DISSOLUTION AND ANALYTICAL CHARACTERIZATION OF TANTALITE ORE, NIOBIUM METAL AND OTHER NIOBIUM COMPOUNDS

by

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DECLARATION

I declare that the dissertation hereby submitted by me for the M.Sc. degree at the University of the Orange Free State is my own independent work and has not previously been submitted by me at another university/faculty. I further more cede copyright of the dissertation in favour of the University of the Free State.

Motlalepula Nete

Date

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Motlalepula Nete

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LIST OF ABBREVIATIONS

Analytical equipment

AAS	Atomic absorption spectroscopy
FAAS	Flame atomic absorption spectroscopy
GFAAS	Graphite furnace atomic absorption spectrometry
ETAAS	Electrothermal atomic absorption spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectroscopy
LA-ICP-MS	Laser ablation inductively coupled plasmas mass spectrometry
ETV-ICP-MS	Electrothermal vaporization inductively coupled plasma mass spectroscopy
ETV	Electrothermal vaporization
NAAS	Neutron activation analysis spectrometry
ENAA	Epithermal instrumental neutron activation
XRF	X-ray fluorescence
XRD	X-ray diffraction
UV/VIS	Ultra violet visible spectroscopy

Chemistry and statistics terms

conc. Or c.	concentration
% rec.	percentage recovery
M_xO_y	Metal oxide
TAN	Tantalite (for tantalites A and B)
SAM	Sample (for Sample 1)
b	y-intercept
m	slope
s	Standard deviation
RSD	Relative standard deviation
l	path length
A	absorbance

$\in$	molar extinction coefficient

Ligands

diars	*o*-phenylenebisdimethylarsine, *o*-$C_6H_4(AsMe_2)_2$
Et	Ethyl
NEt_2	diethylamido
Me	Methyl
$NMet_2$	dimethylamido
py	pyridine
THF	Tetrahydrofuran

KEYWORDS

Niobium

Tantalite

Impurities

Microwave

Fusion

Dissolution

Qualitative

Quantitative

Analysis

Recovery

SUMMARY

Qualitative and quantitative analyses of solid samples using a wet analytical technique, such as ICP-OES, are entirely dependent on the complete dissolution of the samples. Since 1866 niobium and tantalum samples have been successfully dissolved by hydrofluoric acid digestion. However, this method is not preferred in industry due to the dangerous nature of hydrofluoric acid as dissolution reagent. This study was aimed at finding alternative, economically viable and ecologically-friendly conversion methods for the dissolution of Nb metal, Nb_2O_5, NbF_5 and three niobium containing minerals demarcated as Tantalite A, Tantalite B and Sample 1.

Acid digestion of Nb and Nb_2O_5 on a hot plate was investigated with HNO_3, HCl, H_2SO_4, H_3PO_4 and aqua regia. Both Nb and Nb_2O_5 dissolved to a greater extent in H_2SO_4 and H_3PO_4 (0.94% and 0.36% respectively) than in the other acids but the results were very inaccurate in all the acids. Good recoveries were obtained for NbF_5 with recoveries of 95% and 93% from the dissolution of this sample in sulphuric acid and water respectively. Microwave-assisted acid digestion was also investigated with the same acids and high accuracy was obtained with recoveries of 99+% for Nb and Nb_2O_5 and 100% for NbF_5 with H_2SO_4 digestion. Microwave-assisted digestion of the mineral samples produced 90+% Nb recoveries at digestion periods longer than that for the pure Nb samples. The calibration curves for all the elements showed good linearity as well as high precision ($R^2 \geq 0.999$) with low y-intercept values which indicated proper background corrections.

Flux fusion digestion was investigated with different flux reagents for the dissolution of pure Nb_2O_5 and the mineral samples. Lithium tetraborate flux produced excellent results for niobium with recoveries of 98.56 to 109.59% Nb_2O_5 and other major and minor elements. The melt was dissolved in the mixture of H_2SO_4 and methanol to remove the excess of boron as the $B(OMe)_3$ ester which

otherwise resulted in the formation of an insoluble boric acid which co-precipitated with some of the analytes of interest. This dissolution method produced accurate results for pure Nb_2O_5 (102.76% Nb recovery) and for most of the analytes which were identified through the qualitative analysis in the mineral samples (98.56 to 109.59% Nb_2O_5, 100.58 to 108.57% Ta_2O_5, 101.03 to 103.29% TiO_2 and 99.23 to 100.55% Fe_2O_3. Other analytes such as SiO_2, ThO_2 and WO_3 showed lower accuracy with recoveries in the range 61.38 to 85.68%. Good linearity and precision was observed in the standard addition calibration curves for all the elements studied, which illustrates the reliability of the results.

Semi-quantitative analyses of the solid mineral samples were done by means of XRF. The XRF results were in good agreement with the results obtained by fusion with $Li_2B_4O_7$ and ICP-OES analysis. Finally, the mineral samples were qualitatively analysed by X-ray diffraction spectroscopy, Scintillometer, Microscope and a hand magnet to get positive identity of the test samples, mainly the sample demarcated as Sample 1. The XRD patterns for Tantalites A and B were identical and these minerals were radioactive but showed very little magnetic properties. Grains of euxenite, garnet, microlite, tourmaline, quartz, muscovite and manganotantalite were microscopically identified in both Tantalites A and B. From these tests, Tantalites A and B were identified as variations of manganotantalite with small amounts of microlite, euxenite, garnet, tourmaline and accessory of quartz and muscovite impurities.

