complex matrix of different elements and therefore require a number of separation steps to isolate and purify the elements prior to their application in different products. Although the complete removal of impurities from a metal of interest in any mineral is almost impossible, it is vitally important that the purification methods that are selected should be able to reduce the concentration of the impurities substantially to acceptable or desired levels. In **Chapter 2** the different methods of purification and separation for tantalum and niobium were critically discussed. It is clear from this literature survey that some of the separation and purification procedures have been tested only on a laboratory scale, some on a fairly large scale while others have become important commercial production methods.

This chapter will deal with a selection of the purification and separation techniques (for niobium and tantalum) that were used in the study to try and find alternative separation processes or improvements to the current methods (with limitations) for mineral beneficiation. The choice of the techniques was made in such a way that the intended beneficiation process utilised both the mineral's chemical and physical properties as well as those of the impurities in the mineral ore. The discussion will also include the most important chemical principles underlying each of the selected purification or separation techniques with emphasis on their advantages and disadvantages. The chapter entails discussion of the following topics:

- a) The methodology of the study which describes the general processes/steps that were followed in this study

- b) The dissolution techniques for the conversion of tantalum and niobium into soluble compounds which enabled subsequent separation and purification of these elements
- c) Separation and purification techniques specifically applicable for tantalum and niobium
- d) Analytical techniques that assessed the success of the dissolution, separation or purification methods.

3.2 Methodology of the study

The current study forms part of a much larger project and has been preceded by three other studies^{52,53,112} with its overarching aim to find new or improved methods to separate and isolate niobium and tantalum from its ore. These studies investigated different aspects of niobium and tantalum chemistry such as the identification of successful dissolution methods of the oxides and the mineral and the accurate determination of the main elements as well those of the impurities present in the mineral.^{50,51} Some of these studies also investigated the successful removal of the major impurities such as iron and radio-active elements from the ore prior to its complete dissolution. The final beneficiation process that is proposed in this study will therefore include some of the steps or processes that were investigated in these previous studies. A summary of the major findings from these studies are presented in **Table 3.1**.

Table 3.1: Major observations from the tantalite dissolution studies

Method studied	Observation
Fusion with $\text{Li}_2\text{B}_4\text{O}_7$	Complete dissolution of tantalite ⁵³
H_2SO_4 leaching	Removal of 50% U and 70% Th ¹¹²
Magnetic separation	Removal of 90% Fe and Ti ⁵²

In order to understand the chemistry of the most probable dissolution products it was decided to begin the study with the dissolution, subsequent separation and isolation of the two main elements from synthetic niobium/tantalum fluoride and oxide mixtures

112. Koko, F., 2012, Beneficiation of tantalum and niobium from tantalite mineral, [MSc study in progress], Bloemfontein: University of the Free State

using different dissolution methods. The successful dissolution, separation and isolation techniques identified from these studies were then employed on the tantalite samples (main elements present as Ta_2O_5 and Nb_2O_5 , see **Table 1.5** and **Figure 3.1**) to try and separate and purify these two metals from one another with the least amount of impurities.

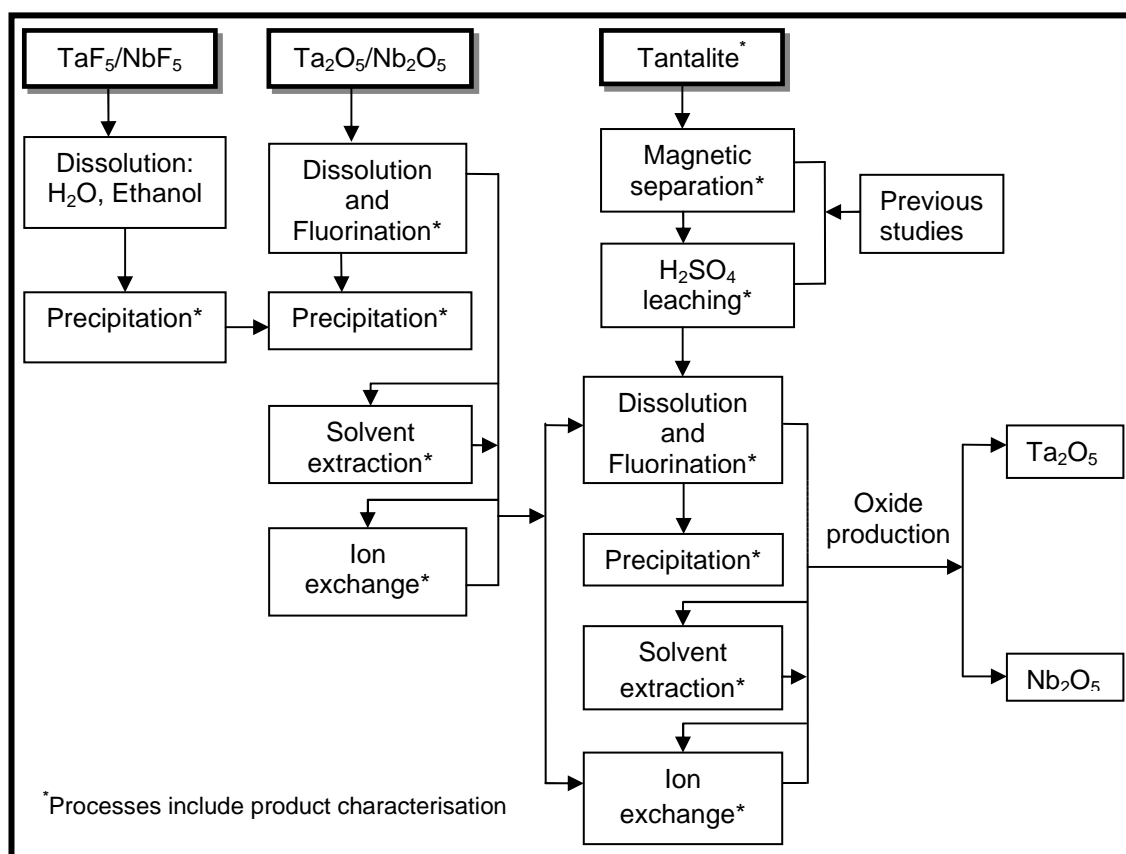


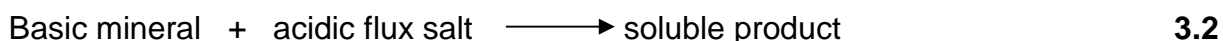
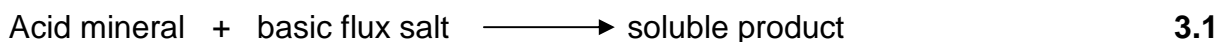
Figure 3.1: Illustration of the methodology that will be used in this study for the separation of Ta and Nb.

3.3 The dissolution techniques used in this study

3.3.1 Fusion dissolution

Flux fusion is often used as an alternative to acid dissolution. This dissolution method is often used for the dissolution of samples such as mineral ores, slags and some metal oxides which are resistant to acid attack. Flux fusion techniques involve the heating a homogenous mixture which entails an excess of salt (flux) added to a mineral sample at temperatures which exceed the melting point of the flux salt in an appropriate container such as a crucible.

The flux salt and the sample react with one another at these elevated temperatures as a molten mixture in a water free environment. The sample is converted into a form that is soluble in acids, bases or water due to a combination of oxidation and acid/base reactions which take place between the flux and inorganic sample according to the following reactions (**Equations 3.1 to 3.3**):



The choice of the flux salt is therefore very important for this dissolution method and fluxes range from acidic to basic and from non-oxidising to strongly oxidising salts as indicated in **Figure 3.2**.

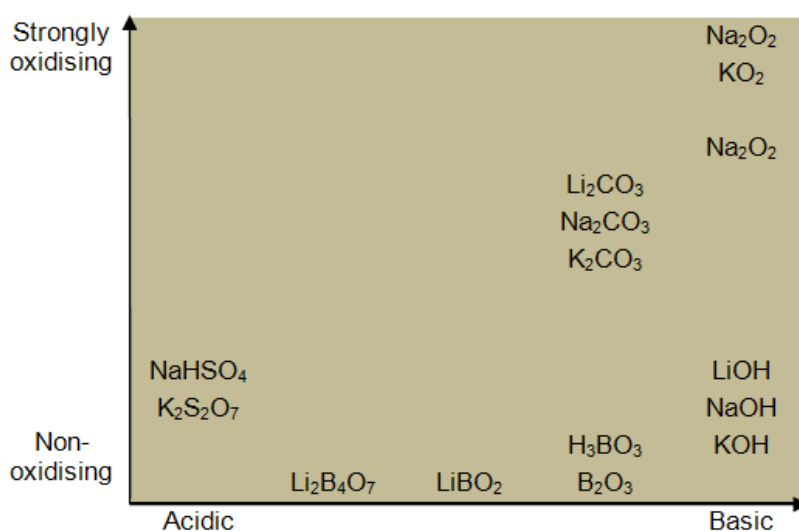


Figure 3.2: Acid/base and oxidising ability properties of the flux salts.¹¹³

The dissolution of the sample is normally dependent on the sample: flux weight ratio as well as the melting point of the flux salt. When the reaction is complete, judged by

113. Dulski, T. R., *A Manual for the Chemical Analysis of Metals*, 1996, Library of Congress Cataloging-in-Publication Data, West Conshohocken, pp. 83 – 88

visual inspection which is indicated by the disappearance of all the starting material, the melt is allowed to cool and then dissolved in acid, base or water.

The flux fusion technique is often employed for dissolution of mineral samples for several reasons: (i) it avoids the use of the potentially toxic HF hence a safer method; (ii) the complete dissolution of the sample due to the high ion concentration and melting temperature of the salts which is difficult to reach using conventional acids and therefore enables complete analysis of the sample and (iii) the resultant melts are often soluble in dilute acid/base or water solutions due to the formation of the corresponding fluoride which have low boiling points (see **Table 3.2**).

Table 3.2: Examples of metal fluorides and their boiling points

Metal fluoride	Boiling point (°C)
BF ₃	100.3
SiF ₄	-86.0
TaF ₅	229.2
NbF ₅	234.5

Most fusion procedures are however accomplished at high temperatures which makes this method an energy intensive technique. There is also a possible loss of analytes due to volatilization. For example, the fluoride flux-fusion will result in the loss of silicon, boron, lead and polonium.¹¹⁴ Tantalum, niobium and molybdenum may also be lost at temperatures greater than 400 °C in fluoride fusions. Moreover, large amounts of the flux are added to the sample (often 10 to 20 times the sample weight) which may result in contamination of the sample by impurities. The choice of a solvent for the dissolution of the melt is also an important step as some acids dissolve the crucible. For example, *aqua regia* attacks and dissolves the platinum crucible. Finally, the resultant solutions contain high salt content which may decrease the accuracy of the subsequent analysis steps.

114. Multi-Agency Radiological Laboratory Analytical Protocols Manual: MARLAP, July 2004, [Internet]. [cited 2012 June 21]. Available from <http://www.epa.gov/rpdweb00/docs/marlap/402-b-04-001b-13-final.pdf>

3.4 Separation and purification techniques in this study

A more detailed outline of the different steps in the tantalite beneficiation in this study is given in **Chapter 6, Figure 6.10**. The separation and purification processes used can generally be classified into two groups namely (i) physical and (ii) chemical methods.

3.4.1 Physical processing routes: Magnetic separation

Magnetism in minerals results from properties that are specific to certain elements in those minerals. For example, the presence of Fe, Ti and Mn in a mineral can result in a certain portion of the mineral samples being attracted to an external magnetic field. The magnetic properties of the elements in these ores are mainly determined by the oxidation state of the elements. The ligand field theory¹¹⁵ successfully describes the correlation between the magnetic properties of the transition metal compounds and the oxidation state. This theory predicts magnetic properties for high spin d^4 , d^5 , d^6 and d^7 electron configurations and less or diamagnetic properties for low spin electron configurations. Two different kinds of magnetism exist for these types of materials namely paramagnetism and ferromagnetism.

Paramagnetic materials are weakly attracted to magnetic field but possess the magnetic properties only in presence of the applied magnetic field. The paramagnetic properties in these materials arise from the presence of unpaired electrons and the realignment of the electron paths in the direction of the externally applied field. Most metals which include Mg, Mo, Li and Ta have the paramagnetic properties. Ferromagnetic materials on the other hand are strongly attracted to magnetic fields and retain their magnetic properties even after the externally applied field has been removed. Metals with ferromagnetic properties include Fe, Co and Ni.¹¹⁶

115. Cotton, F. A., Wilkinson, G. and Gaus, L. P., *Basic Inorganic Chemistry*, 3rd ed., 1994, John Wiley & Sons, Inc., New York, pp. 503-519

116. Diamagnetic, Paramagnetic, and Ferromagnetic Materials, [Internet]. [cited 2012 July 24].

Available from:

<http://www.ndted.org/EducationResources/CommunityCollege/MagParticle/Physics/MagneticMatls.htm>

The electron alignment which leads to the presence of magnetism in the material only occurs below the Curie temperature (a critical temperature at which materials lose their net magnetisation even though they still possess paramagnetic properties) of that material. Above the Curie temperature compounds cease to exhibit the spontaneous magnetism properties. Examples of some magnetic compounds together with their Curie temperatures are given in **Table 3.3**.¹¹⁷

Table 3.3: List of selected magnetic materials

Magnetic material	Curie temperature (K)
Co	1388
Fe	1043
Fe ₂ O ₃	948
Fe ₃ O ₄	858
Ni	627
NiOFe ₂ O ₃	858
MnAs	318
CuOFe ₂ O ₃	728
Dy	88

The magnetic separation is made possible by the difference in responses of different materials in a mixture to the external field. The paramagnetic and ferromagnetic materials are selectively extracted from the sample mixture by introduction of the magnetic field to the samples thereby separating them from the non magnetic material (diamagnetic). However, it is important to note that not every magnetic material can be successful separated with the magnetic separation technique. Whether the sample has enough magnetism for a magnetic separation is determined by the measurement and determination of its magnetic susceptibility, a constant which indicates the degree of magnetisation of material by the external field and is calculated using **Equation 3.4**.

$$\chi_g = \frac{C_{bal} \cdot I \cdot (R - R_0)}{(10^9 \cdot m)} \quad \mathbf{3.4}$$

where: χ_g = mass magnetic susceptibility

117. Ferromagnetism, [Internet]. [cited 2012 June 13]. Available from <http://en.wikipedia.org/wiki/Ferromagnetism>

l = sample length (cm)

m = sample mass (g)

C_{Bal} = balance calibration constant

R_0 = reading from the digital display for the empty tube

R = reading from the digital display for the tube plus sample

The magnetic separation is generally a low cost method of purification (**Figure 3.3**). The magnetic attraction forces work against frictional forces and sometimes a stronger field is required to attract weakly magnetic particles in the sample. Another advantage of the magnetic separation technique is that there are no chemicals involved in the process which eliminate environmental concerns with this purification step.



Figure 3.3: Electromagnet with power supply used in study.

However, magnetic particles can become trapped in more coarse non-magnetic particles (or *vice versa*) and get carried along by the magnetic force. Hence the ore has to be milled to very small particle sizes to liberate the elements before magnetic separation can be done. There is also a risk of cross contamination of the sample during this milling step if the milling equipment is not properly cleaned prior to the milling process.

3.4.2 Chemical processing routes

3.4.2.1 Acid leaching

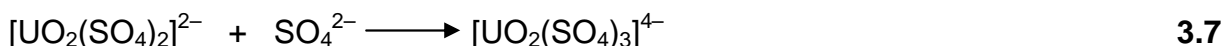
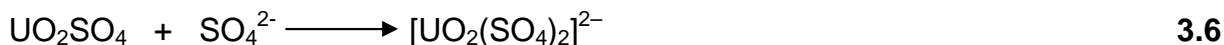
The chemical separation and quantification of the different elements require the sample to be in solution. Thus, the complete dissolution of the mineral sample for the chemical separation of the elements becomes the first and foremost important step. The literature study (**Chapter 2**) has indicated that vigorous conditions such as the use of concentrated HF with other mineral acids and high temperature fusion digestion techniques are commonly used for mineral dissolution. It has also been observed that the presence of fluoride ions from the HF dissolution is extremely important in the subsequent separation of niobium and tantalum.

Despite its success in leaching the main elements in the tantalite mineral while also providing the necessary fluoride ions for the separation of Ta and Nb, HF digestion procedure often results in incomplete dissolution of the mineral samples.^{40,64,118} Some fusion procedures may also produce incomplete digestion or incomplete recoveries due to subsequent precipitation reactions that form during the melt dissolution³⁹ and are normally overcome by addition of steps or in some cases the modification of some of the steps in the process.

Acid leaching or partial dissolution of the mineral sample was used in this study for the selective dissolution of certain metal(s) from a solid sample. This method involves the conversion of the target impurities into soluble salts that can be separated from the solid residue by filtration, decantation or centrifugation. For example, uranium was leached from the minerals with H₂SO₄ which possibly converts the uranium oxide into soluble uranyl sulphate complexes as indicated by the reactions in **Equations 3.5 to 3.7**. Acid leaching is an easy process to perform and is much less harmful (depending on the acid used).



118. El-Hussaini, O. M. and Mahdy, M. A., 2001, "Extraction of Niobium and Tantalum from Nitrate and Sulfate Media by using MIBK", *Mineral Processing and Extractive Metallurgy Review: An International Journal*, **22**(2): pp. 633 – 650



The disadvantages of acid leaching include: (i) the highly acidic and in some cases toxic residual effluent and (ii) lack of complete selectivity which sometimes requires intensive investigations to get the best conditions to improve the efficiency of the method. For example, the sulphuric acid used during the uranium leaching step as indicated in the above chemical reaction, is highly corrosive and non-selective even at low at a temperature range of 40 – 80 °C resulting in many other metal species such as the target elements also being leached from the sample. The efficiency of acid leaching like in other dissolution and purification techniques depends on the grain size and the leaching efficiency increases with decreasing grain size due to increased surface/volume ratio.¹¹⁹

3.4.2.2 Precipitation separation

Precipitation occurs when an ion(s) in solution reacts with a suitable counter ion to form an insoluble compound. First, supersaturation of the solution has to occur followed by nucleation. The nucleation takes place when a minimum number of particles come together to form nuclei of the solid phase. The fundamental equation that summarises the precipitation process is that given by the Von Weimarn ratio (**Equation 3.8**):¹²⁰

$$\text{Relative supersaturation} = (Q - S)/S \quad \mathbf{3.8}$$

where Q is the combined concentration of the reagents before precipitation occurs and is also the degree of supersaturation and S is the solubility of the precipitate at equilibrium.

119. Geälinas, Y., Barnes, R.M., Florian, D., and Schmit, J.P., 1998, Acid Leaching of Metals from Environmental Particles: Expressing Results as a Concentration within the Leachable Fraction” *Environ. Sci. Technol.*, **32**, pp. 3622 – 3627

120. Christian, D. G., *Analytical Chemistry*, 5th ed., 1994, John Wiley & Sons, Inc., New York, pp. 484 – 492

The mechanism for precipitation entails the alternate arrangement of positive and negative ions in a fixed pattern as indicated in **Figure 3.4** (using AgCl as an example). For stoichiometric reactions the net surface charge is zero. However, when one of the ions in the solution is in excess, there will be adsorption of the excess ions on the surface creating a charge that will attract ion of opposite charge from the solution. The process results in the formation of larger particle sizes in precipitates and settles to the bottom of the container.^{118,120,121} This process, which is normally enhanced by the slow heating of the precipitate in the presence of high ion concentration is called coagulation.

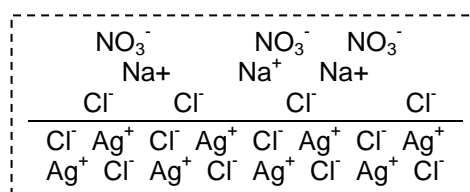


Figure 3.4: Coagulation of the precipitate.

The rate of crystal growth or of the coagulation process influences the purity of the precipitate. Slowly formed precipitates are normally purer than the quickly formed coagulated precipitates. The newly formed solid compound becomes insoluble when the solubility product (K_{sp}) has been attained or exceeded as illustrated by the general reaction (**Equations 3.9 and 3.10**):



$$K_{sp} = [M^+][A^-] \tag{3.10}$$

where M^+ is the cation and A^- is the anion

The precipitation process has three main uses namely (i) gravimetric and volumetric quantitative analyses, (ii) isolation of analytes form solution and (iii) separation of

¹²¹. Skoog, D. A., West, D. M., Holler, J. F. and Crouch, S. R., *Fundamentals of Analytical Chemistry*, 8th ed., 2004, Thomson Brooks/Cole, Australia, pp. 318, 804 – 807

chemical species from one another or from the impurities. In gravimetric determination the analyte in solution is converted into an insoluble compound with known chemical formula which can then be weighed. The masses of the product and the starting material are compared to determine the analyte amount. A volumetric determination of an unknown involves the titration of the analyte with a standard solution. Precipitate formation indicates the stoichiometric end point of the reaction. The analyte amount is determined using the stoichiometric reaction between the metal ion and the counter ion.

In this study the precipitation method was used to chemically separate a specific analyte or element from contaminants present in solution or other analytes by forming an insoluble compound in their presence and is isolated from the rest by filtration. Alternatively, the unwanted ions could be precipitated and removed from the solution leaving the ion of interest in solution which can subsequently be purified or isolated. Examples of the most common precipitants and the type of ions usually precipitated are given in **Table 3.4**.

Table 3.4: Some of the commonly used precipitants for metal isolation

Name	Formula	Example of ions precipitated
Sodium tetraphenylboron	$\text{NaB}(\text{C}_6\text{H}_5)_4$	Ag^+ , Tl^+ , Cs^+ , Cu^+
Tetraphenylarsonium chloride	$(\text{C}_6\text{H}_5)_4\text{AsCl}$	MnO_4^- , I_3^- , ReO_4^-
Ammonium nitrosophenylhydroxylamine (Cupferron)	$\text{NH}_4[\text{C}_6\text{H}_5\text{N}(\text{O})\text{NO}]$	Zr^{4+} , Ti^{4+} , U^{4+} , V^{5+}
Sodium diethyldithiocarbamate	$(\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Na}$	Many metals from acidic solution
Chloride ion	Cl^-	Ag^+

In order to obtain the required selectivity of the precipitation process, certain conditions have to first be fulfilled namely (i) a complete dissolution of the parent matrices of the reacting ions, (ii) concentrations of the reagents have to exceed the solubility product of the resulting compound and (iii) the pH should be fixed or known

since most compounds are only stable in certain pH ranges. Other factors which affect the precipitation process include the presence and concentrations of other constituents as well as the temperature of the solution.

For a separation by means of the precipitation process to be feasible three main requirements should be met:

- The precipitate should first be sufficiently insoluble that the amount that will be lost due to its residual solubility will be negligible.
- The resulting precipitate should be in a form suitable for subsequent handling; it should consist of large crystals or coagulated precipitate so that they can be easily separated from the solution and should not adhere to the container walls.
- The precipitation of the targeted species should preferably be quantitative to avoid repetitions of the process.

Precipitation is a simple process and it can be sufficiently selective if the precipitate forms slowly. This separation technique is also not energy or resource intensive compared to other techniques such as chromatography.

However, it is time consuming to separate the precipitate from the mother solution (filter or centrifuge), then to wash the precipitate and finally to digest the precipitate for chemical analysis. Another disadvantage of the technique is its lack of selectivity, especially when the precipitation rate is high. It is normally extremely difficult to get a completely selective separation technique based on precipitation especially for mineral processing due to coprecipitation (through surface adsorption or occlusion) which cannot be completely avoided for the sample which normally consists of a large number of elements such as tantalite in this study (see **Table 1.5**).

3.4.2.3 Solvent extraction

Solvent extraction or liquid–liquid extraction is a very popular and effective technique to separate metal ions from one another or from interfering matrices. This separation method induces the selective transfer of a chemical compound from one solvent to another immiscible solvent. Examples of immiscible pair of solvents include water and methyl isobutyl ketone.

The separation of the metal ions can be accomplished in a number of different ways which include extracting metal as fluoride or chloride complexes from the solution of HF or HCl respectively.¹¹⁸ The most widely used method of extracting the metal ions is the formation of metal chelate complexes with the addition of chelating agents at appropriate pH. Many of these organic chelating agents are weak organic acids (see **Table 3.4**) which react at a certain pH (pK_a of the weak acid) with the metal ion in the aqueous solvent to form a neutral or uncharged molecule which are highly soluble in organic solvent. The success of any extraction of a solute is determined by the distribution constant, K_D and the extraction ratio, D . The relatively large values of these two terms indicate a successful transfer of the solute from the aqueous into the organic phase. By definition the distribution constant, K_D , is presented by the relative solubility of a solute in two immiscible solvents as indicated in **Equation 3.11**:^{120,122}



with

$$K_D = \frac{[A]_{org}}{[A]_{aq}} \quad 3.12$$

while the extraction ratio, D , is given by the total amount of species A in the organic compared to that in the aqueous layer as indicated in **Equation 3.13**:

$$D = \frac{\sum[A]_{org}}{\sum[A]_{aq}} \quad 3.13$$

The general extraction process of the metal ion in the aqueous phase into the organic layer is shown in **Figure 3.5**. The neutral chelate metal complex is transferred from the water layer to the immiscible organic layer by the mixing of the two solvents. It is therefore important that the analyte(s) are first converted into compounds which are soluble in the organic solvent beforehand.

122. Peters, D. G., Hayers, J. M. and Hieftje, G. M., *Chemical Separations and Measurements: Theory and Practice of Analytical Chemistry*, 1974, W. B. Saunders Company, London, pp. 487 – 489

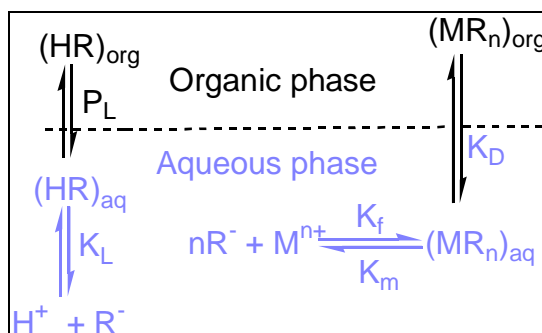
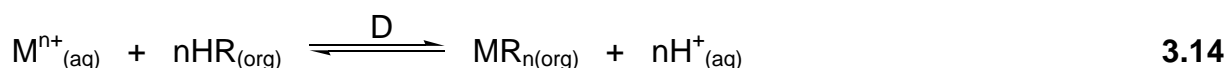


Figure 3.5: Chemical reactions involved in the extraction of metal complexes.^{120,121}

The overall reaction during the extraction process as indicated in **Figure 3.5**, can be written as one reaction (**Equation 3.14**) with an equilibrium constant or extraction ratio (*D*) indicated by **Equation 3.15**:



with

$$D = \frac{[MR_n]_{org}[H^{+}]_{aq}^n}{[M^{n+}]_{aq}[HR]_{org}^n} \quad \mathbf{3.15}$$

where *D* is the extraction ratio for all the species in solution, $[MR_n]_{org}$ = the concentration of the metal chelate in the organic phase, $[M^{n+}]_{aq}$ = the concentration of the metal ions in the aqueous phase and $[HR]_{org}$ = the concentration of the chelating agent in the organic phase.

The extraction process can also be presented as consisting of four equilibrium steps (**Figure 3.5**) each with an equilibrium constant as indicated by **Equations 3.16** to **3.23**:



with

$$K_m = \frac{([M^{n+}]_{aq}[R^-]_{aq})^n}{[MR_n]_{aq}} \quad 3.17$$

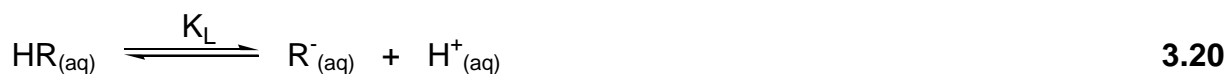
where K_m = the dissociation constant of the neutral metal chelate in the aqueous phase.



with

$$K_D = \frac{[MR_n]_{org}}{[MR_n]_{aq}} \quad 3.19$$

where K_D = the distribution constant of the metal chelate between organic and aqueous layers.



with

$$K_L = \frac{([H^+][R^-])_{aq}}{[HR]_{aq}} \quad 3.21$$

where K_L = the dissociation constant of the chelating agent or weak organic acid in the aqueous layer.



with

$$P_L = \frac{[HR]_{org}}{[HR]_{aq}} \quad 3.23$$

where P_L = the distribution constant of the chelating agent between the organic and the aqueous layers.

Equations 3.24 and **3.25** can be obtained by dividing **Equations 3.19** by **3.17** and **3.21** by **3.23** respectively.

$$\frac{[MR_n]_{org}}{[M^{n+}]_{aq}} = \frac{K_D}{K_m} [R^-]_{aq}^n \quad \mathbf{3.24}$$

$$[R^-]_{aq} = \frac{K_L}{P_L} \cdot \frac{[HR]_{org}}{[H^+]_{aq}} \quad \mathbf{3.25}$$

Substitution of **Equation 3.25** into **3.24** gives the following **Equation 3.26**:

$$D = \frac{K_D K_L^n}{K_m P_L^n} = \frac{[MR_n]_{org} [H^+]_{aq}^n}{[M^{n+}]_{aq} [HR]_{org}^n} \quad \mathbf{3.26}$$

or

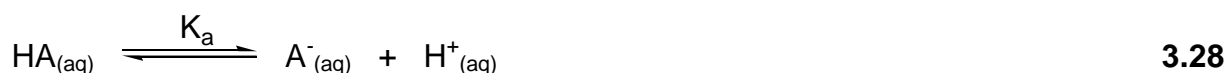
$$D = K_D \frac{[H^+]_{aq}^n}{[HR]_{org}^n} \quad \text{where} \quad \frac{[MR_n]_{org}}{[M^{n+}]_{aq}} = K_D \quad \mathbf{3.27}$$

It is clear from **Equation 3.26** that D is composed of four different equilibrium constants namely, the dissociation constant, (K_m), of the metal chelate, the distribution constant, (K_D), of the metal chelate between the two immiscible layers, the dissociation constant (K_L) of the chelating agent and finally the distribution constant (P_L) of the chelating agent between the two layers. For favourable extraction ($D \gg 1$):

- i. $K_D > 1$ – metal chelate should be highly soluble in organic layer
- ii. $K_L > 1$ – chelating agent should easily dissociate in aqueous layer
- iii. $K_m < 1$ – metal chelate should be stable in aqueous layer (not dissociate)
- iv. $P_L < 1$ – chelating agent should be highly soluble in aqueous layer (insoluble in organic layer)

Equation 3.27 also clearly predicts that the extraction ratio, D, is directly proportional to the $[H^+]$, suggesting an increase in D value with an increase in $[H^+]$.

Another way to determine the relationship between D and K_D of an acid (which it is in the case for $H^+ + MF_6^- \rightleftharpoons HMF_6$ for $M = Ta$ and Nb) is as follows:



where K_a is the dissociation constant of the acid

with

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad 3.29$$

Rewriting **Equation 3.29** gives **Equation 3.30**:

$$[A^-] = \frac{K_a[H^+]}{[HA]} \quad 3.30$$

For the total amount of HA in the aqueous layer as given by **Equation 3.31**:

$$[HA]_{aq}^T = [HA] + [A^-] \quad 3.31$$

Substituting **Equation 3.30** into **3.31**, rearranging and substituting into **Equation 3.12**

$\left(D = \frac{\sum[HA]_{org}}{\sum[HA]_{aq}} \right)$ produces **Equation 3.32**.

$$D = K_D \left(\frac{1}{1 + \frac{K_a}{[H^+]}} \right) \quad 3.32$$

Equation 3.32 clearly indicates that D becomes directly proportional to the $[H^+]$ (especially at $[H^+] \gg K_a$) and will therefore increase in magnitude as the $[H^+]$ increase, as it approaches the K_a value or when it exceeds the K_a value until $D \cong K_D$.

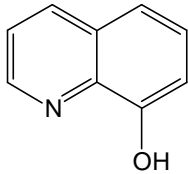
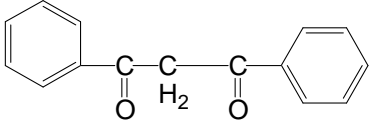
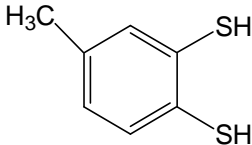
The distribution constant, K_D , for successive extractions can be easily calculated using the following **Equation 3.33**:

$$q_n = \left(\frac{1}{K_D V_r + 1} \right)^n \quad \text{3.33}$$

where q is the fractional amount of solute which remains in the aqueous phase after extraction and V_r is the ratio of organic volume to aqueous volume and n is the number of successive extractions.

Some of the commonly used organic chelating agents are given in **Table 3.5**. These chelating agents are only selective towards certain metal ions at a specific pH range.

Table 3.5: Some organic chelating agents¹²³

Name	Structure	pH of exaction	Extractent	Metal ion
8-Hydroxyquinoline		9.00-9.40	Chloroform	Niobium(V)
Dimethylglyoxime	$\begin{array}{c} \text{H}_3\text{C}-\text{C}=\text{NOH} \\ \\ \text{H}_3\text{C}-\text{C}=\text{NOH} \end{array}$	7.50	Chloroform	Nickel(II)
Dibenzoyl methane		6.00-7.00	Dibenzoyl methane/benzen	Uranium(VI)
Dithiol		-	Diisobutyl ketone	Molybdenum(VI)

A measure of the ability of the system to separate the metal ions, Nb^{5+} and Ta^{5+} for example from one another, is given by the separation factor α which is calculated using **Equation 3.34**¹²⁰ and separation of the different metal species is only viable when $\alpha > 1$. The higher the α -value, the better the separation and less consecutive steps are required.

123. Stary, J. and Irving, H., *The Solvent Extraction of Metal Chelates*, 1964, The Macmillan Company, New, York, pp. 94 – 137

$$\alpha = \frac{K_{D(\text{Nb})}}{K_{D(\text{Ta})}}$$

3.34

The choice of the extracting solvent (organic) is mainly governed by the stability and solubility of the analyte complex, the primary solvent from which the solute is extracted as well as other requirements which are normally dictated by the quantification methods. Some of the basic requirements to be met by the choice of system are as follows:

- Extracting solvent must be insoluble in the primary solvent of the liquid mixture
- The extracting solvent's density should be different from that of the liquid mixture
- There should be a distinct separation of the liquid phases
- The extracting solvent should have a low viscosity since it is difficult to get quantitative separation in viscous medium
- The solvent should be cost effective, non-toxic and non-flammable
- The extracting solvent should have high selectivity for either of the analytes under investigation; that is, increase the separation factor, α value
- The extracting solvent must have a low boiling point for easy removal and concentration after extraction¹²⁴ without a significant loss of the analyte especial when an analysis is to be performed with ICP-OES.

The physical properties of some of the most widely used solvents for the separation of tantalum and niobium are listed in **Table 3.6** below (see also **Chapter 2, Section 2.3.3**).

124. Majors, R. E., 2008, "Practical Aspects of Solvent Extraction" [Internet]. [cited 2012 May 02]. Available from: <http://www.chromatographyonline.com/lcgc/article/articleDetail.jsp?id=570534>

Table 3.6: Physical properties of the most commonly used extractants for the separation of tantalum and niobium.

Extractant	Density (g/ml)/ 20 (°C)	Solubility in water	Boiling point (°C)	Flash point (°C)
Methyl isobutyl ketone	0.802	1.91%, 20 °C	116.5	14
Diiso propyl ketone	0.811	0.43%, 20 °C	124	15
Tributyl phosphate	0.973	0.4%, 20 °C	289 (decomposition)	146
2-Octanol	0.819	0.096%, 25 °C	180	60 – 88

Equally important to the extraction of solutes into the organic phase is the recovery of the analyte from the organic extract. There are several ways to recover the solute from the extractant solvent. These include evaporation of the solvent or the stripping (back extraction) of the solute from the organic solvent. The evaporation of the solvent requires that the solute is non-volatile and thermally stable. The commonly used method of solute recovery is the stripping of the solute using an aqueous solution with a different pH (from the original solution) or which contains a complexing agent that forms complex which dissolves quantitatively in the aqueous layer. The use of solvent extraction as separation technique is generally simple and separations may be performed using inexpensive equipment such a separating funnel (for laboratory scale operations). Large amounts of literature on solvent extraction techniques are available and method development is relatively simple.

However, the separation process is performed after dissolution of a solid sample and the conversion of an analyte into an extractable form. Other disadvantages of the solvent extraction method include emulsion formation that may occur during extraction with some solvents and require a high concentration of acid in the aqueous layer to overcome the problem, the need to evaporate the organic solvent since this makes the process lengthy and labour intensive and large amounts of organic waste can be generated especially when the extraction step needs to be repeated with additional portions of the solvent. Distillation however can recover most of the organic solvent for the subsequent separation.

3.4.2.4 Ion exchange separation

In this study ion exchange was used as the chromatographic separation process. This process entails the competition between metal ions in the mobile phase with ionic sites that are available on the stationary phase. The difference between the ionic bonds between the mobile metal ions and the stationary counter ionic sites enable the successful separation of the different metal species in solutions.

Chromatography generally refers to the separation of components in a sample which is based on the difference in their distribution between two phases namely, stationary and mobile phases as illustrated by the general reaction in **Equation 3.35**. The distribution coefficient can be calculated from **Equation 3.36**.¹²⁵



where m = mobile phase and s = stationary phase.

$$K_s = \frac{[X]_s}{[X]_m} \quad \text{3.36}$$

where $[X]_m$ and $[X]_s$ are the concentrations of component X in the mobile and stationary phase at equilibrium respectively.

A large K_s value indicates that the solute is being strongly retained by the stationary phase. Whether the mixture components will be separated depends on the difference between their retention factor (or capacity factor), k , which is calculated as indicated in **Equation 3.37**.¹²⁰

$$k = \frac{t_r - t_o}{t_o} \quad \text{3.37}$$

125. Skoog, A. D., Holler, F. J. and Nieman, A. T., *Principles of Instrumental Analysis*, 5th ed., 1998, Harcourt Brace College publisher, Philadelphia, p. 675

where t_0 is the time required for the mobile phase to pass through the column and it is the same for all the components and t_r is the time taken to the appearance of the analyte peak.

Retention factor between 1 and 10 is normally preferred or indicative of successful separation. The value of k is also influenced by the charge or oxidation state of the metal ion. The k value for a SO_3^- cation exchange resin is for example in the order $\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+} < \text{Th}^{4+}$.

The separation factor, α , is used to indicate the degree of separation between two different solutes X and Y. This factor is defined as the ratio of the distribution constant (or coefficient) of the more retained species, e.g. X to the distribution constant of the less retained species Y as indicated by **Equation 3.38**.¹²⁵

$$\alpha = \frac{k_X}{k_Y} \qquad \qquad \qquad \mathbf{3.38}$$

Successful separation is normally indicated by α -value larger than 1 and the larger the better. Other experimental parameters that may affect the separation of components by the column include:

- a) Stationery phase particle size; smaller particle size have a larger surface area and better separation of the components,
- b) Column packing
- c) Column length
- d) Column diameter
- e) Flow rate of the mobile phase: elution process is usually carried very slowly if better separation is to be achieved and may require high volume of eluent
- f) pH and temperature of the solutions and
- g) Volume of eluent

The number of theoretical plates, N , in the column are regarded as a measure of column efficiency and the larger the number of the theoretical plates the higher the column efficiency. The number of theoretical plates can be determined using **Equation 3.39**. For high column efficiency, the height equivalent of a theoretical plate

(H) which is the column length divided by the number of the theoretical plates should be as short as possible.¹²⁰

$$N=16 \left(\frac{t_r}{w} \right)^2 \quad 3.39$$

where N= number of the theoretical plates and w = the peak width.

Alternatively N can be calculated using the width of the peak measure at half its maximum height according to the following **Equation 3.40**:^{120,125}

$$N=5.54 \left(\frac{t_r}{w_{1/2}} \right)^2 \quad 3.40$$

An example of a typical anion exchange resin structure is given in **Figure 3.6**. The exchange reaction occurs on the quaternary ammonium functional group. The possible exchange reaction is shown in **Equation 3.41**.

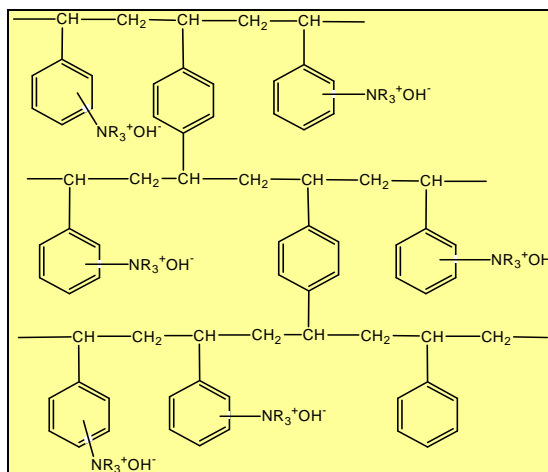
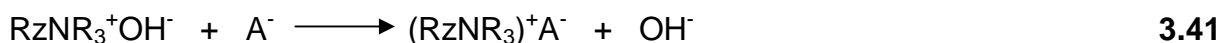


Figure 3.6: Anion exchange resin structure.



Resins are divided into cation exchangers or anion exchangers depending on the functional groups substituted onto the stationary phase which also determines the charge of the resin. The cation exchange resins have affinity for positive ions while

anion exchangers have affinity for negative counter-ions. Resins are further grouped into strong or weak ion exchangers. Strong ion exchange resins are general characterized by the stability of their exchange capacity in a broad pH (2 to 12) range.¹²⁶ The advantages of strong ion exchange resins include simple method development and experimental conditions optimization as well as normally having wider applicability since the separations are not easily affected by pH change. The exchange capacity of weak ion exchange resins is strongly dependent on the pH and is only able to enable exchange in a very narrow pH range. Advantages of both strong and weak ion-exchange resins are high selectivity, use of simple equipment (commonly columns in the laboratory) and wide applicability.

Ion exchange separation method is generally a relatively slow process. The narrow pH control required for weak ion exchange resins can also make optimization of the separation condition difficult. Sometimes high volumes of eluent/s are required to obtain complete separation analytes.

3.5 Analytical techniques used in this study

The success of any separation and purification process is finally evaluated by the percentage recovery and the purity of the different target elements. It is therefore extremely important that every step of the beneficiation procedure is monitored and assessed for its successfulness. This is achieved by the quantification of all the elements isolated during that specific step. This determination of the chemical composition at every level also assists with the mass balance of all the main elements as well as that of the impurities obtained during the whole process which is extremely important for the optimization of the different processes or steps in the beneficiation process. Therefore, the selection of the methods that are suitable for the accurate determination of tantalum and niobium in this study, as well as that of the impurities involved is very important.

The overriding factor in the method selection in this study was the complexity of the tantalite mineral in terms of the elemental composition, the high degree of inertness

126. Levin, S., Analytical Consulting, Medtechnica, "Ion Exchange Theory" [Internet]. [cited 2012 July 20]. Available from: http://www.forumsci.co.il/HPLC/IC_Pharm.pdf

of tantalum and niobium towards many chemical reagents as well as the chemical similarities of the two main elements. The analytical techniques used in this study were selected on the basis of their availability as well as their applicability for the different stages of the beneficiation process. These techniques include X-ray diffraction analysis (XRD) and infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), microanalyser, UV-Vis, ICP-OES and ICP-MS. A concise description of the basic theoretical concepts behind these techniques will be discussed in the following paragraphs.

3.5.1 Characterisation of products

3.5.1.1 UV-Vis analysis

UV-Vis spectroscopy was used in this study as a complementary technique for the characterization of some of the products isolated in the study. Three different spectroscopic techniques were used for the stoichiometric determination of the metal-ligand ratio namely (i) the Job's method of continuous variation, (ii) the mole ratio method and (iii) the slope ratio method.

Job's method of continuous variation entails mixing of the solutions of the ligand and the metal with identical concentrations but varying mole ratio while in the mole ratio method, the metal concentration is kept constant and only the ligand concentration is varied. In both methods the absorbances are plotted against the mole fraction of either the cation or the ligand as illustrated in **Figure 3.7a** (continuous variation method).

In the mole ratio method, the metal concentration is kept constant while the ligand concentration is varied. The absorbance of the solution increases with the increasing mole ratio of the ligand until a stoichiometric amount of the ligand has been added and the absorbance becomes constant as indicated in **Figure 3.7b**.

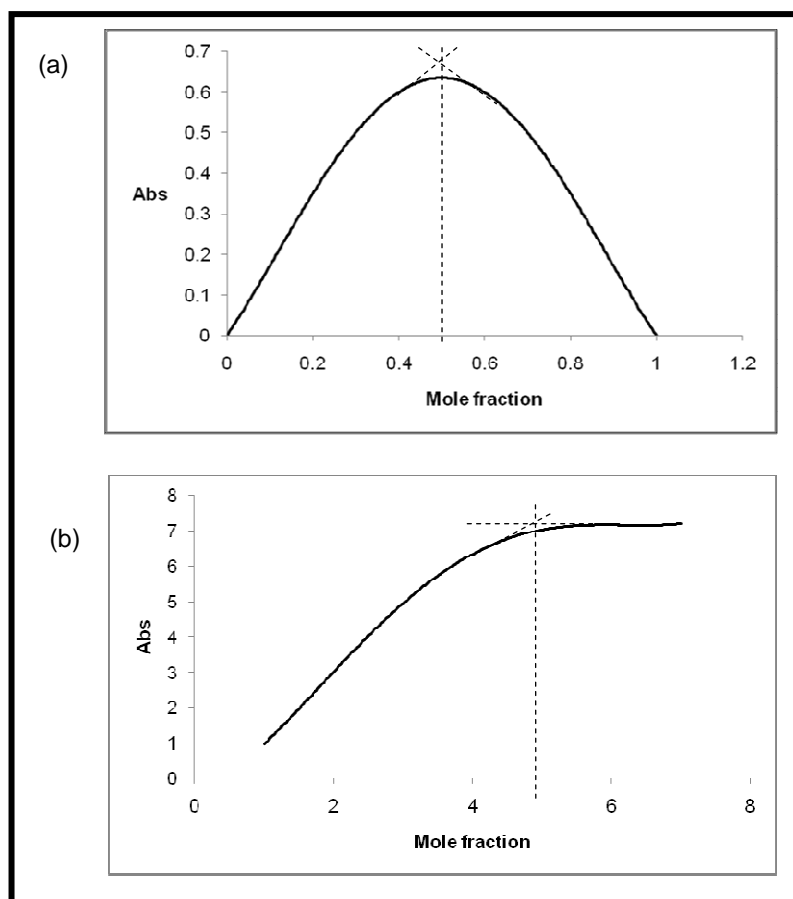


Figure 3.7: (a) Continuous variation and (b) mole ratio methods for complex stoichiometric determination.

Tangents are then drawn on both sides of the maximum (or minimum) of the curve in the continuous variation method and on the increasing and the plateau sides in the mole ratio method. The point where the two tangents meet corresponds to the stoichiometric ratio between the metal and ligand. A line perpendicular to the x-axis is drawn from the point where the two tangents cross each other to determine the mole fraction of the metal.

In the slope ratio method two graphs of absorbance *versus* concentration is constructed for a constant ligand concentration while the metal concentration is varied or *vice versa*. The ratio of the slopes of the two graphs is the stoichiometric ratio between ligand and metal.

The applicability of all the three abovementioned requires that the following conditions be met:

- a) Concentration range should obey the Beer' law
- b) Single complex must exist under the experimental conditions since the methods are effective only when one complex is formed
- c) Total concentration of the two reacting species must be maintained constant
- d) Ionic pH and strength of the solutions should stay constant

3.5.1.2 IR analysis

Infra red spectroscopy was used to try and identify any stretching frequencies which could add to the positive identification of the unknown compounds obtained in different steps in the study. The IR spectrum lies between the microwave and visible regions of the electromagnetic spectrum as indicated in **Figure 3.8**.

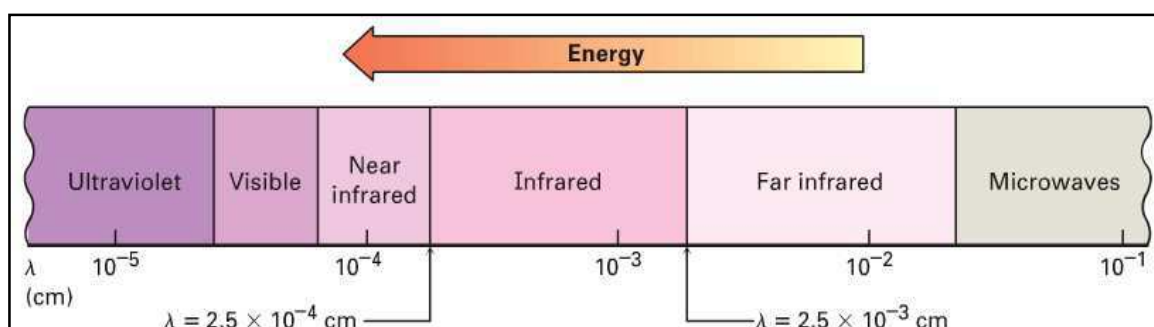


Figure 3.8: The electromagnetic spectrum.

The technique deals with the absorption measurement of the IR radiation by the sample. The IR radiation causes different types of vibrations of the bonds within the molecule. The vibrations include stretching and bending modes. The different vibration modes are indicated in **Figure 3.9**.

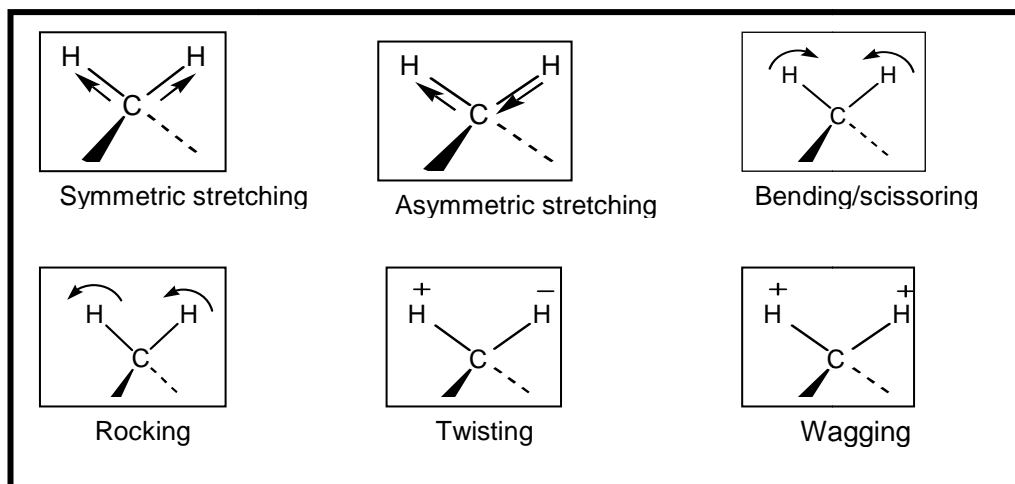


Figure 3.9: Infrared vibrational modes.¹²⁷

The application of IR for structural elucidation is based on the fact that different functional groups absorb characteristic wavelengths of the IR radiation. The regions where certain types of groups absorb the IR radiation are summarized in **Figure 3.10**.

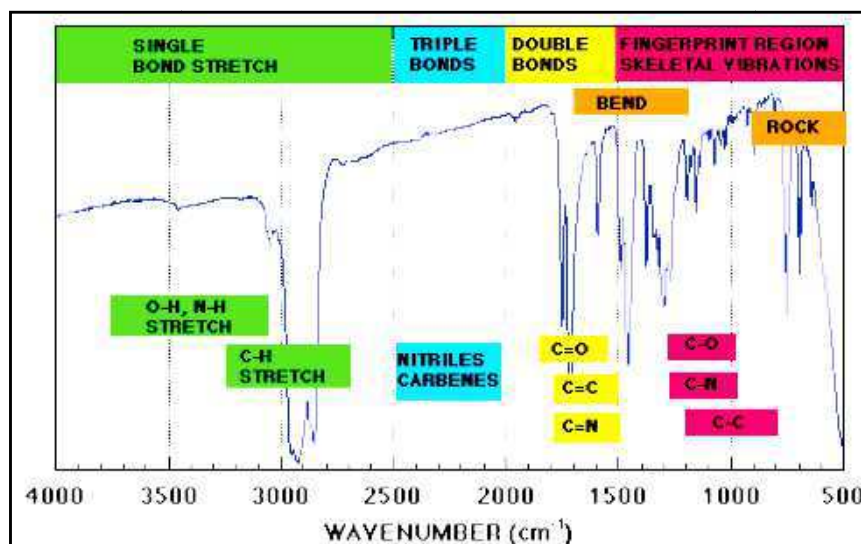


Figure 3.10: Characteristic regions of the infrared absorptions.

127. Williams, D. H. and Fleming, I., Spectroscopic methods in organic chemistry 3rd ed., 1980, McGraw-Hill Book Company (UK) limited, London, p. 39

3.5.1.3 XRD analysis

X-ray diffraction is a result of the scattering of X-rays when it strikes a crystalline material. An X-ray beam hits a crystal surface at an angle θ and gets reflected at the same angle. The unscattered portion of rays penetrates through the material to the second layer where further scattering takes place and the process continues to the third and fourth layers (see **Figure 3.11**).⁶⁸ The whole process of irradiation and scattering is summarized in Bragg's law (**Equation 3.42**) which relates the scattering angle (2θ), the wavelength of the radiation (λ) and the spacing of the diffracting planes in the material (d).

$$n\lambda = 2d \sin \theta$$

3.42

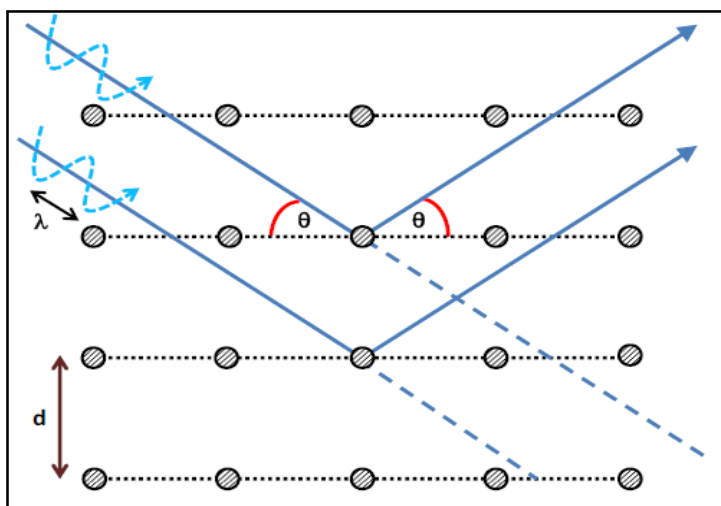


Figure 3.11: Illustration of the basic principles in X-ray diffraction.¹²⁸

The qualitative analysis by XRD is based on the fact that an X-ray diffraction pattern is unique for each material and a positive identification of an unknown sample can be made by matching its diffraction pattern with reference samples.

XRD allows for rapid and non-destructive analyses of multi-component mixtures with a simple sample preparation. There are several databases which include the International Centre for Diffraction Data's Powder Diffraction which allows for the

128. Mitchell, S. and Pérez-Ramírez, J., "Surface Science and Methods in Catalysis, 529-0611-00L, X-ray diffraction", ETH Zürich, Switzerland

comparison of the unknown sample diffraction patterns with that of known standards to obtain a positive identification of the sample. One of the disadvantages of XRD technique is that an identification of characteristic spectra becomes complex and difficult if the sample contains a mixture of different crystalline compounds such as those observed in geological samples. Additionally, the technique does not provide elaborate X-ray patterns for amorphous samples which prevent or hamper their identification using this process.

3.5.1.4 Quantitative analysis by ICP-MS and ICP-OES

The inductively coupled plasma optical emission spectroscopy (ICP-OES) technique is based upon the measurement of the spontaneous emission of photons from atoms, ions and molecules after they have been excited in a RF discharge (**Figure 3.12**). The plasma (6000 to 10000 K) is used to excite these particles (atoms, elemental ions and molecules) in the nebulised spray containing the analyte sample.

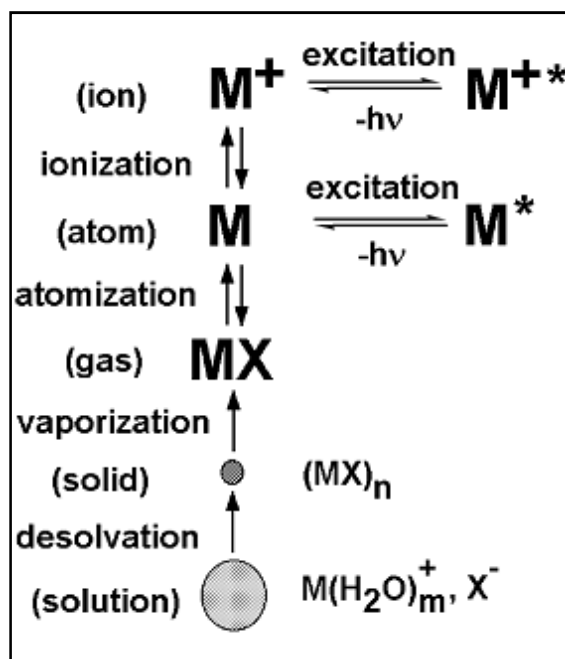


Figure 3.12: Processes from sample droplet introduction to excitation and photon emission in an ICP RF discharge.¹²⁹

129. Boss, C. B. and Fredeen, 1997, Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, [Internet]. [cited 2012 June 28]. Available from <http://atoomspectrometrie.nl/lcpconceptsbook.pdf>

The sample introduction system consists of a peristaltic pump connected to a nebuliser. The nebuliser produces an aerosol that is sprayed into the spray chamber, and in the spray chamber the smallest aerosols follow the gas flow into the plasma. The main analytical advantages of the ICP-OES include its multi-elemental analysis capabilities in various sample matrices. Other advantages include the high operating temperature of the ICP which enables the excitation of refractory elements, and also makes the technique less susceptible to matrix effects. Additionally, ICP-OES has relative low detection limits (see **Figure 3.13**) which allows for trace element analysis as well as target elements with substantially high concentration levels and produce linear calibration curve in orders of magnitude.

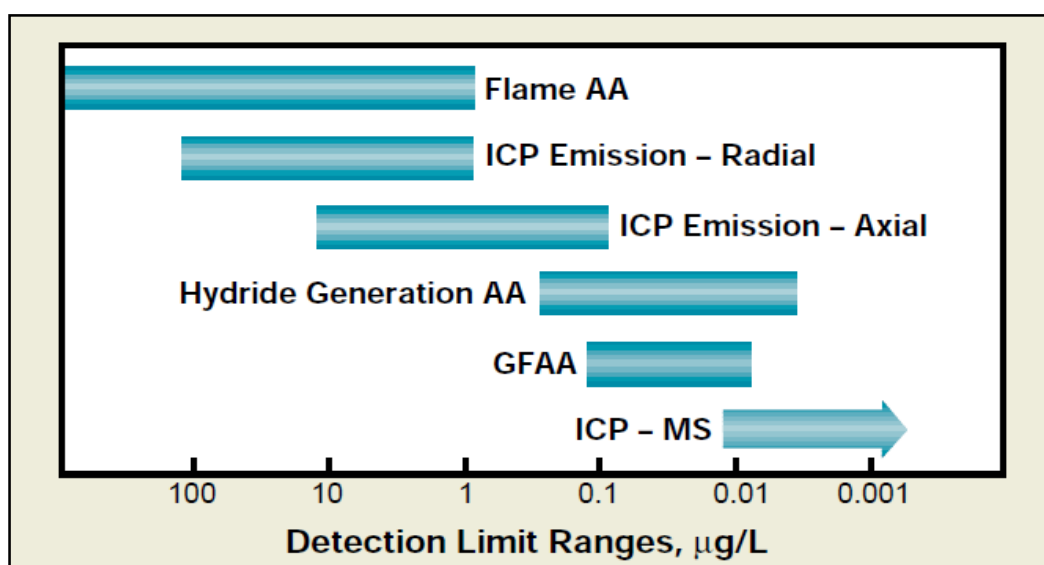


Figure 3.13: Comparison detection limit ranges for the major atomic spectroscopy techniques.¹³⁰

The main disadvantages of the ICP-OES technique are the spectral interferences mainly when a complex matrix such as a mineral sample is analysed. The interferences include the spectral overlap and matrix effects. Spectral overlap is normally due to the presence of other elements in solution which emit at a similar line to the analyte line. An example is the interference of the As 228.812 nm line upon the

130. AAS, GFAAS, ICP or ICP-MS? Which technique should I use? *An elementary overview of elemental analysis*, February 2001, [Internet]. [cited 2012 June 29]. Available from http://www.thermo.com/eThermo/CMA/PDFs/Articles/articlesFile_18407.pdf

Cd 228.802 nm line¹³¹ during Cd analysis. Matrix effects originate from a combination of sources from the sample preparation (chemical reagents) to the instrument settings.

Spectral overlap can however be avoid by proper line selection for each analyte analysis. Matrix effects on the other hand can be overcome by using a blank solution, dilution of solutions or matching the sample and standard matrices. Alternatively, analytical techniques such as standard addition method can be used to minimize the matrix interferences.

The processes from the sample introduction to the plasma formation are exactly the same in both OES and MS. The plasma is formed (see **Equation 3.43**) by the interaction the argon gas with the fluctuating magnetic field produced by the RF generator.



In ICP-OES, the role of the plasma torch, which is normally vertical, is to generate photons of light due to the excitation of a ground state atom to a higher energy level. Upon relaxation the activated atoms are allowed to fall to the ground state and this decrease in energy is released as photons at the element characteristic wavelength (see **Figure 3.14**). The emission signal is directly proportional to the concentration of the element in the sample.

131. Winge, R.K., Fassel, V.A., Peterson, V.J., Floyd, M.A., *Inductively Coupled Plasma – Atomic Emission Spectroscopy. An Atlas of Spectral Information*. 1993. Appendix B

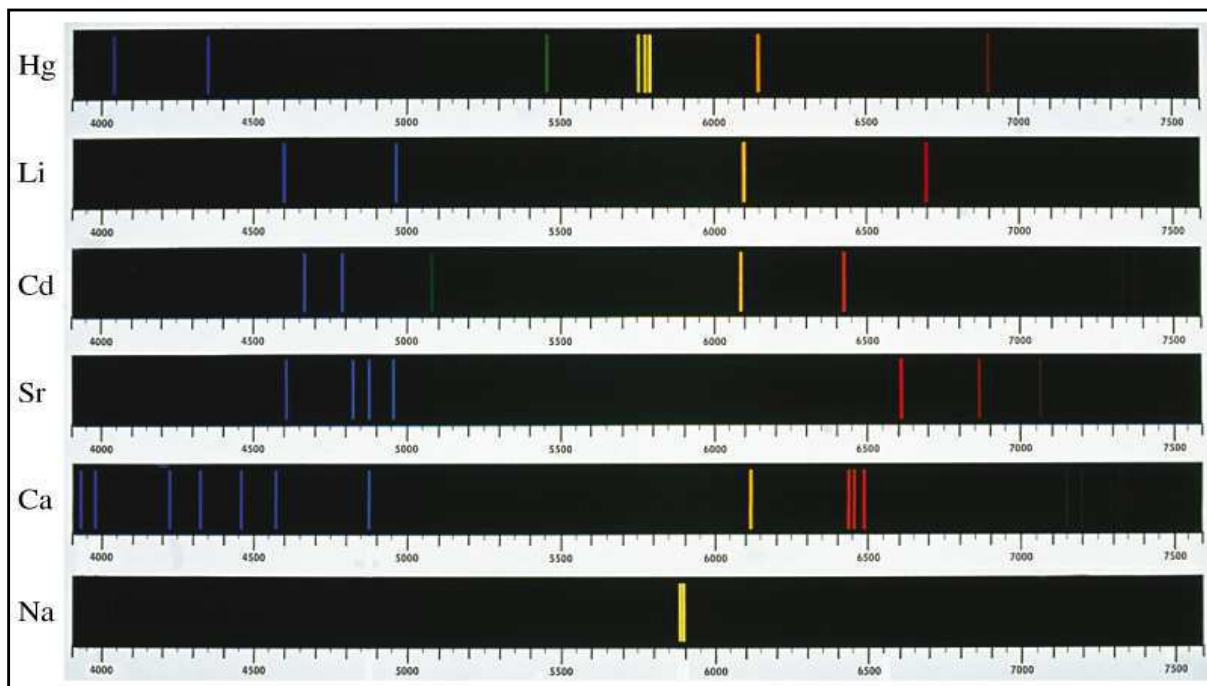


Figure 3.14: Characteristic emission spectra of selected elements.¹³²

Apart from the detection method, the major difference between ICP-MS and ICP-OES is in the role of the plasma torch. In ICP-MS the torch is used to produce positively charged ions by bombarding the analyte atoms, which are typically neutral, with high energy electrons as indicated in **Equation 3.44**.^{133,120}



Once produced, the ions are directed into the mass spectrometer through the MS interface region (see **Figure 3.15**) which consists of two cones, usually made of nickel, each with a small orifice to allow passage of ions into the ion optics where they are directed to the mass separator.¹³⁴ In the separation device, the separation of the ions is based on the mass to charge ratios (m/z) and only the analyte ions with a

132. Line spectra of selected elements, [Internet]. [cited 2012 July 20]. Available from http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/07.html

133. Thomas, R., "Practical Guide to ICP-MS" [Internet]. [cited 2012 June 07]. Available from <http://www.instrument.com.cn/ilog/upfile/file/20110110/2011110171340.pdf>

134. Skoog, D. A., Holler, F. J. and Nieman, T. A., *Principles of Instrumental Analysis 5th ed.*, Harcourt Brace & Company, Philadelphia, 1998, pp. 262 – 263

certain mass-to-charge ratio are allowed through to the detector and all the nonanalyte, interfering, and matrix ions are filtered out. The ions then pass to the detector which gives an electrical signal which is proportional to the concentration of the elements in the sample.

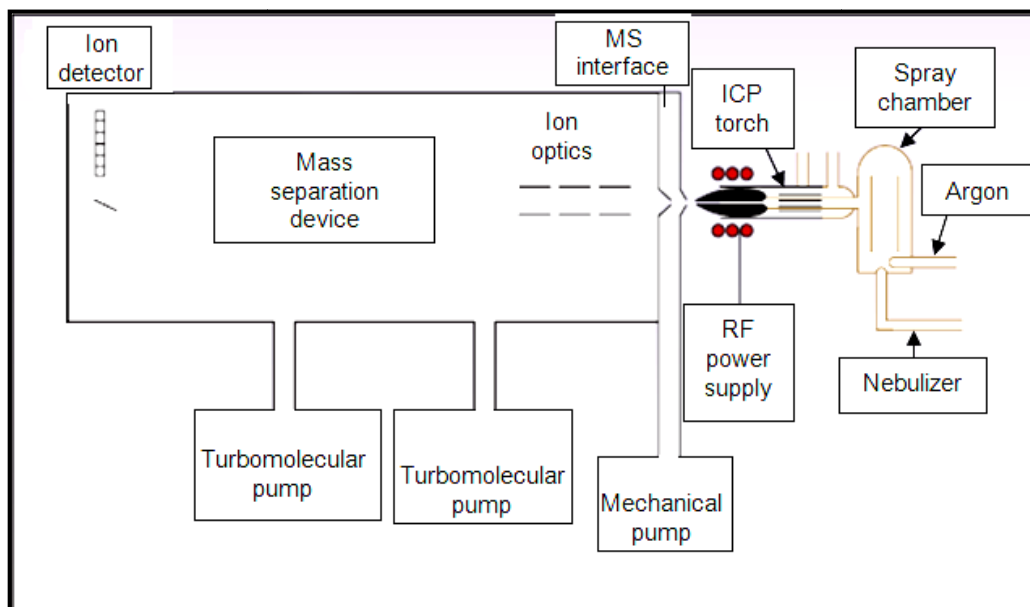


Figure 3.15: The basic components of the ICP-MS instrument.¹³⁵

The high sensitivity of the ICP-MS which enables achievement of the detection limits in the part per trillion (ppt) range originates from the generation of relatively large quantities of positively charged ions.¹³³ ICP-MS has detection capabilities which are 10-100 times better than those of the ICP-OES (see **Figure 3.13**). Additionally, ICP-MS has the ability to measure isotopic ratios. Other advantages include a wide dynamic range and multi-elemental analysis capabilities.

ICP-MS instruments are however much more expensive than ICP-OES. Another disadvantage of ICP-MS is that its measurements are highly affected by high levels of total dissolved solids compared to that of ICP-OES. The high levels of total dissolved elements can result in deposition of salts on the sampler cones, especially during prolonged analytical runs and caused signal changes and reduce the signal

135. Thomas, R., "A Beginner's Guide to ICP-MS", [Internet]. [cited 2012 June 07]. Available from http://matematicas.udea.edu.co/~carlopez/beginner_guide_icpms.pdf

stability. Additionally, higher levels of dissolved salts may cause polyatomic interferences (discussed below) on key target elements. Other requirements such as the need for a sample dissolution step prior to analysis are the same for both the ICP-MS and ICP-OES.

Although interferences in ICP-MS are relatively fewer than in ICP-OES,¹³⁶ proper measures have to be taken upfront to minimize or correct for the type of interferences discussed above during the analyte measurements. Common interferences in ICP-MS are due to isobaric (interelement), molecular (or polyatomic) and doubly-charged ions. Interelement interferences are normally caused by the isotopes of different elements with similar mass-to-charge ratios. Polyatomic ion interferences on the other hand are caused by ions consisting of more than one atom while doubly-charged ions interferences are due to the presence ion with twice the mass of the analyte in solution. Some examples of common interferences are given in **Table 3.7**.

Table 3.7: Examples of interferences which occur in ICP-MS

Element	m/z	% Abundance	Potential interferences		
			Interelement	Polyatomic ions	Doubly-charged ion
Ca	40	199,80	⁴⁰ Ar		-
As	75	100	Sm ²⁺ Eu ²⁺ Nd ²⁺	⁴⁰ Ar ³⁵ Cl	-
Ba	138	71,7	La Ce	-	-
Cu	63	69,2	-	⁴⁷ Ti ¹⁶ O	-
Ga	69	60,1	Ce ²⁺ Ba ²⁺	VO	-
Mn	55	100	-	⁴⁰ Ar ¹⁵ N	-
Sc	45	100	-	-	⁹⁰ Zr ²⁺

Corrections due to these types of interferences usually include the compensation for background ions which are contributed by the constituents of the sample matrix, plasma gas and other reagents such as acid. Working with dilute solutions also helps to minimize the clogging of the skimmer cones and the nebulizer.

136. van de Wiel, H. J., 2003, "Determination of elements by ICP-AES and ICP-MS" National Institute of Public Health and the Environment (RIVM) Bilthoven, The Netherlands

3.5.1.5 C, H and N quantification using a CHNS-microanalyser

For the quantitative determination of carbon, hydrogen and nitrogen atoms, microanalysis using TruSpec Micro was found to be extremely useful. The method involves the burning of a small sample of known mass of sample in an excess of oxygen which have been introduced to oxidisable tin capsules in a high temperature (900 °C) furnace (Figure 3.16). During the combustion process the elements C, H and N are converted into gaseous oxidation products, CO₂, H₂O and mixture of N₂ + NO_x. The oxidation of the elements is catalysed by the tin container and tungsten trioxide. The resulting gasses (CO₂, H₂O, SO₂ and N₂+ NO_x) are transported with helium gas (a carrier) through a silica tube which is packed with copper granules which in turn absorb the excess oxygen in the system and reduce the nitrogen oxide to elemental nitrogen. The gases are then passed to a thermal conductivity detector.¹³⁷

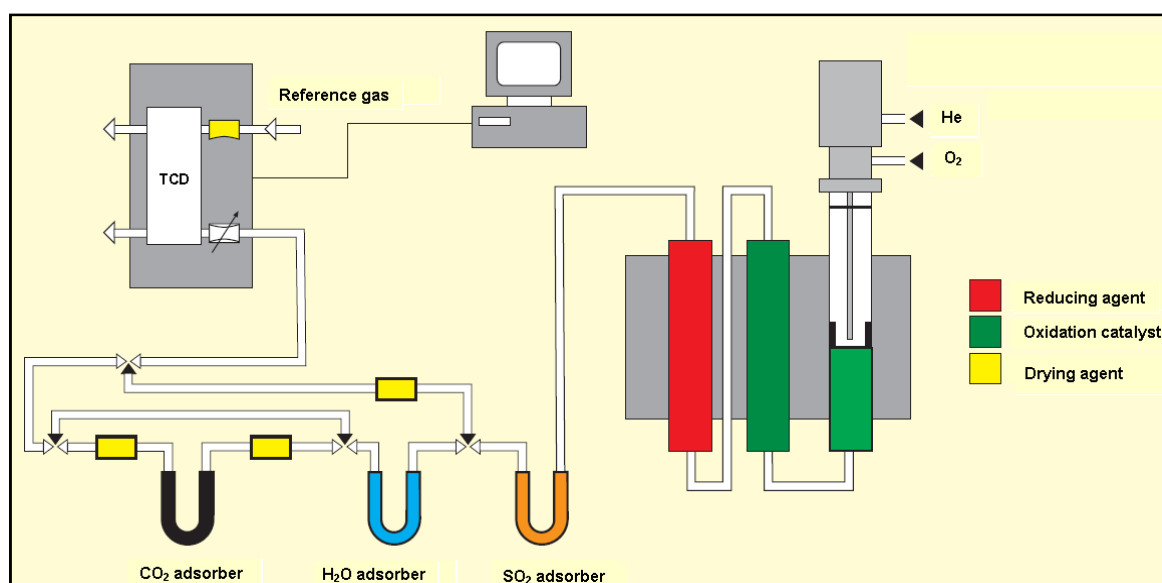


Figure 3.16: The basic set up for a CHNS microanalyser¹³⁸

Major advantages of this technique include the quick (less than 5 min) and simultaneous determination of C, H, N and S as well as a simple sample preparation

137. Rouessac, F. and Rouessac, A., *Chemical Analysis: Modern Instrumentation Methods and Techniques*, 2nd ed., 2007, John Wiley & Sons, Ltd, San Francisco, pp. 356 – 360, 441 – 447

138. vario MACRO Elemental analysers [Internet] (cited 15 June 2012) Available from http://www.tecnologiaaplicada.com/productos/Elementar/pdf/vario_MACRO_Bochure_e.pdf

procedure. The application of this technique is mainly in organic and organometallic compounds but is also use extensively in metal analysis where C, H, N, S are critical.

Weighing of samples for analysis which are normally in mg sizes increases require special care to reduce potential for errors in the final results. As indicated above, the CHNS microanalyzer is a combustion technique. As such excess oxygen is required to ensure a complete conversion of the sample to products. This in turn means that for larger sample amounts large copper filled silicon tubes for removal of excess oxygen will be need and thus the copper usage is significant.

3.5.1.6 Fluoride quantification by NMR

In this study the fluoride content in some of the isolated products was determined/quantified using nuclear magnetic resonance (NMR) spectroscopy. This technique exploits elements with non-zero nuclear spin, that is, nuclei which possess a magnetic moment. An example of NMR active nuclei together with their respective relative sensitivities (probability of a spin transition) is given in **Table 3.8**.

Table 3.8: Example of magnetic isotopes for NMR spectroscopic analysis¹³⁹

Element/Name	Isotope Symbol	Nuclear Spin	Sensitivity vs ^1H
Hydrogen	^1H	1/2	1.000000
Fluorine-19	^{19}F	1/2	0.829825
Boron-11	^{11}B	3/2	0.132281
Tantalum-181	^{181}Ta	7/2	0.03579
Magnesium-25	^{25}Mg	-5/2	0.00027
Carbon-13	^{13}C	1/2	0.000175
Europium-151	^{151}Eu	5/2	0.084211

The application of NMR in quantitative analysis is based on the fact that the integral intensity of the NMR peak is proportional to the number of nuclei that are spinning to

139. Landau, L. D. and Lifshitz, E. M., *Quantum Mechanics*, 2nd ed., 1965, Pergamon Press, Oxford, p. 452

produce it.¹⁴⁰ The ^{19}F (with a spin $\frac{1}{2}$ nuclei) natural abundance of 100% and high sensitivity of ^{19}F to NMR detection¹⁴¹ makes the ^{19}F NMR spectroscopy technique an efficient tool for microanalysis of fluorine. However, because ^{19}F NMR exhibits a wider range of chemical shifts which are sensitive to the chemical environment, it is important to identify a fluoride signal that changes with the fluoride concentration for quantitative analysis. Other than the NMR instrument being relatively expensive, quantitative analysis of fluorine by this technique is a fairly easy process.

3.6 Conclusion

The chemical processes discussed in the above sections have been investigated with commercial samples which have simple matrices. The knowledge which was acquired from these studies was passed onto the mineral samples with complex matrices as indicated in the study methodology section. The dissolution study using Ta_2O_5 and Nb_2O_5 which have similar properties to the tantalite mineral towards dissolution has indicated that a flux fusion method using $\text{NH}_4\text{F}\cdot\text{HF}$ as a flux salt would be effective for the digestion of the tantalite mineral and the separation of Ta and Nb.

Based on the results from other studies (see **Section 3.2**), other processing methods such as magnetic separation for the removal of magnetic impurities and acid leaching using H_2SO_4 for radioactive material removal were also studied for the beneficiation of tantalite. Other separation and purification techniques studied include precipitation, solvent extraction using aliphatic ketones and ion exchange chromatography. The understanding of the working principles as well as the strengths and limitations of these techniques is extremely important for the optimization of the processes.

ICP-OES and ICP-MS were the main methods for the quantification of all the elements in this study while additional information was obtained using techniques

140. He, W., Du, F., Wub, Y., Wang, Y., Liu, X., Liu, H. and Zhao, X., 2006, "Quantitative ^{19}F NMR method validation and application to the quantitative analysis of a fluoro-polyphosphates mixture", *J. Fluorine Chem.*, **127**: pp. 809 – 815

141. Chekmenev, E. Y., Chow, S. K., Tofan, D., Weitekamp, D. P., Ross, B. D. and Pratip Bhattacharya, P., 2008, "Fluorine-19 NMR Chemical Shift Probes Molecular Binding to Lipid Membranes" *J Phys Chem B.*; **112**(20): pp. 6285 – 6287

such as UV-VIS, IR, NMR and microanalysis where necessary. In general the separation and purification of tantalum and niobium from the tantalite mineral in this study was accomplished using a combination of carefully selected digestion procedure(s), separation and determination techniques.

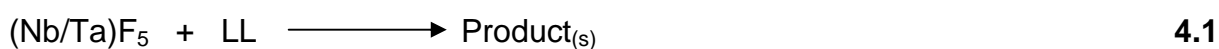
4 Separation of TaF₅ and NbF₅ by selective precipitation

4.1 Introduction

The separation and production of niobium and tantalum from their mineral ores have always depended heavily on the utilisation of the halogen chemistry of these elements. The most important processing routes entail the halogenation of the primary mineral ores by two main methods, namely chlorination and fluorination (see **Chapter 1, Section 1.4.2** and **Chapter 2, Section 2.3.2**) followed by distillation, liquid-liquid extraction and to a lesser extent fractional crystallisation as the K₂MF₇ salts. It is mainly the differences in the physical and chemical properties of the halogen compounds that allow for the successful separation and isolation of the two elements. The difference in the boiling points of the pentachloride complexes (248.2 and 239.4 °C) for example enables the separation of the two elements by fractional distillation.⁴² The fluoride compounds on the other hand are important for the successful separation by solvent extraction. The success of solvent extraction is based on the solubility differences of the niobium and tantalum fluoride complexes (HTaF₆ and HNbF₆) in organic solvents at different acidic conditions. Excellent separation is achieved with this method and as such has become an important industrial method for the separation and production of Ta and Nb. The major disadvantage however, is the use of potentially toxic chemicals such as HF for the dissolution of the mineral ores as well as the subsequent separation steps. It is therefore important to investigate other dissolution methods which are compatible with separation techniques such as precipitation, solvent extraction and ion exchange chromatography.

In this part of the study a new separation method for Ta and Nb was developed using a simple matrix sample (synthetic mixture of TaF₅ and NbF₅) before applying the method to the more complicated tantalite matrix. The chapter describes the development of a precipitation method for the separation of niobium and tantalum (see **Figure 4.1**). The pentafluorides were selected due to their solubility in a

relatively wider range of solvents which include organic solvents such as ethanol and carbon tetrachloride as well as their possible formation from the ammonium bifluoride dissolution of the pentoxides (see **Chapter 5**). The high solubility of the pentahalide complexes would also facilitate the evaluation of a wider range of chelating or precipitating agents. A prerequisite for using selective precipitation as separation method is that either niobium(V) or tantalum(V) should form insoluble, but stable products with the addition of a precipitant (**Equation 4.1**) in the presence of the other metal.



The chapter will also include the characterisation of the isolated precipitate using microelemental analysis, IR, UV-Vis spectroscopy, ^{19}F -NMR and ICP-OES.

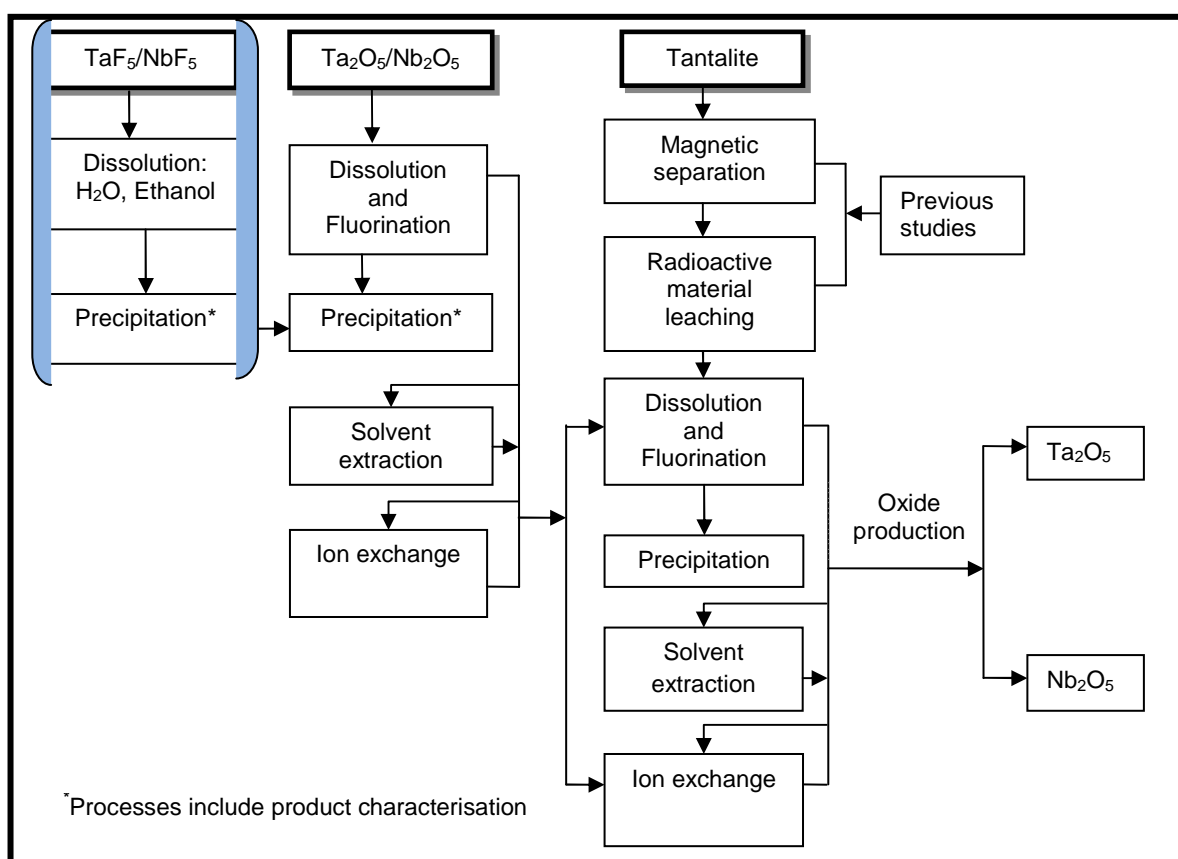


Figure 4.1: Flow diagram illustrating this part of the study (highlighted section) in the separation of Ta and Nb.

4.2 General experimental methods

4.2.1 Reagents and equipment

High purity TaF₅ (98%), NbF₅ (99.9%), 2,2-bipyridine-4,4'-dicarboxylic acid, 2-hydroxyquinoline, neocupoine, sodium citrate dihydrate and imminodiacetic acid were bought from Sigma Aldrich while L-tryptophan, 4-(dimethylamino)-pyridine, *o*-phenylenediamine, *m*-phenylenediamine and *p*-phenylenediamine were sourced from Merck. ICP standard solutions containing 1000 mg/L Ta and Nb, analytical grade methanol, ethanol and D₂O were also bought from Merck while the analytical grade H₂SO₄ (97%) was bought from Associated Chemical Enterprises. Double distilled water was used in all cases.

Grade B glass volumetric flasks and micro-pipettes bought from Merck and Lasec respectively were used for samples preparations. Centrifugation was performed in a rotor supplied by MSE while a Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer controlled by a computer was used for the qualitative and quantitative analysis of Ta and Nb in the solutions. A Bruker Avance II 600 NMR spectrometer was used for the quantitation of the fluoride content while a TruSpec Micro CHNS bought from LECO was used for the elemental carbon, hydrogen and nitrogen analyses. Absorbance measurements were performed on a Cary 50 UV-visible spectrophotometer using a 1 cm path length quartz cell while the infrared spectra were obtained with a Scimitar Series Digilab spectrometer. pH data was collected using a Eutech CyberScan pH 1500 bench Meter. The average values for the results in this chapter are reported based on the standard deviations to indicate the uncertainty in the last digit of the value.

4.2.2 Preparation of ICP-OES calibration solutions and measurements

Standard solutions for ICP-OES analysis were prepared by adding the appropriate volumes of the 1000 mg/L ICP-OES standard solution/s to 10 ml 97% H₂SO₄ in 100.0 mL volumetric flasks and diluted to the mark with double distilled water to prepare 1.0, 3.0, 5.0, 10.0, and 20.0 mg/L concentrations. The blank solutions were prepared by diluting 10.00 mL H₂SO₄ to the 100.00 ml mark of the volumetric flask and were used for background correction. Quantitative analyses were performed at 309.418 nm for Nb and at 240.068 nm for Ta while the detection limits were determined as

0.0094 and 0.024 mg/L for Nb and Ta respectively.⁵³ The ICP-OES conditions indicated in **Table 4.1** were maintained constant throughout the study. Calibration curves with the slopes of 0.89 to 1.04 for Nb and 0.12 and 0.14 for Ta and y-intercepts of 0.001 to 0.038 for Nb and -0.005 to 0.024 for Ta as well as R^2 values of 0.999 to 0.9999 were obtained and used for quantitative analyses.

Table 4.1: ICP-OES operating conditions

Parameter	Value
RF power	1.2 kW
Coolant gas flow	14.0 L/min
Plasma gas flow	1.2 L/min
Carrier gas flow	1.0 L/min
Sample uptake method	Peristaltic pump
Spray chamber	Glass cyclonic spray chamber with concentric nebuliser

4.3 Experimental methods for selective precipitation

4.3.1 Selection of the appropriate precipitant for NbF₅ and TaF₅ separation

The first step in the possible separation of tantalum and niobium by selective precipitation was to add different chelating or precipitating agents to solutions containing pure TaF₅ and NbF₅ as indicated in **Table 4.2**. The study was started by investigating the possible precipitation of the metal complexes using a number of well known nitrogen and oxygen donor ligands. Approximately 0.1 g (0.5 mmol) of NbF₅ and 0.14 g (0.5 mmol) TaF₅ (accurately weighed to 0.1 mg) was dissolved in 10 mL and about 0.16 g (1.5 mmol) of ligand was separately dissolved in 10 mL of solvent (the actual masses of the samples weighed in this chapter can be viewed in the accompanying CD attached to the thesis in the file with the name: **Chapter 4**). The solvents used were water, methanol and ethanol depending on which dissolves both the metal fluoride and ligand samples completely. After complete dissolution, the ligand solution was added to the metal solution (1:3, metal fluoride:ligand mole ratio). The mixture was stirred for about 5 min and then left overnight to allow for precipitation to occur. The results obtained from this preliminary investigation are presented in **Table 4.2**.

Table 4.2: Reactions of NbF₅ and TaF₅ with different precipitating agents

Chelating or precipitating ligand	Solvents	Reaction with NbF ₅	Reaction with TaF ₅
2,2-Bipyridine-4,4'-dicarboxylic acid	Water, ethanol	Clear solution	Light pink solution
2-hydroxyquinoline	Water, ethanol	Light yellow solution	Light yellow solution
Neocupoine	Ethanol	Glassy crystals	Amorphous solid
L-Tryptophan	Water, ethanol	Faint pink/orange ppt* formed after a day	Insoluble solid
4-(Dimethylamino)-pyridine	Methanol	Milky ppt*	Clear solution
Iminodiacetic acid	Water, ethanol	Fine crystals formed overnight	Clear solution
1,4-phenylenediamine (PPDA)	Water, ethanol	Fine crystals formed overnight	Clear solution
Sodium citrate dihydrate	Water	Clear solution	Fine ppt*

*ppt = precipitate

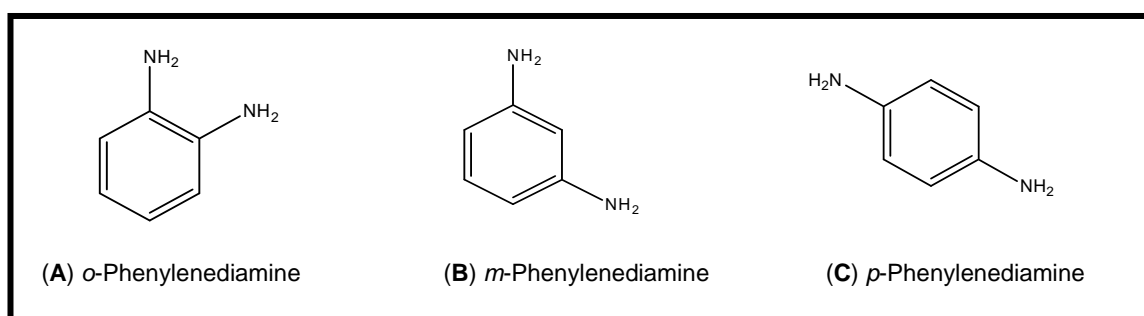
The results in **Table 4.2** indicated that separation of tantalum and niobium by selective precipitation can possibly be expected from 4-(dimethylamino)-pyridine, sodium citrate dihydrate, iminodiacetic acid and *p*-phenylenediamine which showed precipitate formation for the one element, but no precipitation was observed for the other after the 12 hrs (see shaded area of **Table 4.2**). Precipitation with 4-(dimethylamino)-pyridine and sodium citrate dihydrate however produced very fine precipitate that was difficult to separate from the solution and it was decided to concentrate on PPDA and iminodiacetic acid in the next steps of the study.

The same preparative procedure was repeated for these two potential precipitating agents and the niobium and tantalum were quantified by ICP-OES (**Table 4.3**) in the isolated precipitates. The quantitative results in **Table 4.3** indicate a 10:1 Nb:Ta ratio with mixing a 1:1 mixing of NbF₅:TaF₅ ratio for PPDA while iminodiacetic acid only produced a 1:1 and 2:1 ratio for the same elements. It was therefore decided to only continue the investigation with the phenylenediamine ligand as a potential selective precipitant. The mixing of (Nb/Ta)F₅ and PPDA also resulted in blue colour solution which has a maximum absorption at 660 nm being obtained.

Table 4.3: Recovery of Nb and Ta from a mixture of (Nb/TaF)₅ and two different precipitants in ethanol

Precipitating ligand	% Recovery	
	Nb	Ta
<i>p</i> -Phenylenediamine	47.39	4.69
<i>p</i> -Phenylenediamine	67.90	6.06
Iminodiacetic acid	11.50	10.43
Iminodiacetic acid	11.48	5.26

The apparent or potential successful separation of Nb and Ta when using PPDA as reagent also motivated the expansion of the study to include the other two phenylenediamine ligands namely, *o*-phenylenediamine and *m*-phenylenediamine (see **Figure 4.2**). The preliminary results indicated a yellow colour development with a maximum absorption at 450 nm for the *o*-phenylenediamine indicating a possible complex formation with both Nb and Ta while there was no observable change in the solution made with the *m*-phenylenediamine. However, no precipitate was observed for any of the two metals with *o*-phenylenediamine and *m*-phenylenediamine as potential precipitating agents using the identical conditions as described in the above paragraphs. It was therefore decided to continue the study using only the *p*-phenylenediamine (PPDA) for the selective precipitation of Nb from the pentafluoride mixture.

**Figure 4.2:** Different phenylenediamine ligands.

4.3.2 Separation of Nb and Ta from (Nb/Ta)F₅ mixture using PPDA as precipitant

The next step in this investigation was to evaluate the effectiveness of PPDA as selective precipitant on a mixture containing both NbF₅ and TaF₅. NbF₅ (0.1 g, 0.5 mmol) and TaF₅ (0.14 g, 0.5 mmol) were accurately weighed (0.1 mg) and dissolved in 10 mL of ethanol while 0.16 g (1.5 mmol) of PPDA was dissolved in 10 mL of ethanol. The two solutions were mixed and the colour change and precipitate formation were immediately observed. The precipitation reaction was allowed to go on for 12 hrs. The precipitate was isolated by centrifugation followed by the decantation of the filtrate/supernatant solution.

The supernatant was decanted into a 100 mL beaker. About 30 mL of distilled water was added to the supernatant solution and the volume of the solution was reduced to 20 mL on a hot plate at 40 °C to remove most of the ethanol, cooled down and quantitatively transferred to a 100.0 mL volumetric flask. The acidity of this supernatant solution was adjusted by adding 10 mL of 97% H₂SO₄, cooled down to room temperature and the flask was then filled to the mark with double distilled water.

The precipitate in the glass tube was firstly dissolved by the addition of 10 mL 97% H₂SO₄ and the translucent solution was then quantitatively transferred to a 100.0 mL volumetric flask and filled to the mark with double distilled water. Both the precipitate and the supernatant solutions were subsequently analysed for Nb and Ta content using ICP-OES (see **Section 4.2.2**). The results from this study indicated that NbF₅ is preferentially precipitated by the addition of PPDA compared to TaF₅ and that a separation factor of 4 can be obtained by these experimental conditions. The results also indicated that more than 50% of the NbF₅ is recovered in the precipitate while a maximum of only 15% of the TaF₅ is recovered (**Table 4.4**).

Table 4.4: Recovery of Ta and Nb in the precipitate using PPDA

Precipitating ligand	% Recovery	
	Nb	Ta
PPDA	55.71	15.12
PPDA	55.56	13.28
PPDA	59.37	14.42

After it was found that PPDA selectively precipitates niobium from a 50% mixture of niobium and tantalum fluorides, it was decided to refine the experimental conditions to ensure the maximum separation as well as the possible quantitative metal recovery using this method. The parameters which were investigated include pH and PPDA concentration variation. It was decided to reduce the quantities of starting materials (from 0.1 g to 0.02 g NbF₅ and 0.025 g TaF₅ and from 0.15 g to 0.06 g for PPDA) to further reduce the degree of TaF₅ precipitation.

4.3.2.1 Investigation of the pH effect

HCl/KCl buffer (pH ~ 2)

The effect of pH on this precipitation process was firstly investigated using a buffer solution of pH 2.0 which were prepared from HCl and KCl.¹⁴² About 0.02 g NbF₅ (0.053 mmol Nb) and 0.025 g TaF₅ (0.053 mmol Ta) were weighed accurately (to 0.1 mg) in a clean dry 50 mL beaker and dissolved in 10.0 mL ethanol followed by addition of 5 mL of pH 2.0 buffer solution. A PPDA solution was prepared by dissolving 0.06g (0.56 mmol) in 10.0 mL ethanol and was then added to the metal/buffer solution (1:10, metal:ligand mole ratio). The mixing of the two solutions was immediately followed by an immediate blue colour development and a precipitate formation. The precipitate was separated from supernatant solution by centrifugation followed by decantation of the solution.

The precipitate in the glass tube was firstly dissolved by the addition of 10 mL 97% H₂SO₄ and the translucent solution was then quantitatively transferred to a 100.0 mL volumetric flask and filled to the mark with double distilled water. ICP-OES analysis indicated that the precipitate contained Nb and Ta in the same ratios (see **Table 4.5**).

142. Bassett, J., Denney, R. C., Jeffery, G.H. and Mendham, J., *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th ed., Longman group Limited, London, 1978, p. 886

Table 4.5: Influence of lower pH values on recoveries of Nb and Ta in the precipitate using HCl/KCl buffer

Precipitating ligand	pH	% Recovery	
		Nb	Ta
PPDA	1.61	54.61	66.70
PPDA	1.61	49.05	61.69
PPDA	1.66	74.74	83.8
PPDA	1.82	58.79	72.23
PPDA	2.32	62.45	83.14

Acetate buffer (pH ~ 3–6)

The next step was to evaluate an acetic acid/acetate buffer in the precipitation process. Four solutions containing a mixture of niobium and tantalum fluorides were prepared by dissolving accurately weighed (*ca* 0.02 and 0.025 g respectively) samples in 10.0 mL ethanol. Different acetate buffer solutions with pH ranging between pH 3.0 and pH 6.0 were then prepared from CH₃COONa/CH₃COOH.^{121,142} The acetate buffer solutions with different pH values were prepared by combining various volumes of 0.1 M each of CH₃COONa and CH₃COOH stock solutions in a 100.0 mL volumetric flask. The pH solutions (5 mL) were then added to metal fluoride mixtures.

A PPDA solution was prepared by dissolving 0.06g (0.56 mmol) in 10.0 mL ethanol and was then added to the (Nb/Ta)F₅/buffer solution (1:10 metal:ligand mole ratio). The addition of the PPDA solution to the (Nb/Ta)F₅/buffer solutions led to an immediate colour change (to blue) and precipitation. The precipitate formed in all the solutions and was separated from the solution by centrifugation. These precipitates were dissolved in 10 ml H₂SO₄ and quantitatively transferred to 100.0 mL volumetric flasks which were subsequently filled to the mark with water. The solutions were analysed by ICP-OES and the results are given in **Table 4.6**.

Table 4.6: Influence of pH on recoveries of Nb and Ta in precipitate using PPDA and acetate buffer

pH	% Recovery	
	Nb	Ta
3.05	8.99	3.95
4.02	14.14	4.03
5.06	34.69	4.69
6.10	64.55	81.68

The above procedure was repeated to include more pH points and similar results to those reported in **Table 4.6** were obtained. These results are graphically presented in **Figure 4.3**. It is clear from the Nb and Ta recovery that up to pH 5.2, NbF₅ is precipitated preferentially to TaF₅ (2.5:1 at pH ~ 5), but that the TaF₅ precipitation increased rapidly at high pH values to render separation insufficient at high pH values.

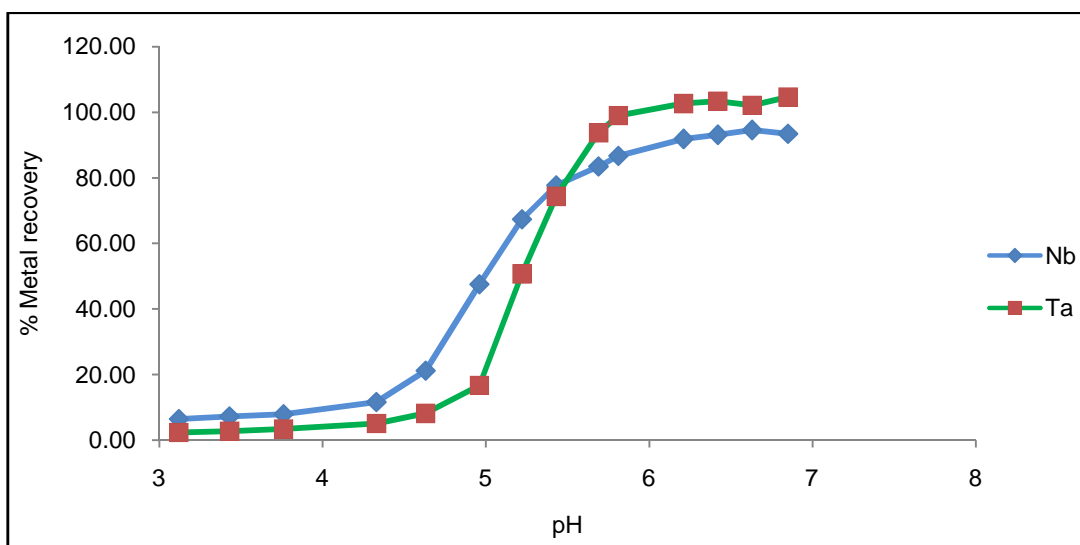


Figure 4.3: Influence of pH on Nb and Ta recoveries in the precipitate using PPDA and acetate buffer.

In order to try and find a possible explanation for the current observation, it was decided to investigate the possibility that acetate can act as a ligand in this separation process. Four portions of NbF₅/TaF₅ mixture (0.02 g (~0.053 mmol) NbF₅ and 0.025 (~0.053 mmol) TaF₅) were dissolved in 10.0 mL ethanol and 5.0 mL of the different acetate buffer (pH ~ 3, 4, 5 and 6) were added to each of these mixtures.

These solutions were left to react for 12 hrs. No precipitate formation was observed in the mixtures of pHs of 3.05 and 4.02, but indeed for pH values of 5.06 and 6.10. These precipitates were separated from the mother solution by centrifugation and dissolved as described earlier. The quantitative results of the precipitates (**Table 4.7**) are in accord with the rapid increase in TaF₅ as was observed in the presence of PPDA as ligand.

Table 4.7: Influence of acetate buffer on recoveries of Nb and Ta at different pHs

Ligand	pH	% Recovery	
		Nb	Ta
Acetate buffer	3.05	---	---
Acetate buffer	4.02	---	---
Acetate buffer	5.06	2.42	4.95
Acetate buffer	6.10	15.70	43.04

--- No precipitate

4.3.2.2 Influence of concentration variation

The next step in this study was to investigate the influence of concentration variation of PPDA on both the recovery and separation of the two metals from the isolated products without the addition of any buffer to the reaction mixture. A mixture of NbF₅ and TaF₅ was prepared in a 1:1 mole ratio by accurately weighing about 0.02 g NbF₅ (0.053 mmol Nb) and 0.025 g TaF₅ (0.053 mmol Ta). This mixture was dissolved in 10.0 mL of absolute ethanol. The concentration of PPDA was varied according to the metal:ligand mole ratio ranging from 1:1 to 1:20 by accurately weighing masses between 0.0057 and 0.11 g and dissolving them in 10.0 mL volumes of ethanol. The metal fluoride solution and the PPDA solution were mixed in a clean and dry beaker. Precipitate formation and colour change were immediately observed at the higher ligand concentrations. A visual comparison of the solutions 5 min after the ligand solution was added is shown in **Figure 4.4**. The pH of all the solutions was measured and was found to be about 5.10.



Figure 4.4: Influence of PPDA concentration on precipitation of NbF_5 and TaF_5 in ethanol ($\text{pH} = 5.10$).

These precipitates were separated from the supernatant liquid and treated as described previously. The quantitative analysis for the tantalum and niobium contents of the precipitate and the supernatant liquid by ICP-OES are presented graphically in **Figures 4.5** and **4.6** respectively.

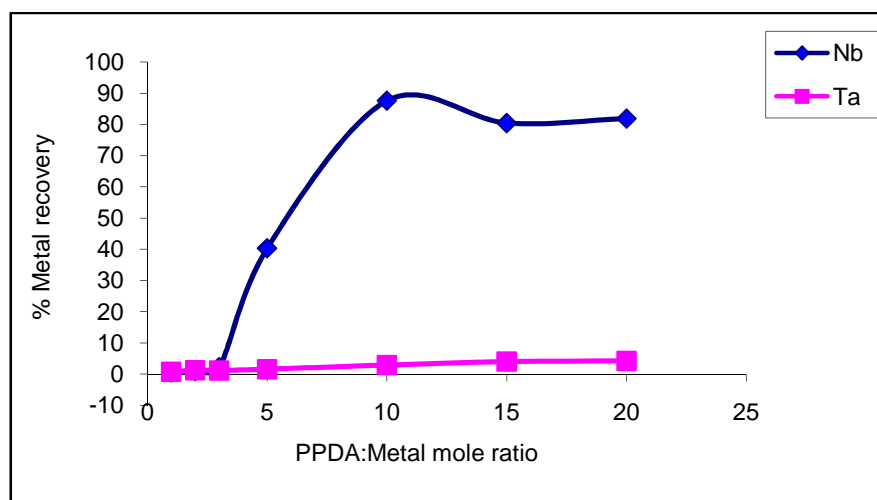


Figure 4.5: Recoveries of Nb and Ta in precipitates from different concentrations of PPDA in ethanol ($\text{pH} = 5.10$).

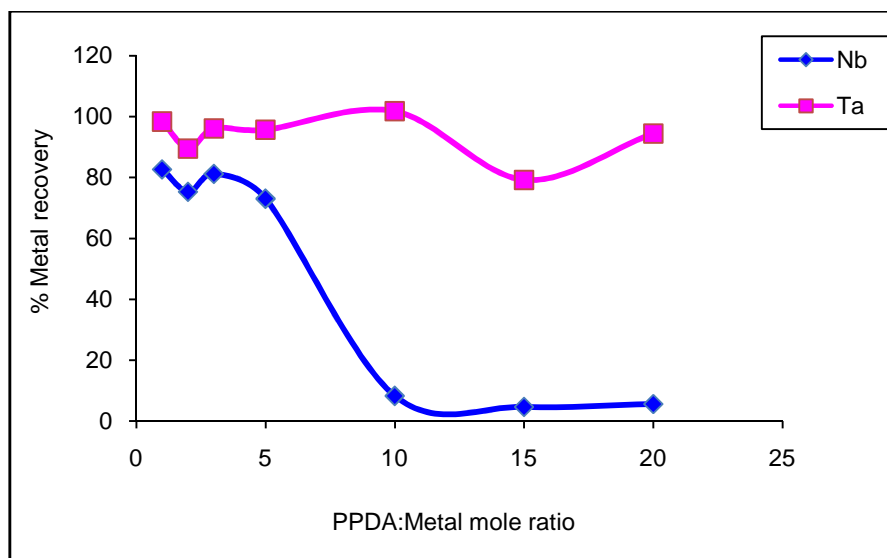


Figure 4.6: Recovery of Nb and Ta in supernatant solution after precipitation with different PPDA concentrations (pH = 5.10).

The experiment was repeated two more times and the results of metal quantification in the precipitate are presented in **Table 4.8**. These results were found to follow the same trend which is presented in **Figure 4.5**.

Table 4.8: Recoveries of Nb and Ta in precipitates at different PPDA concentrations (pH = 5.10)

Metal:PPDA	% Recovery*	
	Nb	Ta
1:1	0.2(4)	0.3(5)
1:2	0.4(6)	0.5(8)
1:3	1(1)	0.4(7)
1:5	42(1)	1.5(2)
1:10	83(4)	3.3(3)
1:15	80.8(5)	4.5(5)
1:20	81.9(3)	4.32(9)

*Average recovery and standard deviation for n = 3

4.3.2.3 Reproducibility test for 1:10 metal:PPDA mole ratio results

To determine the reproducibility of the precipitation results for Nb and Ta, the mole ratio of metal:PPDA was maintained at 1:10. The solutions of (Nb/Ta) F_5 and PPDA

were prepared by dissolving 0.02 g NbF₅, 0.025 TaF₅ (weighed to 0.1 mg accuracy) and 0.0571 g PPDA in 10.0 mL ethanol. The solutions were mixed and the precipitates which formed were separated from the solutions and treated for ICP-OES analysis as previously described. The recovery results obtained from this study are presented in **Table 4.9**.

Table 4.9: Reproducibility of Nb and Ta recoveries of in the precipitate for the 1:10 metal:PPDA mole ratio

Ligand	pH	% Recovery	
		Nb	Ta
PPDA	5.10	80.72	2.68
PPDA	5.10	80.84	4.00
PPDA	5.10	81.29	3.92
PPDA	5.11	78.36	4.06
Mean		80.30	3.67
SD		1.32	0.66
RSD		1.64	17.91

4.4 Results and discussion on selective separation

4.4.1 Selection of the precipitating agent

The initial evaluation of eight different precipitating agents only pointed to two potential reagents namely, iminodiacetic acid and *p*-phenylenediamine which resulted in precipitation after mixing the ligand with the metal halide complexes. The metal quantification results however clearly indicated the preferential precipitation reaction between NbF₅ and *p*-phenylenediamine (PPDA) which resulted in an initial enrichment from a 1:1 Nb:Ta ratio to a 4:1 Nb:Ta ratio after precipitation while a maximum of 2:1 Nb:Ta ratio was obtained from the same 1:1 Nb:Ta mixture with iminodiacetic acid.

4.4.2 Separation of NbF₅ and TaF₅ using PPDA as a selective precipitant in ethanol

Based on the results obtained for the selective precipitation of NbF₅ and TaF₅ using the initial eight precipitating agents and the results obtained in the study involving the comparison between the three phenylenediamine ligands (**Figure 4.2**), the PPDA was selected for the selective precipitation of NbF₅ over TaF₅. Precipitation of NbF₅ and TaF₅ from ethanol was accomplished using PPDA ligand dissolved in the same

solvent. The results in **Table 4.4** clearly indicated that there is a possibility that niobium forms a complex of low solubility with PPDA. The tantalum complex with this ligand on the other hand has a different solubility and remains dissolved in ethanol during the precipitation process. However, the tantalum recoveries of 13.28 and 15.12% were considered too high for separation purposes and re-precipitation process may be necessary. Moreover, niobium recoveries of maximum 59.39% also indicated a need for improvement in the procedure. At this stage the poor results could be attributed to co-precipitation of tantalum with niobium since relatively high concentrations of 0.1 g (~[Metal] = 0.03 M) metal fluorides were used. The co-precipitation problem was solved by working with dilute metal solution. The concentrations of NbF₅ and TaF₅ were decreased to about [Metal] = 5x10⁻³ M (~0.02 g NbF₅ and ~0.03 g TaF₅).

As indicated in **Chapter 3, Section 3.4.2.2**, precipitation is dependent on the concentration of the reagents and the pH of the solution. The concentrations of both the reagents are important for attainment of the K_{eq}, an equilibrium constant at and above which precipitation occurs. The pH of the solution on the other hand does not influence only the complexation and precipitation of the metals by the ligand but also the acid-base properties of the ligand as well as the stability of the precipitate formed thereof.

It was decided at this stage to investigate the pH effects on the precipitate formation between (Nb/Ta)F₅ and PPDA. The pH of the final solutions from which precipitation occurred was controlled using buffer solutions to try and understand as well as to improve the separation and the subsequent metal recoveries.

4.4.2.1 Determination of pH effects using a buffer system

The lower pH values were investigated using the HCl/KCl buffer solutions of pH 1.60 to 2.32. The results obtained from the precipitation under the HCl/KCl buffer condition were found (see **Table 4.5**) to be an opposite of what was expected according to the results obtained earlier in the absence of a buffer solution (see **Table 4.4**). Contrary to the expected high Nb recoveries, at low pH values Ta recoveries were slightly higher than those of Nb. The high recoveries for both Nb and Ta may be due to

possible competition between PPDA and Cl^- for Nb/Ta which seems to react preferentially with Ta compared to Nb.

The next step was to investigate the effect of pH using a different buffer system. The acetate buffer which operates in the pH range 3.5 to 5.5 was used. The precipitation results (**Table 4.6**) indicated recoveries for both Nb and Ta which increase with increasing pH. In acetate buffer system a preferential precipitation towards Nb was observed up to pH \sim 5.50 and above this pH, Ta was precipitated more than Nb (**Figure 4.3**). The high Ta precipitation may be attributed to the competition from the anions in the buffer solutions (chloride and acetate ions). The possible contribution of the ions from the buffer solution in the precipitation of Nb and Ta was investigated with the acetate buffer system. The results (**Table 4.7**) obtained from this study indicated that the acetate ion indeed contributes significantly to the precipitation of the two metals and that the precipitation of both elements increases with pH (which is essentially an increase in the CH_3COO^- concentration). From these results it appears that the acetate ligand acts as chelating agent which reacts with both metal ions to affect the subsequent increase in product formation.