The XRD pattern of Sample 1 showed the presence of manganotantalite, garnet, quartz and muscovite. These minerals were also identified under the microscope. Different from the Tantalite minerals, Sample 1 showed no radioactivity but intense magnetic properties. Sample 1 was identified as a mixture of manganotantalite and garnet with quartz and muscovite impurities.

OPSOMMING

'n Nat analitiese tegniek soos IGP-OES wat vir die kwantitatiewe en kwalitatiewe analises van vastestof monsters gebruik word, is afhanklik van die algehele oplossing van hierdie monsters. Sedert 1866 is niobium en tantaal monsters suksesvol deur waterstoffluoriedsuur-vertering, opgelos. Aangesien waterstoffluoriedsuur as oplossingmiddel gevaarlik en moeilik hanteerbaar is, word hierdie metode minder geredelik deur maatskappye en navorsers aangewend. Die doel van hierdie studie was om alternatiewe, ekonomies uitvoerbare en omgewingsvriendelike metodes vir die oplossing van niobiummetaal (Nb), niobium(v)oksied (Nb_2O_5), niobium(v)fluoried (NbF_5) sowel as drie niobium bevattende minerale naamlik, "Tantaliet Naquissupa A", "Tantaliet Naquissupa B" en "Monster 1", te vind.

Vertering van Nb-metaal en Nb_2O_5 op warmplaat-verhitting is met die volgende sure ondersoek: HNO_3, HCl, H_2SO_4, H_3PO_4 en koningswater. Resultate het getoon dat beide Nb-metaal en Nb_2O_5 beter in H_2SO_4 en H_3PO_4 (0.94% en 0.36% onderskeidelik) as in die ander sure oplos, maar die resultate vir al die sure was baie onakkuraat. Goeie herwinnings met hierdie verteringsmetode is vir NbF_5 verkry met opbrengste van 95% en 93% in swawelsuur en water onderskeidelik. Mikrogolf-geassisteerde suurverterings was ook met dieselfde sure ondersoek en hoë akkuraatheid met opbrengste van 99+% vir Nb-metaal en Nb_2O_5 en 100+% vir NbF_5 is met H_2SO_4 vertering verkry. Mikrogolf-geassisteerde vertering van die mineraalmonsters het Nb opbrengste van 90+% vir langer verteringsperiodes gelewer. Die kalibrasie krommes van al die elemente wat ondersoek is, het goeie lineariteit ($R^2 \geq 0.999$), hoë mate van presisie (% herwinning) en klein y-afsnitte gehad wat op betroubare analitiese resultate dui.

Vloeimiddelsmelting is met verskillende smeltmiddels vir die oplossing van suiwer Nb_2O_5 en ander mineraalmonsters ondersoek. Litiumtertraboraat as smeltmiddel

het uitstekende opbrengste vir Nb (98.56 tot 109.59%) sowel as die ander hoof- en newe elemente wat ondersoek is, gelewer. Die oormaat boor is met die byvoeging van metanol uit die smeltoplossing as die $B(OMe)_3$ ester verwyder. Hierdie oplossingsmetode het akkurate resultate vir suiwer Nb_2O_5 (102.76% Nb herwinning) asook die meeste ander analiete in die ertsmonsters, gelewer, byvoorbeeld 98.56 tot 109.59% Nb_2O_5, 100.58 tot 108.57% Ta_2O_5,101.03 tot 103.29% TiO_2 en 99.23 tot 100.55% Fe_2O_3. Ander onsuiwerhede soos SiO_2, ThO_2 en WO_3 het laer vlakke van akkuraatheid getoon, met herwinningsvlakke in die omgewing van 61.38 tot 85.68%. Die betroubaarheid van die resultate wat met behulp van die standaard-addisie metode uitgevoer is, is deur kwaliteit eksperimentele data soos lineariteit en hoë herwinningsvlakke gekenmerk.

Semi-kwantitatiewe analises vir die erts monsters is met behulp van XRF uitgevoer. Daar was goeie ooreenstemming tussen die XRF en ICP-OES ($Li_2B_4O_7$ smelting) resultate. Die samestelling van die ertsmonsters was ook kwalitatief deur X-straal diffraksie spektroskopie en mikroskoop identifikasie gekarakteriseer. Die XRD spektra vir die Tantaliet A en B ertse is identies, beide toon onder andere radio-aktiewe eienskappe maar toon baie min magnetiese eienskappe. Brokstukke van euxeniet, graniet, mikroliet, toermalyn, kwarts, muskowiet en manganotantaliet is mikroskopies in beide Tantaliet A en B identifiseer. Vanaf hierdie toetse is Tantaliet A en B as variasies van manganotantaliet met klein hoeveelhede van mikroliet, euxeniet, granaat, toermalyn en bykomende kwarts en muskowiet onsuiwerhede gekarakteriseer.

Die XRD spektrum van Monster 1 het ook die teenwoordigheid van manganotantaliet, granaat, kwarts en muskowiet getoon terwyl hierdie minerale ook onder 'n mikroskoop positief waargeneem is. Monster 1 het dan ook geen radioaktiewe eienskappe getoon nie maar wel intense magnetiese eienskappe. Monster 1 is dan ook met behulp van die mikroskoop as 'n mengsel van manganotantaliet, graniet met kwarts en muksowiet as onsuiwerhede identifiseer.