Based on its pK_a value of 6.04,¹⁴³ it is also evident that a small portion of PPDA exists at 5.10 in its deprotonated form. It is therefore possible that there are not enough of $-\text{NH}_2$ groups to react with TaF_5 . As the pH is increased from 5.10 to the pK_a value (6.04) and above, the deprotonation of the amine group occurs and the concentration of the $-\text{NH}_2$ groups is increased and hence the rapid increase in the TaF_5 precipitation (**Figure 4.3**).

4.4.2.2 Effects of PPDA concentration on the precipitation of NbF_5 and TaF_5 in ethanol

A major requirement for a precipitation reaction (see **Chapter 3, Section 3.4.2.2**) is that the ions involved in the precipitate formation have to exist in solution in sufficient concentrations to produce a supersaturated solution and to achieve or exceed the

143. Dong, S., Chi, L., Yang, Z., He, p., Wang, Q. and Fang, Y., 2009, "Simultaneous determination of dihydroxybenzene and phenylenediamine positional isomers using capillary zone electrophoresis coupled with amperometric detection", *J. Sep. Sci.*, **32**: pp. 3232–3238

solubility product (K_{sp}) value of the resulting compound. The concentration of the ligand for the precipitation to occur was determined following the procedure outlined in **Section 4.2.4.2**. The precipitate formed immediately at higher ligand concentration for a fixed metal concentration. No observable precipitate was formed in the 12 hrs period for the ligand concentration of up to 1:3 (Nb (0.02 g, 0.053 mmol):PPDA (0.0171 g, 0.16 mmol)) mole ratios. The precipitation was immediately observed at the metal:PPDA molar ratios of 1:5, 1:10, 1:15 and 1:20. The metal content determination of the precipitate by the ICP-OES indicated good separation of Nb from Ta fluoride solution in all these precipitates with niobium recoveries up to 87.6% and a maximum Ta recovery of 4.32% at a metal:PPDA mole ratio of 1:20. It was found that the increase in ligand concentration up to a metal:PPDA mole ratio of 1:10 was optimum for maximum recovery of Nb and its separation from Ta and that a further increase of PPDA concentration to a metal:PPDA mole ratio of 1:15 and 1:20 had no additional influence on the recovery of Nb (**Figures 4.5**). Repetitions of the experiment under identical conditions indicated that the results were reproducible (**Table 4.8**). The experimental procedure was also repeated for a 1:10 metal:PPDA ratio. The results obtained (**Table 4.9**) from this part of the study indicated a satisfactory reproducibility of %Nb and Ta recoveries in the precipitate.

It was decided in the next step of the study to compare the quantities of Ta and Nb in the precipitate to those in the supernatant solution to ensure there is no significant loss of matter (for example, due to adherence to the container walls) in the sample preparation steps. The precipitation was carried out at a fixed metal:PPDA mole ratio of 1:10 as described above. The precipitates were separated from the solutions and both prepared for ICP-OES analysis as previously described. The results from this study are given in **Table 4.10**. It follows from these results (see also **Figures 4.5** and **4.6**) that there is no significant loss of matter in the separation process.

Table 4.10: Recoveries of Nb and Ta in both the precipitate and supernatant solution

Sample	% Recovery	
	Nb	Ta
Precipitate	81.76	2.77
Solution	15.77	93.15
Total % Mass	97.54	95.93
Precipitate	77.86	5.08
Solution	16.35	89.88
Total % Mass	94.22	94.96
Precipitate	82.06	4.68
Solution	14.06	97.87
Total % Mass	96.12	102.55
Precipitate	83.02	5.25
Solution	16.96	92.11
Total % Mass	99.99	97.36

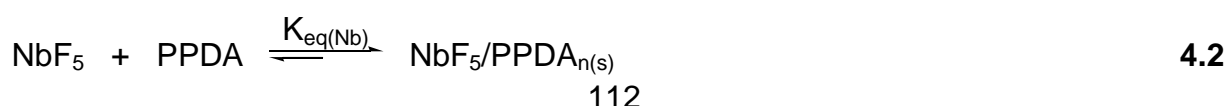
The equilibrium constant for the precipitate formation for both Nb and Ta were calculated using the following the **Equation 4.5**

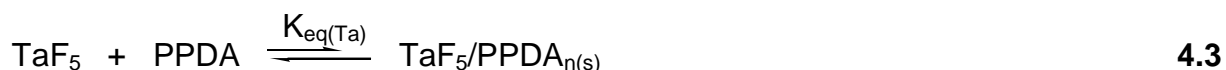
$$K_{eq(M)} = \frac{[M]_{ppt}}{[M]_{aq}} \quad 4.4$$

Where $K_{eq(M)}$ is the precipitate formation constant for a metal ion (Nb or Ta) and $[M]_{ppt}$ and $[M]_{aq}$ is the concentration of the metal ion in the precipitate and in the supernatant solution respectively.

The $K_{eq(Nb)}$ calculated under these experimental conditions (Nb:PPDA 1:10) for 80% product formation (precipitation) is 5.2(5). The $K_{eq(Ta)}$ at this PPDA concentration is substantially lower (0.05(1)) indicating a much larger tendency to form niobium product compared to the equivalent tantalum product. The separation factor, α , which was calculated as a ratio of $K_{eq(Nb)}:K_{eq(Ta)}$ (see **Chapter 3, Equation 3.17**) was found to be 100(9) indicating a successful separation between niobium and tantalum.

The results obtained from different studies (**Section 4.3**) indicated that the reactions between $(Nb/TaF)_5$ and PPDA can be generalised as follows (**Equations 4.2 and 4.3**):





The equilibrium constant for product formation between NbF_5 and PPDA as presented in **Equation 4.2** indicates that the forward reaction is favoured compared to the reverse reaction. The opposite has been observed for the same reaction between TaF_5 and PPDA (**Equation 4.3**). This indicates a more thermodynamically favourable reaction for NbF_5 compared to that of TaF_5 . In addition, the PPDA concentration will decrease as a result of the reaction with NbF_5 and may therefore increase the extent of the reverse reaction for TaF_5 and decrease the overall TaF_5/PPDA precipitate formation, thereby improving the separation of the two metals in this reaction. It is however anticipated from the equilibrium constant determination that by increasing the $[\text{PPDA}]$ the equilibrium in **Equation 4.3** will be shifted to the right and therefore increase the concentration of the insoluble $\text{TaF}_5/\text{PPDA}(\text{s})$ product. It is therefore important that the $[\text{PPDA}]$ is controlled to give maximum precipitation of Nb without causing the increase in TaF_5 precipitation.

4.5 Experimental procedures for the characterisation of the NbF_5/PPDA precipitate

The reaction between the metal pentafluorides and PPDA has clearly indicated two different, very fast reactions, namely, the rapid blue complex formation as well as the white precipitate formation at relatively high PPDA concentrations (see **Section 4.3.2.2** and **Figure 4.4**). From these experimental results uncertainty exists whether the final product formation is the result of a successive or a parallel process. The two possible processes that may take place during the reaction of NbF_5 with PPDA are illustrated in **Figure 4.7**.

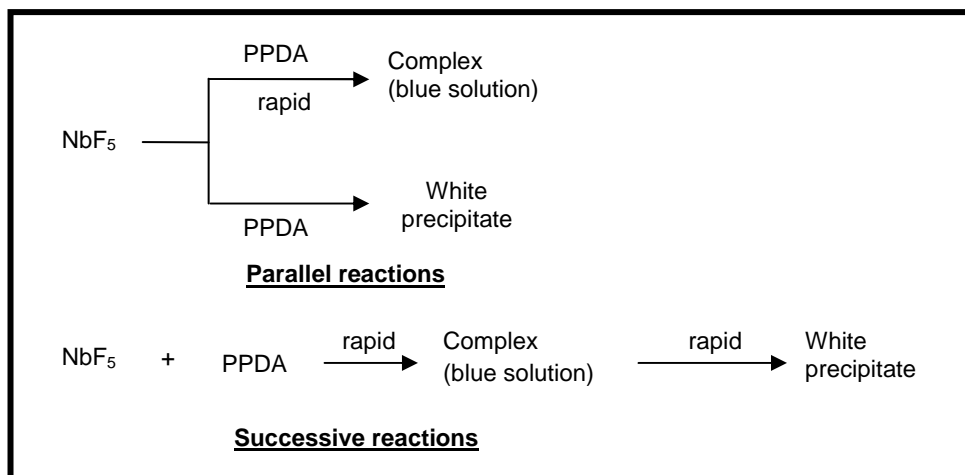


Figure 4.7: Reaction scheme indicating the possible reactions between NbF_5 and PPDA.

In the parallel reactions in **Figure 4.7**, the blue complex formation results from a reaction between NbF_5 and PPDA while the precipitate formation results from another, but different reaction between these two starting materials. Both reactions were however too fast to identify which reaction occurs first. In the successive process, the formation of a blue complex is a prerequisite for the formation of the precipitate product.

The general reaction between the PPDA ligand and NbF_5 is proposed in **Equation 4.4**. Both the precipitate and the coloured solution obtained from this reaction were studied with analytical techniques such as ICP-OES, CHN microanalyser, ^{19}F -NMR, IR and UV–Vis spectrophotometer to obtain the stoichiometry and nature of interaction between the ligand and the two metal fluorides. A flow-chart indicating the production and characterisation of the NbF_5 /PPDA precipitate in this study is outlined in **Figure 4.8**.

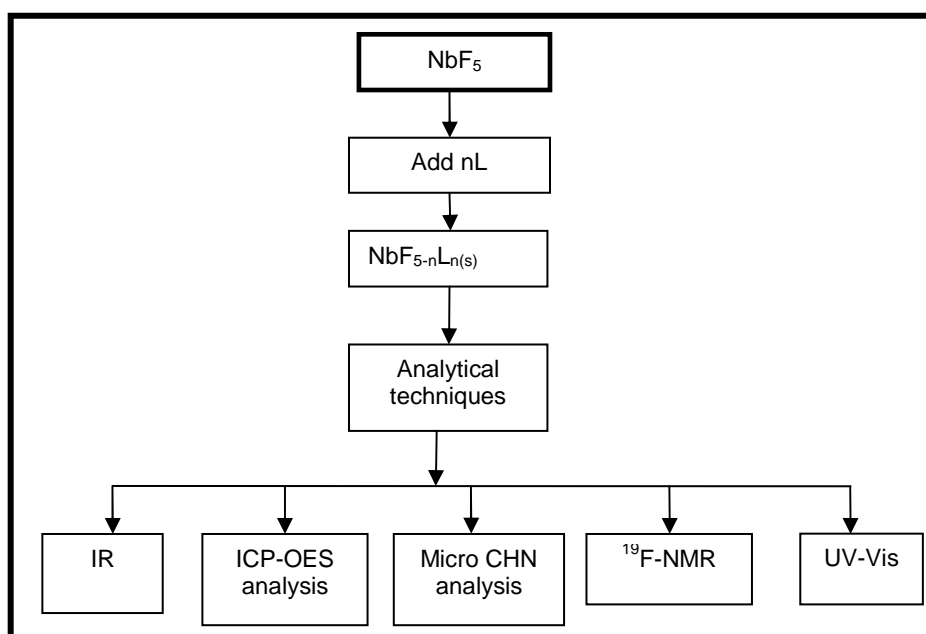
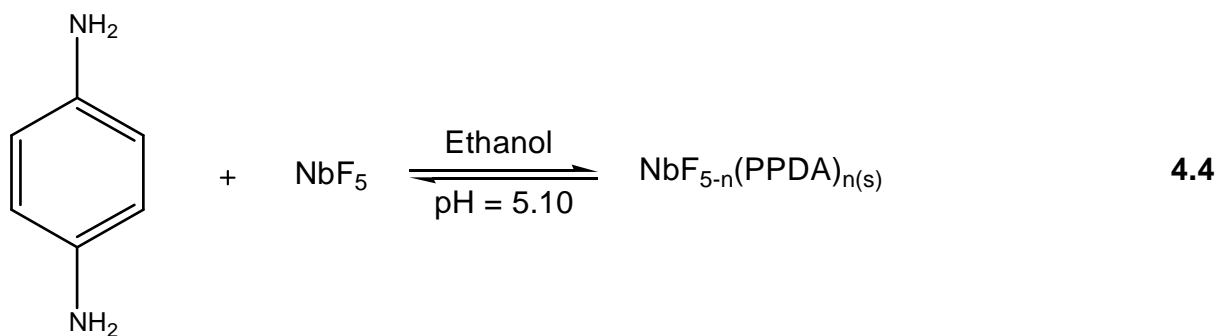


Figure 4.8: Flow chart for niobium precipitate formation and characterization.

4.5.1 Infrared analysis

An accurately weighed NbF_5 sample (0.02 g, 0.11 mmol) was dissolved in 10.0 mL ethanol. PPDA was prepared by dissolving 0.06g (0.56 mmol) in 10.0 mL ethanol and was then added to the NbF_5 solution. The addition of the PPDA solution was followed by an immediate blue colour development and precipitate formation. The precipitate was separated from the supernatant solution by centrifugation followed by the decantation of the solution. The precipitate was washed by repeating the centrifugation of the precipitate in 10 mL ethanol solutions. At the end of the centrifugation process, the ethanol was decanted and the precipitate was dried at 80 °C for 1 hr in an oven. The IR spectrum of the precipitate was then recorded together with that of the two starting materials (**Figure 4.9**).

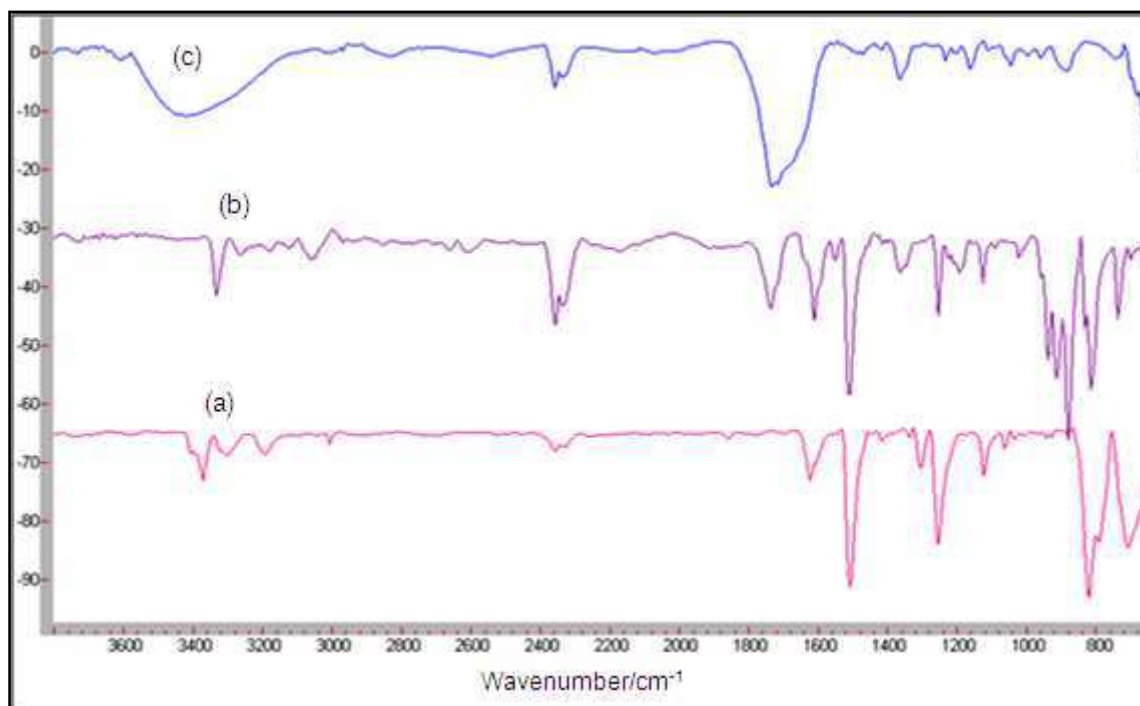


Figure 4.9: IR spectra of (a) PPDA, (b) precipitate product of NbF_5 and PPDA, (c) NbF_5 .

4.5.2 Complex formation determination by spectrophotometric analyses

4.5.2.1 Determination of wavelength of maximum absorbance

A solution (0.001M) of NbF_5 was prepared by dissolving 0.02 g (accurately weighed to 0.1 mg) of NbF_5 in 100.0 mL ethanol in a 100.0 mL volumetric flask. A PPDA solution was prepared by dissolving 0.06g (0.56 mmol) in 10.0 mL ethanol in a 10.0 mL volumetric flask. A PPDA solution (1.5 mL) was then added to the NbF_5 solution (1.5 mL) and the resultant blue solution was scanned over a 200 to 800 nm range on a UV-Vis spectrophotometer to determine the wavelength of maximum absorbance of the solution. A pure PPDA solution (3 mL) which had developed a brown colour during the same time was also scanned alone under identical experimental conditions to determine its wavelength of maximum absorbance as a contrast to ensure that the colour development in the Nb/PPDA solution is indeed due to a reaction not due to the PPDA decomposition. The spectra were collected over a period of 8 hours. The PPDA brown solution had a maximum absorption at 430 nm (**Figure 4.10 A**). The blue solution of the metal fluoride and PPDA on the other hand had a maximum absorption at 660 nm (**Figure 4.10 B**).

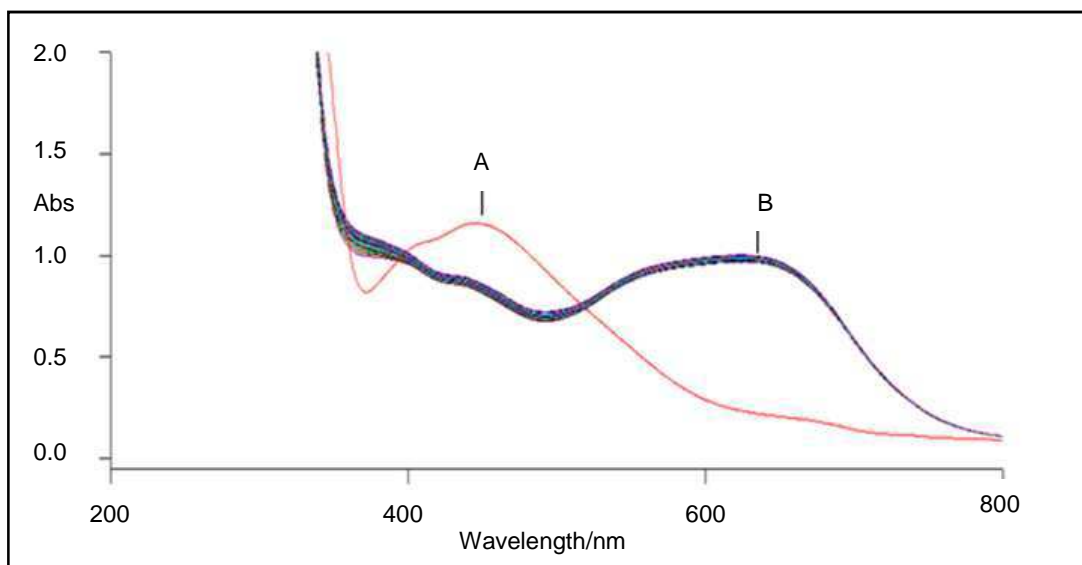


Figure 4.10: UV-Vis spectra of (A) brown ligand solution and (B) blue complex solution.

4.5.2.2 Complex ratio determination by Job's method of continuous variation

A solution of 0.001M NbF_5 was prepared by dissolving 0.02 g (accurately weighed to 0.1 mg) of NbF_5 in 100.0 mL ethanol in a 100.0 mL volumetric flask. A PPDA solution (0.053 M) was prepared by dissolving 0.6g (accurately weighed to 0.1 mg) in 10.0 mL ethanol in a 10.0 mL volumetric flask. Mixtures of 0:10, 1:9, 2:8...10:0 PPDA: NbF_5 volume ratio were prepared in 10.0 mL volumetric flasks. The absorbances of these solutions were measured at 660 nm. The plot of absorbance against the ligand volume ratio is given in **Figure 4.11**.

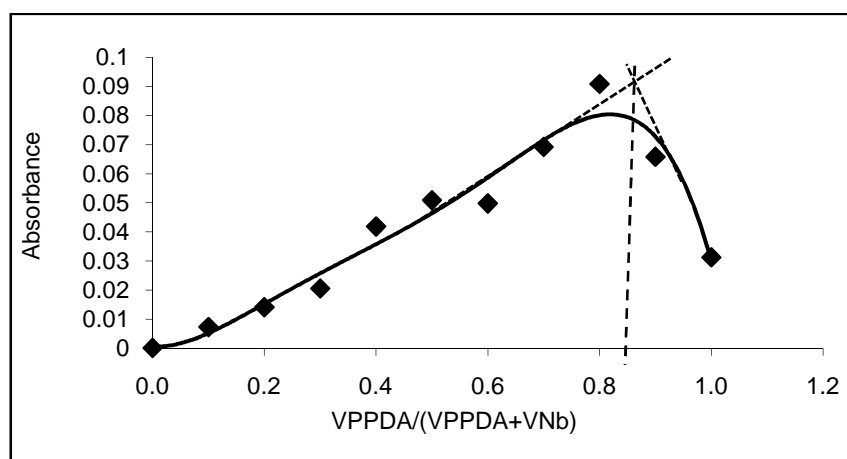


Figure 4.11: Plot of absorbance versus PPDA volume ratio.

4.5.2.3 Complex ratio determination by mole ratio method

Solutions of NbF_5 and PPDA were prepared as described in **Section 4.5.2.1**. Volume mixtures of NbF_5 and PPDA were prepared by mixing a fixed volume of 1.0 mL NbF_5 with PPDA volumes ranging from 0.1 to 5.5 mL in 10.0 mL volumetric flasks. The volumetric flasks were filled to the mark with ethanol and the absorbance of the solutions was then measured at 660 nm. A plot of the absorbance against the ligand concentration is presented in **Figure 4.12**.

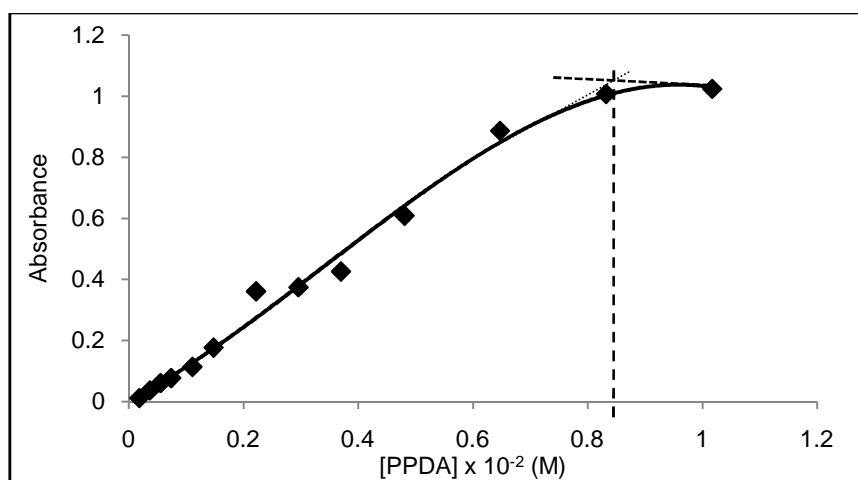


Figure 4.12: Plot of absorbance versus [PPDA] ($[\text{Nb}] = 1.0 \times 10^{-2} \text{ M}$).

4.5.2.4 Complex ratio determination by slope ratio method

Solutions of NbF_5 and PPDA were prepared as described in **Section 4.5.2.1**. Volume mixtures of NbF_5 and PPDA a fixed NbF_5 volume of 1.0 mL and PPDA volumes ranging from 1.0 to 7.0 mL were prepared in 10.0 mL volumetric flasks. Another set of solutions was prepared by mixing a fixed volume of 2.0 mL PPDA with NbF_5 volumes ranging from 0.1 to 0.7 mL in 10.0 mL volumetric flasks. The volumetric flasks were filled to the mark with ethanol and the absorbances of all the solutions were then recorded at 660 nm. The plots of absorbance against the ligand concentration for the first set of solutions and against the metal concentration for the second set of solutions are presented in **Figure 4.13**.

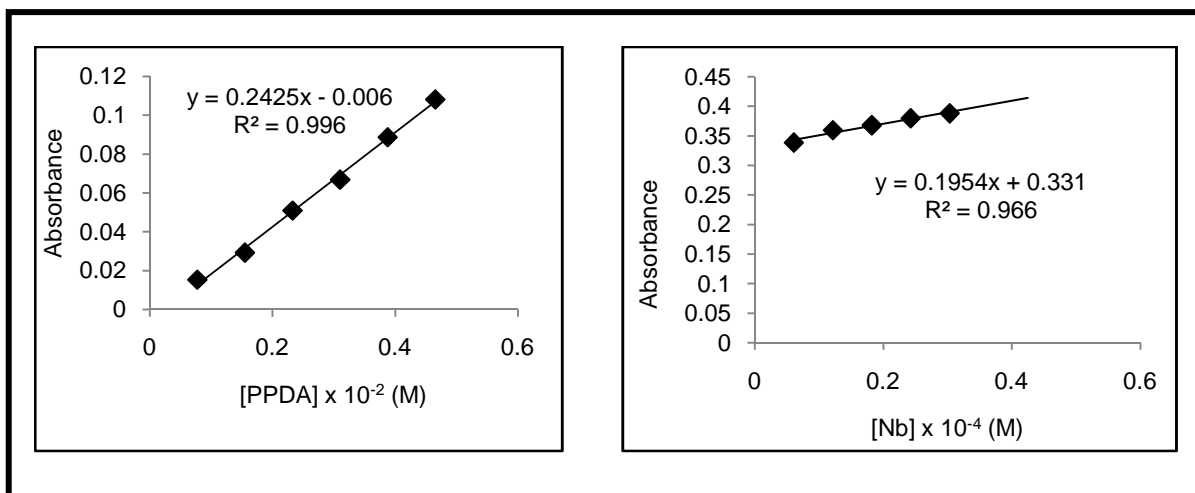


Figure 4.13: Plot of absorbance *versus* [PPDA] and [NbF₅].

4.5.2.5 Determination of formation Nb-PPDA constant and molar extinction coefficient

A 0.001M NbF₅ solution was prepared as described in **Section 4.4.5.1**. A PPDA stock solution (1.0 M) was prepared by dissolving 1.1 g (accurately weighed to 0.1 mg) in 10.0 mL ethanol in a 10.0 mL volumetric flask. PPDA concentrations ranging from 0.01 to 0.5 M were prepared by pipetting appropriate volumes of the stock solution into 10.0 mL volumetric flasks. A constant volume of 2.0 mL NbF₅ solution was added to each volumetric flask and the solutions were allowed to stand for 15 min for full colour development before filling the volumetric flasks to the mark with ethanol. The absorbances of the solutions were measured at 660 nm.

Figure 4.14 is a graph of [Nb]/Abs vs 1/[PPDA]. The formation constant and the molar extinction coefficient were calculated from the Benesi-Hildebrand **Equation 4.5**:¹⁴⁴

$$\frac{[\text{Nb}]}{\text{Abs}} = \frac{1}{\epsilon K_f} \cdot \frac{1}{[\text{PPDA}]} + \frac{1}{\epsilon} \quad 4.5$$

Where K_f is the formation constant and ε is the molar extinction coefficient of the Nb-PPDA complex.

144. Benesi, H. A.; Hildebrand, J. H. 1949, "Spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons", *J. Am. Chem. Soc.*, **71**: p. 2703

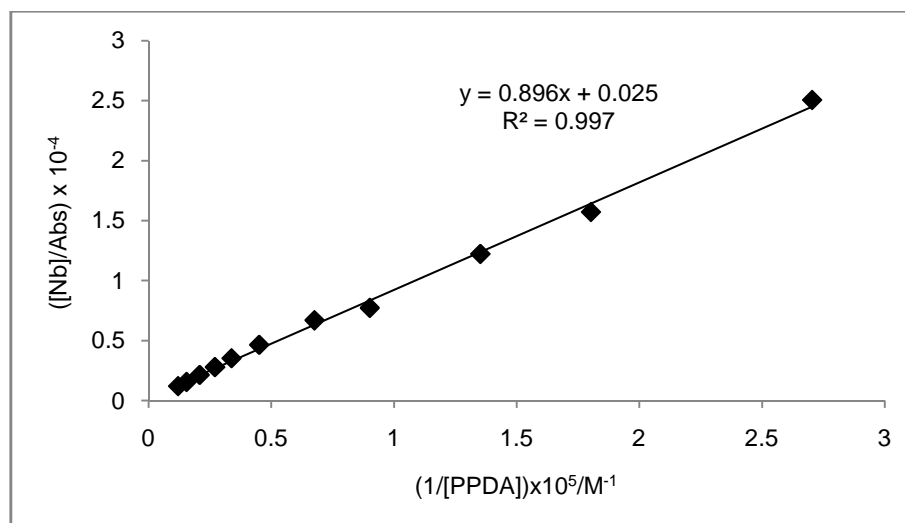


Figure 4.14: Benesi-Hildebrand plot of $[Nb]/Abs$ vs $1/[PPDA]$.

4.5.3 Micro-analysis of C, N and H in precipitate

A $NbF_5/PPDA$ precipitate was prepared, separated from the solution, purified and dried as described in **Section 4.5.1**. Three portions of the precipitate sample with a mass of approximately 2.0 mg were accurately weighed in tin capsules and then presented to the micro CHNS analyser for determination of C, H and N concentrations. Subsamples of this precipitate sample were used for %Nb and %F determination by the ICP-OES and ^{19}F -NMR respectively. The elemental analysis results for C, N, H and the niobium metal content of the precipitate are given in **Table 4.11**.

Table 4.11: Elemental analyses results for the $NbF_5/PPDA$ precipitate

Element	Nb*	C	H	N
%	25.5(1)	28.5(9)	4.0(1)	10.8(4)

*ICP-OES analysed

4.5.4 Determination of niobium concentration in the $NbF_5/PPDA$ precipitate by ICP-OES analysis

Three portions of approximately 0.01 g (weighed to 0.1 mg accuracy) of the $NbF_5/PPDA$ precipitate (from **Section 4.5.3**) were dissolved in 10 mL of 97% H_2SO_4 in a 100.0 mL volumetric flasks. The solution was then allowed to cool to room

temperature and the volumetric flask was filled to the mark with double distilled water. The solutions were then analysed by ICP-OES for Nb determinations and the results are given in **Table 4.11**.

4.5.5 NMR determination of precipitate

4.5.5.1 Selection of fluoride standard

The selection of an appropriate standard for the quantitative determination of fluoride by ^{19}F -NMR technique was the most important part. The selection was based on the following requirements; (1) solubility of the standard in the solvent in which the sample was dissolved, (2) standard should have chemical shifts that are similar to that of the analyte, (3) at least one of the signals in the standard spectrum should change with the concentration of the fluoride and (4) the fluoride salt should not react and destroy the NMR glass tubes (especially at high fluoride concentrations) under the sample preparation conditions used. For this purpose, NaF, KF, TaF₅, NbF₅, NH₄F•HF and NH₄F salts were evaluated as possible standards.

About 0.01 g of each fluoride salt was accurately weighed (0.1 mg) and dissolved in 1 ml of 97% H₂SO₄ in a 10.0 mL volumetric flask. About 3 mL of D₂O was added to each of the volumetric flasks, as internal frequency lock, before filling the volumetric flask to the mark with double distilled water. A 0.6 mL volume of these fluoride solutions were transferred to NMR glass tubes and the spectra were recorded. The ^{19}F -NMR spectra of the evaluated salts are given in **Figure 4.15**.

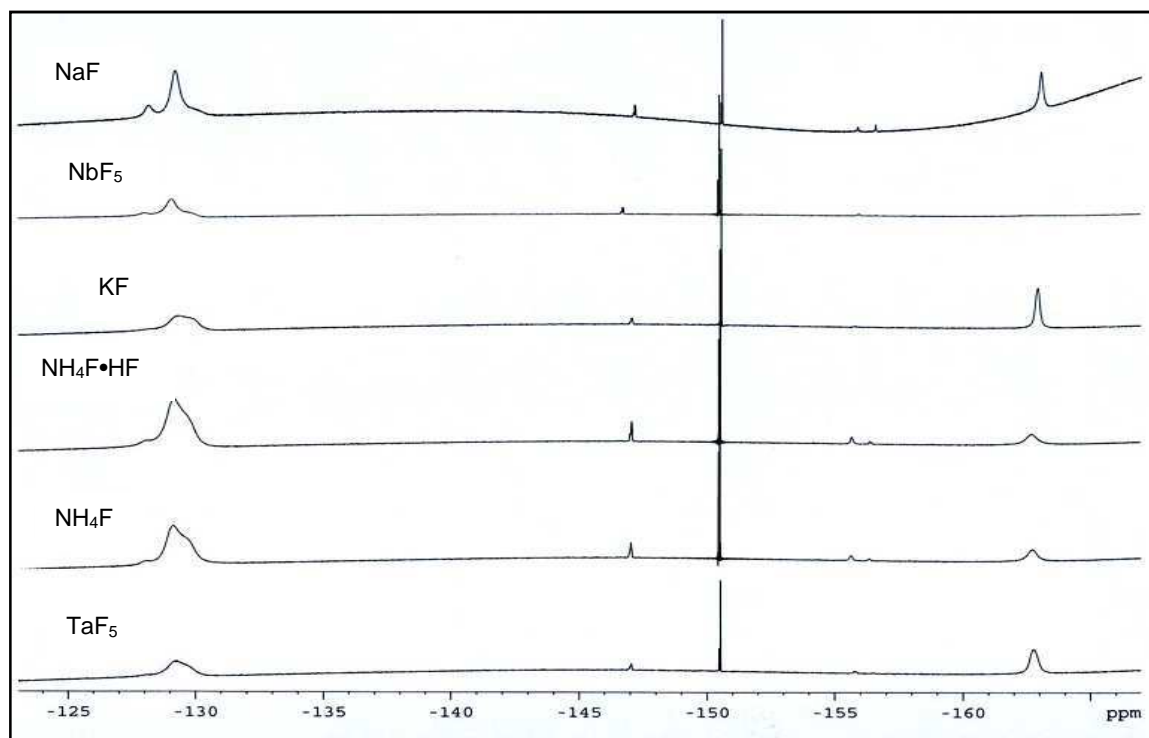


Figure 4.15: ^{19}F -NMR spectra of selected fluoride salts in acidic medium.

It is clear from **Figure 4.15** that there is no significant difference in the chemical shifts of the ^{19}F NMR spectra of the different fluoride salts that were analysed although small differences in the shapes are apparent. It can be deduced from these results that the ^{19}F chemical shift is independent of the sample under the conditions used and this can be attributed to the dissociation of the salts in the acid medium so that the NMR signals are due to free fluoride ions in solution. This may imply that any of these salts could be used as a standard for quantification purposes. NaF was chosen as the fluoride standard based on its relatively high solubility, similarity between its peaks and the unknown sample as well as its non reactivity with the NMR tubes. The ^{19}F -NMR analysis showed the presence of four peaks in the precipitate (NbF_5/PPDA) spectrum. The intensity of the peak at -162 ppm seemed to decrease at higher fluoride concentrations in some solutions while the intensity of the peak at -128 ppm was found to increase with the fluoride concentration in all the standard solutions. The latter peak (-128 ppm) was chosen for quantification of the fluoride.

4.5.5.2 Sample preparation

Three portions of approximately 0.01 g (weighed to 0.01 mg accuracy) of the precipitate sample (from **Section 4.5.3**) were dissolved in 1 mL of 97% H₂SO₄ in 10.0 mL volumetric flasks. About 3 mL of D₂O was added and the volumetric flask was filled to the mark with double distilled water. The ¹⁹F-NMR spectra were recorded together with those of fluoride salts tested (to ensure that the analyte spectra are recorded under exactly the same experimental conditions). The ¹⁹F-NMR spectra of the sample are presented in **Figure 4.16**.

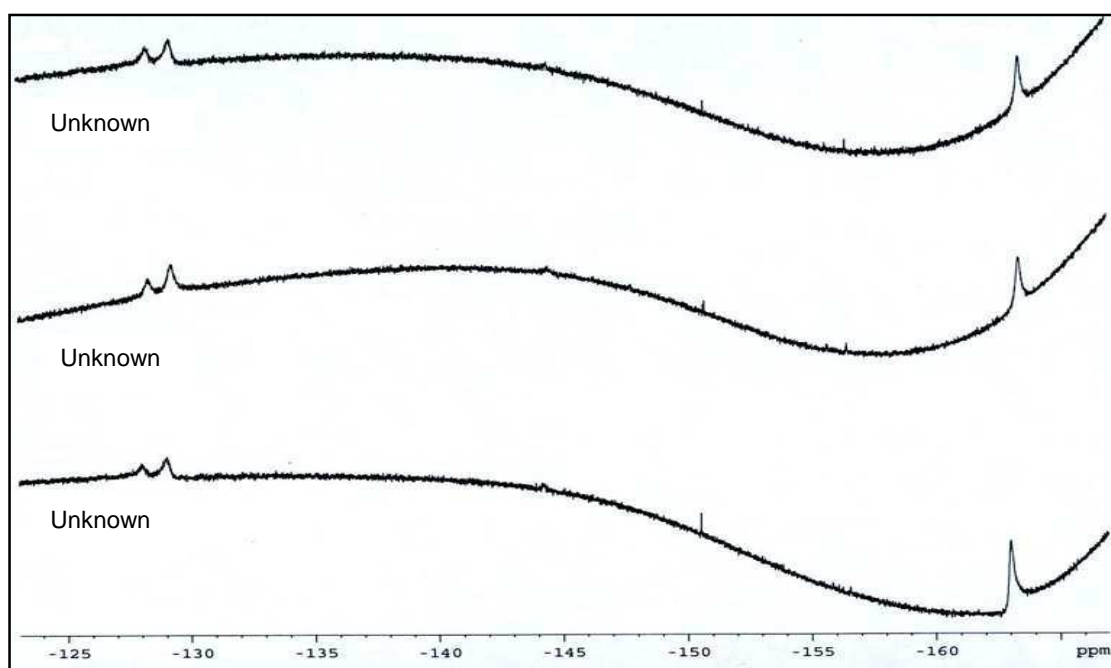


Figure 4.16: ¹⁹F-NMR spectra of the unknown Nb-PPDA compound in acidic medium.

4.5.5.3 Calibration curve and sample determination by ¹⁹F-NMR

A stock solution of 1500 mg/L fluoride was prepared by dissolving 0.3323 g of NaF in double distilled water in a 100.0 mL volumetric flask. Standard fluoride solutions of 150 to 1000 mg/L were prepared by diluting the appropriate volumes of the stock solution in 10.0 mL glass volumetric flasks. The acidity of the standard solutions was adjusted by the addition of 1 mL 97% H₂SO₄. About 3 mL of D₂O was added and the volumetric flasks were filled to the mark with double distilled water. Approximately 0.01 g (accurately weighed to 0.01 mg) of the precipitate sample (from **Section 4.5.3**) was dissolved in 1 mL 97% H₂SO₄ and then prepared the same way as the standard

solutions in 10.0 mL volumetric flask. Six replicates of the precipitate sample were prepared and measured to evaluate the precision of the method. The calibration curve was constructed from a plot of the peak intensity against the concentration (Figure 4.17).

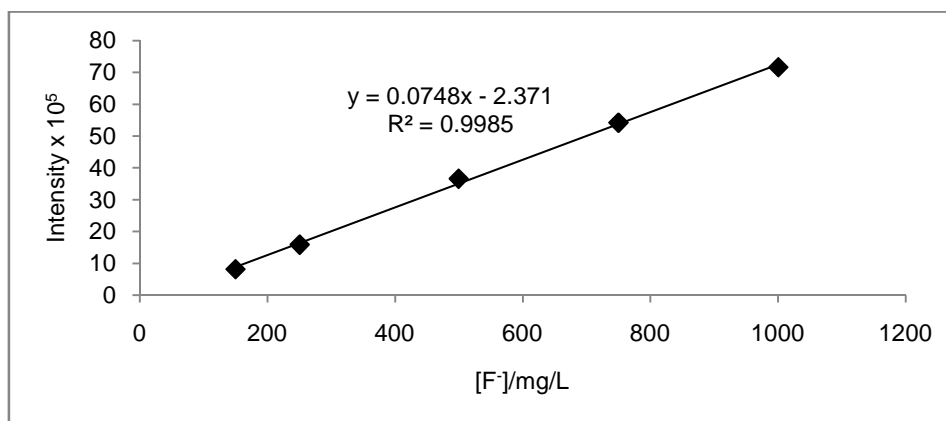


Figure 4.17: Calibration curve for fluoride quantification by ^{19}F -NMR at -128 ppm.

4.6 Results and discussion on characterisation of the NbF_5 /PPDA precipitate

4.6.1 Infrared analysis

The infrared spectra (Figure 4.9) of PPDA, NbF_5 and precipitation product of NbF_5 and PPDA were recorded and compared to determine if there has been any chemical reaction between NbF_5 and PPDA. The comparison of the IR spectra obtained for the final product with that of the two reagents clearly indicate the successful isolation of a new product. The stretching frequencies of 1615, 1514, 1258 and 818 cm^{-1} in the product (Spectrum b) corresponds very well with the peaks at 1626, 1513, 1259 and 822 cm^{-1} that was obtained for the PPDA ligand (Spectrum a) while the stretching frequency at 1740 and 1366 cm^{-1} in the product compared well with the NbF_5 stretching frequency at 1737 and 1367 cm^{-1} (Spectrum c). The appearance of a large number of new stretching frequencies in the 1000 – 900 cm^{-1} region clearly indicate a more complicated product that is formed during the reaction between NbF_5 and PPDA.

The stretching frequencies at 3065 cm^{-1} in the precipitate product and at 3196 cm^{-1} in the PPDA spectra could be due to the aromatic C-H stretching vibration. The stretching frequency at 1626 cm^{-1} in the PPDA spectrum which is also observed at 1615 cm^{-1} in the NbF_5/PPDA product spectrum can be attributed to $-\text{NH}_2$ bending vibrations. The strong stretching frequencies at 1514 cm^{-1} in the product spectrum and 1513 cm^{-1} in the PPDA spectrum are due to the C=C stretching vibrations.¹⁴⁵

4.6.2 Spectrophotometric analyses

It was observed that the reaction between the metal fluorides and PPDA also produced a coloured complex (observed at higher PPDA concentrations). The UV-Vis spectrum of a concentrated solution of PPDA was determined (**Figure 4.10 A**) together with UV-Vis spectra of the blue solution (**Figure 4.10 B**) resulting from the reaction between the NbF_5 and PPDA. The colour change in the PPDA solution from brown to blue upon mixing with the metal solution could be due to some charge transfer between the metal ion and PPDA.

The blue colouration of the reaction mixture was observed in both Ta (in much high [PPDA]s) and Nb solutions which indicated that the ligand reacted in a similar manner with both tantalum and niobium pentafluorides and the selective precipitation of niobium could be only due to the difference in the solubility products (k_{sp}) between the PPDA and the two metals. To prove this assumption the TaF_5 concentration was increased up to 0.01 M and then the UV-Vis absorption spectra of the blue solution were collected over 8 hrs. The obtained TaF_5/PPDA spectra (**Figure 4.18**) were similar to those of NbF_5/PPDA . The slow but constant increase in absorption for the reaction between TaF_5 and PPDA (see **Figure 4.18**) is attributed to precipitate formation under the prevailing conditions and was also visually confirmed by the non-translucence of the solution after 5 min. It is important to note that the $[\text{TaF}_5]$ was substantially higher compared to that of Nb complex which yielded the precipitate formation.

145. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed., Wiley-Interscience, New York, 1970, pp. 151, 225

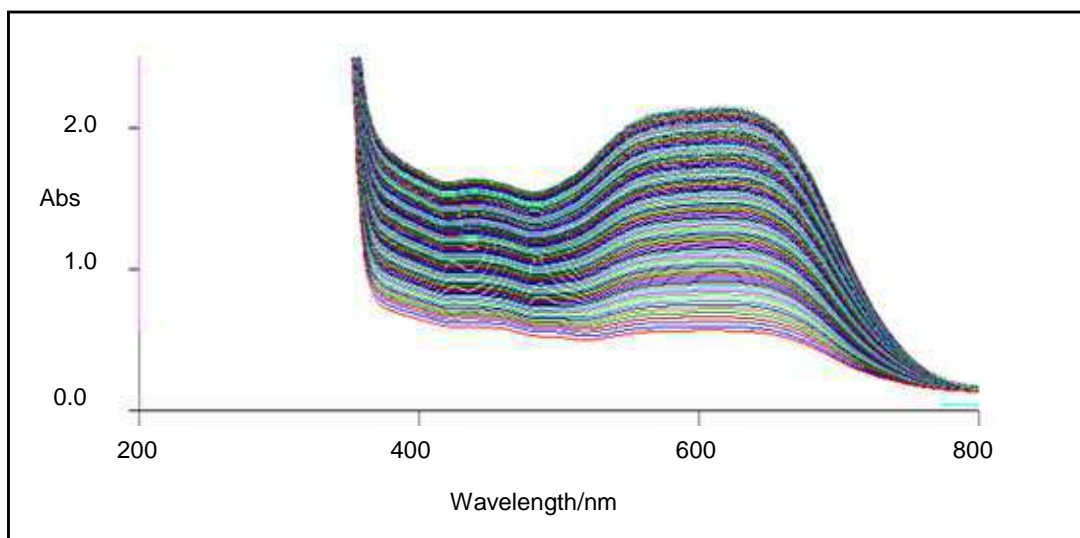


Figure 4.18: UV-Vis spectra for the reaction of 0.01 M TaF_5 and PPDA (100 scans at 1 scan/min).

The colour change of the solutions was utilised in the next step to determine the ratio of the ligand to metal in the newly metal complex. Mixtures of dilute solutions of NbF_5 and PPDA were prepared according to continuous variation, mole ratio and slope ratio procedures (**Section 4.4.5**). The absorbances of the solutions were measured using the UV-Vis spectrophotometer and the mole ratio between Nb and PPDA was determined as described in **Chapter 3, Section 3.5.1.1** for each method. The results (see **Table 4.12**) from this experiment indicated that the complex formed by niobium (or tantalum) and *p*-phenylenediamine is in a 1:1 metal:ligand ratio.

Table 4.12: Stoichiometric ratio of Nb/Ta:PPDA by different methods

Method	Ligand to metal ratio
Job's continuous variation	0.85
Slope ratio	1.24
Mole ratio	0.84
Average	0.98 ± 0.2

It is important to point out that the kinetic study of the product formation (blue colour) was also attempted. This part of the investigation was however unsuccessful due to the high PPDA concentration (reaction completed in ms) and the immediate precipitate formation from this reaction which makes the system unfavourable for a stop flow kinetic study.

Finally, the spectrophotometric analysis of the NbF₅/PPDA solutions was performed to determine the formation constant and molar extinction coefficient of the product. A linear plot of [Nb]/Abs vs 1/[PPDA] (**Figure 4.14**) whose slope = $1/\epsilon K_f$ and a y-intercept = $1/\epsilon$ was obtained. The formation constant and molar extinction coefficient which were calculated from the slope and the y-intercept were found to be $K_f = 7.74 \times 10^2 \text{ M}^{-1}$ and $\epsilon = 1.48 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. The magnitude of the formation constant obtained for the blue complex clearly indicates a thermodynamically favourable reaction for the formation of this complex. This in turn would produce the complex in large amounts for a rapid subsequent precipitation reaction (**Figure 4.7**) if the complex is an intermediate in the formation of the final precipitation (successive reaction).

4.6.3 Product formation

Based on the assumption that the precipitate obtained in this study has a similar stoichiometry to that of the blue complex, atoms of the starting materials were determined in the precipitate to confirm the spectrophotometric results. The elemental analysis results for C, N, H and the niobium metal content of the precipitate are given in **Table 4.11**. The fluoride percentages which was determined by ¹⁹F-NMR techniques was found to have an average %F = 18.7±0.9%. Although the reproducibility of the fluoride results was good, the accuracy of these results may be doubtful due to the fact that quantitative ¹⁹F-NMR is a new technique for fluoride analysis which may require a complete method validation. This falls outside the scope of this study.

The different elemental analyses of the final precipitation indicated the presence of Nb, C, H and N as well as fluoride ions (**Table 4.13**). Different combinations of metal:PPDA:F have been calculated, keeping in mind the formal oxidation state of

the metal ion, the possible charge/s of the PPDA ligand as well as its consequence to the total amount of fluoride that may then be associated with the final product.

Table 4.13: Elemental percentages for NbF₅/PPDA compounds with different Nb:PPDA ratios

Ratio	Possible compound	%				
		Nb	C	H	N	F
	Experimental results	25.5(1)	28.5(9)	4.0(1)	10.8(4)	18.7(9)
2:1	Nb ₂ (C ₆ H ₄ N ₂ H ₂)F ₈ ^a	41.80	16.22	1.36	6.31	34.24
	Nb ₂ (C ₆ H ₄ N ₂ H ₃)F ₉ ^a	40.06	15.52	1.52	6.04	36.86
	Nb ₂ (C ₆ H ₄ N ₂ H ₄)F ₁₀ ^{bc}	38.40	14.88	1.67	5.79	39.26
1:1	Nb(C ₆ H ₄ N ₂ H ₄)F ₅ ^{bc}	31.39	24.33	2.72	9.46	32.10
	Nb(C ₆ H ₄ N ₂ H ₃)F ₄ ^c	33.67	26.09	2.56	10.15	27.54
1:1.5	Nb ₂ (C ₆ H ₄ N ₂ H ₄) ₃ F ₁₀ ^{bc}	27.14	30.86	3.46	12.00	26.54
	Nb ₂ (C ₆ H ₄ N ₂ H ₃) ₃ F ₉ ^{ac}	27.33	31.76	3.41	12.36	25.15
	Nb ₂ (C ₆ H ₄ N ₂ H ₂) ₃ F ₈ ^{ac}	28.24	32.83	3.06	12.77	23.10
	Nb ₂ (C ₆ H ₄ N ₂ H ₂) ₃ F ₇ ^{ac}	29.13	33.86	3.00	13.17	20.85
	Nb ₂ (C ₆ H ₄ N ₂ H ₂) ₃ F ₆ ^{ac}	30.07	34.95	2.94	13.60	18.45
1:2	Nb(C ₆ H ₄ N ₂ H ₄) ₂ F ₅ ^{bc}	22.99	35.64	3.99	13.86	23.51
	Nb(C ₆ H ₄ N ₂ H ₃) ₂ F ₄ ^{ac}	24.26	37.60	3.68	14.62	19.84
	Nb(C ₆ H ₄ N ₂ H ₃) ₂ F ₃ ^{ac}	25.52	39.56	3.88	15.39	15.66

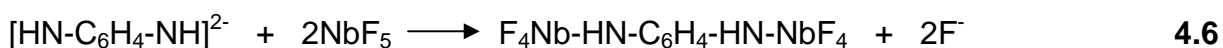
^aConsecutive reaction, ^bNeutral ligand and no F⁻ loss, ^cParallel reaction

The calculations in **Table 4.13** were also based on two possible reactions between NbF₅ and PPDA. The first reaction (formation of blue complex) is based on the possible oxidative deprotonation of the amino functional in PPDA which has been indicated in the literature.¹⁴⁶ These researchers confirmed the existence of the [Mn](THF)-PPDA and [Mn](THF)-PPDA-[Mn](THF) with [Mn] = (η⁵-C₅R₅)(CO)₂Mn(THF). The PPDA acts in the first complex as a one electron oxidation ligand to produce 1:1 and 2:1 metal:ligand complex in the second instance with the PPDA acting as a bridging ligand. In the latter both the NH₂ groups in the para-positions lose a H⁺ and an electron. These intensely blue and red coloured complexes, also known as Wurster's salts, and which are normally being produced by one e⁻

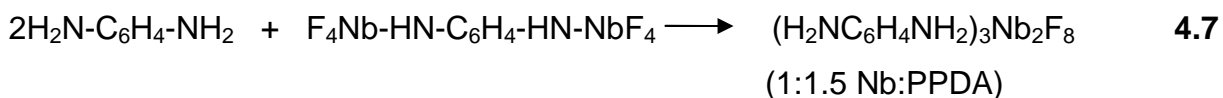
146. Gross, R. and Kaim, W., 1987, "Deprotonated *p*-Phenylenediamines as Non-innocent Ligands. Metal-to Ligand Spin Transfer in the Ground State and Ligand-to-Metal Charge Transfer in the Lowest Excited State of Low-Spin Manganese(II) Complexes" *Inorg. Chem.*, **26**: pp. 3596–3600

oxidation reactions, have been known for more than a century.^{146,147} It is clear from these results that the PPDA ligand can act as a neutral, mono as well as bivalent anion which complicate the possible type of complexes that may be formed with metal complexes such as NbF₅.

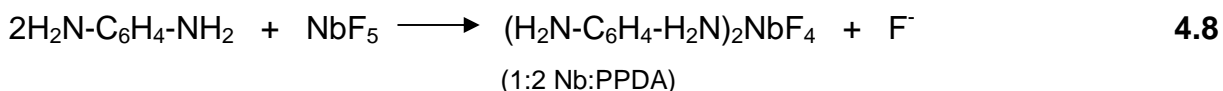
According to this type of reaction, aerial oxidation of the amine group through a loss of a proton and an electron, results in the formation of PPDA⁻ anion. This anion can then react with the NbF₅ complex to produce an intensively coloured intermediate complex. The addition of a negatively charged PPDA ligand to the metal fluoride requires the displacement of a fluoride ion in the final product in order to maintain complex neutrality (precipitate formation) if the Nb maintains a formal oxidation state of +5. The oxidative deprotonation on both amino functional groups of this ligand would be expected to produce a 2:1 Nb:PPDA complex indicated in **Equation 4.6**.



Alternatively, the precipitate could be a result of second consecutive reaction in which the PPDA is coordinated to the Nb through a lone pair of electrons on the nitrogen of the amino group after the initial reaction of the PPDA ligand to produce a number of different metal:PPDA complexes as indicated by the following reactions (**Equations 4.7 and 4.8**):



or



147. Sibert, J. W., 2002, Inventor; Earst Carolina University, assignee. Wurster's crown ligand. United States Patent US 6441164 B2. 2002 Aug 27.

The different combinations with metal and PPDA⁻ ligand ratios contribute to the large number of Nb:PPDA type of complexes that are listed in **Table 4.13**. The composition of final product (precipitate) is postulated using a combination of the reactions proposed by Gross and Kaim¹⁴⁶ as well as the quantification results obtained in this study. The possible different complex compositions which were calculated, were compared to the elemental composition that was experimentally obtained (see **Table 4.13**). It is clear from these results that not any of the proposed metal:PPDA ratios completely match that of the experimental results that were obtained for Nb-PPDA precipitate. The niobium and fluoride content clearly suggest a metal:PPDA ratio larger than 1:1.5 with a close match to that of a 1:2 ratio. The carbon content however for this ratio becomes completely disproportionate. A closer C content is observed for a 1:1 and 1:1.5 ratios while this ratio then again increases the Nb content compared to that which was experimentally obtained. The best fit for the most important elements (assuming some doubt about the newly developed, yet unvalidated F analysis) is the 1:1.5 metal to ligand ratio complexes in **Table 4.13**.

The following mechanism (**Figure 4.19**) is proposed for the formation of a 1:1 blue complex as well as for the subsequent precipitate formation (highlighted in blue in **Table 4.13**). In this case the blue complex would exist as an intermediate step in the precipitate formation process.

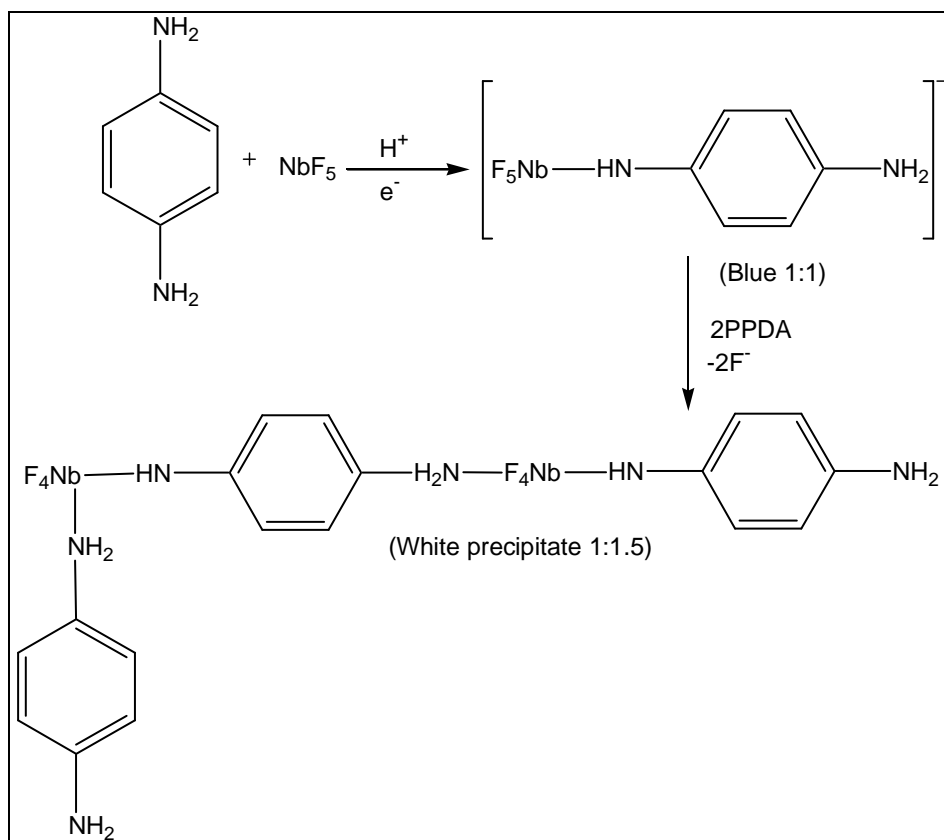


Figure 4.19: Schematic illustration of the possible reactions leading to the formation of the coloured complex and the precipitate between NbF₅ and PPDA.

4.7 Conclusion

This study which investigated the separation of niobium and tantalum(V) fluoride by selective precipitation using an inorganic ligand demonstrated that the *p*-phenylenediamine preferentially precipitates niobium from a 50% mixture of NbF₅ and TaF₅. Niobium recoveries in excess of 80% with only 4% tantalum were obtained in the precipitate from the reaction of (Nb/Ta)F₅ with PPDA in ethanol. The determination of Nb and Ta content in the supernatant solution by ICP-OES indicated that more than 95% of the initial tantalum complex remained in solution. It was found that PPDA reacted in a similar way with both TaF₅ and NbF₅, but that the precipitation as well as the selectivity was mainly governed by the initial concentrations of TaF₅, NbF₅ and PPDA.

The semi-quantitative analyses of the NbF₅ and PPDA product were accomplished using ICP-OES, IR, UV-Vis spectroscopy, micro CHNS analysis and ¹⁹F-NMR. Based

on the quantitative results of a precipitate compound obtained from the reaction between NbF_5 and PPDA, a formula $\text{Nb}_2(\text{C}_6\text{H}_4\text{N}_2\text{H}_4)_3\text{F}_{10}$ or $\text{Nb}_2(\text{C}_6\text{H}_4\text{N}_2\text{H}_2)_3\text{F}_8$ for a 1:1.5 Nb:PPDA ratio can be suggested due to the similarity of the elemental percentage in the unknown compound.

In conclusion, the reaction between PPDA and the metal pentafluorides selectively precipitated Nb in preference to Ta, and thereby successfully achieved the initial goal of separating the two metals from the same solution. The next step of the study (**Chapter 5**) is to test the applicability of this separation method on tantalum and niobium separation from a mixture of Ta_2O_5 and Nb_2O_5 before it is applied to the tantalite mineral as indicated in **Figure 4.1**.

5 Dissolution and separation of Nb_2O_5 and Ta_2O_5

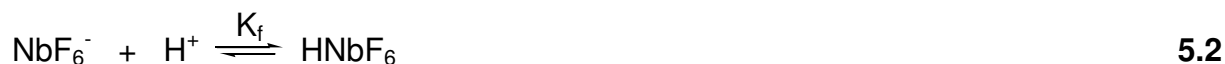
5.1 Introduction

The chemical similarity between metallic Nb and Ta, and their different chemical compounds, as well as the high chemical inertness of the host minerals such as tantalite, make the choice of a chemical process for the separation and the isolation of these elements an interesting challenge. The successful separation of Nb and Ta from each other and from other elements in a complex mineral matrix depends firstly on the selection of appropriate sample dissolution techniques. Despite the large amount of work that has been done on the dissolution and the accurate determination of Ta and Nb in various matrices (see **Chapter 2, Section 2.2**), only a few of these dissolution techniques proved to be effective and could be used for the subsequent successful separation for these elements.

A well known technique which is very successful in producing good separations between Ta and Nb entails the extraction of the tantalum compound alone or sometimes with the niobium compound from hydrofluoric acid solutions using methyl isobutyl ketone (MIBK) as extractant. The disadvantage of this separation method lies in the sample preparation and the handling of the reagents such as HF. In addition, this dissolution procedure produces highly acidic solutions in which the selective separation (extraction in this case) of these elements is in many cases highly ineffective and the separation process is characterised by numerous extraction steps until a more selective step is reached which makes the process extremely tedious.⁴² It is therefore essential to use alternative dissolution methods which involve the use of milder reagents, but which may support the subsequent separation technique such as MIBK extraction.

Research⁴² indicated that the successful and subsequent isolation of the two metal compounds is centred around the formation of the TaF_6^- and NbF_6^- compounds. The

difference in the formation of the acid compounds, HTaF₆ and HNbF₆, appears to be the key for the extraction into MIBK as indicated in the **Equations 5.1** and **5.2**:



The difference in the K_f values (as indicated by the equilibria above) allows for the extraction of HTaF₆ at lower acid concentration into MIBK, compared to HNbF₆. It is anticipated that the use of an alternative fluoride source such as NH₄F•HF may not necessarily yield the same fluoride compounds in solution as HF and may therefore change the separation chemistry. In **Chapter 4** the separation of other Ta and Nb fluoride compounds were investigated in order to explore new separation techniques on newly anticipated fluoride compounds from a change in dissolution method. These newly developed techniques would then be also tested on the products obtained from the dissolution of the metal oxides and/or the mineral.

This chapter comprises two parts. The aim in the first part is to identify a dissolution method which is ecologically acceptable, cost-effective, allow for the complete dissolution of the starting compounds and enables the subsequent separation of these two elements. The second part of the study aims to investigate different separation techniques and to find the optimum conditions for the separation of Nb and Ta from each other using these methods. It was decided to begin the study with the dissolution and subsequent separation of these two elements from a synthetic mixture of niobium and tantalum pentoxides (see **Figure 5.1**) using flux fusion methods. The metal oxides were selected for this study due to their presence in the tantalite mineral and any positive result may then be transferred and evaluated on the mineral itself.

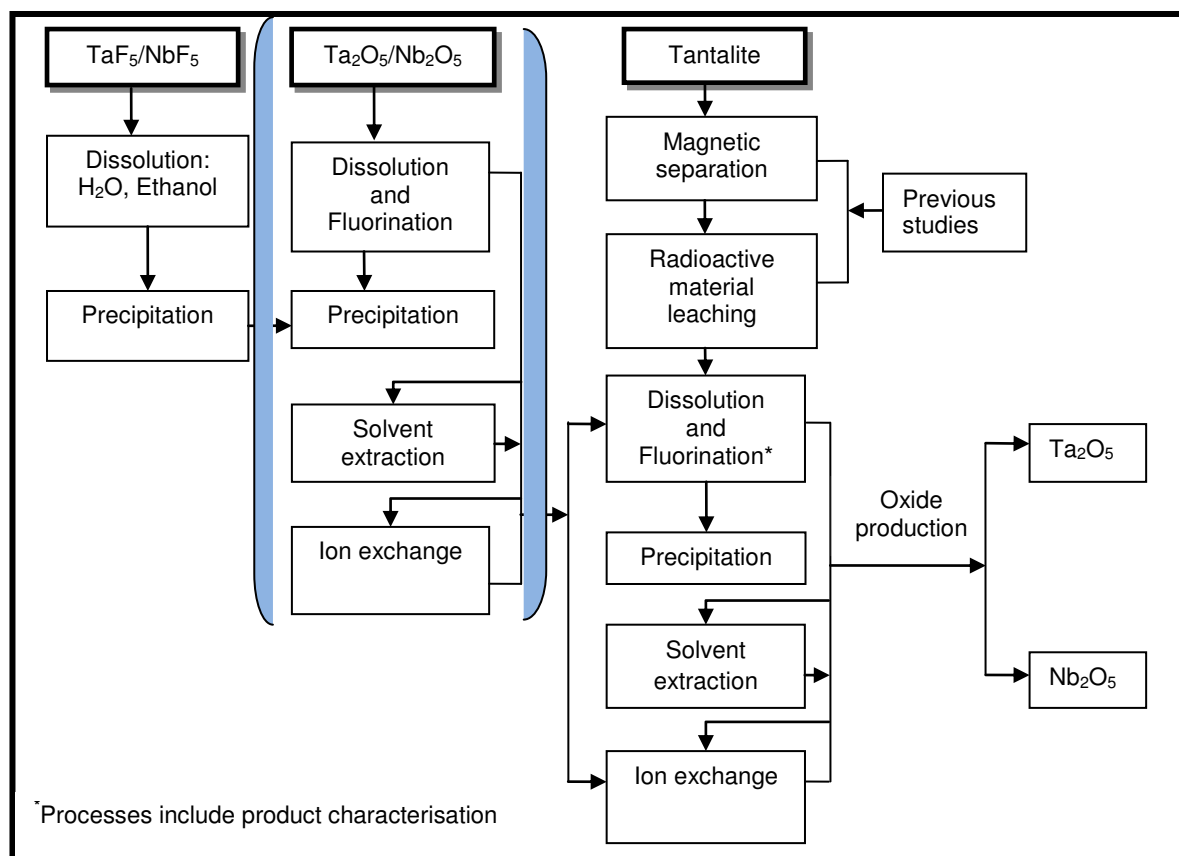


Figure 5.1: Flow diagram with the highlighted area indicating the focus in this part of the study in the separation of Ta and Nb.

5.2 Experimental methods

5.2.1 Reagents and equipment

A strong basic anion exchanger, Amberlite IRA-900 (16 - 50 mesh), as well as a weak basic anion exchanger Dowex marathon (350 – 450 μm), were purchased from Sigma Aldrich. Clinobrite 814 zeolite (cationic filter medium) was supplied by Pratley (Pty) Ltd. High purity Ta_2O_5 (99.99%), Nb_2O_5 (99.9%), as well as Na_2HPO_4 , $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, KF and NaF were also bought from Sigma Aldrich while ammonium bifluoride ($\text{NH}_4\text{F} \cdot \text{HF}$) and *p*-phenylenediamine were sourced from Merck. ICP standard solutions containing 1000 mg/L Ta and Nb were also obtained from Merck. Methyl isobutyl ketone (MIBK) was sourced from Saarchem. Analytical grade H_2SO_4 (97%), H_3PO_4 (85%) and HCl (32%) were bought from Associated Chemical Enterprises. Double distilled water was used in all cases.

Flux fusions were performed in a Thermo Scientific Thermolyne Compact Benchtop Muffle Furnace. The Boeco SP series adjustable volume pipettes and grade B glass and polytetrafluoroethylene (PTFE) volumetric flasks which were bought from Merck were used for sample solution preparations. Merck glass columns with an internal diameter of 1.2 cm were used for ion exchange separations. Centrifugation was performed in a centrifuge supplied by MSE while a Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer controlled by a computer was used for the qualitative and quantitative analysis of Ta and Nb in the solutions. X-ray diffraction spectrometric (XRD) analyses were performed using a Siemens D5000 Diffractometer while the infrared spectra were obtained with a Scimitar Series Digilab spectrometer. The pH measurements were carried out using a Eutech CyberScan pH 1500 bench meter. The average values for the results are reported based on the standard deviations to indicate the uncertainty in the last digit of the value throughout the chapter.

5.2.2 Preparation of ICP-OES calibration solutions and measurements

Standard solutions for ICP-OES analysis were prepared by adding the appropriate volumes of the 1000 mg/L stock solutions to 10.0 mL 97% H₂SO₄ (or 5.0 mL 85% H₃PO₄ when phosphate flux mixture was used) in 100.0 mL volumetric flasks and diluted to the mark with double distilled water to prepare 1.0, 3.0, 5.0, 10.0, and 20.0 mg/L concentrations. The blank solutions were prepared by diluting 10.0 mL H₂SO₄ (or 1:1 Na₂HPO₄:NaH₂PO₄•H₂O fusion melt in 5.0 mL 85% H₃PO₄ for phosphate fusion analysis) to the 100.0 mL mark of the volumetric flask with distilled water and were used for background correction. Quantitative analyses were performed at 309.418 nm for Nb and at 240.068 nm for Ta while the detection limits were determined as 0.0094 and 0.024 mg/L for Nb and Ta respectively.⁵³ The ICP-OES conditions indicated in **Table 4.1** were used for quantitative analyses.

5.2.3 Dissolution of synthetic mixture of Nb₂O₅ and Ta₂O₅ by phosphate fusion

Accurately weighed 0.05 g (to 0.1 mg) samples of Nb₂O₅ and Ta₂O₅ (1.7:1 Nb:Ta mole ratio) were thoroughly mixed with 0.4 g Na₂HPO₄ and 0.4 g NaH₂PO₄•H₂O in a platinum crucible. The actual masses of the samples weighed in this chapter can be viewed in the accompanying CD attached to the thesis in the file with the name: **Chapter 5**. The mixture was fused at 900 °C in a high temperature oven for 30 min. The fusion process was interrupted after 15 min and the mixture was swirled to

facilitate the decomposition process. The obtained melt was then cooled to room temperature and dissolved with double distilled water. The clear solution which indicated a complete dissolution of the melt was then quantitatively transferred to a 100.0 mL volumetric flask and filled to the mark with distilled water. From this solution, a 1.0 mL aliquot was transferred to another 100.0 mL volumetric flask. The acidity of the dilute (1.0 mL) solution was adjusted to match the 0.74 M of the blank and the standard solutions using 5 mL 85% H₃PO₄. The volumetric flask was finally filled to the mark with distilled water. The solution was analysed using ICP-OES for determination of the Nb and Ta recoveries (**Table 5.1**).

Table 5.1: Analytical results for (Nb/Ta)₂O₅ and Na₂HPO₄/NaH₂PO₄•H₂O fusion digestion

Sample	% Recovery	
	Nb	Ta
1	99.44	100.63
2	100.28	99.86
3	99.96	101.40
4	99.71	100.58
Average	99.85	100.62
SD	0.36	0.63
% RSD	0.36	0.62

5.2.4 Separation of Nb₂O₅ and Ta₂O₅ using the phosphate fused solutions

5.2.4.1 Selective precipitation of Nb₂O₅ and Ta₂O₅ using PPDA

A solution of Nb₂O₅ and Ta₂O₅ mixture prepared in **Section 5.2.3** was used to evaluate the applicability of the selective precipitation method which was developed in **Chapter 4** in the separation of the oxides. A *p*-phenylenediamine (PPDA) solution was prepared by dissolving 0.06 g (accurately weighed to 0.1 mg) PPDA in 10.0 mL water. The PPDA solution (5.0 mL) was added to the solution (5.0 mL) containing the (Nb/Ta)₂O₅ mixture. The pH of the solution was determined and was found to be 6.89. The mixture was left to stand for 12 hrs for precipitation to occur. No precipitation or colour change was observed at the end of this period.

The experiment was repeated with four more 5.0 mL aliquots of the (Nb/Ta)₂O₅ mixture. The PPDA solution (5.0 mL) was added to each of the pentoxides solutions

and the pH of the resultant solutions was dropped from 6.89 to 5.10 and 4.30 using 0.1 M H_3PO_4 solution and then left for 12 hrs for precipitation to occur. No precipitate formation was observed at the end of this period.

The fact that the separation procedure of the selective precipitation of the two elements using PPDA was developed using TaF_5 and NbF_5 prompted the additional need to add the fluorides to the separation mixture. The precipitation experiment was repeated as described previously, but this time 0.5 g of $\text{NH}_4\text{F}\cdot\text{HF}$ was added to the $(\text{Nb}/\text{Ta})_2\text{O}_5$ solution before adding the PPDA solution. No precipitation was observed upon the addition of the precipitating agent, but the solution became milky on standing for 12 hours. However, the precipitate particles were too fine for a quantitative separation from the solution. This fine precipitate formation in the presence of F^- ions could also indicate the importance of fluorides in the separation of the two elements.

5.2.4.2 Solvent extraction from phosphate fused solutions

A solution containing the Ta and Nb mixture obtained from the phosphate fusion dissolution (**Section 5.2.3**) was brought into contact with methyl isobutyl ketone (MIBK) to evaluate the possible liquid extraction of one or both elements. A 5.0 mL aliquot of the sample solution containing Nb and Ta was pipetted into a glass separatory funnel followed by the addition of 5 mL of 1.0 M H_3PO_4 . A 10.0 mL portion of MIBK was added to this solution and the mixture was shaken for 5 min. The mixture was then allowed to stand for another 5 min to allow for the separation and equilibration attainment of the liquid phases.

The aqueous solution which formed the bottom layer in the separating funnel, was collected in a 100 mL beaker. The organic solution was stripped with a 10 mL portion of distilled water. The solution was again allowed to stand for 5 min for the phases to separate and the water layer was then collected in a separate 100 mL beaker. The two solutions (acidic aqueous and water strip) were then heated on a hot plate at 40 °C for 50 min to evaporate any MIBK that remained in this layer (to prevent the carbon build-up and subsequent clogging of ICP torch) ensuring that not all the water is removed in this step. The solutions were then cooled to ambient temperature and then quantitatively transferred into 100.0 mL volumetric flasks. The acidity of the

solutions was adjusted to match the 0.74 M of the blank and standard solutions with 85% H₃PO₄ and then the solutions were cooled and subsequently filled to the mark with distilled water. This extraction procedure was repeated at 3.0 M and 5.0 M H₃PO₄ concentrations. The solutions were analysed using ICP-OES and the results are given in **Table 5.2**.

Table 5.2: Solvent extraction results for separation of Nb₂O₅ and Ta₂O₅ using MIBK from phosphate fused mixture

[H ₃ PO ₄] (M)	% Recovery			
	Aqueous phase		Organic phase	
	Nb	Ta	Nb	Ta
0.5	99.77	100.42	0.68	0.23
1.5	100.98	98.36	0.63	0.82
2.5	98.58	100.36	0.69	0.26

5.2.4.3 Separation of Nb and Ta using cation exchange resins

The solution obtained from the phosphate fusion (**Section 5.2.3**) was also tested on cation exchange column for the separation of Nb and Ta. A glass column with 1.2 cm diameter was packed with a weakly acidic clinobrite zeolite cation exchange resin. A zeolite resin was added to distilled water in a 250 mL beaker and stirred to form a free flowing slurry. The slurry was then transferred to the column by means of a funnel. The resin was allowed to settle up to a height of 20 cm. The excess water was then allowed to run out until it was about 1.5 cm above the resin bed. The column was washed with 20 mL of 0.1 M H₃PO. A 5.0 mL aliquot of the sample solution from **Section 5.2.3** was transferred to a column and sequentially eluted with 30 mL aliquots of H₃PO₄ of different concentrations at a rate of 0.7 mL per min. Effluent of each acid concentration was collected at the bottom of the column in a 100.0 mL volumetric flask. The solutions were diluted to the 100.0 mL mark with distilled water for ICP-OES analyses. The quantitative results of this separation experiment are presented in **Table 5.3**.

Table 5.3: Recovery of Nb and Ta from column chromatographic separation on weakly acidic zeolites (by elution with H_3PO_4)

[H_3PO_4] (M)	% Recovery	
	Nb	Ta
0.01	100.43	100.08
0.1	0.02	0.66
1	0.74	0.61
3	0.28	0.31

The results in **Table 5.3** indicated that both Nb and Ta are readily eluted from the weakly acidic cation exchange (zeolite) with dilute H_3PO_4 solutions. It was then decided to investigate a possible separation of these metals on a strong cation exchange resin.

A glass column of 1.2 cm diameter was packed to the height of 20 cm with Amberlite IR-130C. The column was washed with 20 mL of 0.1 M H_3PO_4 . A 5.0 mL aliquot of the sample solution from **Section 5.2.3** was transferred to a column and sequentially eluted with 30 mL aliquots of H_3PO_4 of different concentrations at a rate of 0.7 mL per min. Eluate for each acid concentration was collected at the bottom of the column in a 100.0 mL volumetric flask. The solutions were diluted to the mark with distilled water and then analysed using ICP-OES. The results of this separation experiment are given in **Table 5.4**.

Table 5.4: Recovery of Nb and Ta from column separation using a strong Amberlite cation exchange (by elution with H_3PO_4)

[H_3PO_4] (M)	% Recovery	
	Nb	Ta
0.01	96.62	96.20
0.1	0.25	0.31
1	0.24	0.31
3	0.22	0.33
5	0.26	0.36

5.2.5 Sample dissolution by fluoride fusion

5.2.5.1 Different salts as fluoride sources

The flux fusion method was investigated for the dissolution and fluorination of Nb₂O₅ and Ta₂O₅ using fluoride containing salts. The fluoride salts which were evaluated are KF, NaF and NH₄F•HF. A mixture of Nb₂O₅ and Ta₂O₅ powder was prepared by accurately weighing 0.05 g (to 0.1 mg) of each metal oxide (1.7:1 Nb:Ta mole ratio) in a platinum crucible. A 1.0 g mass of finely ground flux salt (KF, NaF and NH₄F•HF) was added (1:10 metal to flux mass ratio). The samples were mixed homogeneously and then fused in a high temperature oven under the conditions indicated in **Table 5.5**.

Table 5.5: Operating conditions for the (Nb/Ta)₂O₅ mixture digestion using selected fluoride salts as fluxes

Flux	Flux mp (°C)	Fusion temperature (°C)	Time (min)	Metal:flux mass ratio
NH ₄ F•HF	125	200	30	1:10
NaF	992	1100	30	1:10
KF	857	950	30	1:10

The clear liquids obtained for NH₄F•HF and KF after the fusion solidified into white amorphous solids upon cooling. The NaF fusion however produced a white turbid solution which also solidified to become an amorphous solid upon cooling. All the fusion products were cooled to room temperature and then dissolved in water. Only the NH₄F•HF melt dissolved completely in water and this solution was quantitatively transferred to a 100.0 mL PTFE volumetric flask and filled to the mark with distilled water.

A solution of 1.0 M H₂SO₄ was added to try and dissolve the KF and NaF fusion products. The KF and NaF melts did not dissolve completely even in 1.0 M H₂SO₄ solution. The remaining solids were filtered and the filtrates were quantitatively transferred to 100.0 mL PTFE volumetric flasks and filled to the mark with distilled water. Dilute solutions of each of the fusion products were prepared by transferring 1.0 mL of the original solutions into 100.0 mL volumetric flask. The acidity of the dilute solutions was adjusted to match 1.810 M of blank and standard solutions using 97% H₂SO₄. The solutions were cooled and the volumetric flasks were filled to the

mark with distilled water. The quantitative determination of Nb and Ta in these dilute solutions was performed using ICP-OES and the results are presented in **Table 5.6**.

Table 5.6: Recovery of Nb and Ta from fluoride flux digestion in a 1:10 M_2O_5 :flux mass ratio

Flux	Solvent	% Recovery	
		Nb	Ta
KF	0.1 M H_2SO_4	97.04	69.29
KF	0.1 M H_2SO_4	99.47	70.37
$NH_4F \cdot HF$	Water	100.05	98.72
$NH_4F \cdot HF$	Water	101.39	97.17
NaF	0.1 M H_2SO_4	21.37	21.02
NaF	0.1 M H_2SO_4	22.70	13.43

The results in **Table 5.6** indicate successful recovery of the two compounds using $NH_4F \cdot HF$, partial, but potentially promising recovery with KF and poor recovery of the elements using NaF. The low Ta recoveries with the KF fusion compelled a modification in the fusion procedure using this flux.

5.2.5.2 Influence of KF concentration on tantalum recovery

The flux fusion experiment was repeated with KF and the amount of flux was doubled. A mixture of Nb_2O_5 and Ta_2O_5 powder was prepared by mixing approximately 0.05 g (accurately weighed to 0.1 mg) of each metal oxide in a platinum crucible. About 2.0 g of finely ground flux salt (KF) was added (1:20 metal:flux ratio) and the mixture was fused at 950 °C for 30 min. The fusion products were prepared for ICP-OES determinations as previously described. The recovery results from this fusion are presented in **Table 5.7**.

Table 5.7: Recovery of Nb and Ta from KF flux digestion in a 1:20 $(Nb/Ta)_2O_5$:flux ratio

Flux	Solvent	% Recovery	
		Nb	Ta
KF	0.1 M H_2SO_4	99.91	83.64
KF	0.1 M H_2SO_4	99.02	83.14

5.2.5.3 Influence of time on tantalum recovery from KF solution

The recoveries of Ta increased with an increase in KF concentration, but Ta was still not 100% recovered as indicated by the results in **Table 5.7**. The next step in this study was to study the stability of the Ta in the KF solutions and the solutions were analysed over a period of 3 days.

A reaction mixture was prepared by mixing 0.05 g (accurately weighed to 0.1 mg) of each metal oxide in a platinum crucible. About 2.0 g of finely ground KF flux salt was added and the mixture was fused at 950 °C for 30 min. The obtained melt was cooled to room temperature and then dissolved in 1.0 M H₂SO₄. Visual inspection indicated that not all the sample was dissolved. The remaining solid was removed by filtration and the filtrate was quantitatively transferred to a 100.0 mL volumetric flask which was then filled to the mark with distilled water. From this stock solution 1.0 mL was immediately transferred to a 100.0 mL volumetric flask. The acidity of the solution was adjusted to 1.810 M with 97% H₂SO₄ and the volumetric flask was filled to the mark with distilled water for ICP-OES analysis.

After 20 hrs the stock solution which indicated the presence of a precipitate was filtered and a 1.0 mL volume of the solution was transferred to another 100.0 mL volumetric flask and treated as indicated previously for ICP-OES analysis. The process was repeated again after another 20 hrs. The results obtained from this experiment are graphically presented in **Figure 5.2**.

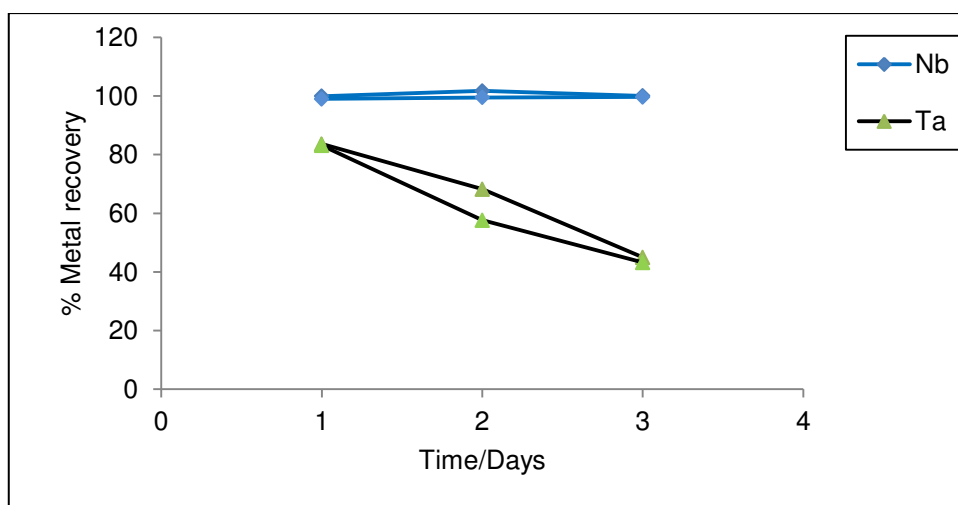


Figure 5.2: Niobium and tantalum recoveries in KF flux solutions over time.

5.2.5.4 Dissolution of Nb₂O₅ and Ta₂O₅ by flux fusion using NH₄F•HF

Approximately 0.05 g Ta₂O₅ and 0.05 g Nb₂O₅ were accurately weighed (to 0.1 mg) in a platinum crucible. About 1.0 g NH₄F•HF was added to the Ta₂O₅/Nb₂O₅ mixture and the contents were mixed thoroughly. The crucible was then placed in an oven at 200 °C and fused for 30 min. After 15 min the melt was shaken briefly and then fused for another 15 min at the end of which it was cooled to room temperature and then dissolved with distilled water. Visual inspection indicated that the entire sample had dissolved in less than 5 min of constant stirring. The clear solution was quantitatively transferred to a 100.0 mL PTFE volumetric flask and diluted to the mark with distilled water. A 1.0 mL aliquot of this solution was subsequently transferred to a 100.0 mL volumetric flask. 10 mL of 97% H₂SO₄ was added to the volumetric flask and the solution was cooled and then filled to the mark with distilled water. This dilute solution was analysed for Nb and Ta concentrations using ICP-OES and the results are presented in **Table 5.8**.

Table 5.8: Reproducibility of Nb and Ta recoveries from NH₄F•HF in a 1:10 M₂O₅:flux mass ratio

Flux	% Recovery	
	Nb	Ta
NH ₄ F•HF	101.67	101.01
NH ₄ F•HF	100.16	100.81
NH ₄ F•HF	99.74	98.39
NH ₄ F•HF	99.93	99.80
Average	100.38	100.00
SD	0.88	1.20
%RSD	0.88	1.20

5.2.5.5 Product characterisation using infrared spectroscopy

Approximately 0.1 g Ta₂O₅, 0.1 g Nb₂O₅ and a mixture (Nb,Ta)₂O₅ comprising 0.05 g of each pentoxide were accurately weighed (to 0.1 mg) in separate platinum crucibles. About 1.0 g of finely ground NH₄F•HF was added to each sample. The mixtures were fused at 200 °C for 30 min as described previously. At the end of fusion the melts were allowed to cool to room temperature and their IR spectra were obtained. The vibrational spectra of the fusion products using NH₄F•HF as flux for

dissolution of Nb_2O_5 , Ta_2O_5 , $(\text{Nb/Ta})_2\text{O}_5$ mixture as well as that of $\text{NH}_4\text{F}\cdot\text{HF}$ are presented in **Figures 5.3 to 5.6**.

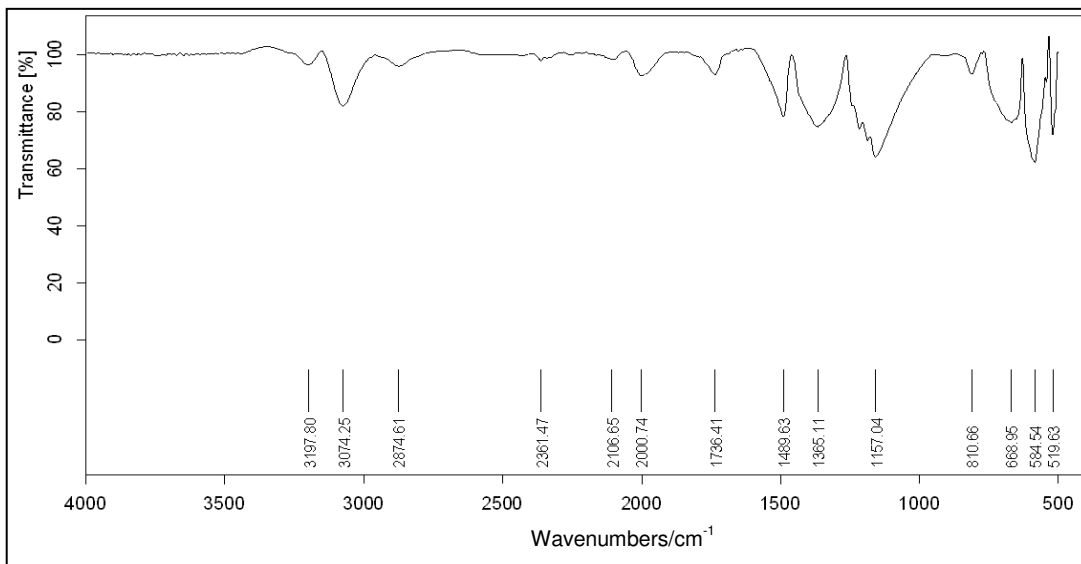


Figure 5.3: IR spectrum of $\text{NH}_4\text{F}\cdot\text{HF}$ flux.

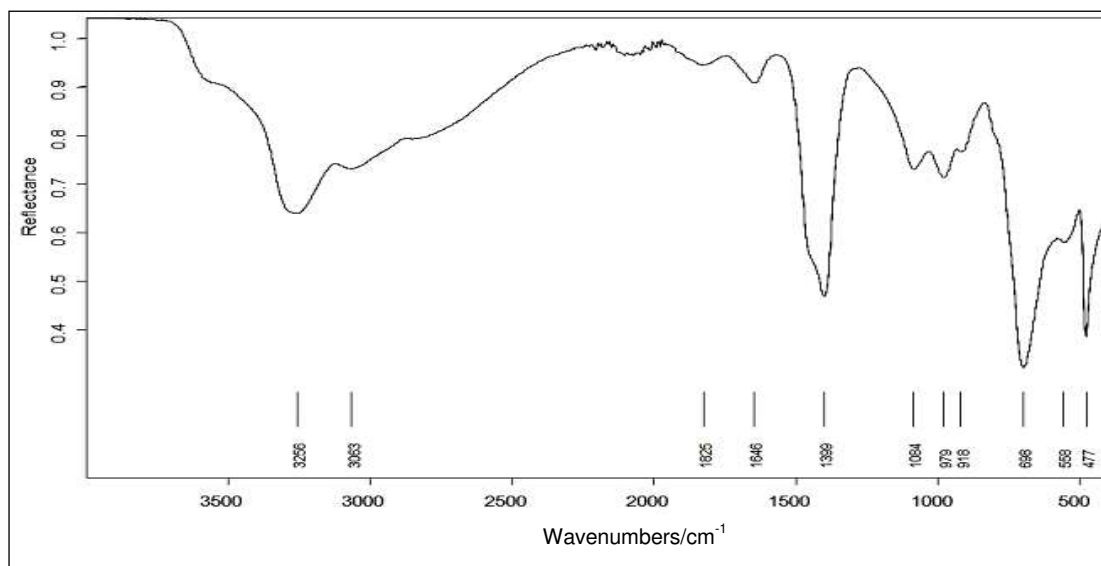


Figure 5.4: IR spectrum of the fusion product between $(\text{Nb/Ta})_2\text{O}_5$ mixtures and $\text{NH}_4\text{F}\cdot\text{HF}$ as flux reagent.

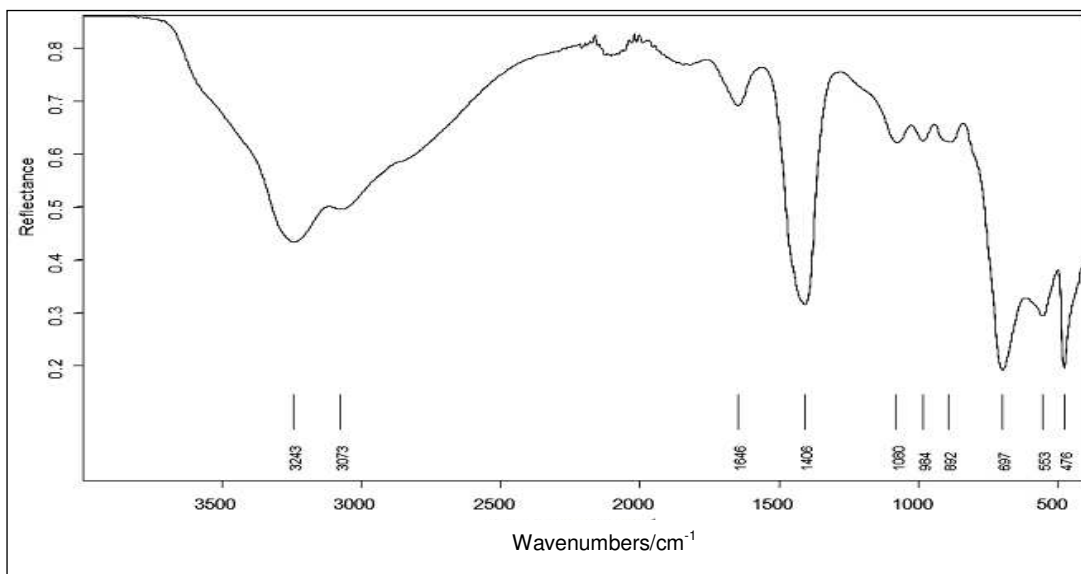


Figure 5.5: IR spectrum of the fusion product between Nb_2O_5 and $\text{NH}_4\text{F}\cdot\text{HF}$ as flux reagent.

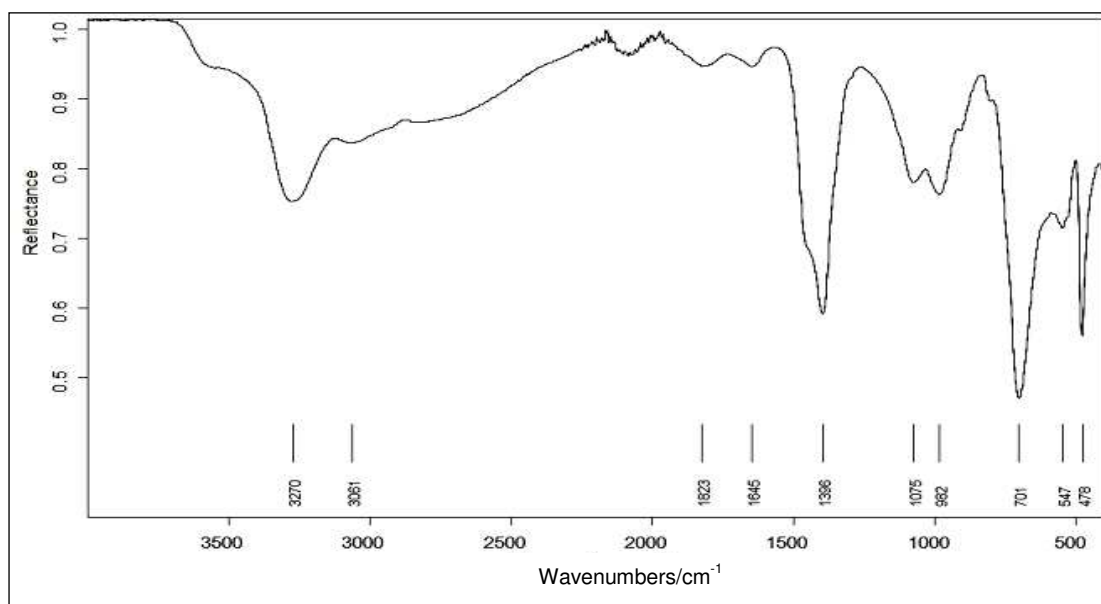


Figure 5.6: IR spectrum of the fusion product between Ta_2O_5 and $\text{NH}_4\text{F}\cdot\text{HF}$ as flux reagent.

5.2.5.6 Product characterisation using X-ray diffraction analysis

Approximately 0.2 g Ta_2O_5 , 0.2 g Nb_2O_5 and a mixture containing both $(\text{Nb,Ta})_2\text{O}_5$ comprising 0.1 g of each pentoxide were accurately weighed (to 0.1 mg) in separate platinum crucibles. About 2.0 g of the finely ground $\text{NH}_4\text{F}\cdot\text{HF}$ was added to each

sample. The mixtures were fused at 200 °C for 30 min as described earlier. At the end of the fusion time the melts were allowed to cool to room temperature and then ground to a fine powder with a pestle and mortar to obtain a homogenous sample. These finely ground samples were then loaded on the XRD sample holder and the surfaces were flattened with a glass slide and the XRD patterns of the different samples were collected. The XRD spectra of the products obtained from the fusion of pure oxides as well as their mixture are given in **Figure 5.7**.

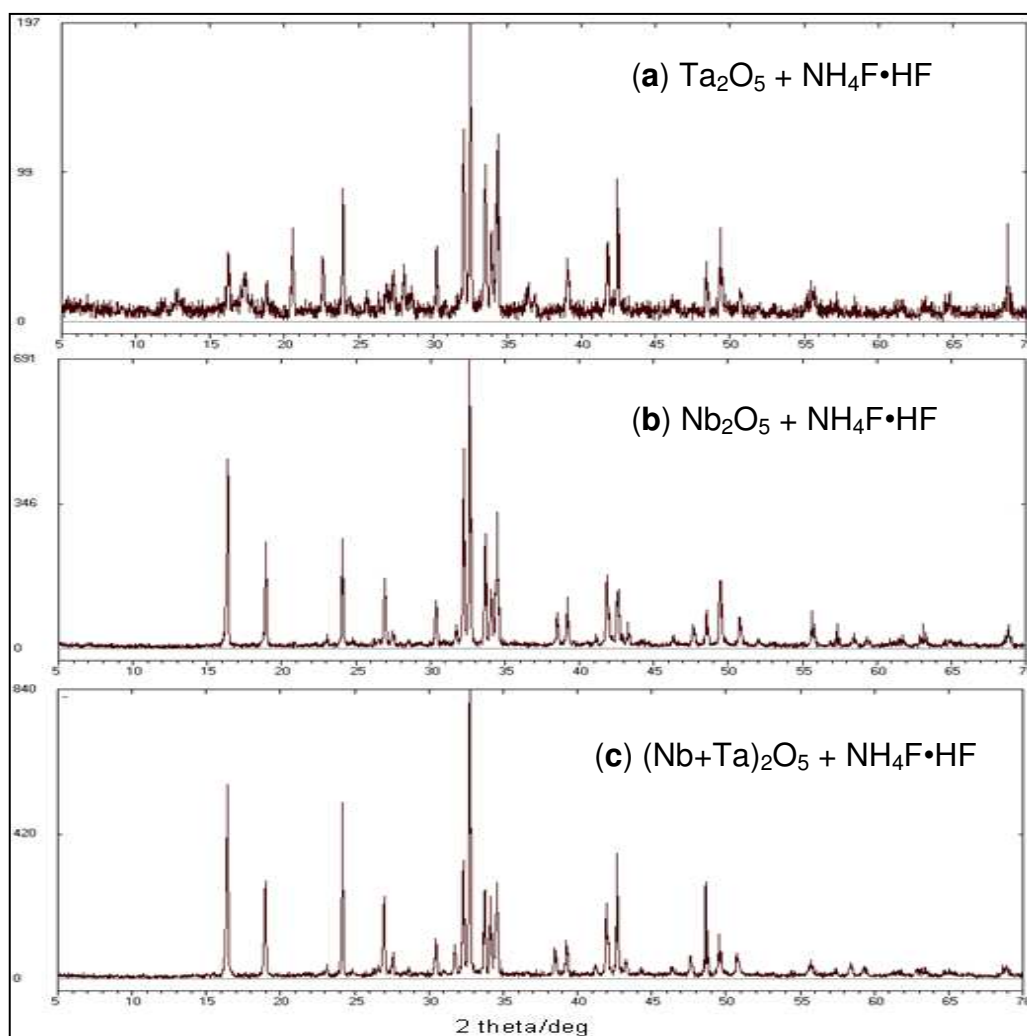


Figure 5.7: X-ray diffraction patterns of (a) $\text{Ta}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$, (b) $\text{Nb}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$, (c) $(\text{Nb}/\text{Ta})_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ fusion products.

5.2.5.7 Selective precipitation of Ta_2O_5 and Nb_2O_5 after $\text{NH}_4\text{F}\cdot\text{HF}$ fusion

A 5.0 mL aliquot of the solution obtained in **Section 5.2.5.4** was transferred to a clean and dry 50 mL beaker. Approximately 0.06 g of PPDA was accurately weighed

and dissolved in 10.0 mL double distilled water. The PPDA solution was added to the $(\text{Nb}/\text{Ta})_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ mixture and this addition was immediately followed by a colour change from colourless to blue and precipitation formation. The pH of the solution was found to be about 5.42. The precipitate was separated from the solution by centrifugation and decantation and then dissolved in 10 mL of 97% H_2SO_4 . The solution was quantitatively transferred to a 100.0 mL and filled to the mark with distilled water.

The filtrate was quantitatively transferred to 100.0 mL volumetric flask and its acidity was adjusted to 1.810 M ($\text{pK}_{\text{a}2}(\text{H}_2\text{SO}_4) = 1.02 \times 10^{-2}$) by addition of 10 mL of 97% H_2SO_4 . The solutions (precipitate and filtrate) were allowed to cool down. The volumetric flask then was filled to the mark with distilled water. The mixtures were then analysed using ICP-OES and the results are presented in **Table 5.9**.

Table 5.9: Precipitation separation results for a synthetic mixture of Nb_2O_5 and Ta_2O_5

Sample	% Recovery	
	Nb	Ta
Precipitate	23(5)	73(3)
Filtrate	76(2)	22(6)
%Total mass	99(4)	95(7)

Average and standard deviations are based on $n = 3$ measurements

5.2.5.8 *Single step solvent extraction and stripping of fluoride fused Ta_2O_5 and Nb_2O_5*

A solution containing Ta_2O_5 and Nb_2O_5 in a fluoride environment was prepared by the flux fusion using $\text{NH}_4\text{F}\cdot\text{HF}$ as described in **Section 5.2.5.4**. A 5.0 mL aliquot of the fluoride solution containing Nb and Ta, was subsequently pipetted into a glass separatory funnel followed by the addition of a 5 mL aliquot of a freshly prepared 0.5 M H_2SO_4 solution. A 10.0 mL aliquot of MIBK was added and the mixture was shaken for 5 min. The solution was then allowed to stand for 5 min to allow for the separation and equilibration attainment of the liquid phases.

The aqueous (acidic) solution which settled as the bottom layer in the separating funnel was released into a 100 mL beaker. Distilled water (10 mL) was added to the

organic layer in the separatory funnel and the mixture was shaken as before. The solution was allowed to stand for 5 min for the phases to separate and this water layer was collected in a separate 100 mL beaker. The two aqueous (water back extraction and acidic solution) solutions were then heated on a hot plate at 40 °C for 50 min to evaporate any MIBK that remained in this layer. The solutions were then cooled to ambient temperature and then quantitatively transferred into 100.0 mL volumetric flasks. The acidity of the solutions was adjusted to match the 1.810 M of the standard solutions with 97% H₂SO₄ and the solution was cooled and then filled to the mark with distilled water. This extraction procedure was repeated at different H₂SO₄ concentrations ranging from 0.5 to 4.0 M. The concentrations of Ta and Nb in each solution were determined by ICP-OES and the recoveries of each element are present in **Table 5.10**.

Table 5.10: Solvent extraction results for separation of Nb₂O₅ and Ta₂O₅ from their synthetic mixture using MIBK

[H ₂ SO ₄] (M)	Aqueous phase		Organic phase	
	% Recovery		% Recovery	
	Nb	Ta	Nb	Ta
0.0	100.91	101.53	0.10	0.08
0.5	101.09	40.57	0.58	61.51
1.0	101.41	32.99	0.60	63.57
1.5	98.74	34.13	0.72	65.90
2.0	97.41	34.56	1.72	69.22
3.0	96.63	26.30	2.04	74.29
4.0	98.11	23.47	1.60	80.59

It is clear from the results in **Table 5.10** that Nb stays mainly in the acidic aqueous solution while Ta is extracted into the organic phase. However, only about 60 to 80% Ta is extracted into the organic solution and the other 20 to 40 % remains in aqueous phase. It was also observed that the extraction of Ta increases slightly with increase in H₂SO₄ concentration.

The number of extractions (n) required to extract in excess of 99.9% of each metal from the aqueous phase was calculated using **Equation 3.33** (see **Section 3.4.2.3**) and the data in **Table 5.10** (to calculate K_{Ds} , see **Table 5.18**). These calculations predict that 2 or more extractions ($n = 2$) are needed to extract Ta quantitatively (see

Table 5.11) under the prevailing experimental conditions from the sample mixture while more than 100 extractions would be needed to quantitatively extract Nb from this mixture under similar experimental conditions. The calculations indicated that the number of extractions required for the Ta extraction decrease from 2.496 at a $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ to 1.546 at the much higher $[\text{H}_2\text{SO}_4] = 4.0 \text{ M}$, clearly indicating the acid dependence on the metal recovery in this extraction process.

Table 5.11: Calculated number of extractions required to extract 99.9% ($q = 0.10\%$) of Nb and Ta using the data in **Table 5.10**

[H ₂ SO ₄] (M)	q ^a (%)	D		n ^b	
		Nb	Ta	Nb	Ta
0.5	0.10	0.006	1.516	403.362	2.496
1.0	0.10	0.006	1.927	393.190	2.144
1.5	0.10	0.007	1.931	316.592	2.142
2.0	0.10	0.018	2.003	131.888	2.094
3.0	0.10	0.021	2.824	110.405	1.717
4.0	0.10	0.016	3.434	142.660	1.546

^aq = Fraction of solute remaining in aqueous layer

^bn = Calculated successive extractions

5.2.5.9 Influence of numerous extractions on tantalum recovery and crystallisation of the products

A 5.0 mL aliquot of the fluoride solution was pipetted into a separatory funnel to which an equal volume of a freshly prepared dilute (1.0 M) H₂SO₄ solution was added and successively extracted with two portions of 10.0 mL of MIBK. The aqueous solution was then heated to evaporate any dissolved organic solvent as previously described. The organic portions were combined and then successively stripped with two portions of 20 mL water. The two stripped solutions were then combined and heated to evaporate any extracted organic solvent. The original acidic aqueous and water strip solutions were quantitatively transferred to 100.0 mL volumetric flasks. The acidity of the solutions was adjusted to match the 1.810 M [H⁺] of the standard and the blank solutions and the volumetric flasks were then filled to the mark with distilled water. These solutions were analysed using ICP-OES and the results are presented in **Table 5.12** and graphically in **Figures 5.8** and **5.9**.

Table 5.12: Solvent extraction results for separation of Nb₂O₅ and Ta₂O₅ from their synthetic mixture using MIBK for $n = 2$

[H ₂ SO ₄] (M)	% Recovery			
	Aqueous phase		Organic phase	
	Nb	Ta	Nb	Ta
0.5	102.51	2.70	0.16	100.92
1.0	103.36	2.56	1.15	100.35
2.5	94.25	1.76	0.15	101.36
4.0	102.78	0.76	0.89	102.77

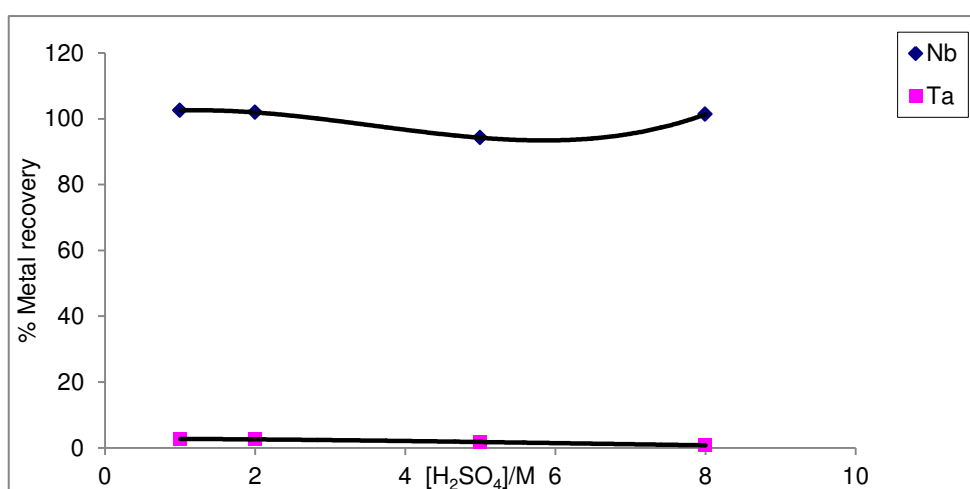


Figure 5.8: Recoveries of Nb and Ta in aqueous solution from a batch extraction procedure using MIBK.

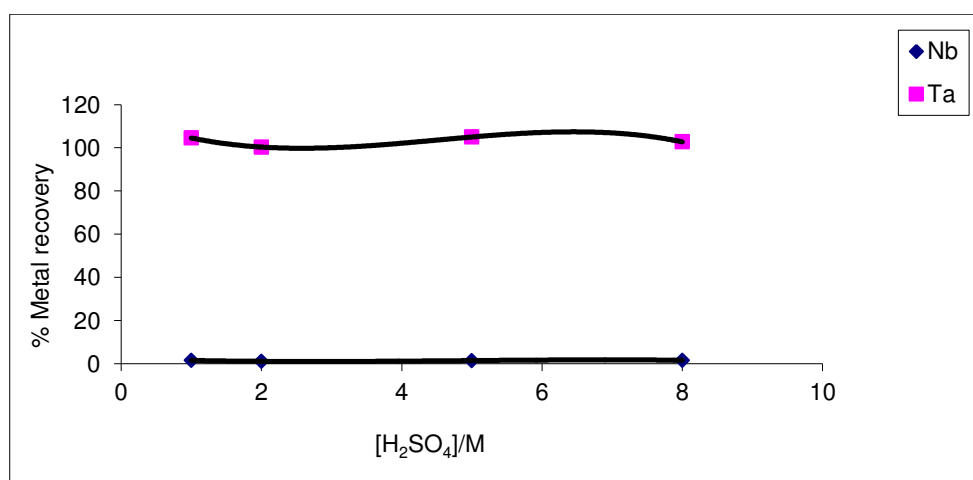


Figure 5.9: Recoveries of Nb and Ta in organic extractant from a batch extraction and stripping procedure using MIBK.

After the separation of Ta from Nb a concentrated solution (1.8 M, 36 mmol) of KF was added to 5.0 mL of the Ta rich solution and then allowed to stand for two days for the crystallisation of the product (K_2TaF_7 or $KTaF_6$) to occur.⁴² The obtained crystallined product was analysed together with the KF using infrared spectroscopy (see **Figures 5.10** and **5.11**).

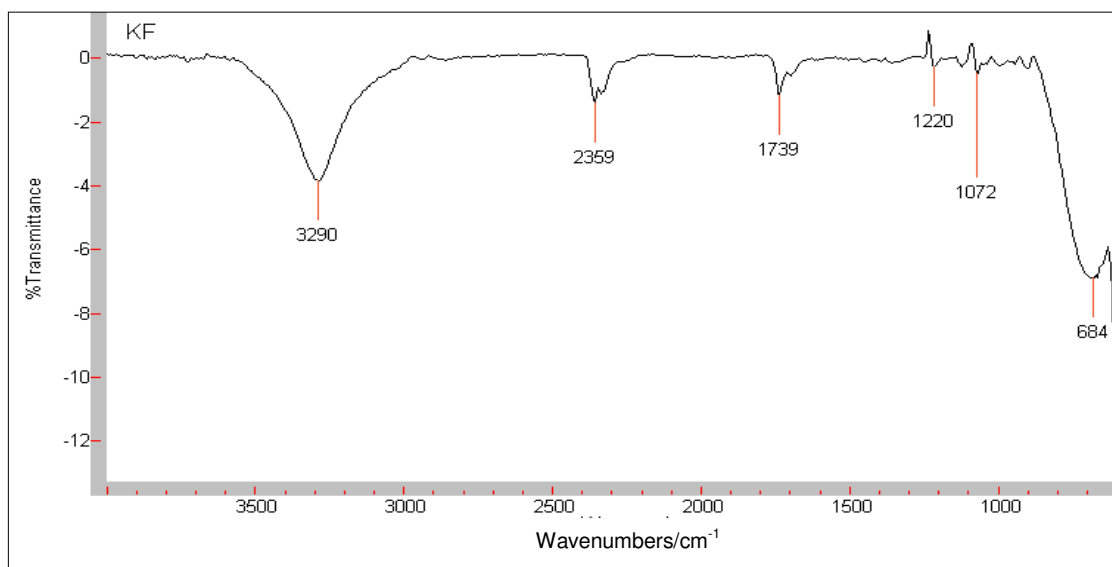


Figure 5.10: Infrared spectrum of potassium fluoride.