1 INTRODUCTION AND SCOPE OF INVESTIGATION

1.1 INTRODUCTION

Niobium (also called columbium), which was discovered in 1801 by the British scientist Charles Hatchett, belongs to the Vb group of elements which also contain vanadium and tantalum as members. The chemistry of niobium (Nb) is very similar to that of tantalum (Ta) and the two metals normally occur together in nature, in the form of oxides that were formed from orthoniobic (orthotantalic), metaniobic (metatantalic) and pyroniobic (pyrotantalic) acids. Niobium has an abundance of $1x10^{-3}$ wt. % in the Earth's crust.[1,2]

More than 150 niobium-containing minerals have been reported, but most can be divided into two groups namely titano-niobates or tantalo-niobates. The titano-niobate mineral pyrochlore, which contains up to 66% Nb, is by far the most important source of niobium. Other titano-niobate minerals include microlite and loparide. Minerals of the general formula $(Ca,Na,Ce),(Nb,Ta,Ti)_2(O,OH,F)_7$ are named pyrochlore-microlite and the mineral is called a pyrochlore if niobium predominates and microlite when tantalum predominates. The composition of the pyrochlore varies depending on the process by which it was formed. Pyrochlore from Brazil occurs in alluvial deposits formed by weathering of syenite-carbonatite rocks and has a typical formula $(Ba,Ca)_2(Nb,Ti,Ce)_2O_6(O,OH)$. In Canada, pyrochlore deposits are complex ring structures of alkali carbonatite rock in little weathered areas of the Precambrian

[1] Angulyansky, A., *The Chemistry of Tantalum and Niobium Fluoride Compounds*. 2004. pp4-13,25,51,84,256-259,318

[2] Mackay, K.M., Mackay, R. A., Henderson, W. *Introduction to Modern Inorganic Chemistry. 5th ed.* 1996. p261

Shield and has a general formula of $(Na,Ca)_2(Nb,Ti)_2O_6(F,OH)$. The most important niobium and tantalum-bearing minerals are given in **Table 1.1**.

Table 1.1: Principal niobium-bearing minerals

Mineral	General formula	Nb_2O_5, wt. %	Ta_2O_5, wt. %	TiO_2, wt. %	Fe_2O_3, wt. %	MnO, wt. %	SnO_2, wt. %
Pyrochlore	$NaCaNb_2O_6F$	40 - 65	0 - 2	1-6	0-2	...	...
Struverite	$(Ti,Ta,Nb,Fe)_2O_6$	12 - 13	12 - 13	56 -57	...	...	5
Columbite	$(Fe,Mn)(Nb,Ta)_2O_6$	40 - 75	1 - 40	0.5 - 3	10-20	2.6	2
Coltan	$(Fe,Mn)(Nb,Ta)_2O_6$	25 - 60	20 - 50	0.5 - 3	10-20	2.6	2
Tantalite	$(Fe,Mn)(Nb,Ta)_2O_6$	2 - 40	42 - 84	0.5 - 3	10-20	2.6	2
Loparite	$(Ce,Na,Ca)_2(Ti,Nb)_2O_6$	5 - 20	0.5 - 3	...	...	...	...
Microlite	$(Na,Ca)_2Ta_2O_6(O,OH,F)$	0 - 7	68 - 77	...	...	...	...
Sumarskite	$(Fe,Ca,U,Y,Ce)_2(Nb,Ta)_2O_6$	40 - 55	15 - 30	...	...	...	...
Euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$	4 - 47	0 - 47	...	...	...	...
Tapiolite	$(Fe,Mn)(Nb,Ta,Ti)_2O_6$	8 - 15	40 - 85	...	...	...	...

Another important source of niobium is the tantalo-niobate mineral columbite-tantalite (coltan) which normally contains mixtures of columbite and tantalite with up to 60% Nb content. Columbite and tantalite are variations of the general formula $(Fe,Mn)(Nb,Ta)_2O_6$ and the mineral is called tantalite when the tantalum pentoxide (Ta_2O_5) content exceeds the niobium pentoxide (Nb_2O_5), and it is called columbite (niobite) when the composition is the other way round.[1,3]

Brazil, Canada, Australia, China, Malaysia, Namibia, Nigeria, Russia, Rwanda, Spain, Thailand, Venezuela, Gabon, Mozambique, Zaire and Zimbabwe contribute to the most of the world's supply of coltan minerals. In 2003 it was reported[4] that Africa

[3] Roskill the Economics of Niobium. 10th ed. Roskill Information Services Ltd. 2005

[4] Roskill the Economics of Tantalum, 9th ed. Roskill Information Services Ltd. 2005

possesses 16% of the world's Ta/Nb feedstock and that Nigeria, which is the dominant producer of niobium containing minerals in Africa, possesses tantalite deposits which are extremely rich in Ta_2O_5 content (40+%).[5] Brazil and Canada are the dominant pyrochlore producers and together account for the majority of the niobium production in 2006. The production data for the known world producers of the niobium raw materials are given in **Table 1.2**.

Table 1.2: World production of niobium raw materials, 1999 to 2004 (t Nb_2O_5)

		1999	**2000**	**2001**	**2002**	**2003**	**2004**
Australia	C-T	200	229	329	415	329	343
Brazil	P	31,317	31,174	39,039	41,327	41,470	-
Canada	P	3,375	3,260	4,547	4,762	4,676	4,719
	C-T	14	16	21	17	16	-
D.R. Congo	C-T	-	157	72	36	19	19
Ethiopia	T	7	10	7	9	9	9
Mozambique	...	-	7	7	11	49	50
Namibia	...	-	1	-	-	1	1
Nigeria	C-T	179	286	358	300	272	286
Rwanda	C-T	66	252	109	43	31	43
Uganda	C-T	-	1	7	4	4	4
Total		**35,158**	**35,394**	**44,492**	**46,924**	**46,876**	**5,474**

Key: P – pyrochlore C-T – columbite-tantalite T – tantalite

[5] Adetunji, A. R., Siyanbola, W.O., Funtua, I. I., Olusunle, S. O. O., Afonja A. A and Adewoye, O. O., *J. Minerals & Materials Characterization & Engineering*. 2005. **4** (2). pp67-73

Brazil, which accounted for about 90% of world production in 2006,[3,6] uses open cast mining and has reserves to last for the next 500 years at current production rates.[7] Together, Brazil and Canada accounted for more than 99% of world production that year (**Figure 1.1**) and it is estimated that Brazil has 460 Mt of ores averaging 2.5-3.0 kg/t Nb_2O_5 (mined ore). Interestingly, the world's largest niobium reserve of 2,897 Mt with 2.81% Nb_2O_5 or 81 Mt was discovered in 1975 at the Amazonas State in Brazil (**Figure 1.2**).

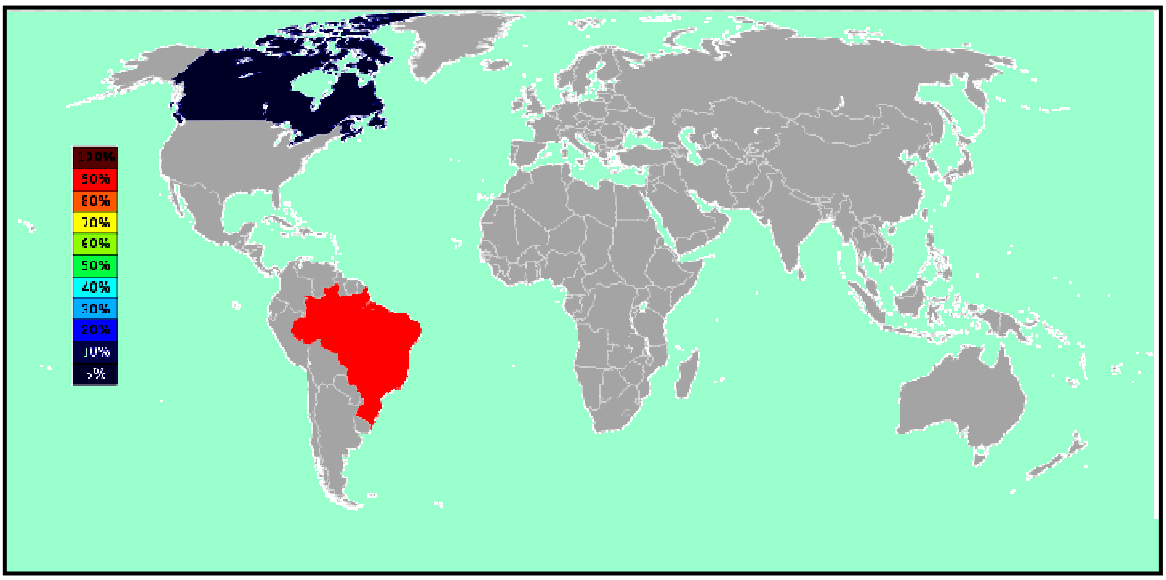


Figure 1.1: Niobium producers 2007.[8]

The geographical distribution of niobium between Brazil, Nigeria, Democratic Republic of Congo and Namibia and between Australia, Malaysia, Thailand and China can possibly be explained by continental drift, which separated the highly localized deposits of Nb containing minerals to different parts of the world.

[6] www.minerals.usgs.gov/minerals

[7] http://www.msm.cam.ac.uk/phase-trans/2006/Nb/Nb.html

[8] http://en.wikipedia.org/wiki/Niobium

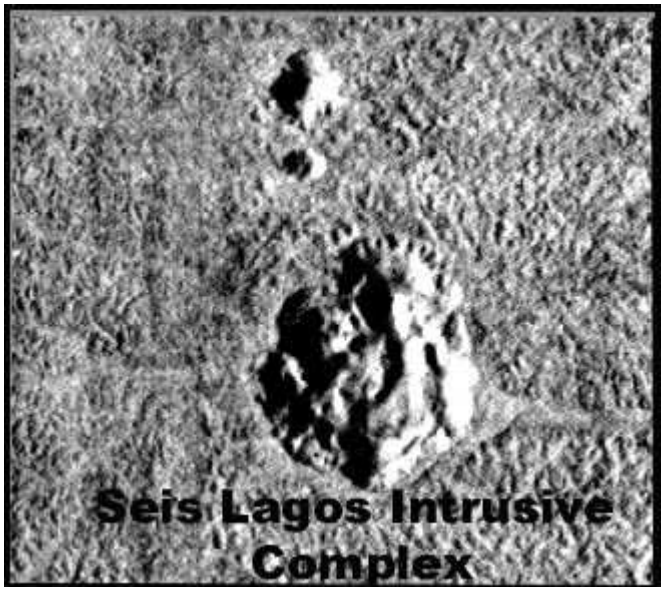


Figure 1.2: Aerial photo of the world's largest niobium reserve at Seis Lagos in Brazil.[9]