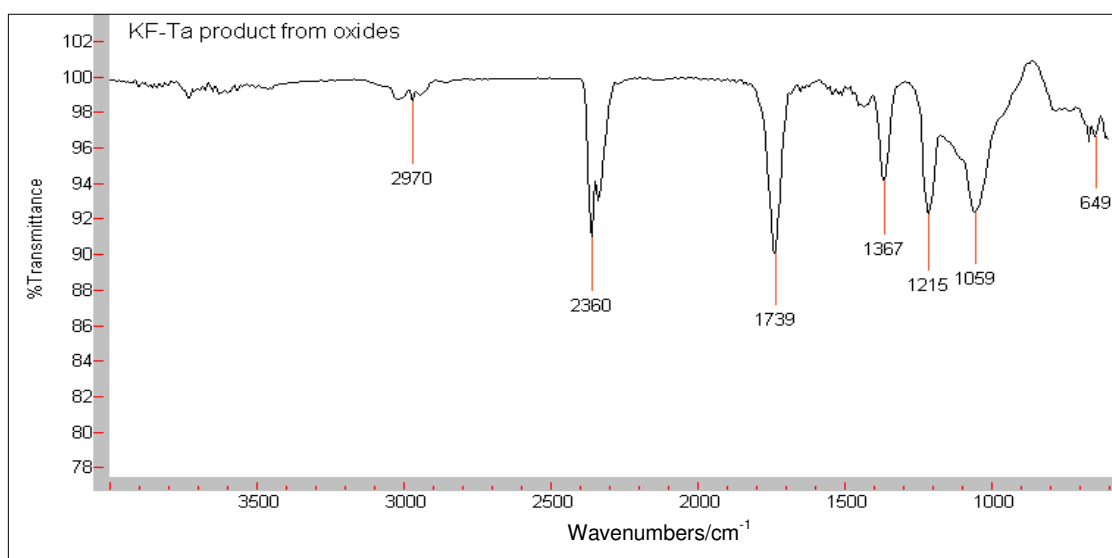


Figure 5.11: Infrared spectrum of the Ta product obtained by addition of KF in Ta rich solution.

5.2.5.10 Separation of fluoride fused (Nb/Ta)₂O₅ on anion exchange resins

Two different anion exchange resins namely, Dowex Marathon wba (a weakly basic anion exchanger, -N⁺H₂CH₃) and Amberlite IRA-900 (a strongly basic anion exchanger, -N⁺(CH₃)₃) were studied to investigate the possible separation of Nb and Ta from a mixture. The two resins were separately added to enough distilled water and stirred in a 250 mL beaker to form a free flowing slurry. The slurry was then transferred to the column of 1.2 cm diameter and packed up to a height of 20 cm. The excess water was released from the column until the water level was about 1.5 cm above the resin bed in the column. The columns were washed by running 20 mL of 1.0 M HCl through the resin. A 5.0 mL volume of the fluoride solution containing the (Nb/Ta)₂O₅ mixture (see **Section 5.2.4**) was then transferred to the column and subsequently sequentially eluted with 30 mL aliquots of HCl of different concentrations at a rate of 0.7 mL per min. The effluent of each acid concentration was subsequently collected in a 100.0 mL volumetric flask and diluted to the mark with distilled water to enable ICP-OES analyses. The results of this separation experiments are presented in **Table 5.13** while the elution curves are shown in **Figures 5.12** and **5.13** for the strong anionic Amberlite and a weak anionic Dowex Marathon exchangers respectively.

Table 5.13: Recoveries of Nb and Ta from a strongly basic Amberlite and a weak basic Dowex Marathon anion exchange columns using HCl as an eluent

[HCl] (M)	% Recovery			
	Amberlite anion		Dowex marathon anion	
	Nb	Ta	Nb	Ta
0.5	6.72	4.60	0.31	0.21
1.0	25.34	18.97	0.87	0.64
2.0	42.42	34.34	1.28	1.54
4.0	17.21	15.48	1.85	1.56
6.0	---	---	86.67	42.85
7.0	---	---	5.06	5.55
Total	91.69	73.39	96.05	52.34

--- Not determined

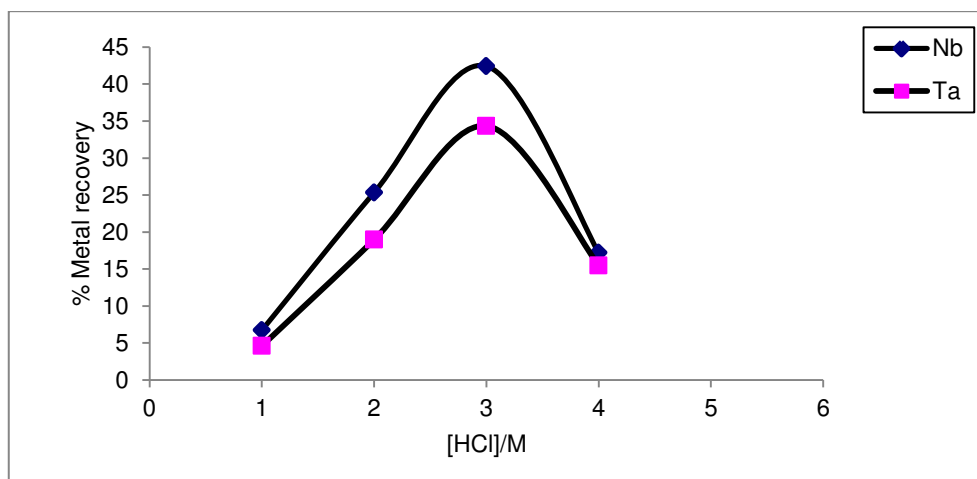


Figure 5.12: Elution of Nb and Ta (in fluoride solution) from strong Amberlite IRA-900 anion exchanger as a function HCl concentration.

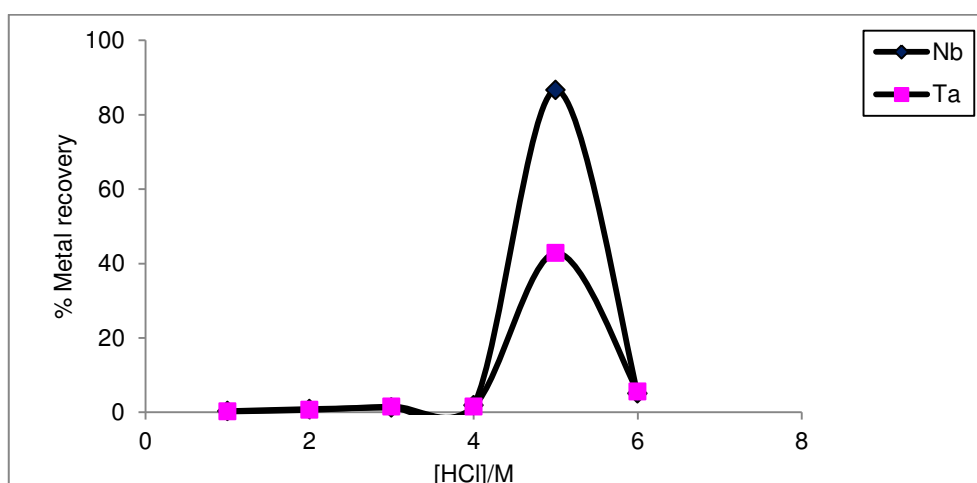


Figure 5.13: Elution of Nb and Ta (in fluoride solution) using weak Dowex Marathon anion exchanger as a function HCl concentration.

5.2.5.11 Determination of the retention times of Ta and Nb

Two different columns using the strong Amberlite IRA-900 and weak Dowex Marathon anion exchangers were prepared according to procedures previously described. The fluoride sample solution (5.0 mL) containing a mixture $(\text{Nb/Ta})_2\text{O}_5$ from **Section 5.2.5.4** was transferred to the column using a micro pipette. Continuous elution was carried with 100.0 mL of a 6.0 M HCl solution (to ensure complete elution of these elements) at a flow rate of 0.6 mL/min. Fractions of 10.0 mL of the effluent were collected and quantitatively transferred to 100.0 mL volumetric flasks. These

solutions were subsequently acidified and diluted for ICP-OES analysis as previously described. The results obtained for the Amberlite IRA-900 elution are given in **Figure 5.14** while the Dowex marathon elution curve is presented in **Figure 5.15**.

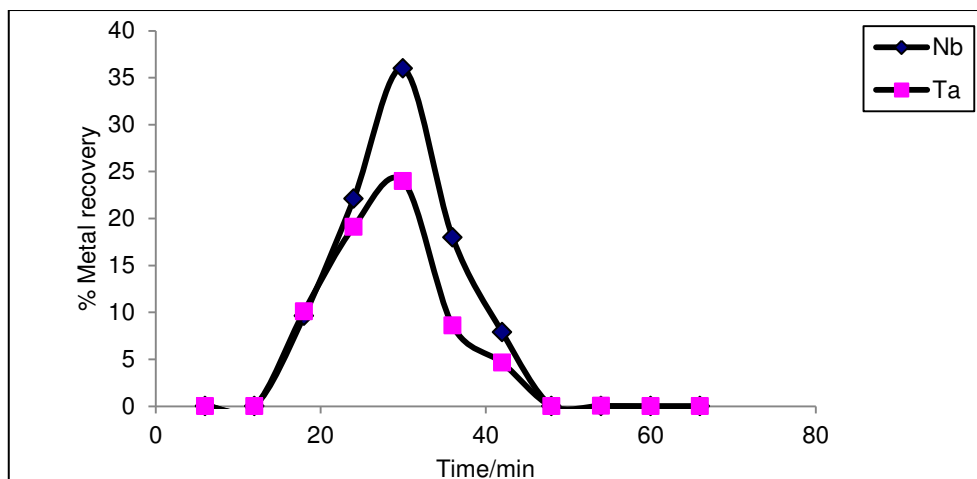


Figure 5.14: Elution of Nb and Ta from a strong Amberlite IRA-900 anion exchange column with 6.0 M HCl as a function of time at a 0.7 mL/min flow rate.

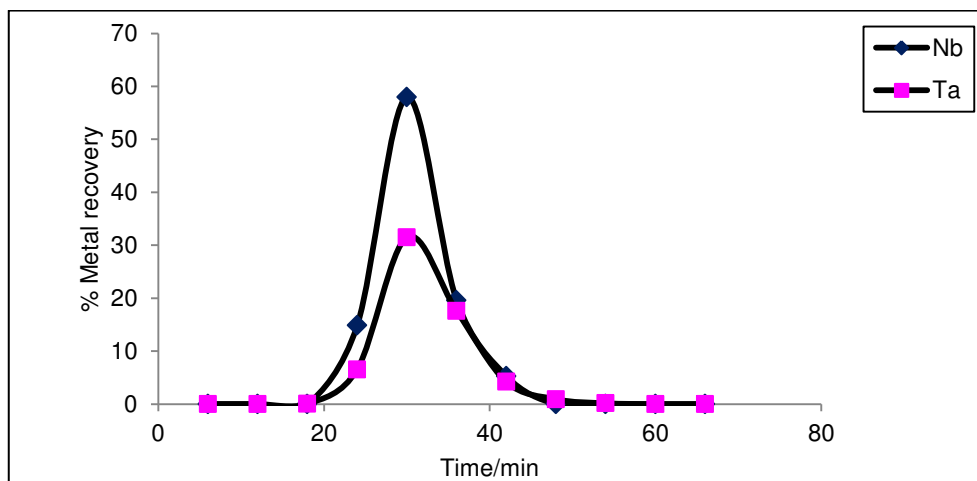


Figure 5.15: Elution of Nb and Ta from weak Dowex Marathon anion exchange column with 6.0 M HCl as a function time at a 0.7 mL/min flow rate.

5.3 Results and discussion

5.3.1 Dissolution of Ta₂O₅ and Nb₂O₅ using Na₂HPO₄/NaH₂PO₄•H₂O fusion

The analytical results obtained for the digestion of the (Ta/Nb)₂O₅ mixture (see **Section 5.2.3** and **Table 5.1**) indicate the complete digestion of the sample mixture within 30 min using a 1:1 phosphate flux mixture (sodium dihydrogen phosphate and disodium hydrogen phosphate). A literature¹⁴⁸ study has indicated that this flux mixture melts upon heating to form linear poly meta-phosphates which are strong complexing agents and which then result in the formation of soluble Nb and Ta complexes. The analytical results indicated excellent recovery of 99.9(4)% and 100.6(6)% with precision of 0.4% and 0.6% RSD (see **Table 5.1**) for Nb and Ta respectively.

5.3.1.1 Selective precipitation of Nb and Ta in phosphate environment using PPDA

The selective precipitation of Nb and Ta using PPDA which was developed in **Chapter 4** indicated that no precipitation (see **Equation 5.3**) of any of these metals in a phosphate solution (**Section 5.2.4.1**). It is clear from these results that the type of Ta and Nb compounds that are formed during the phosphate dissolution (possibly hydrated or phosphate type of complexes) is different from the pentafluoride complexes that were evaluated in **Chapter 4** which do not react in the same way with PPDA to allow for the formation of slightly soluble compounds.



These results clearly illustrate the influence of digestion method on the identity of the chemical products after the digestion step and the subsequent separation methodology of the different metals. The addition of the fluoride in the form of NH₄F•HF to the phosphate digested (Ta/Nb)₂O₅/PPDA (see **Section 5.2.4.1**) solution showed a slight precipitation which was non quantitative for further investigations into

148. Radhamani, R., Mahanta, P. L., Murugesan, P. and Chakrapani, G., 2010, "Novel fusion method for direct determination of uranium in ilmenite, rutile, columbite, tantalite, and xenotime minerals by laser induced fluorimetry" *J Radioanal Nucl Chem.*, **285**:pp. 287–292

this separation method. This observation prompted the continued investigation into the influence of F⁻ ions in the separation of the two metals.

5.3.1.2 Extraction of Nb and Ta by MIBK from phosphate fused solution

The results of separation of Nb and Ta in solution obtained by phosphate fusion dissolution procedure clearly indicated that solvent extraction using MIBK is completely ineffective for the extraction of any of these metals (**Table 5.2**). This observation underlines the difference in chemical identity of these compounds compared to the MF₅ and further proves the importance of the selection of an appropriate sample dissolution method to ensure that the chemical yield is comparative with the subsequent beneficiation processes.

5.3.1.3 Cation exchange for Na₂HPO₄/NaH₂PO₄·H₂O fused (Nb/Ta)₂O₅ mixture

The results obtained from this study indicated that Nb and Ta were readily and quantitatively eluted with dilute H₃PO₄ solutions from both the cationic clinobrite zeolite (**Table 5.3**) and the strong Amberlite IR-130 cation exchange resins. These results clearly indicate that the chemistry of the compounds formed from this (Nb/Ta)₂O₅/phosphate fusion step do not support separation of Nb and Ta by the cation exchange method.

5.3.2 Dissolution and fluorination of Ta₂O₅ and Nb₂O₅ using different F⁻ salts

The next step in this study was to evaluate the effectiveness of different fluoride salts as fluxes for the successful dissolution of the inert (Ta/Nb)₂O₅ oxides. It is anticipated that this process produces metal compounds, most probably fluoride compounds that behave similar to the pentafluorides of the HF-digested products, to allow for the selective separation of the two metals. Three fluoride salts (NH₄F·HF, KF and NaF) were studied as potential dissolution agents (fluxes). The analytical results (**Table 5.6**) obtained from this study indicate a complete dissolution of the sample using NH₄F·HF with recoveries of 100.4(9) and 100(1)% and precisions of 0.9% and ≤ 1.2% RSD (**Table 5.8**) for Nb and Ta respectively. It is expected that fluoride compounds with the formulae (NH₄)₃NbOF₆, (NH₄)₂NbOF₅, (NH₄)₂TaF₇ and NH₄TaF₆ are formed during the fusion step.⁴²

The KF fusion yielded a maximum of 83.6% Ta recovery compared to the 99.9% Nb recovery in the same solution, indicating only the partial dissolution of the sample mixture. The NaF fusion on the other hand produced the lowest recovery for both metals with 21.0% Ta and 22.7% Nb recovered in solution. A literature study⁴² has indicated that compounds with the formulae M_2NbOF_5 , K_2NbF_7 , and M_2TaF_7 , where $M = K$ or Na , are formed in both KF and NaF fusion. It is clear from these results that $NH_4F \cdot HF$ (and to a lesser extent, KF) can be used as flux in the development of an alternative digestion technique compared to that of the toxic HF for the dissolution of $(Nb/Ta)_2O_5$.

5.3.2.1 Comparison of $NH_4F \cdot HF$ fusion with other dissolution techniques

A comparison between the $NH_4F \cdot HF$ fusion and other dissolution methods that were investigated and which do not involve HF, clearly indicated that more than one method can be successful in the dissolution and accurate determination of Nb_2O_5 and Ta_2O_5 . The dissolution methods were compared with regard to the recovery and the experimental requirements needed for the oxide dissolution as summarised in **Table 5.14**. In terms of the element recovery it appears that three different methods, namely sodium phosphate, lithium tetraborate and ammonium bifluoride are equally successful in the complete dissolution of Nb_2O_5 and Ta_2O_5 with 100% recoveries for both elements.

Table 5.14: Comparison of flux fusion dissolution methods and microwave assisted H_2SO_4 digestion not involving HF for dissolution of $(Nb/Ta)_2O_5$

Dissolution method	Fusion Temperature (°C)	Solvent	Dissolution/ stability	~ % Recovery		Reference
				Nb	Ta	
1:1 $NaH_2PO_4 \cdot Na_2HPO_4$ mixture	900	Water	Complete	100	100	61
$Li_2B_4O_7$	1000-1100	97% H_2SO_4 / methanol	Complete	100	100	39, 40
Microwave assisted acid digestion	260	97% H_2SO_4	Incomplete	100	<10	39, 40, 53
$NH_4F \cdot HF$	200-250	Water	Complete	100	100	This study
NaF	900	1 M H_2SO_4	Incomplete	21	20	This study
KF	900	1 M H_2SO_4	Complete/ unstable solution	100	83	This study

The sodium phosphate fusion involved the mixing of the flux mixture (see **Table 5.14**) with sample in a 1:16 sample:flux mass ratio and then the subsequent heating at 900 °C. Complete sample decomposition was achieved in 30 min and the obtained melt completely dissolves in water in less than 10 min. The sodium phosphate fusion method is being regarded as relatively quick, eco-friendly and all the reagents used are easy to handle. However, the sample decomposition is highly energy intensive due to the high fusion temperature required and the sample is contaminated with a high concentration of sodium ions (EIEs) in the process. Lastly and more importantly, this dissolution procedure is only suitable for determination of Nb and Ta in different matrices, but does not support the subsequent separation of these elements from each other using well established methods (see **Section 5.2.4.1** and **Tables 5.2, 5.3** and **5.4**). This is most probably the results of different metallic complexes that are formed or present in solution, probably hydrated metal ions ($M(H_2O)^{5+}$). This clearly indicates the influence of the dissolution step on the separation steps which follow in the process.

The lithium tetraborate dissolution on the other hand involved the fusion of the sample/flux mixture of a 1:15 sample:flux ratio at 1100 °C and the complete sample decomposition is achieved in 90 min.⁵² The addition of methanol to H_2SO_4 during the dissolution of the melt is crucial in this method to prevent any post-precipitation (of the boric acid which may be generated during the dissolution step) which otherwise leads to low elemental recoveries. This additional step lengthened the preparation procedure since the added methanol has to be completely evaporated from the solution before analysis by ICP-OES.^{40,53} In addition, this sample preparation procedure is also highly energy intensive and no results have been reported for the subsequent separation of niobium and tantalum after lithium tetraborate digestion. This method also suffers from the presence of easily ionisable Li contamination.

Microwave assisted acid digestion using H_2SO_4 has advantages which included combining the temperature and pressure to digest the sample at a relatively low temperature (260 °C). However, this dissolution method is only efficient for the selective dissolution of Nb from the mixture of Nb and Ta^{39,40,53} and may be more appropriate as an initial beneficiation step as indicated by the 100% dissolution of the Nb_2O_5 and less than 10% Ta_2O_5 from the oxide mixture.

The sodium fluoride fusion was found to be highly inefficient for the decomposition of the mixture of Nb₂O₅ and Ta₂O₅, while KF fusion indicated the successful decomposition and dissolution for Nb₂O₅, but relatively low Ta recoveries (**Table 5.7**). The results in **Figure 5.2** indicated that tantalum is possibly precipitating from the KF solution leaving the relatively stable niobium complex in solution. The possible precipitation of a Ta product in KF solutions as well as the high fusion temperature of 900 °C makes the KF fusion a less desirable digestion method for the oxide complexes.

The NH₄F•HF fusion method has indicated several advantages as (Nb/Ta)₂O₅ dissolution method which included a low fusion temperature of 250 °C, shorter fusion times (30 min) and the quantitative dissolution (100% recoveries) (**Table 5.8**) using water in less than 10 min. The dissolution of the melt, using only water, simplifies the matrix matching step such as acidity adjustment of the solution and the products obtained with this method proved to be compatible with the well established separation techniques such as solvent extraction and anion exchange (see **Tables 5.9, 5.10 and 5.12**) which have been developed using HF as dissolution agent.^{42,90–92}

One major disadvantage of the fluoride fusion method is that it requires fluoride resistant equipment for every step of the process. The high fluoride concentration chemically attacks the surfaces of the different glass components (see **Equation 5.4**)¹⁴⁹ which results in poor analysis (recoveries) of elements such as Si and B. For analytical determinations using ICP-OES or ICP-MS, the fluoride solutions also have to be extremely dilute to prevent any damage to the ICP glass components such as the plasma torch. This requirement is anticipated to complicate the analyses of any trace elements present in the mineral which will result in some of the elements being analysed near or below the limit of detection (as a result of the large dilution factor) due to a large concentration variation between the elements.

149. Timokhin, A. R. and Komarova, L. A., 1986, "Chemical reaction of ammonium bifluoride with quartz glass" pp. 267–269, Available from:
http://download.springer.com/static/pdf/837/art%253A10.1007%252FBF00697937.pdf?auth66=1353397748_24e33c0ab6ff5c533fd24ef3dd809d02&ext=.pdf



5.3.2.2 Characterisation of $\text{NH}_4\text{F}\cdot\text{HF}$ fusion melts by IR and XRD analyses

Any chemical separation process depends on the chemical properties of the starting material (the fused products in this case) and is therefore essential to try and characterise the products that were obtained after the digestion step (dissolution) prior to the separation processes. A qualitative study of the flux fusion products using $\text{NH}_4\text{F}\cdot\text{HF}$ was carried out using infrared (IR) and X-ray diffraction (XRD) (see **Figures 5.3 to 5.6**). The major vibrational frequencies in the spectra of the ammonium bifluoride fusion products together with that of the $\text{NH}_4\text{F}\cdot\text{HF}$ are listed in **Table 5.15**.

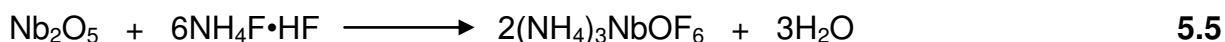
Table 5.15: Infrared stretching frequencies of different Nb and Ta complexes

Medium	Wavenumbers (cm^{-1})									
$\text{Nb}_2\text{O}_5 + \text{NH}_4\text{F}\cdot\text{HF}$	476	553	697	892	934		1080	1406	---	3243
$\text{Ta}_2\text{O}_5 + \text{NH}_4\text{F}\cdot\text{HF}$	478	547	701	---	---	982	1075	1396	---	3270
$(\text{Nb/Ta})_2\text{O}_5 + \text{NH}_4\text{F}\cdot\text{HF}$	477	558	698	918	---	979	1084	1399	---	3256
$\text{NH}_4\text{F}\cdot\text{HF}$	519	584	668	810	---	---	1157	1365	1489	3074, 3198
Nb_2O_5	523	542	591	668	821					
Ta_2O_5	512	543	594	705	833					
NbF_5	641				920			1367	1737	2453
TaF_5	549	585			931				1636	2989

Some of the stretching frequencies of the metal oxides (especially in the 500 – 700 cm^{-1} region) as well as those for the pentafluorides are comparable to those obtained in the fusion products (**Table 5.15**) suggesting possible oxide-fluoride type of compounds. The comparison between the IR spectra of these compounds (Ta_2O_5 , Nb_2O_5 , TaF_5 and NbF_5) with those of the oxides/ $\text{NH}_4\text{F}\cdot\text{HF}$ fusion products also clearly shows that the compounds formed during this $\text{NH}_4\text{F}\cdot\text{HF}$ fusion digestion step are chemically different from both the pentoxides and pentafluorides. The absence of very strong or unique stretching frequencies from both the oxides or the fluoride

compounds (see **Chapter 4**) does not make this method (IR) very effective for the characterisation of the products, but some useful information can be obtained by the comparison of some of the stretching frequencies.

A comparison of the obtained stretching frequencies for the individual and the combined metal oxides with those of different literature reported Nb and Ta fluoride compounds clearly indicated that the products obtained can be a combination of different fluoride and/or oxyfluorides. The $\text{NH}_4\text{F}\cdot\text{HF}$ fused niobium and tantalum samples showed similar infrared spectra (**Figures 5.4 to 5.6**) and which is in many cases very different from that of $\text{NH}_4\text{F}\cdot\text{HF}$. A literature study⁴² has indicated that the reaction between Nb_2O_5 and $\text{NH}_4\text{F}\cdot\text{HF}$ results in the formation of $(\text{NH}_4)_3\text{NbOF}_6$ (**Equation 5.5**) at a temperature of ~ 160 °C which then undergoes a thermal decomposition reaction as the temperature is increased to 200 °C to form $(\text{NH}_4)_2\text{NbOF}_5$ as indicated in **Equation 5.6**.

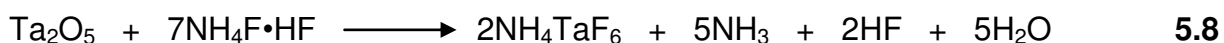


Some literature⁴² stretching frequencies for the compounds $(\text{NH}_4)_3\text{NbOF}_6$ and $(\text{NH}_4)_3\text{TaOF}_6$ which were obtained by a similar digestion procedure are listed in **Table 5.16**. The stretching frequencies for the isolated Ta and Nb products (in this study) which are in the 476 to 477 cm^{-1} region as indicated in **Figures 5.4, 5.5** and **5.6** were found to compare well with the literature stretching frequencies of 470 cm^{-1} for the Nb-F in $(\text{NH}_4)_3\text{NbOF}_6$ and 465 cm^{-1} for Ta-F in $(\text{NH}_4)_3\text{TaOF}_6$ compounds. The stretching frequency at 892 cm^{-1} observed in **Figure 5.5** is similar to 910 cm^{-1} for the Nb-O vibrations in $(\text{NH}_4)_3\text{NbOF}_6$ while the stretching frequencies at 553 – 558 and 918 cm^{-1} regions in **Figures 5.4** are similar to the frequencies of 550 cm^{-1} for Nb-F and 920 cm^{-1} for Nb-O in the $(\text{NH}_4)_2\text{NbOF}_5$.⁴²

Table 5.16: Some assigned vibrational spectra of $(\text{NH}_4)_3(\text{Nb}/\text{Ta})\text{OF}_6$ ⁴²

Compound	Wavenumbers (cm ⁻¹)	Assignment
$(\text{NH}_4)_3\text{NbOF}_6$	916 - 913	M-O
	533 - 535	M-F
	464 - 465	M-F
	410 - 417	M-F
$(\text{NH}_4)_3\text{TaOF}_6$	880	M-O
	550	M-F
	465	M-F

A literature study¹⁵⁰ has also indicated that the fluorination of Ta_2O_5 with molten $\text{NH}_4\text{F}\cdot\text{HF}$ yields mostly ammonium fluorotantalates as indicated in **Equations 5.7** and **5.8**:



The IR spectrum for the $\text{Ta}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ fusion product (**Figure 5.6**) displays a stretching frequency at 547 cm^{-1} which is similar to the literature value of 550 cm^{-1} for the Ta-F vibration in $(\text{NH}_4)_3\text{TaOF}_6$. The IR stretching frequencies in the 1396 to 1406 cm^{-1} region were found to compare well with the vibrations of NH_4^+ ion reported in the literature.¹⁴⁵ The strong stretching frequencies at 693 to 706 cm^{-1} and weak stretching frequencies at 975 to 1087 cm^{-1} observed in all the spectra are similar to the literature values for the vibrations of M-O-M bridges and M-O bond of the metal oxyfluoride^{42,44} indicating a possible mixture of fluorotantalates and oxyfluorotantalates in the case of the $\text{Ta}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ reaction.

The properties of the solid fusion melts were also studied with X-ray diffraction (XRD) (see **Figure 5.7**). The main peaks in these XRD patterns are summarised in **Table 5.17**. The major differences are observed between the $\text{Ta}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ pattern (**bolded** values in **Table 5.16**) and the other two patterns. The XRD patterns (**Figure 5.6**) of these melts indicated that the samples are amorphous which makes crystal

150. Agulyansky, A., 2003, "Potassium fluorotantalate in solid, dissolved and molten conditions", *Journal of Fluorine Chemistry*, **123**: pp. 155–161

structures and lattice parameters' determination complicated. Annealing of the samples to improve crystallization could be important for any structural determination but this was regarded to be outside the scope of this study.

Table 5.17: The XRD reflection angles (2θ /degrees) for the $\text{Nb}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$, $\text{Ta}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ and $(\text{Nb}/\text{Ta})_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ fusion products

Sample mixture		
$\text{Nb}_2\text{O}_5 + \text{NH}_4\text{F}\cdot\text{HF}$	$\text{Ta}_2\text{O}_5 + \text{NH}_4\text{F}\cdot\text{HF}$	$(\text{Nb}/\text{Ta})_2\text{O}_5 + \text{NH}_4\text{F}\cdot\text{HF}$
16.4	16.2	16.4
19.0	20.5	19.0
	22.6	
24.1	23.9	24.2
27.0		27.0
30.4	30.3	30.5
32.2	32.1	32.3
32.6	32.5	32.7
33.7	33.5	33.8
34.1		34.2
34.5	34.4	34.6
39.2	41.8	39.3
41.9	42.4	42.0
42.6		42.7
48.6	48.4	48.7
49.5	49.4	49.6

Although the IR characterization of the products obtained in this study does not conclusively differentiate between the final products as either been KTaF_6 or K_2TaF_7 or any new fluoride compound for that matter, it was decided to discuss and describe the separation chemistry in terms of the MF_6^- compounds ($\text{M} = \text{Ta}$ or Nb). The rationale behind this is the striking similarities of the solvent extraction process for $\text{NH}_4\text{F}\cdot\text{HF}$ and $(\text{HF}/\text{H}_2\text{SO}_4)$ and for which it was reported in literature⁴² that HTaF_6 is the species which is being extracted from the aqueous solution into the organic solvent. Therefore it will be assumed for discussion purposes that the crystallised product is KTaF_6 .

5.3.2.3 Selective precipitation of Nb and Ta after $\text{NH}_4\text{F}\cdot\text{HF}$ fusion dissolution

The same method of selective precipitation which was developed in **Chapter 4** was applied on the $(\text{Ta/Nb})_2\text{O}_5$ mixture after the dissolution of these pentoxides with $\text{NH}_4\text{F}\cdot\text{HF}$ fusion. The results obtained for the selective precipitation method using PPDA to the $\text{NH}_4\text{F}\cdot\text{HF}$ fused $(\text{Nb/Ta})_2\text{O}_5$ sample (**Table 5.8**) indicated a preferential precipitation of Ta which was totally opposite to that obtained for the metal pentafluorides (**Chapter 4, Section 4.3.2.3**). Recoveries of 19.8 to 28.7% for Nb and 70.2 to 76.2% for Ta were obtained in this precipitation study.

The IR study predicts that the flux fusion of $(\text{Nb/Ta})_2\text{O}_5$ with $\text{NH}_4\text{F}\cdot\text{HF}$ produced fluoride compounds as anticipated. Although the chemistry between Nb/Ta and PPDA for the selective precipitation of these is still not completely elucidated in this study, it is apparent that different Nb and Ta fluoride complexes behave differently with regard to PPDA precipitation. The distribution coefficients (D) of Nb and Ta were calculated as the ratio of their concentrations in the precipitate to that in the filtrate/supernatant liquid. The separation factor which is defined as the ratio of distribution coefficient of Ta and that of Nb ($D_{(\text{Ta})}/D_{(\text{Nb})}$) (**Chapter 3, Equation 3.34**) was calculated to be 11(4) (**Table 5.18**) which is at least an order of magnitude smaller than that of the pentafluoride complexes ($\alpha = 100$, see **Section 4.4.2.2, Table 4.10**). The relatively high Nb content in the Ta precipitate as well as the low separation factor obtained render this method insufficient for the separation of these two elements after oxides were digested with $\text{NH}_4\text{F}\cdot\text{HF}$. This observation (different chemical behaviour) also confirmed that the products obtained from the $\text{NH}_4\text{F}\cdot\text{HF}$ dissolution process do not result in formation of the pentafluoride compounds $(\text{Nb/Ta})\text{F}_5$.

Table 5.18: Distribution ratio (D) values of Nb and Ta in precipitate and filtrate and the separation factor (α)

Sample	D (Nb)	D (Ta)	α
1	0.27	1.94	7.20
2	0.27	3.99	15.02
3	0.39	4.20	10.87
Average			11.03
SD			3.91

5.3.2.4 Extraction of Nb and Ta by MIBK from $NH_4F \cdot HF$ fused solution

The experimental results obtained for the Ta/Nb extraction by MIBK from H_2SO_4 solutions indicated that Ta was the major metal compound that was extracted into the organic solvent (MIBK) leaving Nb in the aqueous solution. The single extraction step achieved more than 60% extraction of tantalum and up to 80% with $[H_2SO_4] = 4.0$ M. The distribution ratio (D) for the incomplete extraction of both metal compounds (**Table 5.10**) were determined using **Equations 5.9** and **5.10** (see **Section 3.4.2.3, Equation 3.33**) and excellent agreement between the values by the two calculations was obtained (see **Table 5.19**).

$$D = \frac{[M]_{org}}{[M]_{aq}} \quad 5.9$$

$$q = \left(\frac{1}{DV_r + 1} \right) \quad 5.10$$

where $[M]_{org}$ and $[M]_{aq}$ are the metal concentrations in the organic and aqueous phases.

Table 5.19: The distribution ratios of Nb and Ta between MIBK and aqueous phase at different H₂SO₄ concentrations with one extraction step

H ₂ SO ₄ (M)	Distribution ratio			
	$q = \left(\frac{1}{DV_R + 1} \right)$		$D = \frac{[M]_{org}}{[M]_{aq}}$	
	D _(Nb)	D _(Ta)	D _(Nb)	D _(Ta)
0.5	0.006	1.465	0.006	1.516
1.0	0.006	2.031	0.006	1.927
1.5	0.013	1.930	0.007	1.931
2.0	0.027	1.893	0.018	2.003
3.0	0.035	2.802	0.021	2.824
4.0	0.019	3.261	0.016	3.434

It is clear from the results in **Table 5.19** that the D values (especially for Ta extraction) are influenced by the acid concentration and shows a progressive increase with increase in [H₂SO₄]. This observation can be explained using **Equation 3.32** which predicts that at high acid concentrations ($[H^+] \gg K_a$) $D \approx K_D$.¹²⁰

The obtained D values were then used to calculate the number of extractions necessary (see **Table 5.11**) to achieve complete extraction of both Nb and Ta. The results of this calculation indicated more than 100 successive extractions would be required to achieve 99.9% extraction of Nb while only 2 extractions is necessary for the same amount of Ta extraction which clearly supports the experimental results that indicate good separation between the elements from this reaction mixture.

It is clear from the results in **Table 5.11** that 3 extractions ($n > 2$) are needed to reduce the [Ta] to ~ 0.1% in the aqueous phase at [H₂SO₄] < 2.0 M and decrease to 2 extractions only at [H₂SO₄] > 2.0 M. In practice it means that the amount of Ta extracted can either be increased by increasing the number of extractions at lower H₂SO₄ concentration or decreasing the number of extractions by increasing the [H₂SO₄] (see **Figure 5.14**). The results obtained in this study are in agreement with those of Babkin *et al.* who reported that the H₂SO₄ concentration of 2 – 4 M is sufficient for the selective extraction of Ta while a minimum H₂SO₄ concentration of 6 M is required for the extraction of Nb.⁴² Extrapolation of the linear graph in **Figure**

5.16 predicts that $[\text{H}_2\text{SO}_4] = 6.05 \text{ M}$ will be needed for a single step extraction of Ta (99.9 %) into the MIBK.

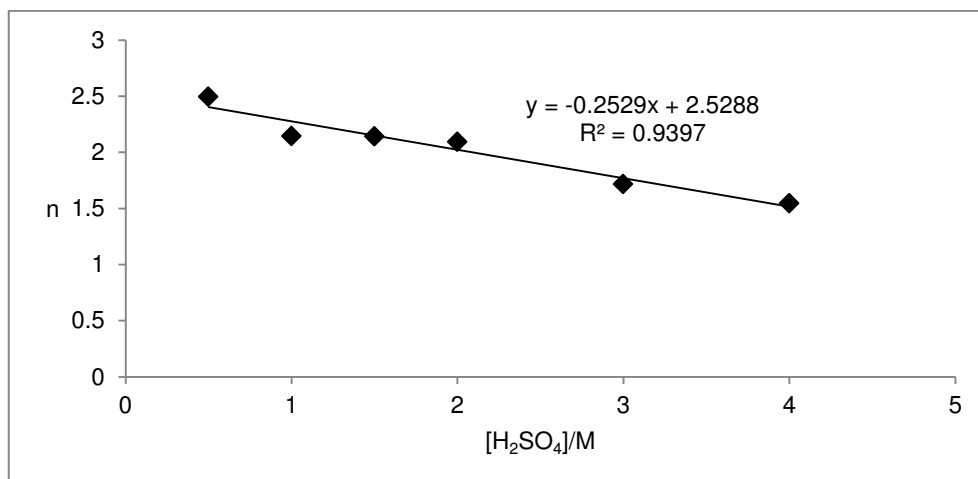


Figure 5.16: Influence of the H_2SO_4 concentration on the successive extractions of Ta from aqueous solution into MIBK.

The extraction ratio, D , was successfully calculated as the ratio of the concentration of metal ion in organic phase to that in the aqueous phase. The separation factor (α) was determined as the ratio of the extraction coefficient of the metal ion in the organic phase ($D_{(\text{Ta})}$ in this case) to that in aqueous phase ($D_{(\text{Nb})}$) (**Table 5.20**).

Table 5.20: Extraction ratio (D) values of Nb and Ta in organic phase and aqueous phase and the separation factor (α) with two extraction steps

$[\text{H}_2\text{SO}_4] \text{ (M)}$	$D_{(\text{Nb})}$	$D_{(\text{Ta})}$	α
0.5	0.005	5.086	1009.64
1.0	0.005	5.255	1043.17
2.5	0.006	6.533	1079.10
4.0	0.005	10.493	2082.79

The values of the extraction ratio for Ta ($D_{(\text{Ta})}$) were found to increase with the increase in sulphuric acid concentration and the plot of $D_{(\text{Ta})}$ against $[\text{H}_2\text{SO}_4]$ (see **Section 3.4.2.3, Equation 3.32**) produced a linear curve (**Figure 5.17**). This curve clearly indicates the dependence of the tantalum extraction efficiency on sulphuric acid concentration.

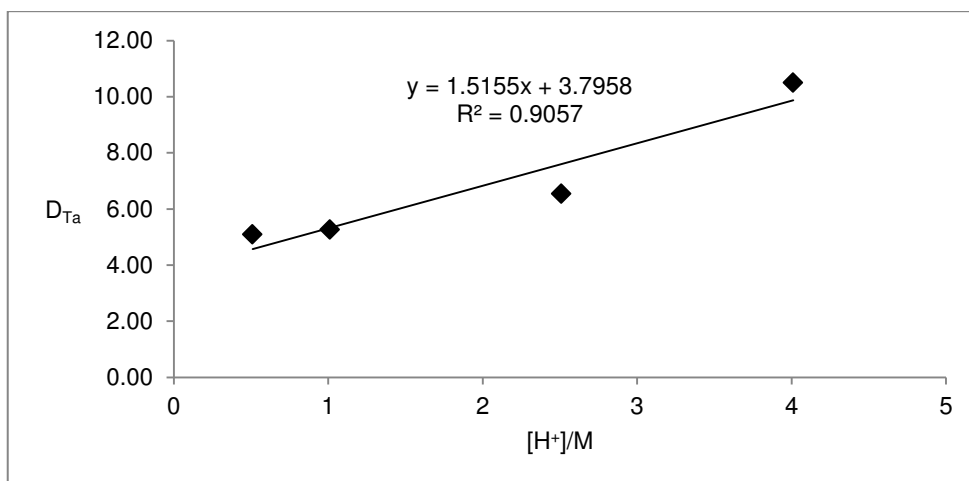


Figure 5.17: Influence of the acidity of the solution on the distribution ratio of Ta (D_{Ta} vs $[H^+]$).

Niobium distribution coefficient on the other hand remains almost constant in this sulphuric acid concentration range (0.5 – 4.0 M) and the overall value of α is only dependent on the extraction coefficient of Ta (D_{Ta}) as indicated in **Figure 5.18**.

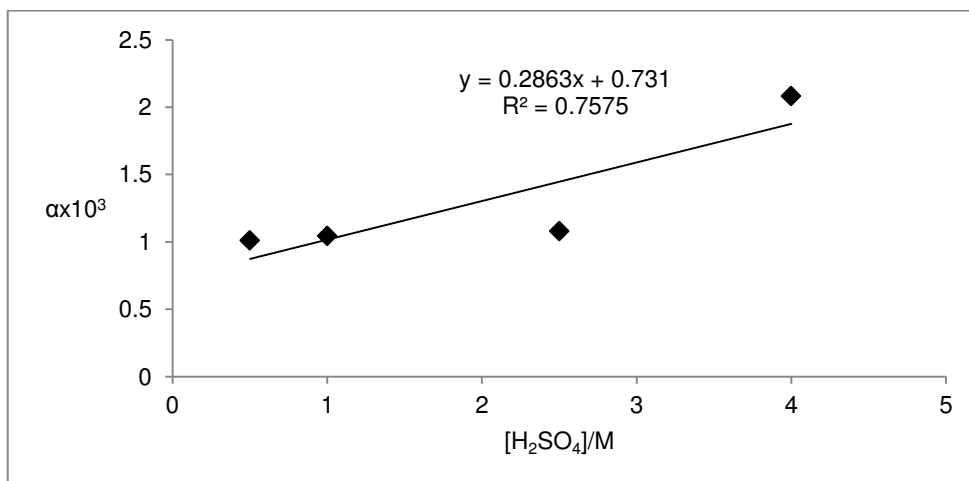
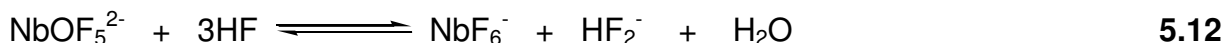


Figure 5.18: Plot of the separation factor (α) against H_2SO_4 concentration.

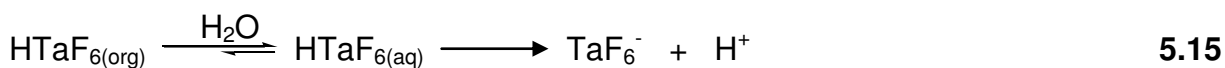
A literature study⁴² has indicated that $NbOF_5^{2-}$ and TaF_7^{2-} are more stable than the NbF_6^- and TaF_6^- complexes in aqueous solutions and that the extraction of Nb and Ta from HF/H_2SO_4 firstly involves the conversion of $NbOF_5^{2-}$ and TaF_7^{2-} into NbF_6^- and TaF_6^- as indicated in **Equations 5.12** and **5.13**.



The role of the acid in this process is probably to convert the NbF_6^- and TaF_6^- ions into neutral compounds (HNbF_6 and HTaF_6) which are soluble in the organic solvent (see **Chapter 1, Equations 1.15** and **1.16**). If the extraction of Ta and Nb into MIBK is dependent on the presence of NbF_6^- and TaF_6^- as indicated in the literature⁴² it is clear from **Equation 5.13** that the production of NbF_6^- from NbOF_5^{2-} (**Equation 5.6**) requires the presence of excess F^- in solution. The TaF_6^- on the other hand can be produced from the $\text{NH}_4\text{F}\cdot\text{HF}$ fusion (**Equation 5.7**) and possibly from TaF_7^{2-} by the addition of an acid as indicated by the following reaction (**Equation 5.14**):



The stripping of tantalum from the organic solution with water can be understood as the reverse of the extraction process as indicated in the following **Equation 5.15**:



Extraction mechanism

The experimental results obtained in this study clearly demonstrated the dependence of the metal extraction process on the $[\text{H}^+]$ (see **Table 5.10**). The different steps in the extraction process are illustrated in **Figure 5.19** and a close inspection of the different individual steps (equilibrium constants) associated with the extraction process (K_{ext} or D), will share light on the importance of $[\text{H}^+]$ in the successful extraction of the Ta product into the organic layer (see **Equation 5.16** or **Section 3.4.2.3 Equation 3.27**).

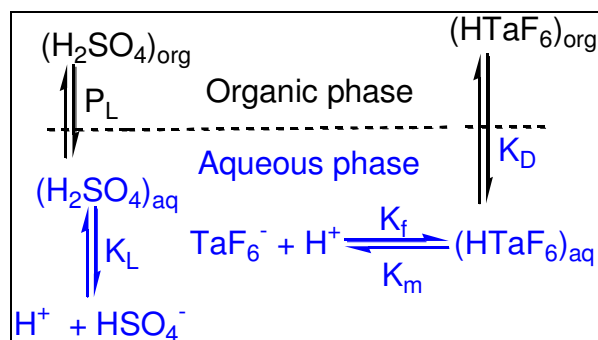
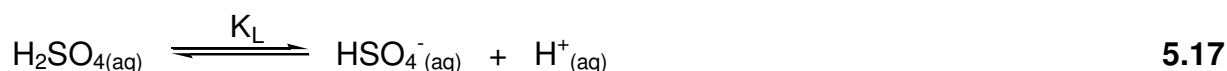


Figure 5.19: Schematic illustration of the tantalum complex distribution between the organic and aqueous phases.

$$D = \frac{K_D K_L^n}{K_m P_L^n} = \frac{[MR_n]_{org} [H^+]_{aq}^n}{[M^{n+}]_{aq} [HR]_{org}^n} \quad 5.16$$

It is anticipated that the solubility of the extractant (H_2SO_4 in this case) and which is represented by P_L ($\ll 1$) in **Figure 5.19**, is extremely low in the organic layer. This can easily be explained since H_2SO_4 is a strong acid and therefore dissociated completely to form H^+ and HSO_4^- (which is also favourable for extraction as K_L (K_a for H_2SO_4) $\gg 1$ in **Equation 5.17**) and these polar or ionic species will be highly insoluble in the organic layer.



The results in **Table 5.10** (zero extraction of Ta with no addition of acid) also clearly demonstrate that the formation of the $HTaF_6$ compound is extremely small ($K_f \ll 1$, as formation constant) or alternatively indicate that $HTaF_6$ is a very strong acid which completely dissociate in the aqueous layer ($K_m \gg 1$). It is therefore argued that the addition of H^+ to the reaction mixture will suppress the dissolution of the $HTaF_6$ compound and forces the equilibrium to the right hand side of the chemical reaction as indicated in **Figure 5.19** or in **Equation 5.18**.



This H^+ addition increases the amount of $HTaF_6$ in the aqueous layer which can now easily be extracted into the organic layer. The K_D value is also favourable for extraction into the organic layer as illustrated by the successful isolation of Ta from the organic layer, but also from the D values that were obtained from this study. **Equation 3.32** predicts that $D \approx K_D$ at high $[H^+]$ and the experimental results indicated a D value of 3.4 at $[H_2SO_4] = 4$ M (see **Table 5.19**), suggesting that the K_D value for the extraction of Ta from the aqueous layer into the organic layer is equal or higher than this value since the experimental K_a for $HTaF_6$ predicted to be large (complete dissolution or $K_a > [H^+]$ at 4 M H_2SO_4) and no convergence of D to K_D was observed ($D \ll K_D$) under the prevailing experimental conditions in this study. The importance of the H^+ influence is also emphasised by its elevation to the power n as indicated by **Equation 5.19** (see also **Section 3.4.2.3**).

$$D = K_D \frac{[H^+]_{aq}^n}{[HR]_{org}^n} \quad 5.19$$

The successful separation of Ta and Nb in this solvent extraction process can also easily be explained or understood by looking at the individual equilibrium steps of the extraction process. The experimental observations of total Ta extraction and little or no Nb extraction suggest that either or both K_f and K_D for Nb is smaller than that of Ta. A smaller K_f value (stronger acid for Nb) suggests the formation of less $HNbF_6$ or $HNbOF_3$ with the addition of H^+ (in the form of H_2SO_4 in this study) and hence less Nb product to be extracted into the organic layer. It can also be seen that the K_D value for Nb is smaller than that of Ta and that the solubility of the neutral Nb compound is less in the organic layer which results in lower quantities of Nb in the organic layer or may be both. The determination of D or K_D for the Nb compounds lies outside the boundaries of this study since the main aim was the separation of the two elements that has been accomplished under the experimental conditions chosen for the study, but a study of Nb extraction as a function of acid will add to the understanding of the extraction or separation process.

The results in **Figures 5.7** and **5.8** showed that Ta can be easily separated from Nb by the solvent extraction method. However, it is anticipated that in a mineral situation this separation procedure may be complicated by a larger number of metal impurities

in the mineral matrix. Therefore, another purification method(s) may be necessary for the removal of impurities which will remain with Nb in the aqueous phase and/or which will be carried with Ta into the organic phase.

The IR measurement of the KF-Ta product (**Figure 5.11**) gave a different spectrum to that of the KF (**Figure 5.10**) with the most prominent differences observed in the region below 1200 cm^{-1} . In addition, the KF-Ta compound also showed a strong stretching frequency at 1367 cm^{-1} which was not observed in the KF spectrum. This result could indicate the formation of a new product between KF and Ta in the stripped Ta solution. A comparison of the IR of this product to that of the $\text{Ta}_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ product (**Figure 5.6**) does indeed indicate similarities between the two products. Corresponding stretching frequencies at 1059 cm^{-1} and 1075 cm^{-1} and at 1367 cm^{-1} and 1396 cm^{-1} were observed for both materials while a difference occurred at stretching frequencies of 547 cm^{-1} and 478 cm^{-1} . This difference in IR stretching frequencies however does not exclude the possibility that the two products are the same since the additional peaks may be due to the presence of the unreacted $\text{NH}_4\text{F}\cdot\text{HF}$ in the flux mixture.

5.3.2.5 Anion exchange separation using the $\text{NH}_4\text{F}\cdot\text{HF}$ fused $(\text{Nb}/\text{Ta})_2\text{O}_5$ mixture

The results of the elution of the tantalum and niobium products obtained from the $\text{NH}_4\text{F}\cdot\text{HF}$ digestion using the strong Amberlite anionic exchange resin with HCl elution (**Table 5.10**) indicated that the separation of the two elements by the strong anionic Amberlite is not very effective. Both Nb and Ta were eluted simultaneously from the column with HCl as elution medium with concentrations ranging between 0.5 and 4.0 M from this column. The weak Dowex Marathon anion exchange column on the other hand retains these elements to a greater extent than the strong Amberlite anion column. However, the elution time of both metals increased with the HCl concentration as expected.

The highest recovery values for both the metals in the Amberlite anion exchange column were achieved with 2 M HCl and it was therefore deemed unnecessary to continue with the increase of the acid concentration to determine the influence of the eluent concentration (see **Table 5.13**). In the Dowex marathon anion exchange

column maximum Nb and Ta recoveries were achieved with 6 M HCl. The extent of separation between Nb and Ta was evaluated by determining the distribution coefficients (or retention factor, k) as well as the separation factor α .

All the relevant semi-quantitative parameters such as k , α and N were calculated for the two resins and are presented in **Table 5.21**. For both the strong Amberlite IRA-900 and Dowex Marathon the $t_{r(\text{Nb})} = t_{r(\text{Ta})} = 30$ min and the $t_o = 6$ min and the k equal to 4 for both metals, corresponding to the $\alpha = 1$ which confirms the ineffective separation of Nb and Ta by this resins. Although the separation of the two metals was not achieved using these resins, the total recovery of these metals indicated that Ta and Nb have somehow different adsorption properties towards these anionic columns with Ta being the more retained element of the two.

Table 5.21: Column parameters for the separation of niobium and tantalum by anion exchange using strong Amberlite IRA-900 and weak Dowex Marathon exchangers

Parameter	Strong Amberlite IRA-900 anion		Weak Dowex Marathon anion	
	Nb	Ta	Nb	Ta
t_r (min)	30	30	30	30
L (cm)	20	20	20	20
W (min)	22.5	24	10	12
N	28	25	64	38
H (cm/plate)	0.71	0.8	0.31	0.53

The number of theoretical plates, N , in the Amberlite IRA-900 and Dowex Marathon anion exchange columns was determined from **Figures 5.14** and **5.15** using **Equation 3.39** (see **Section 3.4.2.4**) and the corresponding height equivalent of a theoretical plate (H) as the column length (20 cm in this study) divided by the number of the theoretical plates.

From **Table 5.21** it is clear that larger peak widths, w , were obtained in the strong Amberlite IRA-900 than in the weak Dowex Marathon anion exchangers for both elements elution. The number of theoretical plates is also smaller hence the height equivalent of a theoretical plate in the strong Amberlite IRA-900 is longer than in the weak Dowex Marathon anion exchangers. The Ta elution curve on the other hand is broader than the Nb curve in both resins indicating that there is some difference in the adsorption properties of these elements by both resins.

5.4 Conclusion

The successful digestion of $(\text{Nb/Ta})_2\text{O}_5$ was accomplished by the fusion of the two oxides with $\text{NH}_4\text{F}\cdot\text{HF}$. The fusion melt was easily and rapidly dissolved with water. The metal recoveries indicated that both Nb and Ta compounds were quantitatively dissolved and recovered. This fusion product was also found to be compatible with the well established separation techniques that were developed for HF dissolution. The results of the flux fusion of the oxides with NaF and KF indicated partial dissolution or post-precipitation from the reaction mixture. This rendered the application of these salts as fluxes ineffective for the dissolution and the subsequent separation.

The low cost of $\text{NH}_4\text{F}\cdot\text{HF}$, the relative ease to handle plus the fact that fusion was performed at relative low temperatures makes this digestion technique worthy to consider as a commercial process and an alternative to HF digestion method. However, it is important to note that necessary precautions have to be taken to avoid inhalation of the fumes produced during the fusion step.

The possible selective precipitation of Nb and Ta was carried from aqueous solutions of $(\text{Nb/Ta})_2\text{O}_5/\text{NH}_4\text{F}\cdot\text{HF}$ fusion product using PPDA as a chelating agent. The results indicated that 73(3)% of tantalum was precipitated from the solution and 23(5)% of niobium. A separation factor of 11(4) was obtained.

Solvent extraction was investigated using MIBK as extractant and the results indicated complete and reproducible separations of Nb_2O_5 and Ta_2O_5 in acidic fluoride solutions. Tantalum was readily extracted into the organic solvent (MIBK) leaving niobium in the aqueous solution. Distribution ratios (D) for Nb and Ta as well as separation factors were determined for different acid concentration. The $D_{(\text{Ta})}$ was found to increase with the acidity of the solution increases while $D_{(\text{Nb})}$ stayed almost constant while the separation factor for Ta increased up to a value of ~ 2000 with an increase in H_2SO_4 concentration to 4.0 M.

Separations of Nb and Ta on the anion exchange column using both strongly and weakly anionic resins were highly ineffective. The results also showed some

difference in the adsorption of Nb and Ta by these resins when elution was carried with hydrochloric acid.