Additional sources of niobium are tin slag, steel and super-alloy scrap.[7] In South Africa, small niobium deposits have been reported in the Northern Cape, the Limpopo Province and Mpumalanga. A number of coltan and beryl-bearing pegmatite deposits are located near Gravelotte in the Limpopo Province. Tantalite and columbite have been mined from pegmatite at Palakop, near the Klein Letaba River in Limpopo Province even though that source is now exhausted. Small amounts of coltan concentrates are also produced from pegmatites in the north-west of Northern Cape Province at Zandkops Drift, 26 km south-west of Garies.[3]

Niobium has numerous applications in everyday life. Small amounts of niobium are added, for example, to other metals to increase their mechanical strength especially when exposed to high temperatures. In the nuclear industries, niobium is used due to its high mechanical strength, melting point (2477 ± 15 ^{o}C), resistance to chemical attack and low capture cross-section for thermal neutrons.[2,7] It is also used in the form of high-purity ferroniobium, nickel-niobium, and cobalt-niobium super-alloys for

[9] http://www.geologo.com.br/seislagos.asp

manufacturing of jet engine components, missiles, cutting tools, pipelines, super magnets and welding rods.

Niobium-tin and niobium-titanium alloys are often used as wires for superconducting magnets capable of producing extremely strong magnetic fields. In its pure form, niobium is also used to make superconducting accelerating structures for particle accelerators.[8] Niobium alloys are often used in surgical implants due to its non-toxic and non-reactive biological properties.[7-10] Along with titanium, tantalum, and aluminium, niobium can also be electrically heated in air and anodized to produce an array of colours and this property makes it attractive for use in jewellery (see **Figure 1.3**).[11,12]

There have been a few reports on photocatalysis processes in which Nb_2O_5 is used for the photocatalytic dehydrogenation of methanol in aqueous solution under deaerated conditions as well as mineralization of acetic acid under aerated conditions.[13] The pattern of total consumption of niobium in the United States of America between 1970 and 1980 has been summarized in **Table 1.3**.

[10] Park, K.S., Kim, N.B., Woo, H.J., Lee, K.Y., Yoon, Y.Y., Hong, W., *Journal of Radioanalytica and Nuclear Chemistry, Articles.* 1994. **179** (1). pp81-86

[11] United States Patent 4040129.

[12] http://www.3rd1000.com/elements/Niobium.htm

[13] http://pubs.acs.org/cen/80th/niobium.html#Anchor-Pamela-11481#Anchor-Pamela-11481

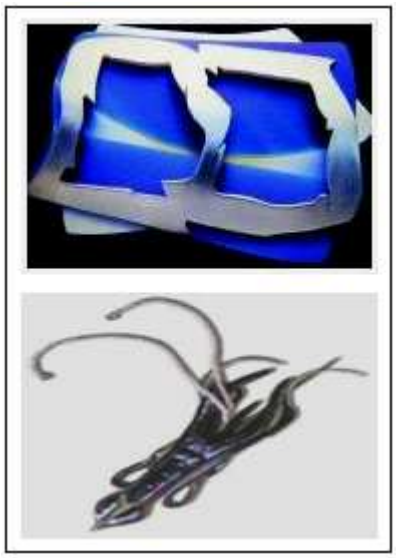


Figure 1.3: Examples of jewels manufactured from anodized Nb

Table 1.3: Consumption pattern for niobium in the USA (US bureau of Mines-1000 LBS)

	1970	**% OF TOTAL 1970**	**1971**	**1972**	**1973**	**1974**	**1975**	**1976**	**1977**	**1978**	**1979**	**1980**	**% OF TOTAL 1980**
STEEL													
Carbon & HSLA	705	26	821	1874	2180	2291	1796	1882	2350	3011	3178	3204	48
Stainless Steel	522	19	588	644	712	564	379	491	588	805	827	696	10
Full alloy Steel	829	31	789	302	361	511	372	538	584	656	505	476	7
Steel Totals	2056	76	2198	2820	3253	3366	2547	2911	3522	4472	4510	4376	65
Super-alloys	472	17	591	665	685	1097	359	423	796	1146	1777	1904	29
Other Alloys	36	1	37	57	67	82	35	50	65	60	32	15	-
Miscellaneous	24	1	51	131	48	78	78	50	20	16	17	7	-
Primary Totals	2588	95	2877	3673	4053	4623	3019	3434	4403	5694	6336	6302	94
Niobium Metal	119	4	115	251	262	161	108	99	190	225	331	346	5
Grand Total	**2707**	**99**	**2992**	**3924**	**4315**	**4784**	**3127**	**3533**	**4593**	**5919**	**6667**	**6648**	**99**

1.2 CHEMISTRY OF NIOBIUM

Niobium is a rare, soft, malleable, ductile, gray-white metal (**Figure 1.4**) and has a body-centered cubic crystalline structure (**Figure 1.5**).

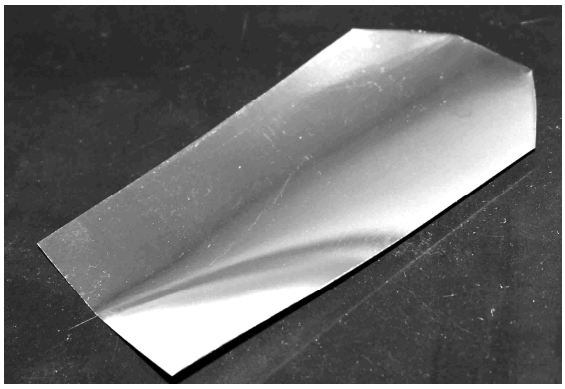


Figure 1.4: Niobium foil

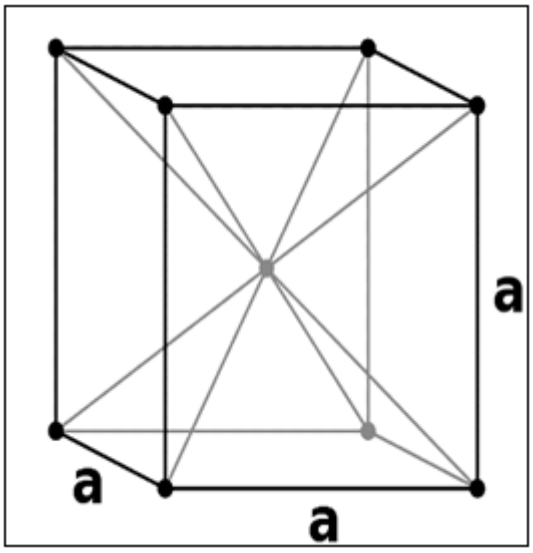


Figure 1.5: Body centered cubic structure of niobium.[6]

The metal starts to oxidize in air at 200 ℃, and must be processed in a protective atmosphere even at moderate temperatures to minimize possible reactions with oxygen, carbon, the halogens (see **Equation 1.1**), nitrogen, and sulphur.[14]

$$2Nb_{(s)} + 5Cl_{2(g)} \longrightarrow 2NbCl_{5(s)} \qquad \textbf{1.1}$$

The metal is inert to acids, even to aqua regia at room temperatures, but is attacked by hot, concentrated acids (Equation **1.2**), and especially by alkalis and oxidizing agents.[1] Some physiochemical properties of niobium are listed in **Table 1.4**.[7]

$$Nb_{(s)} + 6HF \longrightarrow HNbF_6 + 2.5H_{2(g)} + \text{heat} \qquad \textbf{1.2}$$

Table 1.4: Physiochemical properties of niobium

Property	**Niobium**
Atomic radius	2.08 Å
Ionic radius	1 Å
Melting Point	2477 ± 15 ^{o}C
Standard atomic weight	92.91 g·mol^{-1}
Electron configuration	[Kr] 5s^{1} 4d^{4}
Electronegativity (Pauling scale)	1.60
Ionization energies (kJ.mol^{-1})	1st: 652.1
	2nd: 1381.7
	3rd: 2416.0

Niobium forms oxides with a variety of oxidation states namely +II(NbO), +III(Nb_2O_3) and +IV(NbO_2) as well as a +V(Nb_2O_5). The most stable and well-known oxidation state is +V possibly due to its ability to lose the 1s and 4d (in electron configuration [Kr]5s^{1}4d^{4}) electrons to achieve the octet electron configuration for krypton. Niobium in the +V oxidation state has chemistry that is very similar to those of typical non-

[14] Kominami. H. Oki, K., Kohno, M., Onoue, S., Kera, Y., Ohtani, B., *Journal of Materials Chemistry*. 2001. **11**. pp604-609

metals, but forms numerous anionic compounds (for example, $NbCl_6^-$). It also has the ability to form adducts with virtually all types of neutral and anionic donors (Equation **1.3**).

$$Nb_2(OAr)_{10} + 2THF \longrightarrow 2Nb(OAr)_5(THF) \qquad \textbf{1.3}$$

Niobium oxidation states and associated stereo-chemistries are summarized in **Table 1.5**. Research has shown[15] that Nb in its lower oxidation states is much more prone to extended metal-metal bonding. The final products which are obtained *via* the oxidation of the metal are the pentoxides. [15,16]

Table 1.5: Examples of Nb complexes with the metal in different oxidation states

Oxidation state	Coordination number	Geometry	Examples
Nb^{-I}	6	Octahedral	$[Nb(CO)_6]^-$
Nb^{I}	7	π-Complex	$(h^5\text{-}C_5H_5)[Nb(CO)_4]$
Nb^{II}, d^3	6	Octahedral	NbO
Nb^{IV}, d^1	4	Distorted Tetrahedral	$[Nb(NEt_2)_4]$
	6	Octahedral	$[NbX_4]$, $[NbCl_4py_2]$, $[NbCl_6]^{2-}$
	8	Dodecahedral	$[NbX_4(diars)_2]$
Nb^{V}, d^0	4	Tetrahedral	$Sc[NbO_4]$
	5	Trigonal bipyramid	$[NbCl_5]$ (vapour)
	5	Distorted Tetragonal pyramid	$[Nb(NMet_2)_5]$
	6	Octahedral	$[NbCl_5]$, $[NbCl_6]^-$, $[NbOCl_3]$, $[NbCl_5]_2$
	7	…	$K_2[NbF_7]$, $K_3[NbOF_6]$
	8	…	$[Nb(troponate)_4]^+$