6 Separation and purification of niobium and tantalum in tantalite mineral ore

6.1 Introduction

The successful beneficiation of tantalum and niobium ores may vary significantly and its success normally depends on the physiochemical properties (of the ore) such as the presence of radioactive materials, its response to a magnetic field (removal of the magnetic particles), the Ta and Nb content and finally the nature of the ore. For example, the beneficiation process of an ore containing less than 0.1% Ta₂O₅ and Nb₂O₅ usually starts with an enrichment step to enable subsequent separation and accurate determination of these elements.¹⁶ If the ore responds positively to a magnetic field, the first step may involve the magnetic separation of all the magnetic impurities before the dissolution of the sample for the application of the hydrometallurgical processes such as leaching, solvent extraction and ion exchange.

The removal of the radioactive metals such as thorium and uranium from the ore is one of the most important steps in the beneficiation processes and needs to be done in the very early stages of the whole processing. The concentrations of the two elements, thorium and uranium, are vital for the transportation, handling and beneficiation of mineral ores due to their radioactive nature and the implications they have on humans and the environment.¹⁴⁹ Minerals such as tantalite ore containing radioactive levels above 1 Bq/g (e.g. 0.013% ThO₂ plus 0.0048% U₃O₈) are classified as radioactive while levels of 10 Bq/g and above (0.13% ThO₂ plus 0.048% U₃O₈) are considered a concern in terms of transportation.¹¹ If the total radioactivity of the

149. Dampare, S. B., Nyarko, B. J. B., Osaе, S., Akaho, E. H. K., Asiedu, D. K., Serfor-Armah, Y. and Nude, P., 2005, "Simultaneous determination of tantalum, niobium, thorium and uranium in placer Columbite-tantalite deposits from the Akim Oda District of Ghana by epithermal instrumental neutron activation analysis", *J. Radioanal. Nucl. Chem.*, **265**(1): pp. 53–59

sample exceeds 0.5 Bq/g a sample is classified as a Class 7 material in which case a license is required to handle and transport such material.¹⁵⁰

In this study two different tantalum and niobium containing mineral samples were studied in order to evaluate the dissolution and separation methods for the two main elements, normally Nb and Ta, which have been developed and discussed in **Chapters 4** and **5**. The chemical composition of the ore samples, which was determined using ICP-OES and used in this study, is given in **Table 6.1**.

Table 6.1: Chemical compositions of tantalite mineral samples^{51,53}

Analyte	Average concentration (%)	
	Sample A	Sample C
Ta ₂ O ₅	27.8(3)	33.0(2)
Nb ₂ O ₅	27.0(2)	13.7(2)
ThO ₂	0.54(2)	0.29(1)
U ₃ O ₈	2.81(2)	0.14(1)
Al ₂ O ₃	2.04(6)	1.47(1)
SiO ₂	3.5(1)	2.51(4)
WO ₃	1.18(2)	0.16(1)
TiO ₂	2.77(2)	8.19(1)
Mn ₃ O ₄	8.91(7)	3.13(1)
Fe ₂ O ₃	8.3(2)	18.71(6)
SnO ₂	1.64(3)	0.15(1)
Y ₂ O ₃	-	0.24(1)
CaO	-	0.52(4)

The chapter comprises of two parts namely (i) the optimisation and application of the newly developed dissolution and separation methods on the two tantalite mineral samples and (ii) separation and purification of Nb and Ta content in the ore samples using the newly developed methods as well as using other techniques which made use of the physiochemical properties of the mineral samples (see **Figure 6.1**). The

150. Reactor concepts manual, "Transportation of Radioactive Material" [Internet]. [cited 2012 Nov 28]. available from: http://mitnse.files.wordpress.com/2011/03/transportation_11.pdf

main difference between the two samples are the Nb and Ta contents, the high U_3O_8 content in Sample A compared to Sample C and also the Fe_2O_3 content which is much higher in Sample C than in Sample A.

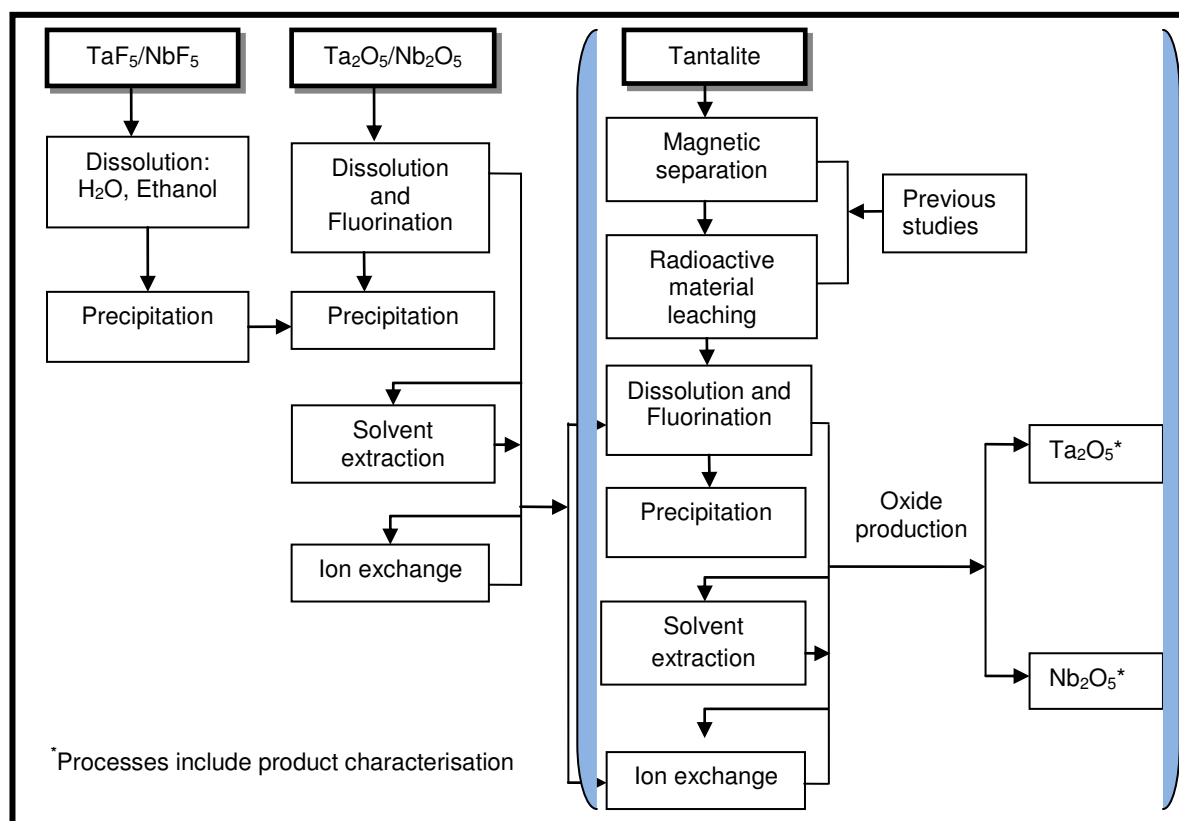


Figure 6.1: Flow diagram with the highlighted area indicating the focus in this part of the study in the separation and purification of Ta and Nb.

6.2 General experimental methods

6.2.1 General procedures, reagents and equipment

Two tantalum/niobium-bearing minerals demarcated as Sample A and Sample C and originating from Mozambique, were supplied by the South African Nuclear Energy Corporation Limited (Necsa). Potassium fluoride and a strong basic anion exchanger, Amberlite IRA-900 (16 - 50 mesh), as well as a weak basic anion exchanger Dowex marathon (350 – 450 μm), were purchased from Sigma Aldrich. High purity ammonium bifluoride ($NH_4F \cdot HF$), *p*-phenylenediamine and 25% ammonia solution were sourced from Merck. ICP standard solutions containing 1000 mg/L Ta, Nb, Ti, Sn, W, Si as well as multi-element standard No. XXVI containing 1000 mg/L each of

Mn, Al, Fe, Ca were also bought from Merck. ICP standard solutions containing 1000 mg/L Th and U were bought from De Bruyn Spectroscopic. Methyl isobutyl ketone, methyl isopentyl ketone, 4-heptanone, 1-octanol and methyl isoamyl ketone were also procured from Merck while the analytical grade HCl (32%) and H₂SO₄ (97%) were bought from Associated Chemical Enterprises. Double distilled water was used in all cases.

Samples were weighed using a Shimadzu AW220 analytical balance while the flux fusions were performed in a Thermo Scientific Thermolyne Compact Benchtop Muffle Furnace. Grade B glass and PTFE volumetric flasks bought from Merck and Boeco SP series adjustable volume pipettes were used for sample preparations. Centrifugation was performed in a centrifuge rotor supplied by MSE while Shimadzu ICPS-7510 ICP-OES sequential plasma and ICPM-8500 ICP-MS spectrometers were used for the elemental analysis of the sample solutions. The infrared spectra were obtained with a Scimitar Series Digilab spectrometer. The average values for the results are reported based on the standard deviations to indicate the uncertainty in the last digit of the value throughout the chapter.

6.2.2 Preparation of standards solutions

Standard solutions for ICP-OES analysis were prepared by adding the appropriate volumes of the standards to 10.0 mL 97% H₂SO₄ (or 5.0 mL 85% H₃PO₄ when phosphate flux mixture was used) in 100.0 mL volumetric flasks and diluted to the mark with double distilled water to prepare 1.0, 3.0, 5.0, 10.0, and 20.0 mg/L concentrations. The blank solutions were prepared by diluting 10.0 mL H₂SO₄ (or 5.0 mL H₃PO₄) to the 100.0 mL mark of the volumetric flask and were used for background correction. Quantitative analyses were performed at selected wavelengths indicated in **Table 6.2**.⁵³ The ICP-OES conditions indicated in **Table 4.1** were used for quantitative analyses.

Table 6.2: Selected analytical wavelengths and detection limits for the elements studied^{40,53}

Element	Wavelength (nm)	Detection limit (mg/L)
Al	394.403	0.0074
Si	251.612	0.012
Ti	336.121	0.0015
Mn	257.610	0.00031
Fe	259.940	0.0035
Ta	240.068	0.0047
Nb	309.418	0.0094
Sn	189.989	0.025
W	207.911	0.030
Th	374.119	0.096
U	367.007	0.30

A set of calibration solutions of Nb and Ta ranging from 1.0 to 10.0 ppb as well as a blank solution were prepared in 10.0 mL 97% H₂SO₄ in 100.0 mL volumetric flasks for analysis of these elements by inductively coupled mass spectroscopy (ICP-MS). The operating ICP-MS conditions given in **Table 6.3** were used for analytical determination of Nb and Ta.

Table 6.3: Working conditions of ICP-MS for Nb and Ta determinations

Parameter	Value
RF power	1.2 kW
Coolant gas flow	7.0 L/min
Plasma gas flow	1.50 L/min
Carrier gas flow	0.60 L/min
Sample uptake method	Peristaltic pump
Sampling depth	5.0 mm
Sample introduction system	Glass cyclonic spray chamber with concentric nebuliser

6.2.3 Handling and preparation of samples

The mineral samples used in this study were received as coarse samples with particle sizes in the 0.1 mm to 5 mm range. The samples were subsequently ground

to a particle size distribution of 9.8 – 11.1 μm using a vibratory disc mill in a closed steel milling vessel. The mineral samples (due to the presence of radioactive elements, 2.81% U_3O_8 and 0.54% ThO_2 in Sample A and 0.14% U_3O_8 and 0.29% ThO_2 in Sample C) together with U and Th stock solutions were stored in closed containers, wrapped in lead foil and kept locked in cabinets which were placed approximately 5 m away from the working area in the laboratory to reduce personnel exposure to any radiation and to prevent any unauthorized access to these materials. Disposable gloves, as well as mouth and nose masks were used when handling the chemicals to avoid any accidental ingestion and where possible, samples were prepared in the fume hood to avoid inhalation of the radioactive dust. All the uranium and thorium containing waste was kept in labelled polyethylene bottles for disposal by a certified waste disposal company as appointed by the University of the Free State.

6.3 Experimental procedures for optimization and application of methods for tantalite processing

The separation and dissolution methods that were developed in this study were evaluated on commercial $(\text{Nb/Ta})\text{F}_5$ and $(\text{Nb/Ta})_2\text{O}_5$ (**Chapters 4 and 5**). In this part of the study these methods are evaluated and optimized for their successful application to the tantalite mineral samples. Sample A was chosen and used for this assessment and the optimum conditions were used for the dissolution and separation of Ta and Nb in the other mineral sample and in the total beneficiation process in **Section 6.5**.

6.3.1 Dissolution of tantalite samples by $\text{NH}_4\text{F}\cdot\text{HF}$ fusion

Approximately 0.1 g of mineral sample was weighed (accurately to 0.1 mg) in a platinum crucible and thoroughly mixed with approximately 1.0 g of $\text{NH}_4\text{F}\cdot\text{HF}$ flux (1:10 sample:flux ratio) (the actual masses of the samples weighed in this chapter can be viewed in the accompanying CD attached to the thesis in the file with the name: **Chapter 6**) and the mixture was fused at 200 $^\circ\text{C}$ for 30 min in a high temperature oven. A clear melt which became an amorphous solid upon cooling was obtained. The melt was dissolved in distilled water and the solution was stirred for 10 min. Visual inspection of the sample after the 10 min period indicated that some solid

sample remained undissolved. The residue was removed by filtration and the filtrate was quantitatively transferred to the 100.0 mL PTFE volumetric flasks and the volumetric flasks were filled to the mark with distilled water. A 5.0 mL volume of the solution was transferred to a 100.0 mL volumetric flask and the acidity was adjusted by the addition of 10 mL 97% H₂SO₄. The solution was cooled and then filled to the mark with distilled water for quantitative analysis using ICP-OES. The ICP-OES results are given in **Table 6.4**. All the results are reported as the equivalent oxides of the most stable oxidation state of these metals mainly for comparison purposes with previously reported results (**Table 6.1**).⁵¹

Table 6.4: Fusion results for a 1:10 Sample A:NH₄F•HF ratio at and 200 °C for 30 min

Analyte	Concentration (%)				
	Found				Expected
	1	2	3	Average	
Ta ₂ O ₅	24.78	23.32	24.67	24.3(8)	27.8(3)
Nb ₂ O ₅	27.92	29.14	28.50	28.5(6)	27.0(2)
ThO ₂	0.40	0.39	0.41	0.40(1)	0.54(2)
U ₃ O ₈	1.09	1.13	1.80	1.3(4)	2.81(2)
WO ₃	1.71	1.62	1.48	1.6(1)	1.18(2)
TiO ₂	2.52	2.55	2.74	2.6(1)	2.77(2)
Mn ₃ O ₄	8.02	8.11	5.87	7(1)	8.91(7)
Fe ₂ O ₃	7.73	7.67	7.56	7.65(9)	8.3(2)
SnO ₂	0.85	0.86	0.79	0.83(4)	1.64(3)

Bold values = highly inaccurate results

The results obtained in this experiment indicated incomplete sample dissolution and incomplete recoveries for some elements such as Ta relative to their expected content values (using **Table 6.1** as a guide). The incomplete sample digestion together with especially the low Ta₂O₅ recoveries obtained in this part of the study, prompted a further investigation into the optimisation of the experimental parameters for the dissolution method of these mineral samples. The parameters were evaluated based on the triplicate analyses and these include the influences of fusion time, sample to flux ratio as well as the fusion temperature on the expected element recoveries. The SiO₂ and Al₂O₃ results are not reported due to the fact that the nebuliser of the ICP-OES was made of glass and which inevitably led to inaccurate Si results (see **Equation 5.4**). The Al results (not shown) on the other hand were found

to be highly inaccurate which according to the literature^{151,152} can be the result of the presence of the residual fluoride.

6.3.1.1 Influence of sample:flux ratio on dissolution of tantalite ore

The effect of the flux concentration on the dissolution of the tantalite mineral was investigated by using a fixed amount of 0.1 g (weighed to 0.1 mg accuracy) of Sample A and mixing with $\text{NH}_4\text{F}\cdot\text{HF}$ flux in ratios of 1:10, 1:15 and 1:20 sample:flux (see **Table 6.5**). The obtained melts were allowed to cool to ambient temperature and then dissolved in water. Visual inspection indicated that some of the sample had not dissolved in the mixtures. The undissolved solids were removed by filtration and the solutions were quantitatively transferred to 100.0 mL volumetric flasks and filled to the mark with distilled water. A 5.0 mL volume of the solution was transferred to another 100.0 mL volumetric flask and treated for ICP-OES analysis as previously described. The obtained results are presented in **Table 6.5**.

Table 6.5: Quantification of elements in the dissolved portion of Sample A as a function of sample:flux ratio at 200 °C, 30 min

Sample:Flux ratio	Concentration (%)								
	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
1:10	2.47	7.66	7.49	28.11	1.53	24.41	2.24	0.29	0.91
1:15	2.29	7.41	7.31	27.23	1.23	23.09	1.77	0.29	0.73
1:20	2.46	7.26	7.38	26.47	1.18	27.31	1.76	0.31	0.90
Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

151. Rettig, S. L., Marinenko, J. W., Khoury, H. N., and Jones, B. F., 1983, "Comparison of rapid methods for chemical analysis of milligram samples of ultrafine clays" *Clays and Clay Minerals*, **31**(6), pp. 440-446

152. Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP): 13 Sample dissolution, [homepage on the Internet]. C2004 [updated 2004 July; cited 2013 April 22]. Available from: <http://www.epa.gov/radiation/docs/marlap/402-b-04-001b-13-final.pdf>

6.3.1.2 Influence of temperature on digestion of tantalite ore

In the next step, the sample:flux ratio was fixed at 1:20 (since more accurate results were obtained for both Nb₂O₅ and Ta₂O₅ at this ratio in the previous experiment) for the investigation of a temperature variation on the dissolution of the tantalite by NH₄F•HF. A 0.1 g (weighed to 0.1 mg accuracy) of Sample A was mixed with NH₄F•HF in a ratio of 1:20 sample:flux in platinum crucibles. The subsequent fusions were carried out at 185, 200 and 250 °C for time duration of 30 min. The obtained melt was cooled to the surrounding temperature and then dissolved in distilled water. The undissolved solids were separated from the solution by filtration. The filtrates were quantitatively transferred to 100.0 mL volumetric flasks and then filled to the mark with distilled water. A 5.0 mL aliquot of the solution was then transferred to another 100.0 mL volumetric flask. The acidity adjustment and dilutions of the solutions were done as previously described (**Section 6.3.1**). The solutions were analysed using ICP-OES and the results are presented in **Table 6.6**.

Table 6.6: Quantification of elements in the dissolved portion of Sample A as a function of temperature with sample:flux ratio =1:20 for 30 min

Temperature / °C	Concentration (%)								
	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
185	2.21	6.51	6.71	24.54	1.01	20.86	1.60	0.28	1.00
200	2.44	7.55	7.39	27.16	1.25	28.12	2.03	0.27	0.68
250	2.40	7.77	7.37	26.60	1.19	27.98	1.72	0.31	0.76
Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

6.3.1.3 Influence of the fusion time on dissolution of tantalite ore

In the next step it was decided to investigate the effect of time on the degree of digestion of tantalite by NH₄F•HF by keeping the ratio of 1:20 and temperature of 250 °C while varying the fusion time between 30 and 120 min. In all the studied fusion times a residue was obtained during the water dissolution step. The solids were separated from the solution by filtration. Solutions obtained after filtration were treated for the ICP-OES measurements as outlined previously (**Section 6.3.1**). The analyses results are presented in **Table 6.7**.

Table 6.7: Quantification of elements in the dissolved portion of Sample A as a function of time with sample:flux ratio = 1:20 at 250 °C

Time (min)	Concentration (%)								
	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
30	2.46	7.26	7.38	26.47	1.18	27.31	1.76	0.31	0.90
60	2.64	8.72	7.50	27.22	1.57	27.19	2.16	0.48	2.54
120	2.81	8.86	7.58	27.74	1.15	27.01	1.82	0.43	3.06
Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

6.3.1.4 Analysis of the residual sample

Visual inspection revealed that some solids had remained undissolved under all the investigated experimental conditions. The residues obtained after the tantalite sample were fluxed with NH₄F•HF at 250 °C for 30 min and dissolution with water, were quantitatively transferred to a pre-weighed platinum crucible by removing the sample from the filter paper with water. The water was evaporated and the samples were dried at 100 °C for 5 hrs. The crucible was re-weighed to determine the sample mass. A 1:1 mixture of Na₂HPO₄ and NaH₂PO₄•H₂O was added to this residue to yield a 1:16 sample:flux ratio. The sample/flux mixture was then fused at 900 °C for 30 min. The obtained melt was cooled to room temperature and then dissolved in water. Visual inspection indicated that all the solids had dissolve and the solution was quantitatively transferred to a 100.0 mL volumetric flask. The acidity of the solution was adjusted by the addition of 5 mL 85% H₃PO₄ and then diluted to the mark with distilled water. The solution was analysed using ICP-OES and the results are presented in **Table 6.8**.

Table 6.8: Quantification of elements in the residual portion of Sample A after the dissolution with NH₄F•HF at 250 °C and leaching with water

Sample	Concentration (%)								
	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Residue	0.29	1.86	0.63	0.06	0.42	0.57	0.02	0.43	1.25

6.3.2 Application of the optimal conditions for the dissolution of Samples A and C

It was decided from the results obtained in the previous investigations that a 30 min digestion at 250 °C was the most promising conditions for the total recovery of Nb and Ta and the other major elements such as Mn, Fe and Ti from the tantalite mineral samples. The $\text{NH}_4\text{F}\cdot\text{HF}$ fusion and dissolution procedures were repeated for Sample A and extended to Sample C. Approximately 0.1 g (accurately weighed to 0.1 mg) of each mineral sample was thoroughly mixed with 2.0 g of $\text{NH}_4\text{F}\cdot\text{HF}$ in platinum crucibles and then fused at 250 °C for 30 min in an oven. The obtained melt was cooled to ambient temperature and then dissolved in water. The residues were separated from the solution by filtration. The filtrates were quantitatively transferred to 100.0 mL volumetric flasks. A 5.0 mL aliquot of each solution was quantitatively transferred to another 100.0 mL volumetric flask. The acidity of the solutions was adjusted with 10 mL 97% H_2SO_4 and then allowed to cool to room temperature before filling them to the mark with distilled water. **Table 6.9** presents the results obtained from the ICP-OES measurements of the solutions.

Table 6.9: ICP-OES measurement results after fusion dissolution of tantalite mineral ores with $\text{NH}_4\text{F}\cdot\text{HF}$ (1:20 sample:flux ratio) at 250 °C for 30 min

Analyte	% M_xO_y			
	Sample A		Sample C	
	Found	Expected	Found	Expected
Ta ₂ O ₅	27.8(9)	27.8(3)	29.6(4)	33.0(2)
Nb ₂ O ₅	27.1(5)	27.0(2)	13.2(3)	13.7(2)
ThO ₂	0.40(8)	0.54(2)	0.27(4)	0.29(1)
U ₃ O ₈	1.0(3)	2.81(2)	0.16(1)	0.14(1)
WO ₃	2.0(2)	1.18(2)	1.1(6)	0.16(1)
TiO ₂	2.5(1)	2.77(2)	10.4(6)	8.19(1)
Mn ₃ O ₄	7.87(9)	8.91(7)	3.7(5)	3.13(1)
Fe ₂ O ₃	7.69(9)	8.3(2)	19.8(6)	18.71(6)
SnO ₂	1.47(3)	1.64(3)	n.d	0.15(1)
Y ₂ O ₃			0.16(6)	0.24(1)
CaO			0.50(5)	0.52(4)

Bold values = inaccurate results

6.3.3 Separation of Nb and Ta in Sample A mineral ore by selective precipitation method

A 0.06 g (accurately weighed to 0.1 mg) *p*-phenylenediamine (PPDA) sample was dissolved in 10.0 mL water. The PPDA solution (5.0 mL) was then added to the Sample A solution (5.0 mL) obtained in **Section 6.3.2**. This addition was immediately followed by a colour change from colourless to blue and precipitate formation (see **Chapter 4, Section 4.3.1**). The pH of the solution was found to be 5.46. The precipitate was separated from the solution by centrifugation and decantation. The precipitate was subsequently dissolved in 10 mL of 97% H₂SO₄. The solution was quantitatively transferred to a 100.0 mL, allowed to cool to room temperature and then filled to the mark with distilled water.

The filtrate (supernatant liquid) was also transferred quantitatively to a 100.0 mL volumetric flask and 10 mL concentrated H₂SO₄ was added. The solution was cooled and then made up to the mark with distilled water. Both the precipitate and filtrate solutions were analysed for Nb and Ta concentrations using ICP-OES and the results are given in **Table 6.10**.

Table 6.10: Quantification of Nb and Ta in the precipitate obtained from flux fusion of Sample A with NH₄F·HF and precipitation with PPDA from water solutions

Sample	Concentration (%)	
	Nb ₂ O ₅	Ta ₂ O ₅
Precipitate	3(1)	21(2)
Filtrate	25.1(8)	6(2)
% Total mass	27.85	27.51
Expected	27.0(2)	27.8(3)

Standard deviations are based on n = 3 analyses

6.3.4 Solvent extraction separation of Nb and Ta in tantalite mineral using MIBK

A 5.0 mL aliquot of the Sample A solution obtained in **Section 6.3.2** was pipetted into a separating funnel followed by the addition of 5 mL of H₂SO₄ solution. This sample-acid mixture was shaken for 5 min and then successively extracted with two portions of 10 mL of methyl isobutyl ketone (MIBK). The sample-acid solution and MIBK

mixture was shaken for 5 min at desired acid H₂SO₄ concentration (1.0 M to 4.0 M). Each time the solution was allowed to stand for 5 min to allow for the complete separation of the two immiscible liquid phases. The aqueous (acidic) solution (the bottom layer) was then collected in a 100 mL beaker. This aqueous solution was stirred on a hot plate set at 40 °C for 50 min to evaporate any dissolved organic solvent.

The two organic portions were combined and then successively stripped with two portions of 20 mL water. The solution was allowed to stand for 5 min for the complete separation of the liquid phases. The water layer was then collected in another 100 mL beaker. The water (strip) solutions were then combined and heated to evaporate any dissolved organic solvent. The acidic aqueous and water strip solutions were then cooled to room temperature and then quantitatively transferred to 100.0 mL volumetric flasks. The acidity of the solutions was adjusted to match the 1.810 M H₂SO₄ of the standard and blank solutions. The solutions were again allowed to cool to room temperature and the volumetric flasks were then filled to mark with distilled water. The solutions were analysed using ICP-OES and the results are reported in **Table 6.11** and the average percentages obtained are graphically presented in **Figures 6.2** and **6.3**.

Table 6.11: Solvent extraction for separation of elements in Sample A using MIBK after fusion with NH₄F•HF for 30 min at 250 °C

M _x O _y (%)	[H ₂ SO ₄] (M)								Expected (%)
	Aqueous				Organic				
	1.0	3.0	4.0	Average*	1.0	3.0	4.0	Average*	
Ta ₂ O ₅	0.47	0.73	0.49	0.56	27.06	27.59	27.91	27.52	27.8(3)
Nb ₂ O ₅	27.47	28.03	26.76	27.42	0.85	0.76	0.76	0.79	27.0(2)
ThO ₂	0.42	0.44	0.37	1.08	0.19	0.37	0.04	0.20	0.54(2)
U ₃ O ₈	2.42	2.50	2.40	2.44	0.35	0.26	0.47	0.36	2.81(2)
WO ₃	1.84	1.74	1.70	1.76	0.05	0.05	0.04	0.05	1.18(2)
TiO ₂	2.49	2.46	2.39	2.44	0.27	0.26	0.24	0.26	2.77(2)
Mn ₃ O ₄	8.04	7.87	7.74	7.88	0.16	0.21	0.10	0.15	8.91(7)
Fe ₂ O ₃	7.42	7.26	7.36	7.34	0.25	0.27	0.23	0.25	8.3(2)
SnO ₂	1.19	1.07	1.05	1.10	0.37	0.43	0.33	0.37	1.64(3)

*Average calculated on the basis of similar results for different H₂SO₄ concentrations

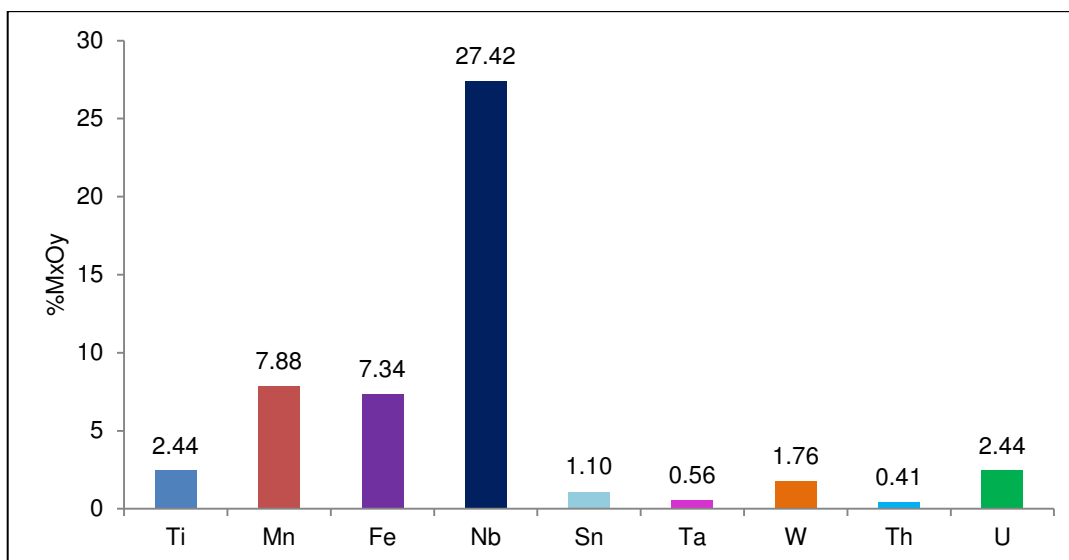


Figure 6.2: Aqueous solution analysis of the average solvent extraction separation of elements at different $[H_2SO_4]$ in Sample A (Al and Si excluded due to inaccurate analysis) using MIBK after fusion with $NH_4F \cdot HF$ for 30 min. at $250\text{ }^\circ\text{C}$.

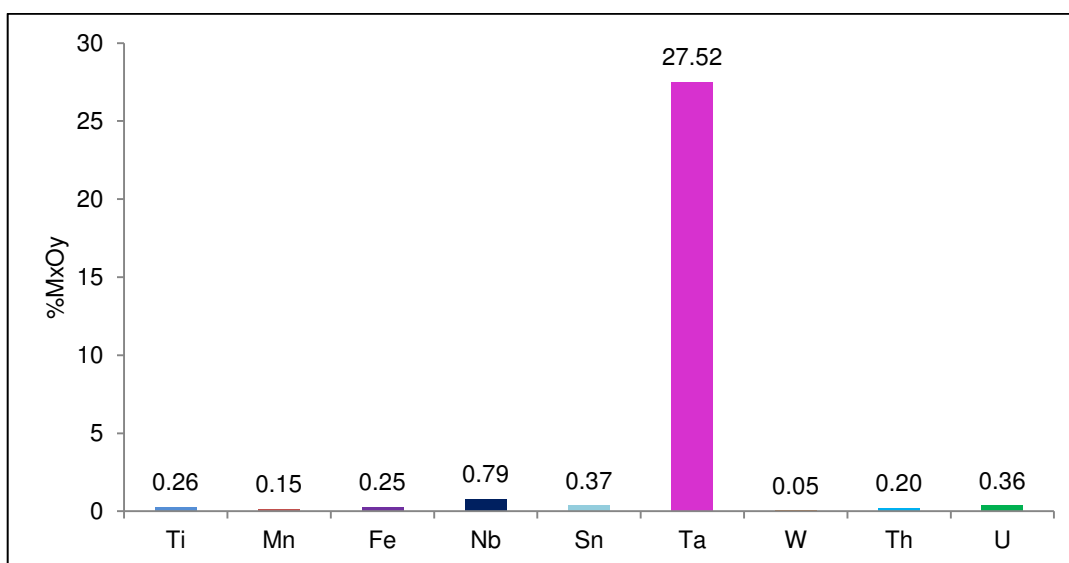


Figure 6.3: Organic phase analysis of the average solvent extraction ($n = 2$) separation of elements at different $[H_2SO_4]$ in Sample A (Al and Si excluded due to inaccurate analysis) using MIBK after fusion with $NH_4F \cdot HF$ for 30 min. at $250\text{ }^\circ\text{C}$.

6.3.4.1 Solvents for extraction separation of elements in tantalite sample

MIBK is the most commercially used solvent for both collective and selective extraction of Ta and Nb due to its low density as well as its ability to extract the

fluoride complexes of these elements from the acidic solutions. Despite its success, MIBK has disadvantages which include a low flash point (14 °C), which makes it very hazardous to handle, as well as a relatively high solubility (1.9%) in aqueous solutions. The high solubility of MIBK in aqueous solution necessitates an additional step to remove the extractant from the aqueous solution¹⁵³ after extraction thereby lengthening the separation process. The presence of organic solvents in the aqueous solutions enhances the analyte and solvent intensities which may lead to positive errors in the element recovery analysis.¹⁵⁴ The use of MIBK in this study was very successful for the selective extraction of tantalum from the aqueous acidic solutions, facilitating the separation of tantalum from niobium as well as from most of the metal impurities in the tantalite mineral sample. This study was however extended to include the investigation of other potential organic extractants. Some of the properties of the organic solvents selected for this study are outlined in **Table 6.12**.

Table 6.12: The properties of the organic solvents selected for the extraction Ta and/or Nb from the tantalite mineral matrix

Solvent/Extractant	Density (g/cm ³)	Solubility in water at 20 °C (%)	Boiling point (°C)	Flash point (°C)
4-Heptanone (4-Hept)	0.817	0.46	145	48
1-Octanol (1-Oct)	0.824	1.0x10 ⁻⁶	194.5	81.1
Methyl isopropyl ketone (MIPK)	0.805	0.6	95	-1
Methyl isobutyl ketone (MIBK)	0.802	1.91	116.5	14
Methyl isoamyl ketone (MIAK)	0.888	0.50	144	43.3

The solvents which were investigated include two MIBK analogues, namely methyl-isopropyl ketone (MIPK) and methyl isoamyl ketone (MIAK) (see **Figure 6.4**) as well as 4-heptanone (4-Hept) and 1-octanol (1-Oct) which has been reported in

153. Qin-gang, L., Kang-gen, Z. and Qi-xiu, Z., 2000, "MIBK Removal from Aqueous Solution by Aeration method", *J. Cent. Souiii Univ. Teo-inol.*, **7**(4): pp. 182–185

154. Grindlay, G., Maestre, S., Gras, L. and Mora, J., 2006, "Introduction of organic solvent solutions into inductively coupled plasma-atomic emission spectrometry using a microwave assisted sample introduction system" *J. Anal. At. Spectrom.*, **21**: pp. 1403–1411

literature^{155, 156} as possible successful extractants for tantalum and niobium from HF solutions.

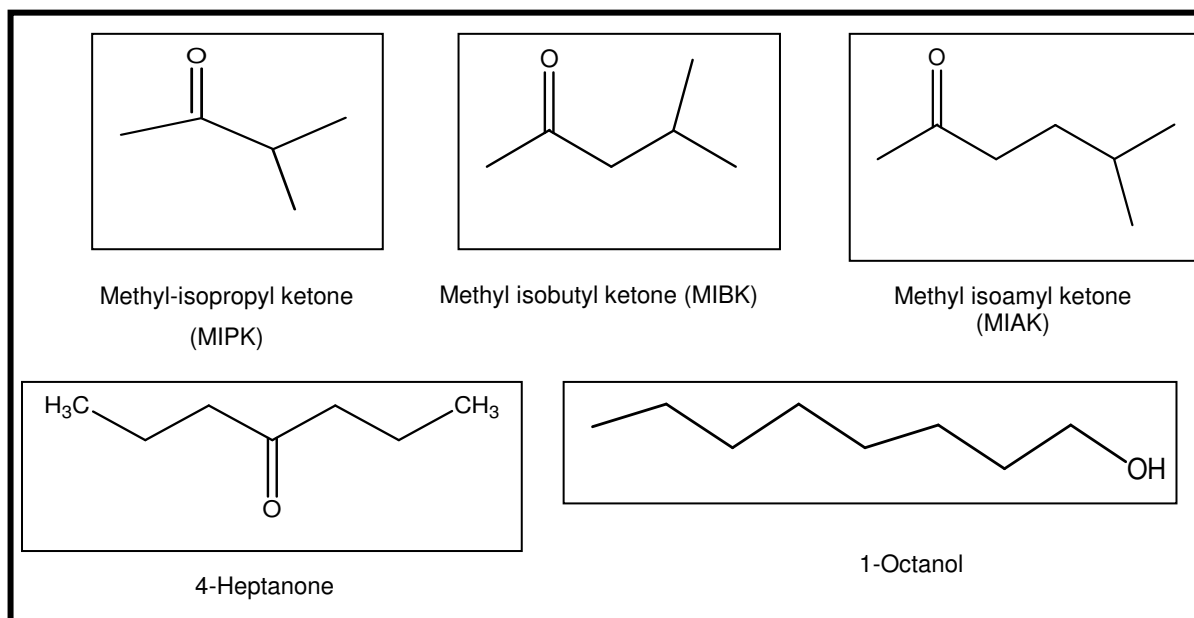


Figure 6.4: Chemical structures of the selected solvents for Nb and/or Ta extraction from the tantalite matrix in this study.

A 5.0 mL aliquot of the Sample A solution obtained in **Section 6.3.2** was mixed with 5 mL of 8.0 M H_2SO_4 solution in a separating funnel. Extraction was carried with two successive portions of 10.0 mL of each solvent and back extraction (from the organic phase) was done with two portions of 20 mL distilled water. All the aqueous solutions were heated to about 40 °C for 50 min in glass beakers to ensure that all the organic solvents are removed prior to analysis by ICP-OES. The acidity of the solutions was adjusted to match the blank and standard solutions with 97% H_2SO_4 . The solutions were allowed to cool to ambient temperature and then filled to the 100.0 mL mark of the volumetric flask with distilled water. All the solutions were analysed using ICP-OES and the results for the duplicate analyses of each solvent are given in **Table 6.13**.

155. Stevenson, P. C., and Hicks, H. G., 1953, "Separation of Tantalum and Niobium by Solvent Extraction", *Anal. Chem.*, **25**(10): pp.1517–1519

156. Maiorov, V. G., Nikolaev, A. I., Sklokin, L. I., and Baklanova, I. V., 2001, "Extractive Recovery of Tantalum(V) and Niobium(V) with Octanol from Hydrofluoric Acid Solutions Containing Large Amounts of Titanium(IV)" *Russ. J. Appl. Chem.*, **74**(6) 2001, pp. 945–949

Table 6.13: Comparison between the different organic solvents investigated for the solvent extractive separation of Ta and Nb in Sample A

Solvent	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
4-Hep-aq	2.95	8.03	7.31	23.70	3.28	1.60	2.20	0.76	2.76
4-Hep-org	0.87	0.29	0.66	1.78	0.24	26.60	0.29	0.93	1.10
MIPK-aq	2.87	8.32	8.18	23.48	3.34	1.39	3.18	0.48	2.19
MIPK-org	0.75	0.00	0.30	0.54	0.19	16.78	0.02	0.66	0.25
MIBK-aq	2.92	7.88	7.92	28.04	3.61	1.28	3.03	0.29	2.20
MIBK-org	0.84	0.15	0.47	0.45	0.20	28.27	0.24	0.57	0.33
1-Oct-aq	2.65	7.20	7.55	20.71	3.54	0.81	2.86	0.38	2.59
1-Oct-org	1.00	0.17	0.62	4.74	0.24	26.89	0.37	0.78	0.46
MIAK-aq	2.68	8.62	8.07	28.23	1.27	0.53	2.15	0.79	3.07
MIAK-org	0.34	0.28	0.22	0.55	0.46	28.96	0.78	0.34	0.33

Aq = aqueous phase, org = organic phase

The results in **Table 6.13** indicate that in all the solvents investigated in this study succeeded in the extraction of Ta into the organic phase leaving Nb and the majority of the other metal impurities in the aqueous phase. The results obtained for MIAK and 1-octanol compare well with those obtained for MIBK. The MIAK was chosen for further evaluation based on the results in **Table 6.13**.

6.3.4.2 Solvent extraction separation of Nb and Ta in tantalite mineral using MIAK

A 5.00 mL aliquot of the Sample A solution obtained in **Section 6.3.2** was pipetted into a separating funnel followed by the addition of 5 mL H₂SO₄ of the appropriate concentration. The extraction was investigated using different H₂SO₄ concentrations ranging between 1.0 M and 4.0 M with two successive portions of 10 mL of MIAK while the stripping was accomplished with two portions of 20 mL distilled water. The aqueous acidic and the water strip solutions were quantitatively transferred to 100.0 mL volumetric flasks. The acidity of the solutions was adjusted with H₂SO₄ to match the blank and standard solutions matrices. The solutions were allowed to cool to ambient temperature and then filled to the mark with distilled water. These solutions were analysed using ICP-OES and the results are given in **Table 6.14** and

presented graphically in **Figures 6.5** and **6.6** for both the aqueous and organic phases respectively.

Table 6.14: Solvent extraction for separation of elements in Sample A using MIAK after fusion with $\text{NH}_4\text{F}\cdot\text{HF}$ for 30 min at 250 °C

M_xO_y (%)	[H_2SO_4] (M)										Expected (%)
	Aqueous solution					Organic solution					
	1	2	3	4	Average	1	2	3	4	Average	
Ta ₂ O ₅	0.86	0.25	0.39	0.37	0.47	28.10	27.53	27.11	27.34	27.52	27.8(3)
Nb ₂ O ₅	28.33	27.08	26.73	28.27	27.60	0.43	0.53	0.52	0.68	0.54	27.0(2)
ThO ₂	0.35	0.39	0.16	0.47	0.34	n.d	n.d	0.04	0.06	0.02	0.54(2)
U ₃ O ₈	1.56	1.47	1.56	1.71	1.58	0.45	0.49	0.41	0.58	0.48	2.81(2)
WO ₃	2.21	2.22	1.80	2.31	2.14	0.81	0.74	0.57	0.63	0.68	1.18(2)
TiO ₂	3.01	2.81	2.81	3.14	2.94	0.46	0.50	0.47	0.47	0.48	2.77(2)
Mn ₃ O ₄	8.74	8.49	8.12	8.33	8.42	0.53	0.45	0.47	0.55	0.50	8.91(7)
Fe ₂ O ₃	8.65	8.29	8.25	8.45	8.41	0.69	0.67	0.65	0.74	0.69	8.3(2)
SnO ₂	1.38	1.29	1.21	1.47	1.34	0.46	0.69	0.51	0.52	0.54	1.64(3)

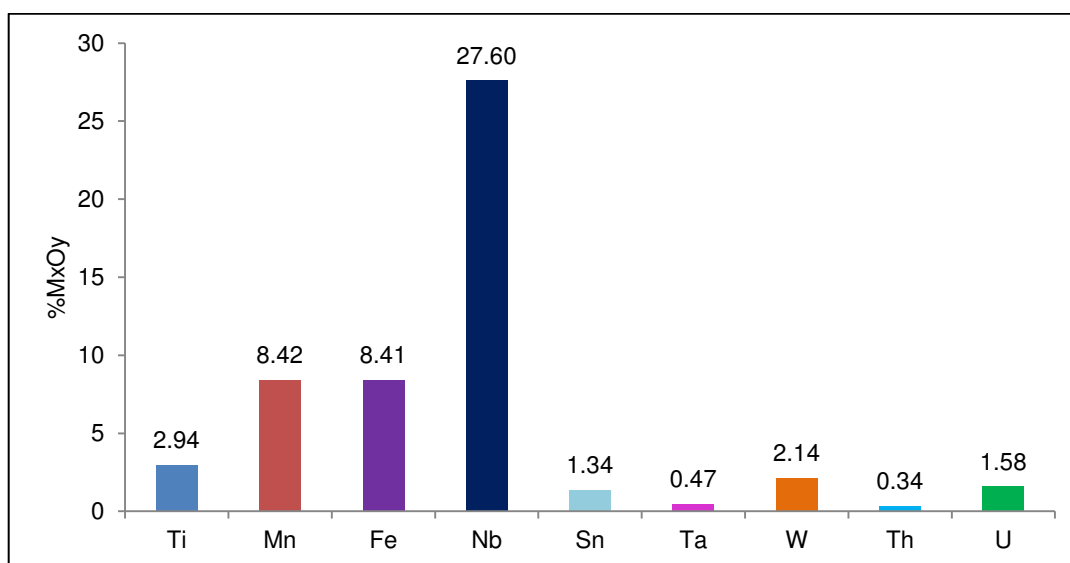


Figure 6.5: Aqueous phase analysis of the average element recovery after solvent extraction separation at different [H_2SO_4] in Sample A (Al and Si excluded due to inaccurate analysis) using MIAK after fusion with $\text{NH}_4\text{F}\cdot\text{HF}$ for 30 min. at 250 °C.

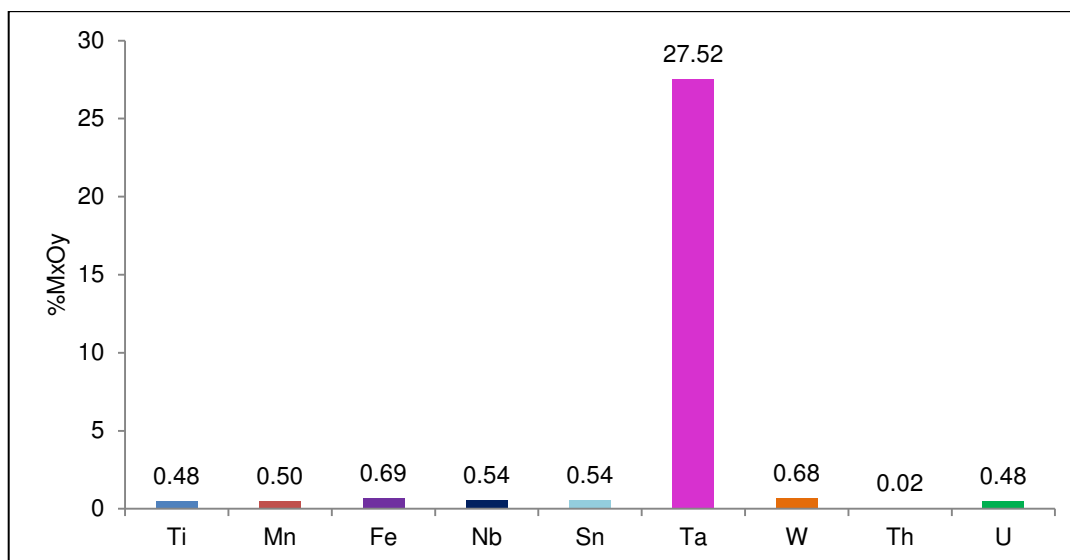


Figure 6.6: Organic phase analysis of the average element recovery using solvent extraction separation of at different $[H_2SO_4]$ in Sample A (Al and Si excluded due to inaccurate analysis) using MIAK after fusion with $NH_4F \cdot HF$ for 30 min. at $250\text{ }^\circ\text{C}$.

The percentage of extraction for each metal was calculated using the data in **Table 6.14** and **Equation 6.1** and the results are presented in **Table 6.15**.

$$\%E = \frac{[S]_{\text{org}}V_{\text{org}}}{[S]_{\text{aq}}V_{\text{aq}} + [S]_{\text{org}}V_{\text{org}}} \times 100\% \quad 6.1$$

where $[S]_{\text{org}}$ and $[S]_{\text{aq}}$ represent the concentration (% metal oxide in this case) of the metal in the two liquid phase and V_{org} and V_{aq} is the organic and aqueous volume respectively.

Table 6.15: Determination of percentage metal oxides in the two liquid phases

Analyte	Total	Concentration (%)	
		Aqueous	Organic
Ta ₂ O ₅	27.99	1.68	98.32
Nb ₂ O ₅	28.14	98.08	1.92
ThO ₂	0.36	94.44	5.56
U ₃ O ₈	2.06	76.70	23.30
WO ₃	2.82	75.89	24.11
TiO ₂	3.42	85.96	14.04
Mn ₃ O ₄	8.92	94.39	5.61
Fe ₂ O ₃	9.10	92.42	7.58
SnO ₂	1.88	71.28	28.72

6.3.4.3 Column chromatographic purification of tantalite ore

From the solvent extraction separation study (**Sections 6.3.2.2 to 6.3.2.4**) it was found that the majority of Nb remains in the original aqueous solution together with most of the other metal impurities present in Sample A when Ta is extracted into the organic phase. The extraction or separation of niobium from these metal impurities was subsequently investigated with ion exchange as separation method. Sample A mineral ore was digested by flux fusion method using NH₄F•HF and dissolved in water as indicated in **Section 6.3.2**. The strongly basic Amberlite IRA-900 and a weakly basic Dowex marathon anion exchange resins were selected for the possible separation of Nb and Ta from the other metals.

6.3.4.3.1 Elution of tantalite elements on Amberlite IRA-900 anion using different HCl concentrations

A glass column with a 1.2 cm internal diameter was packed to a height of 20 cm with the strongly basic Amberlite IRA-900 anion exchange resin. The column was firstly washed by passing 20 mL 1.0 M HCl through the resin. A 5.0 mL aliquot of the sample solution (from **Section 6.3.2**) was then transferred to the column using a micropipette. A sequential elution was done with 20 mL of different HCl concentrations ranging from 0.1 M to 6.0 M (see **Tables 6.16**). The effluent of each acid concentration was collected in 100.0 mL volumetric flask. At the end of the elution process the solutions were filled to the mark with distilled water and then analysed using ICP-OES. The results of this experiment are presented in **Table 6.16**.

Table 6.16: Elution of tantalite elements from a strongly basic Amberlite IR-900 anion exchange columns using HCl as an eluent

[HCl] (M)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
0.1	0.30	7.61	7.88	0.73	n.d	1.23	0.77	0.16	n.d
0.5	0.32	0.33	0.31	0.68	n.d	1.42	0.24	n.d	n.d
1.0	0.38	0.26	0.20	0.46	n.d	3.30	0.40	n.d	n.d
2.0	1.65	0.22	0.13	4.60	n.d	3.41	0.38	0.09	n.d
3.0	0.08	0.17	0.14	8.34	n.d	3.39	0.23	0.11	0.16
4.0	0.08	0.24	0.09	3.96	n.d	3.21	0.28	0.16	0.32
6.0	0.05	0.25	0.01	0.89	n.d	1.09	0.25	0.15	0.24
% Total	2.86	9.07	8.75	19.66	n.d	17.06	2.55	0.68	0.73
% Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

n.d = not detected

6.3.4.3.2 Elution of tantalite elements on Dowex Marathon WBA anion using different HCl and H₂SO₄ concentrations

A glass column with a 1.2 cm internal diameter was packed to a height of 20 cm with the weakly basic Dowex Marathon wba anion exchanger resin. The resin was washed with 20 mL of 1.0 M HCl solution and then 5.0 mL aliquot of the sample solution was quantitatively transferred to the column. Elution was sequentially performed with different concentrations of acid ranging from 0.1 M to 6.0 M (see **Tables 6.17**). The effluent of each elution was collected in a 100 mL beaker and subsequently transferred to a 100.0 mL volumetric flask. The acidity of these solutions was adjusted by addition of the appropriate concentrations of HCl to match the blank and the standard solutions matrix. The solutions were then made up to the mark with distilled water and subsequently analysed using ICP-OES. The results obtained in this study are presented in **Table 6.17**.

Table 6.17: Elemental elution from the tantalite sample using HCl on a Dowex Marathon wba anion exchanger column

[HCl] (M)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
0.05	0.07	0.16	0.13	n.d	0.02	0.01	0.24	0.01	n.d
0.1	0.04	0.43	0.10	n.d	n.d	0.14	n.d	n.d	n.d
1.0	0.05	0.35	0.12	n.d	n.d	0.09	n.d	n.d	2.38
4.0	2.16	3.00	6.62	n.d	0.02	0.82	n.d	0.02	1.28
6.0	0.19	0.04	0.20	12.72	n.d	5.62	0.02	0.22	0.06
%Total	2.51	3.99	7.17	12.72	0.04	6.68	0.25	0.25	3.72
%Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

Bold values = highest values eluted

n.d = not detected

Another column with identical properties to that used for HCl elution was packed with the Dowex Marathon wba to a height of 20 cm and then washed with 20 mL of 1.0 M H₂SO₄ solution. A 5.0 mL aliquot of sample solution was transferred to this column and sequentially eluted with different concentrations of H₂SO₄. The effluents of each elution was collected in a 100 mL beaker and quantitatively transferred to 100.0 mL volumetric flask. The acidity of the solution was adjusted accordingly with H₂SO₄ solution of the appropriate concentration to match the blank and the standard solutions matrix. The solutions were allowed to cool to ambient temperature and then diluted to the mark with distilled water. The solutions were analysed using ICP-OES and the results are give in **Table 6.18**.

Table 6.18: Elemental elution from the tantalite sample using H₂SO₄ on a Dowex Marathon wba anion exchanger column

[H ₂ SO ₄] (M)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
0.05	0.78	3.05	1.58	1.11	0.80	1.06	0.51	0.09	0.08
0.1	0.77	1.83	1.61	1.07	0.81	1.02	0.45	0.16	0.88
1.0	0.79	1.06	1.46	1.12	0.81	1.01	0.72	0.13	1.22
4.0	2.15	1.02	7.06	1.83	1.43	1.87	1.14	0.01	0.32
6.0	2.15	1.02	0.08	1.83	1.43	1.87	1.14	0.01	0.32
%Total	6.63	7.98	11.78	6.96	5.28	6.82	3.96	0.41	2.82
%Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

A comparison of the total recovery for the two different acids, clearly indicate that the elution with HCl effected the highest Nb and Ta and it was therefore decided to continue the study with only HCl as a potential eluent for the selective elution of the elements in this tantalite matrix. The HCl elution results also revealed that the concentrations of the elements in the eluate increased with increasing HCl concentration. A further evaluation of the effect of the HCl concentrations on the elements separation and recovery was performed with HCl concentrations ranging between 4.0 M and 8.0 M.

A column of 1.2 cm diameter was packed with Dowex Marathon wba anion exchanger (a weakly basic anion exchanger) to a height of 20 cm. The resin was washed with 20 mL of 1.0 M HCl solution. A 5.0 mL aliquot of Sample A solution (**Section 6.3.2**) was then quantitatively transferred to the column and then sequentially eluted with 20 mL of HCl of different concentrations. The effluent of each acid concentration was collected in a 100.0 mL volumetric flask. The acidity of the solution was adjusted with HCl to match that of the blank and the standard solutions and then diluted to the mark with distilled water. These solutions were analysed using ICP-OES and the results are given in **Table 6.19**.

Table 6.19: Element recovery from a tantalite sample elusion using HCl on Dowex Marathon WBE anion exchanger column at different HCl concentrations

[HCl] (M)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
4.0	1.25	6.57	7.41	0.80	0.21	1.79	1.06	0.31	2.34
6.0	0.79	0.34	0.22	16.15	0.07	10.18	0.42	n.d	n.d
8.0	n.d	0.10	0.08	n.d	0.10	0.98	n.d	n.d	n.d
%Total	2.03	7.01	7.71	16.95	0.37	12.96	1.48	0.31	2.34
%Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)
%Recovery at 4.0 M	44.96	73.71	89.22	2.98	12.77	6.45	90.25	57.72	83.31
%Total recovery	73.47	78.65	92.87	62.78	22.64	46.61	125.50	57.72	83.31

Bold values = highest values eluted with different acid concentrations

n.d = not detected

6.3.4.3.3 Influence of the total volume of mobile phase on elution of Sample A elements

The effect of HCl volume on the elution process was investigated in order to improve the elution conditions from the Dowex Marathon wba resin. Two columns were packed with the Dowex Marathon wba resin to a height of 20 cm and then washed with 20 mL of 1.0 M HCl. A 5.0 mL aliquot of the sample solution was quantitatively transferred to the columns and sequentially eluted with 4.0 M and 6.0 M HCl solutions. In one column the elements were eluted with 20 mL of each HCl solution while in the other column elution was carried with 40 mL of the same solutions. The effluent of the elution was collected in 100 mL beakers and then quantitatively transferred to 100.0 mL volumetric flask. The acidity of the solutions was adjusted accordingly with HCl to match that of the blank and the standard solutions. The solutions were then analysed using ICP-OES and the results are give in **Table 6.20**.