[15] Wilkinson, G., Gillard, R.D., McClevery, J.A., *Comprehensive Coordination Chemistry.* 1987. **3**. p587

[16] http://www.lentech.com

1.2.1 Chemistry of niobium oxides

Niobium (V) oxide (Nb_2O_5) is an acidic oxide and is thus not soluble in acids with the exception of hydrofluoric acid. Niobium oxides are generally dissolved by alkali fusion or by treatment with concentrated hydrofluoric acid (HF). Fusion of Nb_2O_5 with hydroxides or carbonates results in the formation of niobates such as sodium metaniobate, $NaNbO_3$. Nb_2O_5 can be synthesized by dehydration of niobium hydrate (Equation **1.4**) but the more pure Nb_2O_5 is produced by hydrolysis of $NbCl_5$ (Equation **1.5**).

$$Nb_2O_5.yH_2O \xrightarrow{\Delta} Nb_2O_5 + yH_2O \qquad \textbf{1.4}$$

$$2NbCl_5 + 5H_2O \longrightarrow Nb_2O_5 + 10HCl \qquad \textbf{1.5}$$

It can also be reduced to a dark gray niobium (IV) oxide (NbO_2) (Equation **1.6**) which in turn can be further reduced to niobium (III) oxide (Nb_2O_3) and niobium (II) oxide (NbO) by heating the pentoxide in a stream of hydrogen gas at 1000 ^oC.

$$Nb_2O_{5(s)} + H_{2(g)} \xrightarrow{1000\,^oC} 2NbO_{2(s)} + H_2O_{(g)} \qquad \textbf{1.6}$$

The reaction between Nb_2O_5 and HF results in the formation of fluoro-complexes (see Equation **1.7**). Oxygen and fluorine ions have very similar ionic radii (1.36 and 1.33 Å respectively) and this steric similarity ensures relatively easy substitution of oxides by fluoride ions in the compound. These substitution reactions allow for the synthesis of oxyfluoroniobates from the reaction of Nb_2O_5 with ammonium bifluoride (NH_4HF_2) or alkali hydrofluorides such as $LiHF_2$ and $NaHF_2$ as indicated in Equation **1.8**.

$$Nb_2O_5 + 12HF \longrightarrow 2HNbF_6 + 10H_2O \qquad \textbf{1.7}$$

$$Nb_2O_5 + 6LiHF_2 \longrightarrow 2Li_3NbOF_6 + 3H_2O \qquad \textbf{1.8}$$

It was reported that the average Nb-O bond distance in Nb_2O_5 was determined as 1.96(2) Å in which the Nb centre was tetragonally surrounded by the oxygen atoms.[17] The oxygen atoms form partially covalent bonds with the metal which may account for the high thermal stability and resistance to hydrolysis. The substitution of oxygen atoms by fluorine atoms such as in K_2NbOF_5 results in a shorter Nb-O bond distance (1.68 Å) while the Nb-F_{cis} bond distance was determined as (1.84 Å) and Nb-F_{trans} as (2.06 Å) in the same structure.[1] It was also found that niobium in the V^+ state (pentoxide) reacts with sulphuric acid forming a $HNb_6O_{19}^{7-}$ complex.[18] Other reactions of Nb_2O_5 include its reduction with carbon to the niobium metal (Equations **1.9** and **1.10**) and synthesis of oxychloride and oxybromide as indicated in Equations **1.11** and **1.12** respectively.

$$Nb_2O_5 + 7C \xrightarrow{1800\,^oC} 2NbC + 5CO \qquad \textbf{1.9}$$

$$Nb_2O_5 + 5NbC \longrightarrow 7Nb + 5CO \qquad \textbf{1.10}$$

$$2Nb_2O_5 + 3CCl_4 \longrightarrow 4NbOCl_3 + 3CO_2 \qquad \textbf{1.11}$$

$$Nb_2O_5 + 3Br_2 + 3C \longrightarrow 2NbOBr_3 + 3CO \qquad \textbf{1.12}$$

1.2.2 Chemistry of niobium fluorides

The coordination chemistry of the higher halides is widely developed with their volatility decreasing from fluorides to the iodides. Research has shown[16] that Nb and Ta are among the few elements which form stable pentaiodide compounds as indicated in Equation **1.13**.

[17] Cotton, F.A., Wilkinson, G., *Advanced Inorganic Chemistry, 3rd edition*. 1972. pp934-942

[18] Marlap. Sample Dissolution. July 2004. pp13.1-13.27

$$2Nb_{(s)} + 5I_{2(g)} \longrightarrow 2NbI_{5(s)} \qquad \textbf{1.13}$$

The wide variety of fluoride compounds that have successfully been synthesized and characterized as well as the wide spectrum of their preparation methods are all related to fluorine's high electronegativity, low dissociation energy of the fluorine molecule and its strong oxidizing ability. Some special properties possessed by all niobium fluoride compounds are their relatively low thermal stability and tendency towards hygroscopicity and hydrolysis (Equation **1.14**). These features indicate that special conditions are required for the successful preparation of the fluoride compounds, these being a dry and low pressure atmosphere as well as controlled temperatures.[1]

$$K_2NbF_7 + H_2O \longrightarrow K_2NbOF_5 + 2HF \qquad \textbf{1.14}$$

Numerous niobium fluoride compounds have been synthesized by fluorination of the pure niobium metal or its oxides and it was found[1] that fluorination with hydrofluoric acid can occur spontaneously at low temperatures (≤ 298 K) while fluorination of the metal oxides by ammonium fluoride, NH_4F and ammonium bifluoride, NH_4HF_2 can only occur at higher temperatures (**Table 1.6**).