Table 6.20: Effect of HCl volume on the element elution using a Dowex Marathon wba anion exchanger column

Volume (mL)	[HCl] (M)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
20	4	0.21	6.46	3.83	0.46	0.32	1.27	0.50	1.18	3.83
	6	0.77	1.36	0.95	8.46	0.30	1.97	0.81	0.99	4.83
40	4	1.22	6.59	8.05	0.41	0.28	1.41	0.28	0.81	3.51
	6	1.21	0.27	0.25	23.98	0.25	13.71	1.47	0.81	2.27
% Expected		2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

Bold values = highest values eluted with different volumes

6.3.4.3.4 Influence of the flow rate of HCl on element recovery

The results in **Tables 6.16** to **6.20** clearly indicated that separation of the tantalum from the niobium by these anion exchange resins (Amberlite IR-900 and Dowex Marathon wba) is unfeasible since the optimal conditions for separation from the other elements always indicated the presence of both Nb and Ta in substantial quantities in the final solutions. It was therefore decided to separate Ta from the mineral matrix by solvent extraction prior to the elution procedure and then investigate the possible separation of Nb from the other impurities. The results also indicated that the 40 mL volume of the eluent was not enough for the complete

recovery of both Nb and Ta (**Table 6.20**) and as such a 60 mL volume of eluent was used in the investigations that follow.

A solution of Sample A was prepared by fusion with $\text{NH}_4\text{F}\cdot\text{HF}$ as flux. The melt was subsequently dissolved with in distilled water (see **Section 6.3.2**). A 5.0 mL aliquot of the sample solution was quantitatively transferred to a separatory funnel followed by addition of 5.0 mL of 8.0 M H_2SO_4 solution. The mixture was shaken for 5 min and then extracted with two portions of 10 mL MIAK. The aqueous phase was collected in a 100 mL beaker. The organic phase was stripped with two portions of water and subsequently analysed for Ta content using ICP-OES and the results are given in **Table 6.21**.

Table 6.21: Elemental recovery from the organic portion after the solvent extraction using MIAK

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
MIAK-Org ₁	0.38	0.06	0.42	0.30	0.03	26.83	0.08	0.24	0.07
MIAK-Org ₂	0.05	0.32	0.51	0.35	n.d	27.91	0.15	0.24	0.16
Average	0.21	0.19	0.47	0.33	0.01	27.37	0.11	0.24	0.12

n.d = not detected

In order to test the effect of the flow rate on the separation and recovery of Nb from the mineral matrix, two different flow rates (0.7 mL/min and 1.7 mL/min) were investigated. Two columns (1.2 cm internal diameter) were packed with Dowex marathon wba resin to a height of 20 cm. The resin was then washed with 20 mL of 1.0 M HCl solution. The aqueous portion, after the extraction of Ta using solvent extraction, was quantitatively transferred to the column followed by the elution with 60 mL of 6.0 M HCl. In one column the flow rate was maintained at 0.7 mL/min while in the other column the flow rate was 1.7 mL/min. The effluent from both columns was collected in fractions of 10 mL portions. The effluent portions were then quantitatively transferred to 100.0 mL volumetric flasks. The acidity of the solutions was adjusted with HCl to match the blank and the standard solutions. The concentration of the elements in these solutions was determined using ICP-OES and the results are presented in **Tables 6.22** and **6.23**.

Table 6.22: Elemental recovery from a tantalite sample elution using HCl on Dowex Marathon wba anion exchanger column at 0.7 mL/min flow rate

Time (min)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
14	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.07	n.d
28	0.83	3.70	n.d 0.00	n.d 0.00	n.d	n.d	n.d	0.01	0.36
42	1.63	4.92	5.51	n.d	n.d			0.05	0.09
56	0.39	0.63	0.43	9.01		0.08		0.06	0.15
70	0.00	n.d	n.d	8.60	n.d	n.d	n.d	0.13	n.d
84	0.00	n.d	n.d	5.69	n.d	n.d	n.d	0.14	0.06
98	0.00	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.06
112	0.00	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
126	0.00	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
%Total	2.85	9.24	5.94	23.30	n.d	0.08	n.d	0.47	0.72
%Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

n.d = not detected

Table 6.23: Elemental recovery from a tantalite sample elution using HCl on Dowex Marathon wba anion exchanger column at 1.7 mL/min flow rate

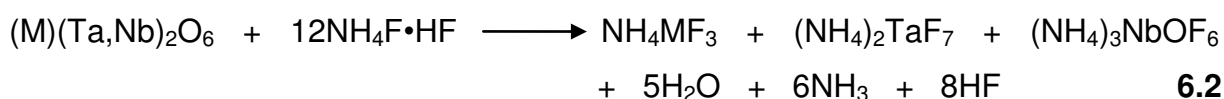
Time (min)	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
6	0.30	0.99	n.d	n.d	n.d	n.d	n.d	0.19	0.64
12	1.20	4.24	8.23	n.d	n.d	n.d	n.d	0.17	0.34
18	1.01	3.62	0.39	n.d	n.d	n.d	n.d	0.10	n.d
24	0.01	0.51	n.d	4.28	n.d	n.d	n.d	0.13	0.21
30	n.d	n.d	n.d	12.34	n.d	n.d	n.d	0.22	n.d
36	n.d	n.d	n.d	9.14	n.d	n.d	n.d	0.10	n.d
42	n.d	n.d	n.d	2.83	n.d	n.d	n.d	0.08	0.01
48	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.07	n.d
54	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.03	n.d
60	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.03	n.d
66	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.05	n.d
% Total	2.52	9.35	8.62	28.60	n.d	n.d	n.d	1.18	1.20
% Expected	2.77(2)	8.91(7)	8.3(2)	27.0(2)	1.64(3)	27.8(3)	1.18(2)	0.54(2)	2.81(2)

n.d = not detected

6.4 Results and discussion on optimization of methods

6.4.1 Dissolution of tantalite mineral samples using $\text{NH}_4\text{F}\cdot\text{HF}$ fusion method

The dissolution of the tantalite mineral was accomplished by the flux fusion with $\text{NH}_4\text{F}\cdot\text{HF}$ and the melt's subsequent dissolution with water. A possible chemical reaction between tantalite and $\text{NH}_4\text{F}\cdot\text{HF}$ as predicted in the literature is as follows (**Equation 6.2**):⁴²



where M = Fe or Mn.

The initial experimental results obtained in this study clearly indicated that the $\text{NH}_4\text{F}\cdot\text{HF}$ fusion digestion method resulted in the incomplete dissolution of the mineral sample as indicated by a solid residue which remained in solution after dissolution. The extent of dissolution of the mineral sample was evaluated by the determination of the concentrations of the metal ions in the solution and the results are expressed as percentage metal oxides of the most stable oxidation state of the element. The Nb_2O_5 and Ta_2O_5 recoveries (**Table 6.4**) are in the range 102.6 to 107.1 % and 84.0 to 89.2% (using **Table 6.1** as a guide, 27.92 to 29.14 of 27.0(2) Nb and 23.32 to 24.78 of 27.8(3) Ta) respectively. The analytical results (See **Table 6.4**) also indicated that the other elements in this mineral sample were successfully dissolved and good recoveries were obtained except for Al and Si with quantities much higher than expected (See **Table 6.4**). Various factors such as sample to flux ratio and temperature were then investigated to try and optimize this digestion method to effect the complete dissolution and total of all the elements, but particularly the Nb and Ta recoveries.

6.4.1.1 *Effect of sample:flux ratio on element recovery*

The effect of the concentration of $\text{NH}_4\text{F}\cdot\text{HF}$ on the dissolution of tantalite mineral was evaluated with the sample:flux ratios ranging from 1:10 to 1:20. The results obtained in this part of the study (**Table 6.5**) clearly indicated a correlation between the sample amount and the amount of $\text{NH}_4\text{F}\cdot\text{HF}$ required for the complete dissolution of the elements in tantalite mineral ore. A sample ratio of 1:10 was found to be satisfactory

for the complete recovery of Nb₂O₅ (103.35%) but not so for Ta₂O₅ (87.81%). The 1:20 sample:flux ratio on the other hand gave satisfactory dissolution for both Nb₂O₅ (98.15%) and Ta₂O₅ (98.24%), see **Table 6.5**) and most of the other metal constituents except for U₃O₈ and ThO₂ whose results seemed some what independent of the amount of flux when compared to expected recoveries as indicated in **Table 6.1**.

6.4.1.2 *Effect of temperature on element recovery*

The effect of temperature on the digestion and dissolution of the tantalite mineral ore were studied for fusion temperatures of 185, 200 and 250 °C. The results obtained in this study (**Table 6.6**) indicated that fusion at 185 °C produced lower recoveries for all the analytes (except for Al and Si) and that the 200 °C temperature is sufficiently high for the digestion of the tantalite mineral and the quantitative recovery of Nb and Ta using water as indicated by the recoveries of 100.59% and 101.04% Nb₂O₅ and Ta₂O₅ respectively. There is no marked improvement in the results upon increasing the temperature from 200 °C to 250 °C, but visual inspection indicated that the amount of residue decreased significantly at this fusion temperature suggesting a more complete reaction with the rest of the elements contained in the mineral sample.

6.4.1.3 *Influence of fusion time on the element recovery*

The next part of the study involved the investigation of the effect of digestion time on the dissolution of the tantalite mineral. The results obtained (**Table 6.7**) in this study revealed that the 30 min digestion time is sufficient for fluorination and dissolution of the main elements in the tantalite mineral as indicated by recoveries of 98.04% Nb₂O₅ and 98.24% Ta₂O₅. The results indicated little or no significant change in dissolution of the elements as observed upon increasing the digestion time from 30 min to 120 min (recoveries of 102.7% Nb₂O₅ and 97.2% Ta₂O₅).

6.4.1.4 *Determination of the composition of the residue obtained after NH₄F•HF fusion and dissolution with water*

The residue obtained after the dissolution of the melt obtained after the NH₄F•HF digestion (sample:flux ratio of 1:20) at 250 °C for 30 min was re-dissolved using a different flux (1:1 mixture of Na₂HPO₄ and NaH₂PO₄•H₂O) and analysed using ICP-

OES first for the determination of the presence of the metal in the remaining residue. The qualitative analysis of solution indicated the positive results for Sn, Ta, Mn, Fe and Ti. However, it was decided to do a quantitative analysis of all the elements to confirm their presence or absence in the residue since the detection of some of the elements such as U by ICP-OES may be poor (due to high detection limits, see **Section 6.6.4**) at low concentrations. The results obtained (**Table 6.8**) in this part of the study indicated that the residue contained 1.25% and 1.86% of U_3O_8 and Mn_3O_4 as the only high concentrations of the metal oxides in the residue. Most of the other metal oxides were successfully converted into their soluble fluoride salts as confirmed by the concentrations in the residue (e.g. 0.06% Nb_2O_5 and 0.57% Ta_2O_5).

6.4.1.5 Digestion of tantalite mineral using the optimal conditions

A combination of the experimental results obtained in **Sections 6.4.1.1 – 6.4.1.3** for the optimal element recovery indicated that the preferred conditions using $NH_4F \cdot HF$ as flux should be 30 min digestion time at 250 °C with a 1:20 sample:flux ratio. Under these conditions, recoveries of 100.2(5)% Nb_2O_5 and 100.0(9)% Ta_2O_5 were obtained from the dissolution of Sample A while 96.53(3)% Nb_2O_5 and 89.8(4)% Ta_2O_5 were recovered for Sample C (see **Table 6.9**). About 90% TiO_2 , Mn_3O_4 , Fe_2O_3 and SnO_2 and 73% ThO_2 were also obtained for Sample A. The Mn_3O_4 and Fe_2O_3 recoveries of 108.6(5)% and 103.7(3)% respectively were obtained for Sample C while most of the other elements indicated inaccurate (using **Table 6.1** as reference) analysis.

6.4.2 Comparison between $NH_4F \cdot HF$ flux fusion and other digestion methods for the dissolution of tantalite ore

The quantitative results obtained in this study were compared with those obtained previously using different digestion methods on the same samples and by different researchers (see **Table 6.24**). The methods were compared on the basis of the metal/element recoveries obtained for each method. All the results are reported as the percentage oxides of the most stable oxidation state of the elements. The results obtained in this study (using $NH_4F \cdot HF$ digestion) showed comparable percentage oxides for most of the target elements in the mineral ores, except for U_3O_8 in Sample A and Al_2O_3 and SiO_2 (results not shown) in both samples (see **Section 6.3.1**).

Table 6.24: Comparison of results of tantalite digestion by different methods and analysts

Digestion method	%								
	Sample A					Sample C			
	NH ₄ F•HF fusion	Micro wave	Li ₂ B ₄ O ₇		Unkown	NH ₄ F•HF fusion	Micro wave	Li ₂ B ₄ O ₇	
Analyst	Nete	Nete	Nete	Theron	Alfred H Knight	Nete	Nete	Nete	Theron
Ta ₂ O ₅	27.79	24.4	27.82	27.69	27.71	29.60	25	32.99	29.98
Nb ₂ O ₅	27.07	24.7	27.01	30.51	27.41	10.74	10.9	8.74	7.26
ThO ₂	0.40	0.60	0.54	0.52	0.65	0.27	0.48	0.29	---
U ₃ O ₈	0.96	2.82	2.81	2.97	2.83	0.16	0.35	0.14	---
WO ₃	1.98	1.33	1.18	0.09	1.61	1.12	0.24	0.16	1.18
TiO ₂	2.46	2.43	2.77	2.85	2.68	10.43	8.85	8.19	10.68
Mn ₃ O ₄	7.87	6.76	8.91	7.08	8.03	3.73	3.1	3.13	0.93
Fe ₂ O ₃	7.69	6.12	8.34	7.35	8.29	19.79	11.9	18.71	18.48
SnO ₂	1.47	0.79	1.64	<0.01	1.41	<0.01	0.09	0.15	<0.01
Y ₂ O ₃						0.16	0.24	0.24	---
CaO						0.50	0.60	0.52	---

Bold values = inaccurate results

The lower than expected U recovery from Sample A was a concern at this point when NH₄F•HF is used as flux when its recovery is compared with other digestion methods such as lithium tetraborate (Li₂B₄O₇). There are three possible reasons for this observation. First, the low percentage values could result from an incomplete decomposition of the U₃O₈, or a formation of volatile uranium fluoride compound (UF₄ or UF₆)¹⁵⁷ which may be lost during the fusion step or the formation of insoluble uranium salts that remains in the residue during the dissolution step. The comparison of the results obtained in this study with the LTB and Alfred H Knight results indicated that the recoveries of Ti, Mn, Fe and Sn were in the range 90 to 96% while only U₃O₈ and ThO₂ were 33 and 73 % respectively, indicating a possible loss of these elements. The results obtained by microwave assisted H₂SO₄ digestion on the other hand were lower than all the flux fusion and the Alfred H Knight results except for ThO₂, U₃O₈ and WO₃ (see **Table 6.24**). These results clearly showed the inefficiency of the microwave/H₂SO₄ dissolution method on the tantalite minerals under study. This microwave procedure also produced incomplete sample dissolution.

157. Yeaman, C. B., 2001, Dry process fluorination of uranium dioxide using ammonium bifluoride, [MSc thesis]. Berkeley: University of California; 2001 [cited 2013 Feb 22]

The analysis of the residual sample from the $\text{NH}_4\text{F}\cdot\text{HF}$ flux fusion procedure however recovered the remaining, but yet undetermined uranium in the undissolved sample, thereby ruling out the possibility of uranium loss from the sample by volatilisation. The concentrations of the other metals (Fe, Mn, Nb, Ta, W, Al, Sn and Si) in the residues (see **Table 6.8**) were very low clearly confirming a complete solubilisation of most of the tantalite constituents in the initial digestion step.

From the above discussions it is clear that the $\text{NH}_4\text{F}\cdot\text{HF}$ is highly successful as a flux for the dissolution and recovery of the main elements in the tantalite mineral ores studied. The $\text{NH}_4\text{F}\cdot\text{HF}$ flux fusion has several advantages over some other known dissolution methods such as $\text{Li}_2\text{B}_4\text{O}_7$ and which are successful in the dissolution of Nb and Ta samples.⁵¹ The advantages include a relatively low fusion temperature (200 °C to 250 °C) and shorter digestion time of 30 min (see also **Section 5.3.2.1** and **Table 5.14**).

6.4.3 Separation of niobium and tantalum in the mineral ore by selective precipitation

Studies on the selective separation of niobium and tantalum from the tantalite ore using PPDA, indicated similar chemical behaviour to that observed for the oxides. The results obtained (**Table 6.10**) in this study indicated that more Ta (68.7%) was precipitated than Nb (14.7%), similar to what was observed with the pure oxides (23(5)% and 73(3)% for Nb and Ta respectively (**Table 5.9**) and can be explained accordingly (see **Section 5.3.2.3**). These results clearly show the correlation of the chemistry of the niobium and tantalum compounds in the tantalite mineral and that of the metal oxides which were studied in **Chapter 5**, confirming that Nb and Ta are present as the oxides within the mineral. The results further indicated the lack of selectivity of the p-phenylenediamine ligand towards precipitation of either Nb or Ta in the tantalite mineral solutions. Tantalum was mainly isolated in the precipitate in relatively higher quantities compared to the Nb, and this is different from the results which were obtained for the NbF_5 and TaF_5 , in **Chapter 4**. This observation indicates a different chemical composition for the products obtained from the reaction of the $\text{NH}_4\text{F}\cdot\text{HF}$ with the Nb and Ta in the tantalite. This would in turn lead to the formation of different chemical compounds between PPDA and these metals in the tantalite solutions resulting in the different solids (ppt) that are formed in this reaction.

6.4.4 Solvent extraction separation of niobium and tantalum in tantalite ore

The solvent extraction of the elements in Sample A was performed with 10 mL portions of MIBK from different H₂SO₄ concentrations ranging from 1.0 M to 4.0 M. The results obtained (**Table 6.11**) from this study demonstrated that the tantalite dissolution using NH₄F•HF as a flux produced a chemical compound which is suitable for selective extraction of Ta from the mineral matrix (see also **Figure 6.3**). The extraction process/chemistry behave similar to the separation process observed for the pure Nb₂O₅ and Ta₂O₅ synthetic mixture as discussed in **Chapter 5**. The analytical results showed that 98.99% Ta were recovered from the organic portion while 101.6% Nb was recovered from the aqueous solution (**Table 6.11**). The poor Nb extractions into the organic phase under these experimental conditions clearly indicate the successful separation of these two elements from one another. In addition, the results also indicated a separation of Ta from the majority of the elements in the mineral sample (see **Figure 6.2**).

Poor extraction (see **Figure 6.3**) of the other metal impurities also indicates the possibility of isolating a Ta compound with a relatively good purity. However, the Ta obtained by this separation is expected to be contaminated with Si, most probably from the use of glass separatory funnel in the extraction step. Other possible contaminants are Al, Th and U which were also found in significant quantities (1.11% Al₂O₃ and 0.36 U₃O₈) in the organic portion (see **Table 6.11**) after the solvent extraction process. The inaccurate analysis of Al makes the judgement of whether it was extracted or not problematic at this stage but this does not rule it out as a potential contaminant in the enriched tantalum portion.

6.4.4.1 Evaluation of different extractants on Ta recovery

Different organic solvents were also evaluated for the selective extraction of Ta and/or Nb from the tantalite mineral. The results obtained from this study indicated that all the evaluated solvents were selective towards the tantalum complex extraction (see **Figure 6.7**). The 4-heptanone and methyl isopropyl ketone were found to extract ~2% Nb, while 1-octanol extracted ~5% Nb along with Ta. In terms of selectivity towards Ta extraction MIBK and MIAK are comparable (see **Figure 6.7** and **Table 6.5**) suggesting that MIAK can be used in place of MIBK to extract Ta and

thus separating it from Nb and from the rest of the other metal constituents of the tantalite mineral ore in the fluoride solutions.

Only the methyl isopropyl ketone (MIPK) extraction produced poor results for both Ta and Nb in the two liquid phases. In addition, the MIPK and 4-Hep extractions showed a formation of emulsions that resulted in poor separation of solvent phases and what required a long waiting time of more than 45 min and addition of excess acidic solution to obtain a complete phase separation. Another problem that was encountered with these two solvents (MIPK and 4-Hep) was the significant loss of Nb that was observed (much lower mass balance than expected, **Table 6.5**) which is probably lost in the raffinate organic solution. The 1-octanol however, has a disadvantage that it also extracts a significant amount of Nb (4.31-5.17 %, **Table 6.5**). The results also showed a significant extraction of Th and U into the organic portion for all the solvents. These results indicate a possible contamination of Ta in the organic portion by these two elements.

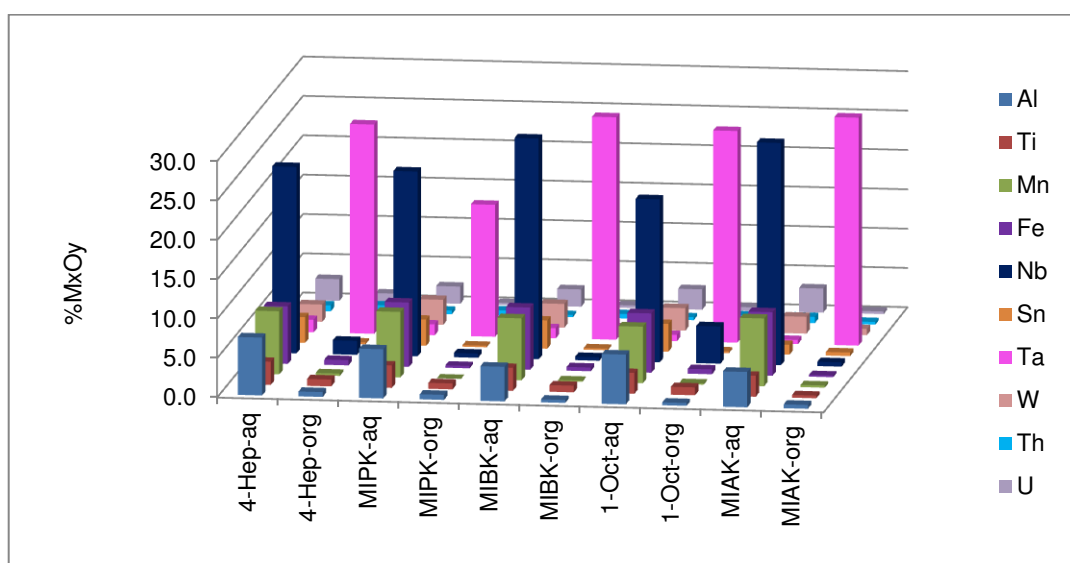


Figure 6.7: Recovery of the elements after solvents extraction of the tantalite ore elements after $\text{NH}_4\text{F}\cdot\text{HF}$ dissolution.

Methyl isoamyl ketone (MIAK) has several advantages over MIBK which include a higher flash point and relatively lower solubility in water. The MIAK is four times less soluble in water (0.50 g/100mL solubility at 20 °C) compared to MIBK (1.91 g/mL, at 20 °C). The low solubility in water eliminates the need to heat solutions after

extraction and stripping in order to remove the dissolved organic solvent from the aqueous solution prior to analysis by instrumental techniques such as ICP-OES. Another practical consideration for the use of MIAK as extractant is the fact that phase separation during the extraction process is much quicker (more immiscible) compared to MIBK, most probably due to its larger molecular weight. In addition, the relatively high flash point (43.3 °C) of MIAK makes this solvent safer to handle compared to MIBK.

The extent of extraction of each metal by the different solvents was determined by calculating its extraction ratio (D), which was calculated as the ratio of concentration of the solute in the organic phase and in the aqueous phase (see **Table 6.25**) and using **Equation 3.33** for Ta (for comparison with the value obtained using this **Equation 3.33** in **Chapter 5**). It is interesting to note that the extraction ratio of tantalum greatly exceeds that of all other metals in solution. With a relatively large D value, Th is the only element ($D_{Th} = 1.54$ in MIBK in **Table 6.25**) that could be extracted together with Ta in all the solvents (highlighted rows in **Table 6.24**). There is also a slight increase of the D value for Nb in 1-octanol indicating that some of this metal compound can be extracted into the organic phase (see also **Figure 6.7**) during this process.

Table 6.25: Distribution ratios for elements present in tantalite mineral after extraction with different organic solvents at 4.0 M H₂SO₄

Metal	D values				
	4-Hep	MIPK	MIBK	MIAK	Octa-1
Al	0.539	0.621	0.085	0.262	0.838
Ti	0.296	0.263	0.271	0.127	0.378
Mn	0.036	<0.000	0.021	0.032	0.026
Fe	0.091	0.036	0.055	0.027	0.088
Nb	0.075	0.041	0.012	0.019	0.222
Sn	0.074	0.058	0.063	0.384	0.069
Ta	3.171	3.4658	3.658	6.210	4.864
W	0.132	0.005	0.087	0.343	0.128
Th	1.217	1.386	1.548	0.416	2.051
U	0.397	0.116	0.148	0.104	0.182

The selectivity, hence the separation of the elements relative to Ta extraction, is indicated by the calculated separation factor (α). The separation factors for all the elements were determined relative to Ta as the ratio of tantalum distribution ratio to that of the impurity metal ($\alpha = D_{(Ta)}/D_{(M)}$) and the results are summarised in **Table 6.26**.

Table 6.26: Separation factors between tantalum and other metals in the tantalite mineral after extraction with different organic solvents

Metal	α values				
	4-Hep	MIPK	MIBK	MIAK	Octa-1
Ta	1.00	1.00	1.00	1.00	1.00
Al	5.89	5.58	43.22	23.66	5.81
Ti	10.72	13.17	13.48	48.74	12.86
Mn	88.72	---	174.12	192.98	189.61
Fe	34.92	96.66	66.94	231.60	55.51
Nb	42.33	84.95	299.93	327.47	21.91
Sn	42.84	59.71	58.16	16.19	70.44
W	24.02	694.07	41.89	18.11	37.89
Th	2.61	2.50	2.36	14.93	2.37
U	7.99	29.92	24.75	59.61	26.75

The large separation factors obtained from this comparison indicate that tantalum extraction from niobium and the other mineral impurities is feasible in all the organic/H₂O-H₂SO₄ solvent systems that were investigated. The emulsion formation for both 4-Hept and MIPK, as well as the low flash point of MIPK (see **Table 6.12**) are however disadvantageous for their application in this kind of separation process. 1-Octanol has the advantage of a very low solubility in water and high flash point, but the separation using this solvent showed relatively poor selectivity between Ta and Nb compared to MIBK and MIAK. The separation factors between MIBK/H₂O-H₂SO₄ and MIAK/H₂O-H₂SO₄ systems are comparable, however, the low flash point and relatively high solubility of MIBK in water solutions makes MIAK a more favourable solvent for the selective extraction of tantalum from the tantalite matrix and was thus selected for application in the purification study (see **Section 6.5**).

The percentage of extraction of each metal using MIAK was calculated by dividing the concentration (%) of the metal oxide in the organic phase by the sum of concentrations in both liquid phases (see **Equation 6.1**). It is evident from **Table 6.15** that the percentage of extraction of Ta using this way of calculation resulted in a higher value than that of all the other elements in the mineral sample. However, low concentrations of other elements contributed to calculation errors of orders of magnitude, compared to the high concentration elements, which led to apparent high percentage extraction.

6.4.5 Anion exchange separation of Nb and Ta in the tantalite ore

6.4.5.1 Selection of the anion exchange resin

The results of the elution of the different metal compounds using a strongly basic Amberlite IR-900 (**Table 6.16**) indicated that both Nb and Ta were eluted by the same HCl concentrations (e.g. 3.96% Nb₂O₅ and 3.21% Ta₂O₅ at 4.0 M HCl), thereby rendering this separation method ineffective for the separation of these elements. Other major elements such as Mn and Fe were eluted at low acid concentrations (7.61% Mn₃O₄ and 7.88% Fe₂O₃ at 0.1 M HCl), thereby separating these elements from Nb and Ta during this process. On the other hand, Ti elution was accomplished (1.65% TiO₂) at 2.0 M HCl in the presence of Nb and Ta, which indicated that the Nb and/or Ta obtained by this method could be contaminated with Ti and to some extent with U and Th. The recoveries of these elements also indicated an increase in extraction with an increase in HCl concentration (0.11 to 0.16% ThO₂ and 0.16 to 0.32% U₃O₈ at 3.0 to 5.0 M HCl respectively). The Sn content on the other hand showed that Sn was completely retained by the resin as indicated by its total recovery (**Table 6.17**) of (<0.0%) zero from the Amberlite IR-900 anion exchange column.

The elution of the different elements in the tantalite mineral from a weakly basic Dowex Marathon anion exchanger using HCl as an eluent, demonstrated some preferential elution of the elements at different HCl concentrations. Maximum recoveries (using **Table 6.1** as reference) of 77.98 for TiO₂, 33.67 for Mn₃O₄ and 79.76% Fe₂O₃ were obtained from a 4.0 M HCl elution. Niobium was only eluted at a 6.0 M HCl concentration (**Table 6.17**) thereby indicating the possible separation of Nb from Ti, Mn and Fe using this resin. The Ta and Th elution also increased

significantly at the same HCl concentration (6.0 M) and thus predicting poor separation between Nb and Ta by the Dowex Marathon wba anion exchange procedure. The Nb_2O_5 and Ta_2O_5 recoveries of 47.11 and 20.22% obtained from this separation step clearly indicate that there is some differences in the adsorption of these two elements on this resin. These results therefore prompted this study to continue with only the Dowex Marathon anion exchanger to try and improve the separation, as well as the recovery of Nb and Ta from the mineral matrix.

6.4.5.2 Selection of an eluent for Dowex Marathon wba anion exchanger

Two different acids, namely HCl and H_2SO_4 with concentrations ranging between 0.05 M and 6.0 M were evaluated to determine the most effective mobile (elution) solvent for the separation of the different elements in tantalite mineral. The results for the HCl elution (**Table 6.17**) indicated that most of the metals are retained on the column at low acid concentrations except for W, Th and U, but these recoveries were highly inaccurate. The quantitative results also indicated smaller quantities for the majority of the elements (compared to the expected results) were eluted at HCl concentrations of 6.0 M and thereby indicating the possible quantitative elution of these elements with the adjustment of the relevant experimental parameters. The results obtained for the elution with H_2SO_4 (**Table 6.18**) indicated that all the elements are eluted at the same rate at all H_2SO_4 concentrations and thereby rendering it inefficient as a mobile phase (eluent) in this separation using the Dowex Marathon wba anion as exchanger.

6.4.5.2.1 Effect of HCl (eluent) concentration on elution of tantalite elements

Results obtained from the previous study (**Section 6.4.5.1** and **Table 6.17**) indicated that the elements that were eluted with the HCl and in combination with the Dowex Marathon wba resin, basically starts at a HCl concentration of 4.0 M. It was therefore decided to study the effect of the mobile solvent concentration (HCl concentrations ranging from 4.0 M to 6.0 M) on the recovery of the different elements. The results which were obtained from this study revealed that the majority of the Fe, Mn, Ti, Th, U and W were eluted using a 4.0 M HCl solution (see **Table 6.19**). At this HCl concentration, only 2.98 Nb_2O_5 and 6.45% Ta_2O_5 were eluted together with 12.77% SnO_2 . Surprisingly, the quantities of all the elements decreased significantly when the concentration of HCl was increased to 6.0 M, resulting in the total recoveries

decreasing to less than 90% for most elements. These results also revealed that the adsorption of Nb and Ta on the anion resin was indeed different and that the Ta compound was the more strongly adsorbed species (total recovery of 62.78% Nb₂O₅ compared to 46.61% Ta₂O₅).

6.4.5.2.2 *Influence of the volume of the mobile phase on elution of tantalite elements*

The effect of the volume on the elution process of the different elements in the tantalite solution using the Dowex Marathon, was investigated with 20 mL and 40 mL of both 4.0 M and 6.0 M HCl solutions. The results obtained in this part of the study indicated an increase in the recovery of the elements with an increase in volume from 20 mL to 40 mL volume (see **Table 6.20**). The concentrations of Nb₂O₅ and Ta₂O₅ increased from 8.46 to 23.98% and 1.97 to 13.71% respectively when the volume of a 6.0 M HCl solution was increased from 20 mL to 40 mL. The concentrations of Fe and Ti also increased from 3.83 to 8.05% and 0.21 to 1.22% respectively as the elution volume was increased from 20 mL to 40 mL using the 4.0 M HCl solution. The results however indicated that even the 40 mL volume was not enough for the complete recovery of Nb and/or Ta and thus suggesting a volume larger than 40 mL of 4 M and/or 6 M HCl solutions is needed (60 mL used in final separation steps) for the maximum separation and recovery of the elements using this Dowex Marathon wba anion exchange resin.

6.4.5.2.3 *Separation of Ta by solvent extraction using MIAK prior to anion exchange process*

From the results obtained in the previous studies (**Sections 6.4.5.1** and **6.4.5.2**) it was found that both niobium and tantalum are always simultaneously removed from the resin (see **Tables 6.17** and **6.19**) and thereby indicating its inefficiency to separate these metals from one another using both the strong Amberlite IR-900 and the weak Dowex Marathon wba anion exchangers. These results therefore indicate that it is essential to separate the tantalum from the mixture by solvent extraction prior to ion exchange separation to effectively separate the two main elements from one another. The results of the solvent extraction (**Table 6.21**) prior to the elution process indicated a successful removal of Ta (98.2%) from the mineral matrix leaving Nb and most of the elemental impurities in the aqueous solution. The aqueous solutions containing Nb together with all the other elements were subsequently

subjected to the separation of the elements using the anion exchange separation process in the following step.

6.4.5.2.4 Influence of the flow rate on the elution of tantalite elements

Elution of the elements using the different acid concentrations (4.0 M and 6.0 M) can be a tedious process which produces large volumes of acid waste. The possibility of a one step separation of niobium from the rest of the metal constituents on the basis of their adsorption properties was investigated by the elution of the elements with two different flow rates at 6.0 M HCl. The elution diagrams of Nb, Ta, Fe, Mn, Ti, U, Sn, Th and W at the different flow rates (Al and Si omitted due to inaccurate analysis) are given in **Figures 6.8** and **6.9** (see also **Tables 6.5** and **6.6**).

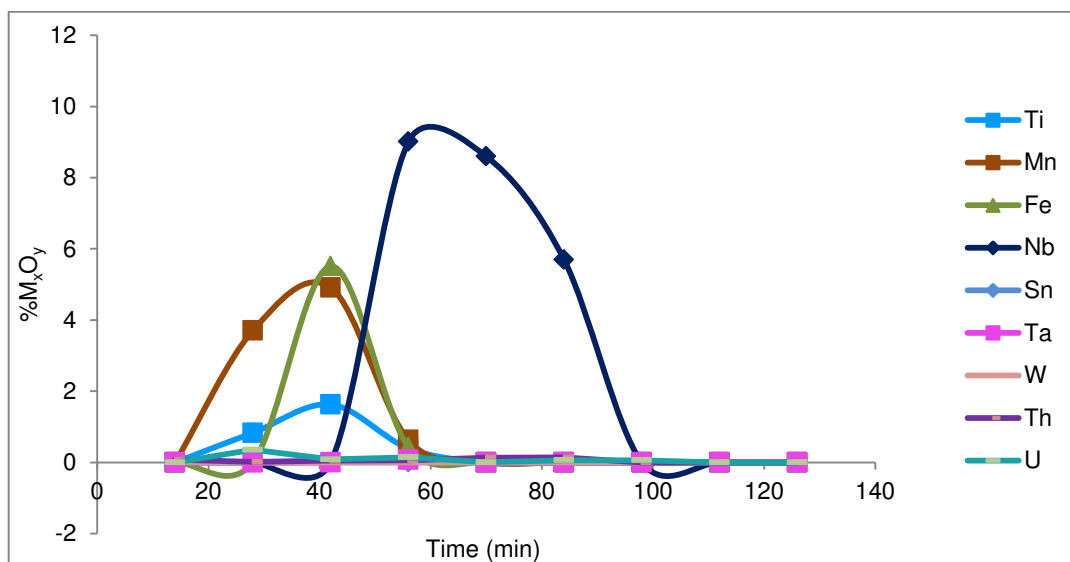


Figure 6.8: Elution of elements as a function of time using 6.0 M HCl solution at a fixed flow rate of 0.7 mL/min.

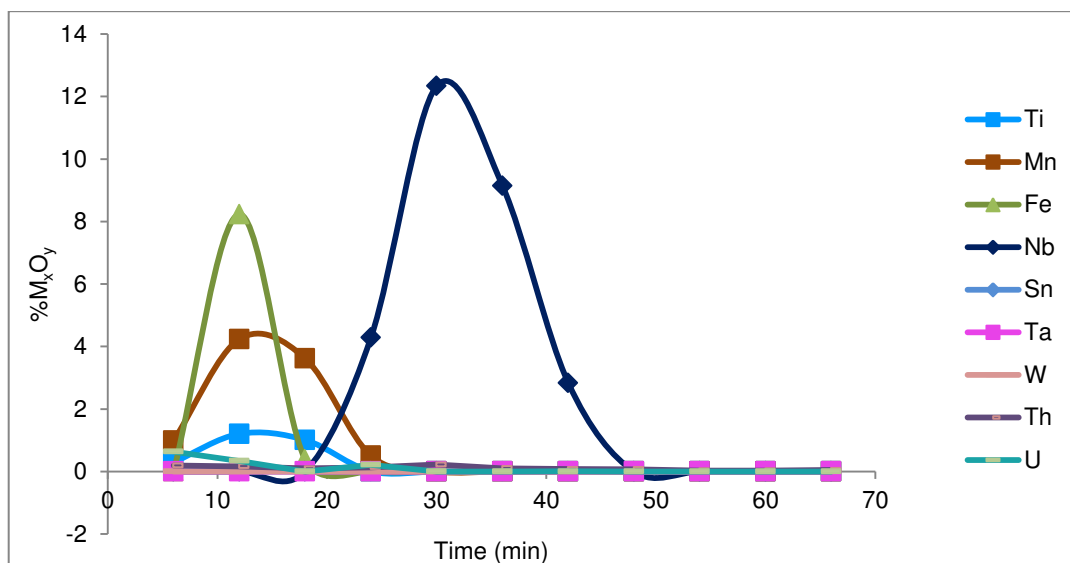


Figure 6.9: Elution of elements as a function of time using 6.0 M HCl solution at a fixed flow rate of 1.7 mL/min.

In **Figures 6.8** and **6.9** it can clearly be seen that the Nb compound is adsorbed differently to the anion exchange resin compared to the rest of the other metals present in solution and as such exhibit good selectivity using the weak Dowex Marathon wba anion exchanger. The results clearly indicate that at a flow rate of 0.7 mL/min (**Figure 6.8**) the elution curves are relatively broader, than that at a 1.7 mL/min flow rate (**Figure 6.9**). This observation can be attributed to the diffusion processes such as longitudinal and eddy diffusions (stationary and mobile phase mass transfer)^{120,125} which result in “tailing” and the overlap of the elution peaks.¹²⁰ As a result, a flow rate of 1.7 mL/min was selected to be the optimum conditions for the quantitative separation and recovery of niobium from the rest of the other metals in the tantalite ore. It is interesting to note that a relatively quicker flow rate is the condition which gives better elemental separation results. Normally the longer the time (slower flow rate) the better the separation but that was not observed in this study. The results however indicated that even at the 1.7 mL/min rate there is still some possible contamination of Nb with small amounts of Mn, U, Th, Ti and Al as indicated by the overlap of the peaks (**Figure 6.9**) of Mn, Ti and U at about 20 min (see also **Table 6.23**) (0.51% Mn₃O₄ and 0.21 U₃O₈%).

Semi-quantitative parameters for this analysis such as the number of the theoretical plates (N) and the theoretical plate height (H) which are used to assess the efficiency

of the column, were calculated for the Dowex Marathon wba using the information obtained from **Figures 6.8** and **6.9** (see **Chapter 3, Equation 3.38**). The highest concentrations (peak maximum) for most of the impurities were recovered at about 12 min and for Nb at 35 min at a flow rate of 1.7 mL/min and at 42 min and 56 min for most of the elements and Nb respectively at 0.7 mL/min. Poorly defined peaks were obtained for some of the trace elements due to their relatively low concentrations (see **Tables 6.22** and **6.23**). The retention factors (k) of the elements were calculated using **Equation 3.36**. The separation factor (α) between Nb and the other elements was calculated from **Equation 3.7** ($\alpha = k_{(Nb)}/k_{(M)}$). The separation factors obtained (see **Table 6.27**) for Nb compared to Mn and Fe clearly predict good, but not complete separation of these elements from Nb as indicated by the overlap of the elution graphs at ~ 20 min (see **Figure 6.9**). The results (see **Table 6.27**) further indicate the importance of the process selection of the optimum flow rate for this separation.

Table 6.27: Column parameters for the separation of niobium from the tantalite impurities by elution with 6.0 M HCl using Dowex Marathon anion exchanger resin

Flow rate (mL/min)	Element	t_r (min)	k	$\alpha = k_{(Nb)}/k_{(M)}$	W (min)	N	L (cm)	H (cm/plate)
1.7	Mn	13.9	1.317	3.291	11.9	8	20	2.65
	Fe	11.7	0.950	4.561	6.2	21	20	0.96
	Nb	32	4.333	1.000	11.5	43	20	0.47
0.7	Mn	42	2.000	1.571	30.8	30	20	0.67
	Fe	42	2.000	1.571	16.5	104	20	0.19
	Nb	56	3.143	1.000	23	102	20	0.20

The shorter retention time for the metal impurities at a flow rate of 1.7 mL/min resulted in smaller numbers of theoretical plates for Mn hence the larger theoretical plate heights (**Table 6.27**). The number of the theoretical plates for Fe and Nb on the other hand was reasonably large resulting in relatively smaller height equivalent of the theoretical plates. Column efficiency as indicated by the number of theoretical plates should be as large as possible with the small plate heights.¹²⁵ The numbers of theoretical plates for the elution of most of the elements increased (for example from 43 to 102 for Nb) and smaller theoretical plate heights were obtained when the elution was done at a flow rate of 0.7 mL/min. However, relatively poor separation

factors between Nb and these elements were obtained due to “tailing” as indicated by the non-symmetrical elution peaks (**Table 6.27**) at a 0.7 mL/min flow rate.

6.5 Experimental procedures for processing of tantalite mineral samples

The final step in this study was to evaluate the total mineral beneficiation process on a step-by-step basis applying all the dissolution and separation processes for the tantalite mineral samples. These steps will include processes that were developed earlier^{52,53} as well as the new flux fusion, solvent extraction and ion exchange processes that were developed earlier in this study (See **Section 6.3.4** and **Figures 6.1** and **6.10**)

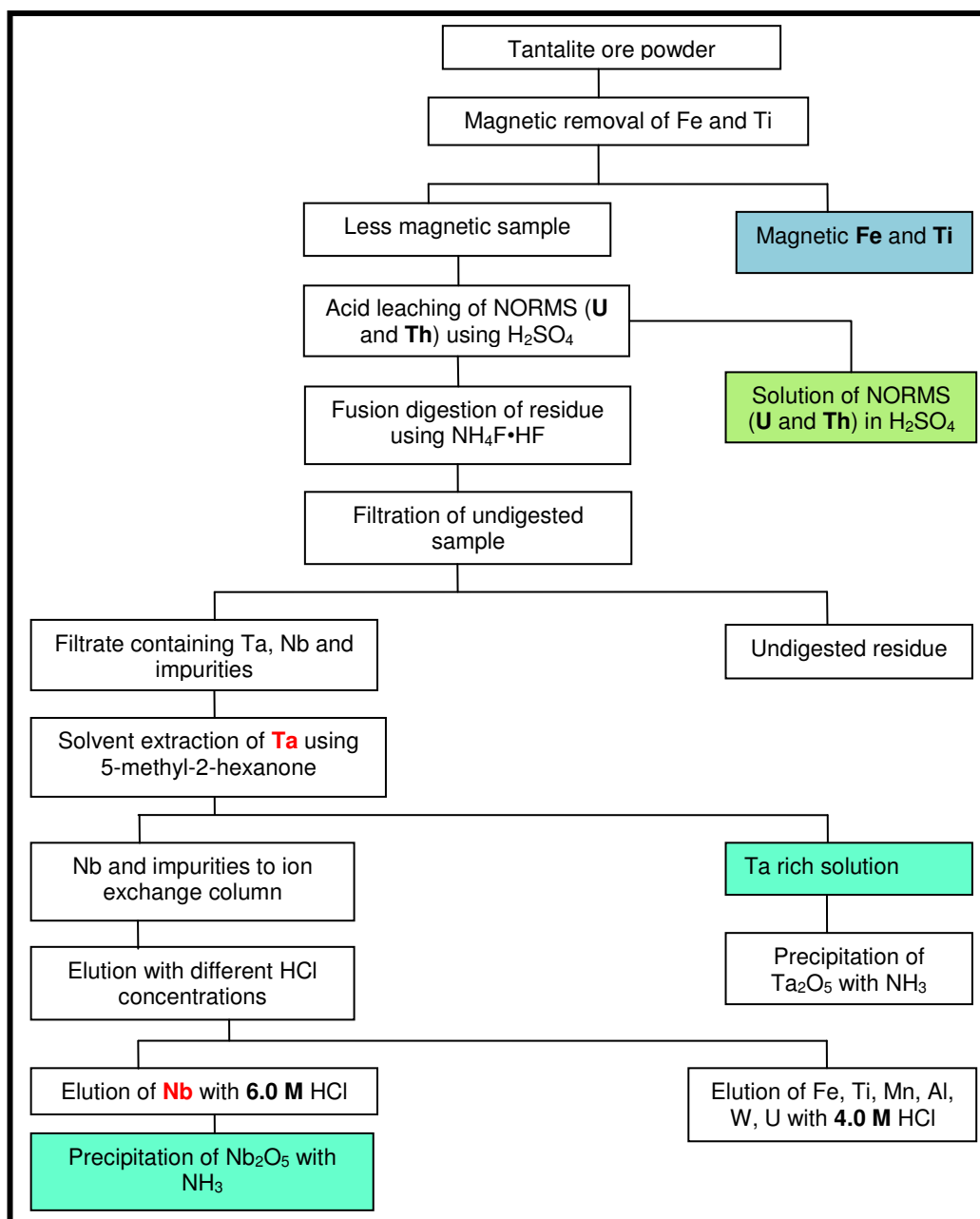


Figure 6.10: Scheme for the tantalite ore treatment for the separation and purification of Nb and Ta.

6.5.1 Step 1: Magnetic separation of impurities from tantalum and niobium

Portions of about 1.0 g Samples (A and C) were accurately weighed and the magnetic and non-magnetic particles were manually removed (using a permanent magnet and an in-house electromagnetic device). The collected magnetic and non-magnetic portions were then re-weighed to determine the amount of mass lost due to the adherence of small amounts of the finely ground mineral sample to the glass

surfaces used during the separation process. The results obtained from the magnetic separation and the magnetic properties of the samples are discussed in the following sections.

6.5.1.1 *Magnetic susceptibility determinations*

The magnetic susceptibility of the bulk samples A and C together with the separated magnetic and non-magnetic portions of Sample C were determined with a Sherwood Scientific magnetic susceptibility balance (MSB) at 20 °C. The MSB balance was reset to zero and the empty capillary tube was weighed and then placed into the balance to determine the R_o value and filled to a height between 1.5 cm and 3.5 cm as required by the manual of the equipment. The actual height of the sample in the tube was measured and the capillary tube (with the sample) was re-weighed and the R value was recorded. The magnetic separation of the different portions using Sample A was problematic due to the small amount of Fe_2O_3 (see **Table 6.2**) and large experimental errors were obtained for this part of the study. It was therefore decided not to perform a magnetic susceptibility determination on the separated portions of this sample. The mass susceptibility (χ_g) of these samples was calculated using **Equation 3.4** and the results are reported in **Table 6.28**. The reported values in **Table 6.28** represent the average of five replicate measurements.

Table 6.28: Mass magnetic susceptibility determinations for the two tantalite samples

Sample		m (g)	l (cm)	R_o	R	C_{bal}	$10^6 \chi_g$ (cm ³ ·g ⁻¹)
Sample A	Bulk	0.0383	2.5	50	1100	1.003918	2.8(2)
Sample C	Bulk	0.0172	2.8	50	4734	1.003918	29.3(7)
	Magnetic C	0.0040	2.5	50	2168	1.003918	53(2)
	Less-magnetic C	0.0291	2.6	50	207.25	1.003918	0.89(9)

6.5.1.2 *Quantitative determination of the elements contained in the magnetic portion of the tantalite samples*

The quantification of the elements present in this magnetic portion involved the dissolution and the quantification of the elements using ICP-OES. Magnetic material was accurately weighed (0.1 mg) and quantitatively transferred to (from **Section 6.2.7**) platinum crucible and thoroughly mix it with $NH_4F \cdot HF$ in a 1:20 sample:flux

ratio. The mixture was then fused at 250 °C for 30 min in the high temperature oven. The fusion melt was then cooled to ambient temperature and then dissolved with distilled water. Visual inspection indicated that the entire sample had dissolved. The obtained solution was quantitatively transferred to a 100.0 mL PTFE volumetric flask and filled to the mark with distilled water. A 5.0 mL aliquot of this solution was transferred to another 100.0 mL volumetric flask and the acidity of the solution was adjusted with of 97% H₂SO₄, cooled and then filled to the mark with distilled water. The solution was analysed using ICP-OES and the results are presented in **Table 6.29**.

Table 6.29: Quantification of the elements contained in the magnetic portion of the tantalite, Samples A and C

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Sam C ₁	4.99	0.40	10.20	1.39	0.05	2.53	0.12	0.32	0.27
Sam C ₂	5.55	0.45	10.82	1.55	0.06	2.75	0.14	0.34	0.24
Sam C ₃	4.98	0.35	13.79	1.59	0.07	2.77	0.20	0.45	0.49
Sam C ₄	3.29	0.45	13.95	1.73	0.07	3.03	0.22	0.45	0.46
Average	4.70	0.41	12.17	1.19	0.03	2.51	0.11	0.18	0.13
Sam A ₁	0.19	0.54	0.63	1.85	0.09	2.05	0.10	0.05	0.20
Sam A ₂	0.25	0.73	0.81	2.60	0.14	2.73	0.14	0.06	0.27
Sam A ₃	0.26	0.77	0.84	2.74	0.12	2.89	0.14	0.07	0.29
Average	0.24	0.68	0.76	2.40	0.12	2.56	0.13	0.06	0.25

Sam A = Sample A and Sam C = Sample C

6.5.2 Step 2: Acid leaching procedure for removal of radioactive materials

The next step of the beneficiation process involved the removal of the NORMs from the solid samples. The non-magnetic sample (portion from **Section 6.5.1**) was quantitative transferred to a pre-weighed 100 mL beaker. A 10 mL volume of 97% H₂SO₄ was added and the sample was stirred on a hot plate at 50 °C for 3 hrs. The obtained ore slurry was centrifuged to separate the solids from the liquid and the supernatant liquid was decanted into a 100.0 mL volumetric flask. The volumetric flask was then filled to the mark with distilled water. The solution was analysed using ICP-OES and the results are given in **Table 6.30**. The ore residue was dried at 100 °C for 2 hrs in an oven and then quantitatively transferred to a platinum crucible for further digestion using NH₄F•HF.

Table 6.30: Quantification of the elements after the acid leaching of the tantalite minerals using 97% H₂SO₄ leaching for 3 hrs at 50 °C

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Sam C ₁	0.60	0.15	0.38	0.17	n.d	0.09	0.03	0.05	0.17
Sam C ₂	0.54	0.10	0.36	0.12	n.d	0.07	0.02	0.03	0.14
Average	0.58	0.13	0.37	0.15	<0.00	0.08	0.03	0.04	0.15
Sam A ₁	0.15	0.44	0.87	1.56	0.05	0.44	0.11	0.34	1.61
Sam A ₂	0.11	0.38	0.68	1.09	0.03	0.23	0.09	0.31	1.84
Sam A ₃	0.11	0.39	0.67	1.10	0.04	0.22	0.10	0.33	1.75
Sam A ₄	0.12	0.37	0.73	1.09	0.03	0.21	0.08	0.33	1.82
Average	0.12	0.40	0.74	1.21	0.04	0.27	0.10	0.33	1.75

Sam A = Sample A and Sam C = Sample C

6.5.3 Step 3: Dissolution of residual ore samples

The next step in the total beneficiation process involved the dissolution of the remaining solid and the quantification of all the elements present using ICP-OES. NH₄F·HF was added in a 20:1 mass ratio to the remaining mineral ore (from **Section 6.5.2**) and the mixture was fused at 250 °C for 30 min in a platinum crucible. The obtained melt was cooled to room temperature and then dissolved in distilled water. The undigested residue was filtered and washed with distilled water. The filtrate was quantitatively transferred into a 100.0 mL PTFE volumetric flask and diluted to the mark with distilled water. This bulk solution was further used for the separation process in the following steps. Aliquots of 5.0 mL of the solution were prepared for ICP-OES analysis as previously described and the results are presented in **Table 6.31**.

Table 6.31: Quantification of the elements after fusion of residual tantalite samples with NH₄F·HF at 250 °C for 30 min

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Sam C ₁	5.25	3.51	7.94	10.68	0.07	26.03	0.34	0.07	0.18
Sam C ₂	6.72	3.47	9.70	10.13	0.06	26.08	0.25	0.06	0.12
Average	6.04	3.53	8.91	10.51	0.06	26.06	0.30	0.06	0.15
Sam A ₁	2.03	6.86	6.25	24.36	0.73	24.56	1.24	0.27	0.95
Sam A ₂	2.06	6.84	5.96	24.87	0.67	24.39	1.16	0.26	0.98
Average	2.04	6.85	6.10	24.62	0.70	24.47	1.20	0.26	0.97

Sam A = Sample A and Sam C = Sample C

6.5.4 Step 4: Solvent extraction separation of Nb and Ta in mineral samples

The next step in this process involved the removal of Ta from the rest of the sample solution using solvent extraction. 5.0 mL of the bulk solution obtained from **Section 6.5.3** was transferred to a separating funnel and 5 mL of 8.0 M H₂SO₄ solution was added to this solution. The solution was thoroughly mixed for 5 min and the Ta was then extracted with two successive portions of 10.0 mL of MIAK. The aqueous solution was collected in a 100 mL beaker for column separation in the following part of the beneficiation process. The organic phase was back extracted with two portions of 20 mL water. The water solutions were combined and quantitatively transferred to a 100.0 mL volumetric flask. The acidity of the solution was adjusted with H₂SO₄ to match the blank and the standard solutions matrices. The solutions were then filled to the mark with distilled water and subsequently analysed using ICP-OES. The results obtained in this study are presented in **Table 6.32**.

Table 6.32: Element quantification after solvent extraction using MIAK (after fusion with NH₄F•HF for 30 min at 250 °C)

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Sam C ₁	0.07	0.01	0.14	0.03	0.02	26.13	0.06	0.03	n.d
Sam C ₂	0.05	0.00	0.03	0.12	n.d	26.26	0.07	0.04	0.41
Average	0.06	0.01	0.09	0.07	0.01	26.19	0.06	0.04	0.20
Sam A ₁	0.20	0.03	0.05	0.03	0.01	24.44	0.20	0.08	0.40
Sam A ₂	0.03	0.01	0.08	0.07	n.d	24.90	0.09	0.03	0.27
Average	0.11	0.02	0.06	0.05	0.01	24.67	0.15	0.05	0.34

Sam A = Sample A and Sam C = Sample C

n.d = not detected

6.5.5 Step 5: Ion exchange separation

The final step in this beneficiation process involved the separation of Nb from the rest of the impurities using ion exchange chromatography. The remaining aqueous solution (10.0 mL) from **Section 6.5.4** was quantitatively transferred to the Dowex Marathon wba anion exchanger column and sequentially eluted with 60 mL of 4.0 M and then 6.0 M HCl at a rate of 1.7 mL per min. The effluent was collected in a graduated cylinder in 10.0 mL fractions and then quantitatively transferred to a 100.0 mL volumetric flask. The acidity of the solutions was adjusted to match that of the blank and standard solutions with 32% HCl. The solutions were then filled to the

mark with distilled water and then analysed using ICP-OES. The results obtained in this study are presented in **Tables 6.33** and **6.34**.

Table 6.33: Quantitation of the impurities from tantalite Samples A and C by column separation using 4.0 M HCl as eluent as a first elution step

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Sam C ₁	3.95	2.18	5.00	0.07	n.d	0.14	0.23	0.35	0.26
Sam C ₂	3.81	1.98	3.83	0.03	0.01	0.15	0.12	0.23	0.00
Average	3.88	2.08	4.42	0.05	0.01	0.14	0.18	0.29	0.13
Sam A ₁	1.72	5.82	5.23	n.d	n.d	0.10	0.90	0.21	0.18
Sam A ₂	1.70	5.64	5.36	n.d	n.d	0.10	0.85	0.21	0.09
Sam A ₃	1.73	5.58	5.03	n.d	n.d	0.15	0.98	0.28	0.16
Sam A ₄	1.60	5.39	4.98	n.d	n.d	0.12	0.90	0.26	0.12
Average	1.69	5.61	5.15	<0.00	<0.00	0.12	0.91	0.24	0.14

Sam A = Sample A and Sam C = Sample C

n.d = not detected

Table 6.34: Elution of Nb from Dowex Marathon wba column separation using 6.0 M HCl as eluent

Sample ID	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈
Sam C ₁	n.d	n.d	n.d	8.16	n.d	0.39	0.06	n.d	0.07
Sam C ₂	n.d	n.d	n.d	9.22	n.d	0.29	0.05	0.01	0.16
Average	<0.00	<0.00	<0.00	8.69	<0.00	0.34	0.05	0.01	0.12
Sam A ₁	n.d	n.d	n.d	24.90	n.d	0.09	0.20	0.12	n.d
Sam A ₂	n.d	n.d	n.d	24.62	n.d	0.07	0.23	0.13	n.d
Sam A ₃	n.d	0.02	n.d	24.98	n.d	0.05	0.07	0.08	0.05
Sam A ₄	n.d	n.d	n.d	24.13	n.d	0.30	0.10	0.05	n.d
Average	<0.00	0.01	<0.00	24.66	<0.00	0.13	0.15	0.09	0.01

Sam A = Sample A and Sam C = Sample C

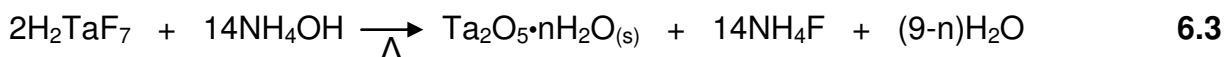
n.d = not detected

6.5.6 Characterisation of the final Nb and Ta products obtained after separation

6.5.6.1 Characterisation of Ta product using IR spectroscopy

The identification and the purity of the main products, namely Ta and Nb concluded the study and the whole beneficiation process. Ta₂O₅ was precipitated after the

extraction and stripping process (from **Section 6.5.4**) by the addition of 25% ammonium hydroxide as indicated in **Equation 6.3**.⁴² The precipitate was air dried and then calcined to 900 °C to remove ammonium fluoride and any residual extractant and to convert the formed hydrated tantalum oxide to the pentoxide.



The identity of the tantalum product was evaluated by the determination of its IR spectrum and comparing the obtained spectrum to that of the commercial pentoxide (**Figures 6.11** and **6.12**).

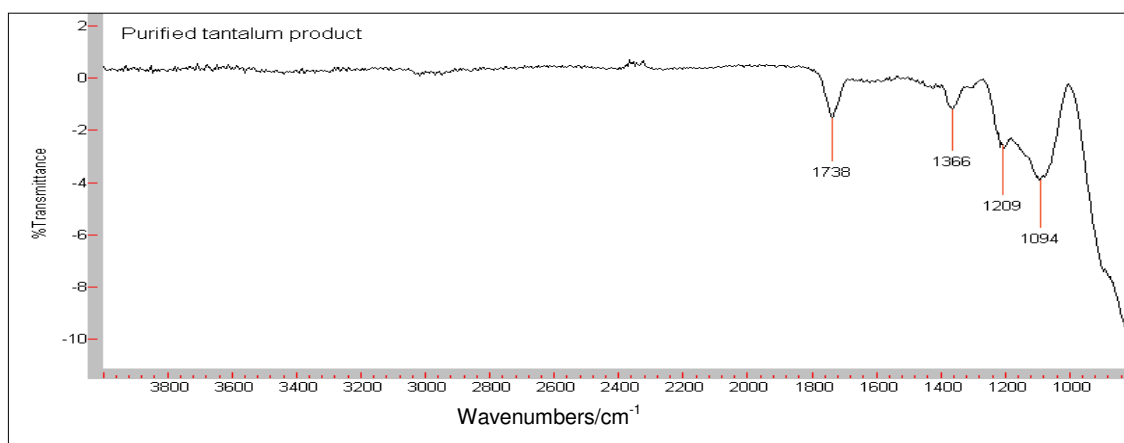


Figure 6.11: IR spectrum of isolated product (Ta_2O_5 calcined at 900 °C).

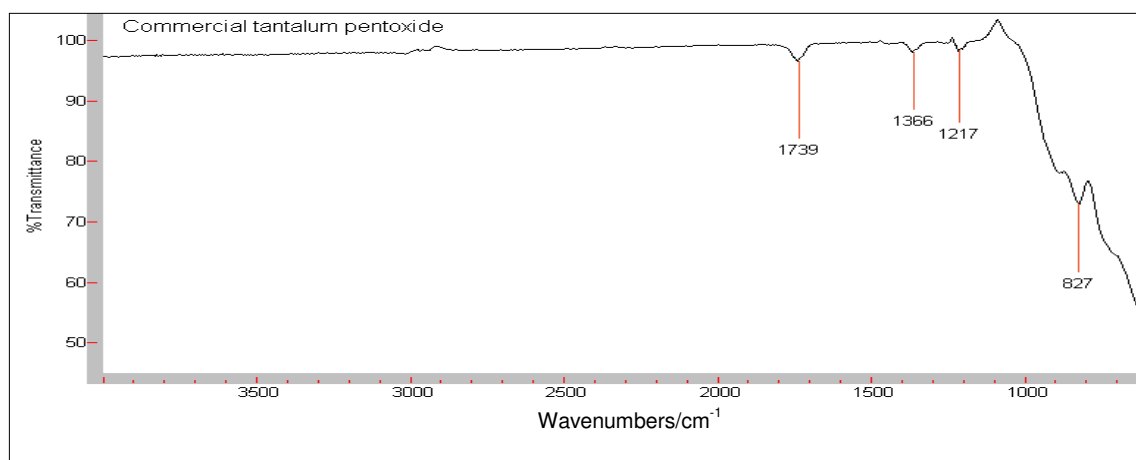


Figure 6.12: IR spectrum of commercial Ta_2O_5 .

An excess of the KF solution was also added to another portion of the Ta rich water strip solution for the possible crystallisation of potassium fluorotantalates compounds such as K_2TaF_7 (**Equation 6.4**). The solution was allowed to stand for two days for the crystallisation to occur. Crystals were successfully isolated and separated from the mother solution by decantation. The IR spectrum of this product is given in **Figure 6.13**.

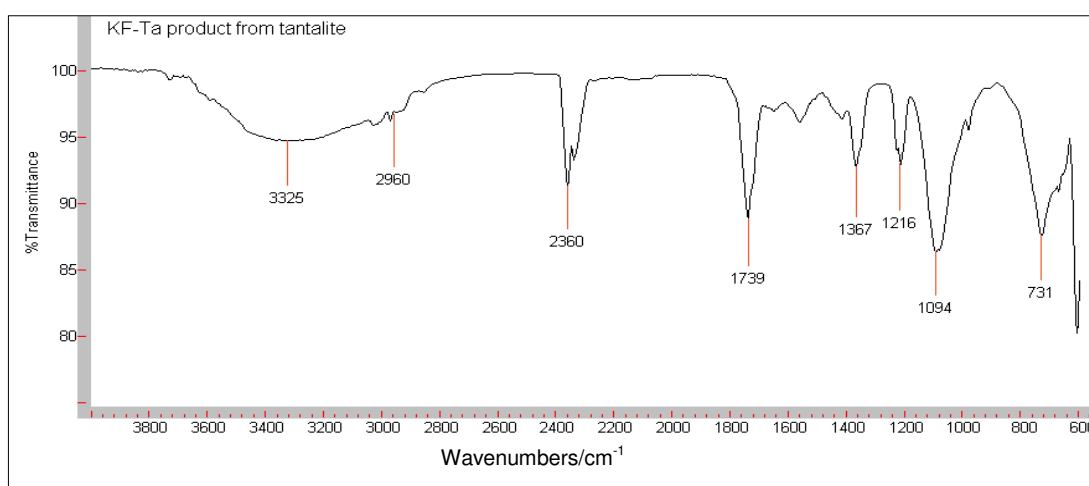
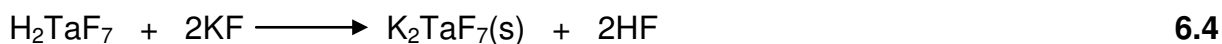
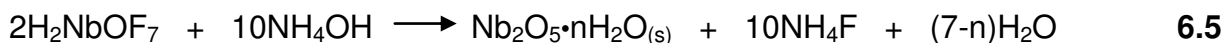


Figure 6.13: Infrared spectrum of potassium fluorotantalate product.

6.5.6.2 Characterisation of the Nb product using IR spectroscopy

The final solutions containing the enriched Nb content were combined and ammonia solution was added to precipitate the Nb as the hydrated niobium pentoxide as indicated in the following **Equation 6.5**:⁴²



The solid was separated from the solution by centrifugation, dried and then calcined at 900 °C. The IR of the isolated product (presumably Nb_2O_5) was compared with that of commercial Nb_2O_5 (99.9%) (**Figures 6.14** and **6.15**).

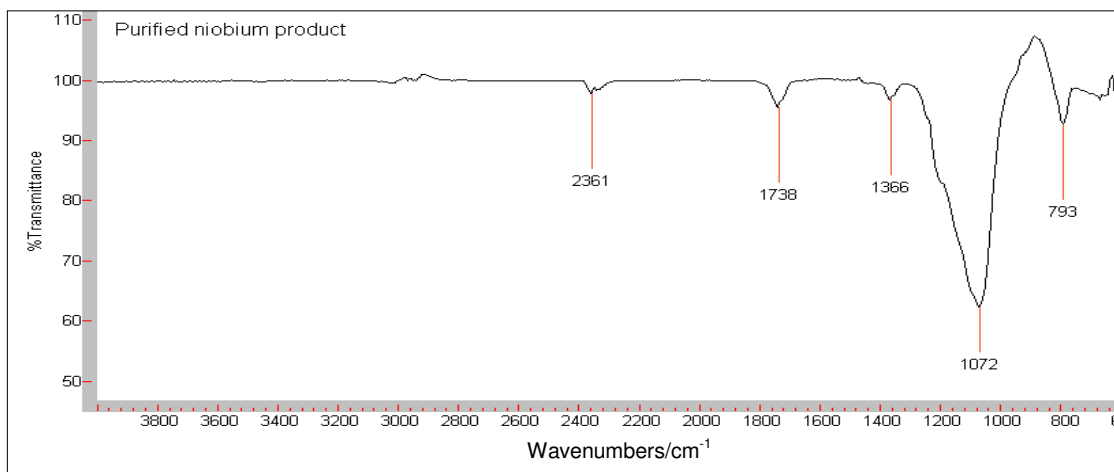


Figure 6.14: IR spectrum of purification product (Nb_2O_5 calcined at 900 °C).

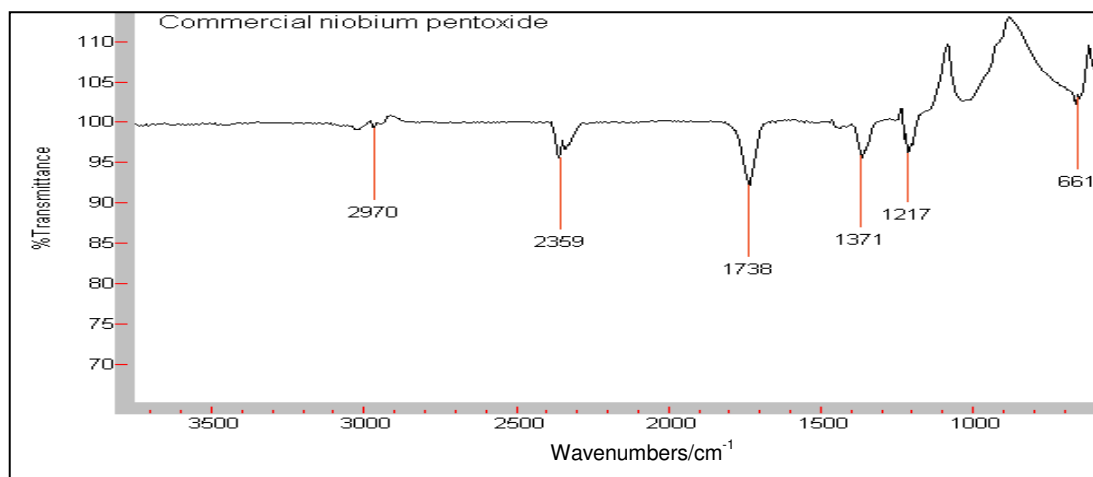


Figure 6.15: IR spectrum of commercial Nb_2O_5 .

The elemental content of the KF/Ta crystals and the Nb and Ta oxides (obtained from all the previous extraction and subsequent isolation steps) were also determined by ICP-OES and ICP-MS. The white solid (Ta and Nb products) obtained after calcination, was accurately weighed (to 0.1 mg) and then fused with $\text{NH}_4\text{F}\cdot\text{HF}$ in a 1:20 sample:flux ratio and the resultant melt was dissolved with distilled water. A visual inspection of the solution indicated that the entire sample had dissolved for both Nb and Ta products. The sample solutions were quantitatively transferred to 100.0 mL volumetric flasks and their acidity was adjusted accordingly with H_2SO_4 to match that of the blank and the standard solutions. Approximately 0.02 g of KF/Ta crystals were accurately weighed (to 0.1 mg), dissolved in 10 mL of concentrated

H₂SO₄ in a beaker and then quantitatively transferred to a 100.0 mL volumetric flask. The solutions were allowed to cool down to ambient temperature and then filled to the mark with distilled water. Results of a chemical analysis of both oxides and KF/Ta crystals are presented in **Table 6.35**. The percentage metal recoveries in **Table 6.35** for the product formed from the precipitation of the tantalum and niobium by NH₃ were calculated as %M₂O₅ (M = Nb/Ta) while solid (crystals) obtained after the addition of KF salt to the tantalum enriched solution was calculated %K₂TaF₇ and %KTaF₆.

Table 6.35: Quantification of Ta and Nb in final product after separation

Sample	% Recovery			
	ICP-MS		ICP-OES	
	Nb	Ta	Nb	Ta
Nb ₂ O ₅	96.19	2.03	95.55	3.42
Ta ₂ O ₅	3.56	96.85	1.05	100.32
K ₂ TaF ₇	0.00	41.24	5.32	49.89
KTaF ₆	0.00	35.13	5.32	42.50

The Nb and Ta oxide samples were also analysed for the other metal impurities using ICP-OES and the results are given in **Table 6.36**. It is important to note that the concentrations of all the elements except Si were extremely low to the extent that the concentration observed were below the lowest point of the calibration range in both the Ta rich and the Nb rich samples and therefore are considered very unreliable.

Table 6.36: Quantitative determination of the impurities in the purified Nb and Ta products using ICP-OES

Sample	Al ₂ O ₃	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃	Nb ₂ O ₅	SnO ₂	Ta ₂ O ₅	WO ₃	ThO ₂	U ₃ O ₈	SiO ₂
Ta ₂ O ₅	n.d	0.60	0.33	0.82	1.40	0.49	97.76	0.66	0.49	0.02	37.08
Nb ₂ O ₅	0.99	0.39	0.17	0.02	94.40	n.d	0.77	0.19	n.d	0.04	53.87

n.d = not detected

6.6 Results and discussion

6.6.1 Step1: Magnetic separation of magnetic materials

The qualitative analysis of these mineral samples in the previous study⁵³ has indicated that a large number of grains/particles in Samples C were magnetically active compared to Sample A. The magnetism in these samples was quantitatively

determined in the current study by the determination of the mass magnetic susceptibility (χ_g) of these samples. The results (**Table 6.26**) indicated that Sample C contains a much higher amount of magnetic particles than Sample A.

A comparison between these mass magnetic susceptibility determinations and the chemical quantification of the samples (**Table 6.29**) clearly indicates that the magnetic susceptibility is largely as result of the presence of iron and titanium within these samples. Sample C, with the higher Fe and Ti concentrations, gave higher magnetic susceptibility values than Sample A which has the lower Fe and Ti content, as was also confirmed by the quantification of the elements using ICP-OES (**Table 6.1**).⁵³ The value of χ_g increased significantly in the magnetic portion of Sample C (after separation and concentration of the magnetic active particles) as expected and the quantitative chemical analysis results indicated that the observed magnetism in this sample is mainly due to Fe and Ti and surprisingly, to a small extent some Nb and Ta. The quantitative analysis of Sample A on the other hand (lower magnetism) indicated approximately the same concentrations of Nb and Ta in the magnetic portion compared to that obtained for Sample C (1.19% and 2.51% for Nb₂O₅ and Ta₂O₅ in Sample C and 2.40% and 2.56% for Nb₂O₅ and Ta₂O₅ in Sample A), but unexpectedly lower Fe and Ti (**Table 6.29**) contents in the magnetic portion.

The presence of Ti, as well as the Ta and Nb in the magnetic portion of the mineral is quite surprising. The most stable oxidation state of Ti is Ti⁺⁴ which is a d⁰ species and which should in theory exhibit diamagnetic properties (zero paramagnetism) and thereby not be influenced by external magnetic field. A possible explanation for its presence in the magnetic portion of the mineral is that it is present as ilmenite/rutile (Ti,Nb,Fe)₃O₆. This close association of the Ti with the paramagnetic Fe can account for its separation with the magnetic portion of the sample. The most stable oxidation state for Nb and Ta on the other hand is +5, which is also a d⁰ species, and as in the case of Ti, should exhibit no paramagnetic properties. A possible explanation for their presence in the magnetic portion of the mineral is that a small percentage of the two elements may be another oxidation state (e.g. +3 for Nb) which may exhibit paramagnetic properties or that the grain size of the mineral is still not small enough to release these two elements from the paramagnetic material and are subsequently

separated from the rest of the Nb and Ta content associated with some paramagnetic Fe.

6.6.2 Step 2: Acid leaching of radioactive Th and U

The results obtained for uranium and thorium leaching with H_2SO_4 are presented in **Table 6.30**. It is evident from these results that reasonable concentrations of uranium and thorium are leached into the H_2SO_4 solution (62.3% U_3O_8 and 61.1% ThO_2). The quantitative results also clearly indicated that there was some loss of two main metals (especially Nb, 4.02% Nb_2O_5 due to its solubility in H_2SO_4) while the radioactive materials which remained in the residue may still be at unacceptable levels. Successful leaching of the radioactive elements from the mineral samples was found to be significantly dependent on the temperature of the acid mixture and the maximum dissolution of these elements with minimum loss of Nb and Ta was determined by the proper selection of experimental conditions¹¹² as selected and used in this study.

6.6.3 Step 3: Dissolution of the residual tantalite samples

The dissolution and subsequent analysis of the residual sample indicated that about 90% of both Nb and Ta had remained in the undissolved mineral after the magnetic separation and acid leaching steps. The loss of Nb and Ta in the magnetic separation process could be due to reasons discussed in the previous section (**6.6.1**). It can be seen from the obtained results that the total Fe_2O_3 and TiO_2 contents were reduced (18.71(6) to 8.82% and from 8.19(1) to 5.99% for Fe and Ti respectively in Sample C and from 8.3(2)% to 6.11% and 2.77(2)% to 2.05% in Sample A (**Table 6.31**). The majority of Fe and Ti in Sample C were separated from the mineral matrix in the magnetic separation step. The total contents of Mn_3O_4 and WO_3 were also slightly affected by the two primary purification processes (magnetic separation and acid leaching) but it is interesting to see that a maximum of ~ 6% Nb_2O_5 was leached by sulphuric acid at 50 °C since this could lead to a future study to investigate the leaching of Nb and Ta ores at low temperatures. It is also interesting to note that Ta on the other hand was very slightly affected by the concentrated H_2SO_4 (**Table 6.30**). About 9% (~2% of 27.8(3)% Ta_2O_5 and ~2% of 27.0(2)% Nb_2O_5) of both Ta and Nb were lost in the magnetic separation step. The two process (magnetic and acid leaching separations) have reduced the total Nb_2O_5 and Ta_2O_5 contents from

27.0(2)% to 24.62% and 27.8(3)% to 24.48% respectively in Sample A and from 13.7(2)% to 10.41% and 33.0(2)% to 26.06% respectively in Sample C (**Table 6.31**).

6.6.4 Steps 4 and 5: Purification of tantalum and niobium by solvent extraction and ion exchange methods

In the solvent extraction step it is clear that Ta was successfully extracted from $\text{NH}_4\text{F}\cdot\text{HF}$ solution using 5-methyl-2-hexanone (MIAK) instead of methyl isobutyl ketone which is commonly used for these extraction purposes. The results obtained (**Table 6.4**) in this part of the study indicated that Ta was selectively extracted into the MIAK leaving Nb and other metal impurities in the acidic aqueous solution. Average recoveries (**Table 6.32**) of 100.78% and 100.54% Ta_2O_5 (using results in **Table 6.31** as a guide) in Samples A and C respectively were obtained. The results also showed relatively low concentrations of other elements (except for Si, not included in the results) in the Ta rich solution in Sample A (**Table 6.32**) compare to the previous results (see **Table 6.14**) which were obtained from the same procedure, but without prior magnetic separation and acid leaching processes. These results (**Table 6.32**) clearly indicate the successful separation of the Ta from the majority of impurities and its subsequent purification or enrichment in this step.

The ion exchange separation step (which follow the solvent extraction of Ta) using a weakly basic Dowex marathon wba anion exchanger resin clearly demonstrated its efficiency in separating Nb from the majority of the accompanying metal impurities. However, it was found that prior removal of Ta from the solution is inevitable in the purification of Nb by this method. All the elements, except Sn, were quantitatively recovered by elution with 60 mL of 4.0 M HCl while Nb was eluted with a 6.0 M HCl solution. The results obtained (see **Table 6.32**) in this part of the study indicated that a relatively pure Nb compound was successfully isolated from tantalite mineral ore.

Average recoveries of 99.27% and 83.63% Nb_2O_5 (using results in **Table 6.31** as a guide) in Samples A and C respectively were obtained. Recovery values of 15.0 % WO_3 and 46.15% ThO_2 were present in the Nb rich Sample A solution (**Table 6.32**). The quantitative results for Th and W in these analyses may be inaccurate since the total recoveries of these elements in all the separation steps are much higher than 100% (e.g. 173.92% ThO_2 was obtained by the addition of all the Th recovered in the

beneficiation process (11.1, 61.1, 11.1, 44.4 and 46.2%) from the magnetic separation, acid leaching, solvent extraction, 4.0 M HCl elution and 6.0 M HCl elution respectively). However this inaccurate analysis results does not eliminate the possibility of contamination (small amounts) in the isolated Nb compound by these elements. The inaccuracy in the Th, U and W can be attributed to their low concentrations in these mineral samples since the quantification of the Th and U in the different steps in the beneficiation process were done in close proximity of their limits of detection and quantification (LOD and LOQ) (e.g. 0.002 to 0.05 mg/L and 0.01 to 0.5 mg/L for Th and U respectively)^{158,159} by the ICP-OES. At these low concentrations the element signal may be interfered with by the background signal of the equipment and thus lead to positives errors.¹⁶⁰

6.6.5 Determination of the quality of Ta and Nb purification products

The final step in the dissolution and separation process of the two tantalite samples was to try and characterise the final products, as well as to determine their final purity. The infrared spectra of the purified Nb and Ta products are expected to be similar to the two corresponding commercially obtained pentoxides. All the four spectra show similar stretching frequencies in the region 1366-1739 cm^{-1} . The Ta product and Ta_2O_5 spectra also showed similar stretching frequencies at about 1200 cm^{-1} . Only the stretching frequency at 827 cm^{-1} in the Ta_2O_5 spectrum was found to be different from the 1094 cm^{-1} stretching frequency observed in the purified Ta product. Both the Nb_2O_5 and the purified Nb product showed a stretching frequency at 2360 cm^{-1} but different stretching frequencies below the 700 cm^{-1} region (793 cm^{-1} and 614 cm^{-1} in the spectrum of the purified Nb product and 661 cm^{-1} in the spectrum of the commercially obtained Nb_2O_5). The IR spectra for both the Ta and Nb purified

158. Evans Analytical group, 2007, ICP-OES and ICP-MS Detection Limit Guidance, [Internet]. [cited 2013 Feb 27], Available from: <http://www.eaglabs.com/documents/icp-oes-ms-detection-limit-guidance-BR023.pdf>

159. PerkinElmer, 2008-2011, Atomic Spectroscopy A Guide to Selecting the Appropriate Technique and System, [Internet]. [cited 2013 Feb 27], Available from http://www.perkinelmer.com/PDFs/Downloads/BRO_WorldLeaderAAICPMSICPMS.pdf

160. Schibler, J., Moore, D. and De Borba, B., PITTCO 2007 Presentation "Setting Meaningful Detection and Quantitation Limits for Chromatography Methods", Dionex Corporation, Sunnyvale, CA, USA, [Internet]. [cited 2013 Feb 27], Available from: <http://www.dionex.com/en-us/webdocs/52823-LPN-1926-Chromeleon.pdf>

products showed a strong stretching frequency at 1072 cm^{-1} and 1094 cm^{-1} (which were not observed in the commercially obtained pentoxides), probably resulting from incomplete conversion of the products obtained after purification to the pentoxides during the calcinations step. This comparison of the IR spectra for each purified metal product to that of the corresponding commercial metal pentoxide indicated that the IR spectra of the purified niobium and tantalum products are generally similar to those of the pure commercially obtained Nb_2O_5 and Ta_2O_5 compounds (**Figures 6.16** and **6.17**). It is therefore reasonable to suppose that the solids which were isolated in the final stage of this study are the expected Nb and Ta pentoxides. It is however believed that this comparison would be more conclusive with the powder XRD analysis which could not be performed due to the larger amount of sample require for the experiment.

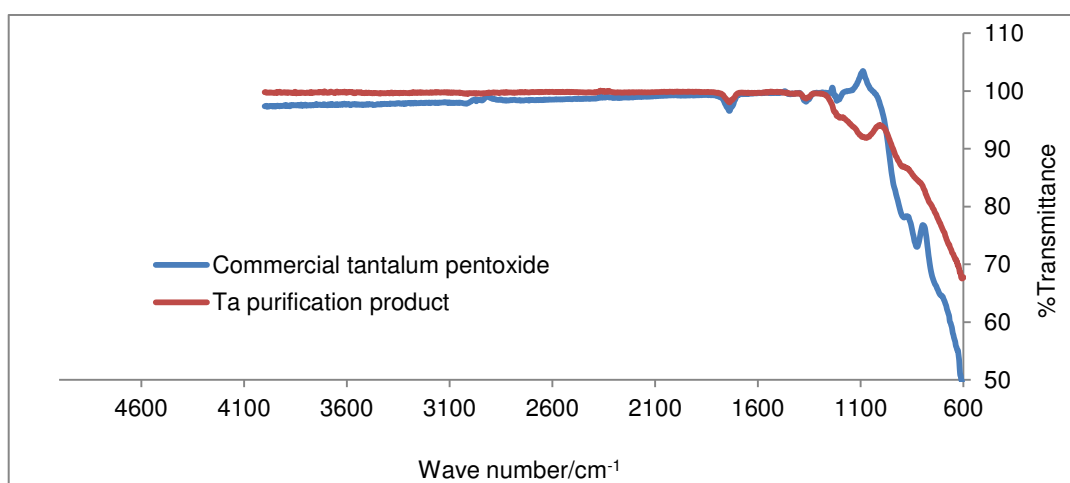


Figure 6.16: Comparison between commercial Ta_2O_5 (99.9%) and the tantalum purification product of the tantalite mineral ore.

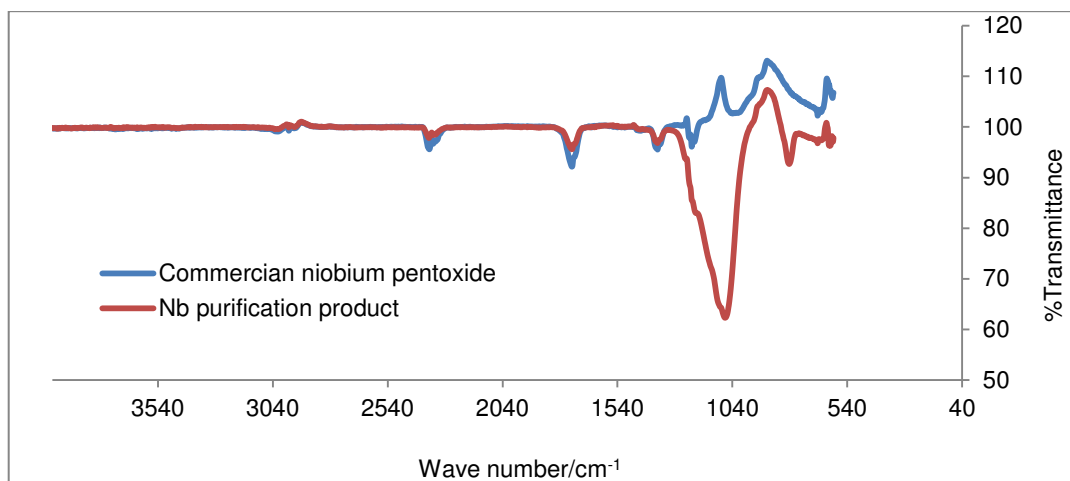


Figure 6.17: Comparison between commercial Nb_2O_5 (99.9%) and the niobium purification product of the tantalite mineral ore.

The purity of the two final products, Nb_2O_5 and Ta_2O_5 , was determined as 96.2% and 96.9% for Nb_2O_5 and Ta_2O_5 using ICP-MS and 95.8% and 96.8% for Nb_2O_5 and Ta_2O_5 from the ICP-OES analysis with the major impurity being silicon (**Table 6.36**). The silicon contamination in this study is probably caused by the reaction of the high fluoride content with the glass components (e.g. glass nebulization systems) of both the ICP instruments. It is believed that this silicon contamination could be completely avoided by the use of a fluoride resistant nebulisation system in the analysis step as well as PTFE volumetric equipment (beakers, volumetric flasks etc).

According to the literature¹⁶¹ the potassium fluorotantalate (K_2TaF_7) is expected to form when the potassium salt such as KF is added to the Ta rich fluoride solution. The solid (crystalline) obtained from the reaction between the KF and the Ta fluoride complex in the Ta rich solution was also analysed with the spectrometric techniques and the IR spectroscopy. The quantitative results obtained by both ICP-OES and ICP-MS showed that Ta recovery from the crystalline product was less than 50% (**Table 6.35**). The IR spectrum of the product (**Figure 6.13**) however indicates the

161. Eckert, J., Reichert, K., Schnitter, C. and Seyeda, H., "Processing of columbite-tantalite ores and concentrates for niobium and niobium compounds in electronic applications" H.C. Starck GmbH & Co. KG Im Schleeke 78–91, 38642 Goslar, Germany

presence of the water peaks (3325 to 2960 cm^{-1}) and thereby suggesting that a hydrated product was obtained. The addition of the crystal water to the proposed formula of K_2TaF_7 indicated some increase in the %recovery of Ta (e.g. 1, 2, 3 water molecules lead to %recovery increase from 49.9 to 52.2, 54.5 and 56.8% respectively). The low Ta recovery in this product could also be due to an incomplete reaction or the formation of other K-Ta products other than the expected hexa or heptafluorotantalate.

The IR spectrum (**Figure 6.13**) of crystalline solid obtained in this part of the study was found to be very similar to that obtained from the oxides separation in chapter 5 (**Figure 5.11**). Both spectra showed the stretching frequency in the region 2960-2970 cm^{-1} , most probably due to the presence of $-\text{OH}$ from water. The two spectra also showed similar stretching frequencies in the region 1059-2360 cm^{-1} clearly indicating the possibility of similar products. The strong stretching frequencies at 1059 cm^{-1} and 1094 cm^{-1} and 2360 cm^{-1} observed in the two spectra (**Figures 5.11** and **6.13**) were found to be similar to those obtained in the KF spectrum (**Figure 5.10**, weak 1072 cm^{-1} and 2359 cm^{-1} stretching frequencies) indicating a possible mixture of the K-Ta product and the unreacted KF salt.

6.7 Summary

The success of this study is clearly demonstrated by the isolation of the relatively pure Ta and Nb compounds after applying all the beneficiation steps that were developed in Chapter 5 to the two different tantalite minerals and the two main elements were completely recovered despite the partial dissolution of the mineral ore (dissolution in excess of 95%) using $\text{NH}_4\text{F}\cdot\text{HF}$ as fluxing agent. Optimum conditions were determined to be a 1:20 sample:flux ratio with a fusion time of 30 min at a temperature between 200 and 250 $^\circ\text{C}$. The results obtained using the $\text{NH}_4\text{F}\cdot\text{HF}$ digestion method was compared with those obtained by other dissolution methods of the same samples. The percentages of the metal oxides in these ore samples were found to be in excellent agreement with the values that have been obtained using different digestion methods. The $\text{NH}_4\text{F}\cdot\text{HF}$ digestion method however has several advantages over these other techniques. These include an economical, relatively safe and effective dissolution of the Nb/Ta samples by forming the water soluble fluoride compounds. In addition, the solutions obtained from this method were found

to be suitable for selective extraction and purification of tantalum from the tantalite matrix and which are very similar to the processes developed for the beneficiation processes using HF as dissolution agent.

Different organic solvents were evaluated for the selective separation of Ta from Nb and other metal constituents in the tantalite ores. It was found that of the five selected solvents, MIBK and MIAK, offer the best separations and have equal efficiency and selectivity towards Ta extraction. However, the MIAK has advantages such as relatively lower solubility in water and higher flash point which makes the handling of this solvent easier than the MIBK counterpart. The ability of the solvents studied in terms of selectivity and other characteristics towards Ta extraction can be summarised as follows: 4-Hept = MIPK < 1-Oct < MIBK < MIAK.

Both the strong Amberlite IRA-900 and the weak Dowex Marathon wba anion-exchange resins were evaluated for the selective extraction of Nb and Ta from the mineral matrix. The results obtained in this study indicated that only the Dowex Marathon wba is suitable to separate Nb and Ta from the rest of the elemental impurities using HCl as a mobile phase and was therefore selected for further investigation in this study. Experimental conditions such as the eluent acid, acid concentration and flow rate time were studied for optimisation of the separation process.

The extraction of niobium and tantalum from tantalite mineral using a combination of magnetic separation, acid leaching, solvent extraction and ion exchange methods was investigated and Nb₂O₅ and Ta₂O₅ of 96% purity were obtained. The entire process resulted in a total loss of approximately 13% of both Nb₂O₅ and Ta₂O₅. The quantitative analysis of the obtained pentoxides indicated that the main impurity in both oxides is SiO₂. The SiO₂ contamination was difficult to avoid because the samples were digested with NH₄F•HF and subsequently analysed with ICP-OES and ICP-MS in which glass nebulisers were used.

In comparison with the direct HF dissolution (industrial procedure), the NH₄F•HF dissolution of the Ta/Nb ore for hydrometallurgical processing has an advantage above the HF process in that it makes use of a more economical and safe reagent

($\text{NH}_4\text{F}\cdot\text{HF}$ and water) in the dissolution step. However, similar to HF, the $\text{NH}_4\text{F}\cdot\text{HF}$ digestion is also characterised by the generation of fumes which may be a health hazard and as such require extreme care and good ventilation when performing the procedure. Once the dissolution has been achieved the subsequent separation and purification operations are somewhat similar to those involved in the HF dissolution process. The $\text{NH}_4\text{F}\cdot\text{HF}$ digestion method is mostly suitable for the selective extraction of Ta. However, literature study¹⁶² has indicated that a collective extraction of Nb and Ta using MIBK is also possible at higher H_2SO_4 concentrations. The complete beneficiation route will always be governed by the characteristics of Nb/Ta ore or concentrate at hand and therefore must be evaluated carefully before application to the sample.

A possible beneficiation process, as illustrated by the flow sheet, was also developed for the purification of Nb and Ta from the tantalite ores. The degree of the success achieved for each step investigated was evaluated and the results are summarised in **Table 6.37**.

Table 6.37: Evaluation of various steps involved in the Ta and Nb purification process investigated in this study

Process	Parameter	Evaluation
Dissolution of the ore by $\text{NH}_4\text{F}\cdot\text{HF}$	Complete dissolution of sample	<< %95
	Complete recovery of Nb and Ta	√√
Separation of elements	Separation of Ta from Nb by solvent extraction	√√
	Separation of Nb from other metal impurities	√
Purification of Nb and Ta	Purification and isolation Ta_2O_5	√√
	Purification and isolation Nb_2O_5	√√

√√- successful to above 95%
 √- successful to about 90%
 X- not successful

162. Kabangu, M.J. and Crouse, P.L., 2012, "Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction", *Hydrometallurgy*, **129–130**: pp. 151–155

The dissolution and separation processes investigated in this study displayed a strong similarity between the chemistries of the pure Nb and Ta oxides and the Nb and Ta compounds in the tantalite samples and thus clearly indicating the relevance of using the pure oxides for the development and validation of the methods for the processing of Nb and Ta in mineral ores. Recoveries of 100.4(9) and 100(1)% for Nb and Ta were obtained in the pure pentoxide dissolution while 100.3(5) and 100.0(9)% for Nb and Ta were obtained in the tantalite dissolution. Additionally, similar results were obtained during the separation of Nb and Ta using solvent extraction method and in both the pure pentoxides and the tantalite minerals studies. Tantalum was selectively extracted into the organic phase leaving the Nb in the aqueous phase. The calculated distribution ratios of 3.43 and 3.66 for Ta in MIBK which were obtained for the pure oxide mixture and the tantalite respectively are in excellent agreement with one another. A general comparison for the treatment of the samples in this study is given in **Table 6.38**.

Table 6.38: Comparison between the reactions of the pure Nb and Ta pentoxide mixture and the tantalite samples

Sample	Dissolution	%Recoveries of Nb and Ta	Separation by solvent extraction	Separation by ion exchange	IR Spectroscopy analysis
Nb ₂ O ₅ + Ta ₂ O ₅	Complete	Complete	Complete	Incomplete	Similar IR spectra between the commercially obtained and isolated products
Sample A	Incomplete	Complete	Complete	Incomplete	
Sample C	Incomplete	Complete	Complete	Incomplete	

Another study¹⁶² done by Kabangu and Crouse and which was done parallel to this study, indicated very similar optimal experimental conditions (e.g. 250 °C fusion time, semi-quantitative and quantitative results for the dissolution of the tantalite ores (dimorph, tapiolite (Fe,Mn)(Ta,Nb)₂O₆)) using NH₄F•HF. Both studies point to the incomplete sample dissolution, but quantitative recoveries for both Nb and Ta (97.24% and 98.66% for Nb and Ta in the study by Kabangu and Crouse and 100.3(5)% and 100.0(9)% for Nb and Ta in this study). Another interesting observation which was made during this comparison is in the solvent extraction procedure. The Ta extraction in the tapiolite study was accomplished with 1-octanol and 2-octanol as extractants while in this study several solvents were evaluated and MIAK was finally selected for the selective extraction of Ta. Both studies revealed

that two successive extractions are needed for quantitative extraction of Ta. However, the distribution ratio for Ta extraction from the tantalite solution in the 1-octanol extraction was calculated to be 4.864 in this study while the extraction from the tapiolite solution in the 1-octanol extraction gave a distribution ratio of 167.753 at 4.0 M H₂SO₄. The main differences between the two studies are in the dissolution conditions for the two tantalite samples. In the tapiolite study the sample digestion conditions of 1:30 sample:NH₄F•HF and 3 hrs fusion time were used while the conditions of 1:20 sample:NH₄F•HF and 30 min fusion were found to be optimum in this study.

6.8 Conclusion

The use of NH₄F•HF as fluxing agent for tantalite minerals proved to be an excellent alternative to HF dissolution which not only succeeded in dissolving the majority of the mineral sample, but also produced metal compounds very similar to the HF digestion which allowed for the subsequent separation and purification of all the metal ions in the solution. Another very important result from this whole study is the similarity of the chemical behaviour of the mineral (containing the metal oxides) oxides and that of pure Nb and Ta pentoxides. These similarities will allow for the development or the investigation of possible dissolution and separation methods on the pure metal oxides which will be extremely relevant for separation of the two main elements in Ta and Nb containing minerals.

7 Evaluation and future studies

7.1 Introduction

The aim of this chapter is firstly to evaluate the achievements of this study as measured against the aims that were set out in the beginning of this study in **Chapter 1** and secondly to identify possible future research projects that were recognized during the investigation.

7.2 Evaluation of the study

The main focus of this project was to investigate the possible dissolution, separation and purification of the main elements in tantalite minerals using environmental friendly reagents which are more easy to handle as well as having the added benefits such as economical and scalable properties. These specific objectives include:

- ❖ Development of a sample preparation method that is safe for the environment and allows further processing of Ta/Nb concentrates to pure Ta and Nb compounds.
- ❖ Use of inorganic and organic ligands as complexing agents for selective precipitation of Ta or Nb using synthetic mixtures of commercial and complex mineral samples.
- ❖ Use of solvent extraction procedures from a non HF solution and the study of other organic solvents for extraction utilising properties such as solubility in aqueous solution, flammability and immiscibility.
- ❖ Utilisation of magnetic properties of the mineral samples to explore a possibility of a separation and purification process.
- ❖ Utilisation of purification methods, such as acid leaching from studies conducted by other researchers in our lab, for removal of the more soluble impurities as well as the use of ion exchange methods to purify the metals of interest and
- ❖ Characterisation and quantification of the products as monitory steps to assess the success of the purification and separation methods that were studied.

These objectives were mainly accomplished as revealed by the results obtained in **Chapters 4 to 6**. The results in **Chapters 5 and 6** clearly indicate that $\text{NH}_4\text{F}\cdot\text{HF}$ can successfully been used as fluxing agent (alternative to HF) for the pure metal oxide

and different tantalite mineral samples. Quantitative recoveries of the main elements at milder experimental conditions clearly demonstrated its usefulness as dissolution agent. The subsequent separation and purification studies also clearly indicated that the $\text{NH}_4\text{F}\cdot\text{HF}$ flux fusion produces fluorinated tantalum and niobium compounds which allowed for the isolation of the main elements using techniques similar to those developed for the HF process.

The successful separation *via* selective precipitation of one of the metal compounds in $\text{NbF}_5/\text{TaF}_5$ and $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ mixtures, using the *p*-phenylenediamine ligand, indicate the usefulness of this ligand in the beneficiation process of the two metals. Excellent separation and purification results (using MIAK as an extractant) were also obtained using H_2SO_4 as the inorganic reagent in combination with the $\text{NH}_4\text{F}\cdot\text{HF}$ flux fusion products. The mechanistic study on this process clearly identified the extraction limiting-step of this process. The successful isolation of a relatively pure Nb compound also illustrates the usefulness of ion exchange for the separation of Nb from the rest of the impurities present in the flux solution.

The evaluation of the whole tantalite mineral beneficiation process in **Chapter 6** clearly confirmed the successful application of both physical and chemical knowledge to the successful development of the proposed process. The removal of the major impurities in large quantities prior to dissolution using magnetic separation not only acted as an initial enrichment step, but also limited the down-stream contamination of the final products. The removal of the radioactive materials, namely U and Th, using H_2SO_4 acid leaching also removed the majority of these harmful elements from the reaction mixture which made it safer to process, to transport and decreased the impurity contamination in the downstream products.

The success of the study is further underlined by the characterization and isolation of the main elements as relatively pure products (> 95%) after two separation steps (solvent extraction and ion exchange chromatography) from the tantalite mineral mixture.

7.3 Future research

A number of interesting projects have been identified for future research. The limited success that were obtained for the separation of the main elements from the useful phosphate and borate flux procedures clearly point to different chemical Nb and Ta compounds (most probably hydrated metal ions) in solution. The failure to separate and isolate the elements from these solutions using the well-established methods, necessitates an in-depth investigation into the chelation (using numerous weak organic acids) of the metal ions and their subsequent extraction and/or separation from these mixtures.

A future study could also involve a more detailed study on the magnetic separation of the Fe and Ti impurities from the mineral. Factors such as magnetic strength and the influence of temperature should form part of such a study.

Another project could involve the detail study on the difference in the chemical behaviour of the MF_5 compounds compared to M_2O_5 using *p*-phenylenediamine as a complexing agent. Characterization of the final products will have to form a major part of the study.

The difference in elemental composition in the tantalite mineral family also requires a detailed study on the applicability of $\text{NH}_4\text{F}\cdot\text{HF}$ as general fluxing agent for Ta and Nb containing minerals as well as their subsequent separation and purification. The loss of ~10% of the major elements in the separation and purification steps may also be the focus of a future study. In addition, no results have been published for the accurate determination of Ta and Nb in other poorly soluble samples such as the pure metals and alloys using the $\text{NH}_4\text{F}\cdot\text{HF}$ dissolution method. The evaluation of $\text{NH}_4\text{F}\cdot\text{HF}$ as a fluxing and fluorinating agent for a wider spectrum of Ta and Nb samples could also be an interesting research project.

Finally, the ion exchange separation of the two main elements using both the strong anion exchange Amberlite IRA-900 and the weak Dowex Marathon wba indicated major differences in the adsorption behaviour between the Ta and the Nb compound. These differences may be investigated in future to try and refine the procedure and even to identify other resins for better separations and recoveries of both Nb and Ta.

7.4 Possible publications from this project

1. Separation of tantalum and niobium compounds by selective precipitation
2. Dissolution and solvent extraction separation of tantalum and niobium pentoxides using ammonium bifluoride as fluxing and fluorinating agent
3. Comparison of the dissolution methods for the tantalite mineral ores
4. Primary beneficiation of tantalum and niobium ores using magnetic separation and acid leaching methods
5. Purification of tantalum and niobium in tantalite using solvent extraction and anion exchange separation techniques

Summary

The aim of this project was to investigate the possible dissolution, separation and purification of tantalum and niobium in synthetic $((\text{Ta/Nb})\text{F}_5$ and $(\text{Ta/Nb})_2\text{O}_5$) and natural (tantalite minerals) compounds using eco-friendly reagents which are easy to handle as well as having benefits such as economical and scalable properties.

The possible separation of Ta or Nb was investigated using the pentafluoride compounds due to their solubility in a wide variety of solvents and their possible formation from the $\text{NH}_4\text{F}\cdot\text{HF}$ flux fusion. Selective precipitation of the two metals was initially investigated with different chelating or precipitating agents and good separations were obtained using *p*-phenylenediamine as reagent. The experimental parameters which were investigated include the influence of concentration and the pH effects on metal recovery. Niobium recoveries in excess of 80% with only 4% tantalum were obtained in the precipitate with the separation factor of 100(9) using a 50% mixture of NbF_5 and TaF_5 . The quantitative determination of Nb and Ta content in the supernatant solution using ICP-OES indicated that more than 95% of the initial tantalum complex remained in solution.

The presence of the pentoxides in the tantalite minerals prompted the investigation into the separation of the metals in a synthetic mixture. It involved the dissolution and subsequent separation of Nb and Ta using a variety of fluxing agents and solvent extraction, selective precipitation and ion exchange techniques. The dissolution of a 50% of Nb_2O_5 and Ta_2O_5 was investigated with $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ mixture, KF, NaF and $\text{NH}_4\text{F}\cdot\text{HF}$ as fluxes in a flux fusion digestion technique. $\text{NH}_4\text{F}\cdot\text{HF}$ was found to be highly successful in the dissolution of the pentoxide mixture with recoveries of 100.4(9)% and 100(1)% for Nb and Ta respectively. In addition, only the $\text{NH}_4\text{F}\cdot\text{HF}$ fusion dissolution was found to support the subsequent separation techniques. The application of the selective precipitation on the $\text{NH}_4\text{F}\cdot\text{HF}$ digestion solutions indicated 23(5) and 73(3)% precipitation of Nb and Ta respectively. The separation of Nb and Ta

using solvent extraction technique indicated that Ta is selectively extracted into the methyl isobutyl ketone (MIKB) with recoveries of 101(1)% and 0.6(5)% for Ta and Nb. The distribution ratio of tantalum ($D_{(Ta)}$) was found to increase with an increase in H_2SO_4 concentration and was determined as 3.46 at $[H_2SO_4] = 4.0$ M. The separation on the strongly basic Amberlite IRA-900 and a weak basic Dowex Marathon anion exchange columns using HCl as an eluent indicate unfeasible separations with recoveries of 91.7 to 96.1% Nb and 52.4 to 73.4% Ta.

The dissolution and separation methods that were successfully developed and evaluated using the synthetic $(Ta/Nb)_2O_5$ mixture were then evaluated on the two tantalite mineral samples. The $NH_4F \cdot HF$ fusion dissolution was successfully applied on the tantalite ore samples and experimental conditions such as the fusion temperature and flux concentration effects were investigated to optimise the procedure. Excellent recoveries of 100.3(5) and 100.0(9)% were obtained for Nb and Ta in Sample A and 96.4(3) and 101.3(4)% for Nb and Ta in Sample C. The application of the selective precipitation, solvent extraction and ion exchange separations produced results similar to the separation of Nb and Ta in the pentoxide mixture. Different solvents were evaluated for the selective extraction of Ta and a pure tantalum compound was isolated using methyl isoamyl ketone (MIAK).

The magnetic removal of some of the impurities and the H_2SO_4 leaching of the NORM's preceded the dissolution of the rest of the minerals. TiO_2 and Fe_2O_3 (57.4(9) and 65(2)%) were removed in the magnetic separation step and 60.77(1)% ThO_2 and 62.4(1)% U_3O_8 were separated in the H_2SO_4 leaching method. Tantalum was selectively extracted into the MIAK after its dissolution using $NH_4F \cdot HF$ with $D_{(Ta)}$ of 6.21 at 4.0 M H_2SO_4 . Niobium was extracted from the mineral matrix using the weak Dowex Marathon wba anion exchanger using HCl as an eluent. Nb_2O_5 and Ta_2O_5 of 96% purity were obtained after precipitation with ammonia.

Opsomming

Die doel van hierdie ondersoek was om die moontlike vertering, skeiding en suiwering van tantaal en niobium in sintetiese $(\text{Ta/Nb})\text{F}_5$, $(\text{Ta/Nb})_2\text{O}_5$ en tantalië minerale te ondersoek deur van omgewingsvriendelike reagente te gebruik wat addisioneel voordele soos goedkoper prosesse, opskaling asook makliker hantering insluit.

Die moontlike skeiding van Ta of Nb is ondersoek deur gebruik te maak van die pentafluoriedverbindings as gevolg van hul oplosbaarheid in 'n wye verskeidenheid van oplosmiddels en die moontlike vorming van dié betrokke verbindings met 'n $\text{NH}_4\text{F}\cdot\text{HF}$ soutsmeting. Selektiewe neerslag van die twee metale is aanvanklik met verskillende kelaatvormende of presipiterende agente ondersoek. Goeie skeidings is met fenileendiamien as reagens verkry. Die eksperimentele parameters wat ondersoek is, sluit onder andere die invloed van konsentrasie en pH op element herwinning in. Niobium herwinning van meer as 80% is verkry en met slegs 4% tantaal in die presipitaat teenwoordig. 'n Skeidingsfaktor van 100(9) vir die 1:1 mengsel van NbF_5 en TaF_5 is bereken. Die kwantitatiewe bepaling van Nb en Ta-inhoud in die filtraat met behulp van IGP-OES het aangedui dat meer as 95% van die aanvanklike tantaal-kompleks in oplossing bly.

Die teenwoordigheid van die pentoksied in die tantalië minerale het aanleiding gegee tot die ondersoek na die skeiding van die metale in 'n sintetiese mengsel. Dit het die ontbinding en daaropvolgende skeiding van Nb en Ta met behulp van verskillende smeltmiddels en ekstraktiewe oplosmiddels, selektiewe neerslag en ionuitruiling tegnieke behels. Die soutsmetingsvertering van 'n 1:1 Nb_2O_5 en Ta_2O_5 mengsel is gevolglik met 'n $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ mengsel, KF, NaF en $\text{NH}_4\text{F}\cdot\text{HF}$ ondersoek. $\text{NH}_4\text{F}\cdot\text{HF}$ is hoogs suksesvol bevind in die ontbinding van die pentoksied mengsel met herwinning van 100.4(9)% en 100(1)% vir Nb en Ta onderskeidelik. Daarbenewens het slegs die $\text{NH}_4\text{F}\cdot\text{HF}$ soutsmeting die daaropvolgende skeidingstegnieke ondersteun. Die toepassing van die selektiewe neerslagvorming op die $\text{NH}_4\text{F}\cdot\text{HF}$ verteringsoplossings

het 23(5) en 73(3)% neerslagvorming van Nb en Ta onderskeidelik aangedui. Die skeiding van Nb en Ta met behulp van oplosmiddel-ekstraksie tegnieke het aangedui dat Ta selektief in metiel-isobutielketoon (MIKB) geïsoleer kan word, met herwinnings van 101(1)% en 0.6(5)% vir Ta en Nb onderskeidelik. Resultate het getoon dat die verspreidingsverhouding van tantaal ($D_{(Ta)}$) direk afhanklik van H_2SO_4 konsentrasie is en is as 3.46 by $[H_2SO_4] = 4$ M bepaal. Die skeiding van die twee metale met behulp van die sterk basiese Amberlite IRA-900 en swak basiese Dowex Marathon anioon-uitruilkolomme en met HCl as 'n elueermiddel, was oneffektief met die gesamentlik herwinning van 91.7 tot 96.1% Nb en 52.4 tot 73.4% Ta.

Die ontbindings en skeidings metodes wat suksesvol op die sintetiese $(Ta/Nb)_2O_5$ mengsel ontwikkel en geëvalueer is, is vervolgens op twee tantaliet bevattende minerale geëvalueer. Die $NH_4F \cdot HF$ soutsmeltingsvertering is suksesvol op die tantaliet erts monsters toegepas en eksperimentele kondisies soos die smelt-temperatuur en soutkonsentrasie-effekte is ondersoek om sodoende die prosedure te optimaliseer. Uitstekende herwinning van 100.3(5) en 100.0(9)% vir Nb en Ta is in een monster verkry en 96.4(3) en 101.3(4)% vir Nb en Ta in 'n ander monster is verkry. Die toepassing van die selektiewe presipitasie, oplosmiddel-ekstraksie, en ionuitruiling het resultate soortgelyk van die skeiding van Nb en Ta in die sintetiese pentoksiedmengsel verkry. Verskillende oplosmiddels is vir die selektiewe ekstraksie van Ta geëvalueer en 'n suiwer tantaalverbinding is met metiel-iso-amielketoon (MIAK) geïsoleer.

Die magnetiese verwydering van sommige van die onsuiverhede en die H_2SO_4 loging van die radio-aktiewe element het die totale vertering van die res van die mineraalmonsters voorafgegaan. TiO_2 en Fe_2O_3 (57.4(9) en 65(2)%) is in die magnetiese skeidingstap verwyder terwyl 60.77(1)% ThO_2 en 62.4(1)% U_3O_8 in die H_2SO_4 uitloging metode geskei is. Tantaal is selektief, ná die vertering met die gebruik van $NH_4F \cdot HF$, met behulp van MIAK geëkstraheer en die ekstraksie-verhouding ($D_{(Ta)}$) is as 6.21 in 4.0 M H_2SO_4 bepaal. Niobium is daarna met hulp van die swak Dowex Marathon ionuitruiler en HCl as 'n elueermiddel as produk geïsoleer. Nb_2O_5 en Ta_2O_5 met 96% suiwerheid is na neerslagvorming met ammoniak verkry.