Table 1.6: Spontaneity of niobium and fluoride reactions expressed in Gibb's energy change

Fluorination process	**ΔG, Kcal/mol, 298 K**
$Nb + 5HF \longrightarrow NbF_5 + 2.5H_2$	-333
$Nb + 2.5NH_4HF_2 \longrightarrow NbF_5 + 2.5H_2 + 2.5NH_3$	-199
$Nb + 5NH_4F \longrightarrow NbF_5 + 2.5H_2 + 5NH_3$	-38
$Nb_2O_5 + 10HF \longrightarrow 2NbF_5 + 5H_2O$	-63.6
$Nb_2O_5 + 5NH_4HF_2 \longrightarrow 2NbF_5 + 5H_2O + 10NH_3$	150
$Nb_2O_5 + 10NH_4F \longrightarrow 2NbF_5 + 5H_2O + 10NH_3$	231

Niobium pentafluoride (NbF_5) is a white solid with a melting point of 79.0 ℃ and boiling near 230 ^{o}C[1,6] and unlike oxides, it is found that the fluoride compounds form mostly ionic bonds which can be attributed to fluorine's high electronegativity compared to that of oxygen. The formation of these ionic bonds with relatively low bond energy account for these complexes to display a tendency towards thermolysis and hygroscopicity and may account for the ease with which NbF_5 dissolves in polar solvents such as hydrochloric acid, nitric acid, concentrated sulphuric acid, ethanol, chloroform, tetrachloromethane and ethanoic acid.[1]

The monomeric NbF_5 crystallizes in a distorted trigonal bipyramidal geometry with Nb-F_{ax} (1.88 Å) and Nb-F_{eq} (1.89, 1.87 Å) while another form of the same compound crystallizes in a tetrameric orientation with fluoride bridging atoms between each pair of metal atoms with Nb-F_{ax} (1.86 Å), Nb-F_{eq} (1.82 Å) and Nb-F_{br} (2.09 Å) (**Figure 1.6**).[2] There is evidence[1] that the liquid phase structure of the same complex possesses the *cis*-bridging bonds with the formation of polymers rather than tetramers. It was also found that vapour phase consists of 98% trimeric Nb_3F_{15} and 2% monomeric NbF_5 compounds.

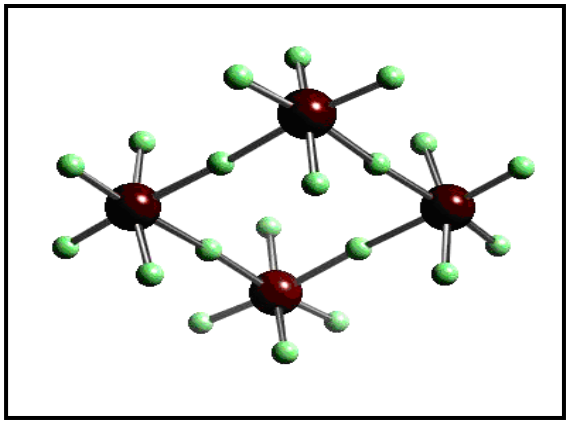


Figure 1.6: The structure of $[NbF_5]_4$.[19]

[19] http://www.webelements.com/niobium/chemistry.html

1.3 CHEMISTRY OF THE MINERAL TANTALITE

In nature the colour of the mineral tantalite can differ from black to brown in both colour and streak (the color left by a mineral dragged across a rough surface) in pegmatites (**Figure 1.7**)[20] while manganese rich tantalites can be brown or translucent. Some specimens may show a bluish iridescent tarnish and have demonstrated weak magnetic properties. Tantalite is largely found mixed with columbite in an ore called coltan[7] which consists of an isomorphous mixture of four salts namely $Fe(TaO_3)_2$, $Mn(TaO_3)_2$, $Fe(NbO_3)_2$, and $Mn(NbO_3)_2$ and almost always contains titanium, tin, tungsten, and other elemental impurities.[21]

Figure 1.7: Tantalite $(Fe,Mn)(Ta,Nb)_2O_6$

[20] http://www.webelements.com/compounds/niobium/Nb-4_F-20.html

[21] Singh, R.P. *J. Electronic Materials*. 2001. **30** (12). p1584

1.3.1 Most common production procedures

The elements niobium and tantalum are produced from the raw material by two main methods namely the chlorination and the fluorination followed by liquid-liquid extraction. The chlorination method involves the chlorination of the raw material followed by separation and purification by distillation of the tantalum and niobium pentachlorides with boiling points of 236 ^{o}C and 248 ^{o}C respectively. The chlorination method can follow two different routes depending on the type of raw materials. The first route is a reductive process in which oxide-type mineral ore or concentrate is chlorinated with chlorine gas in the presence of coal or other related material producing pentachlorides. The second process involves chlorination of ferroalloys (ferroniobium-tantalum) on a sodium chloride melt that contains iron trichloride, $FeCl_3$. Chlorine gas is passed through the melt yielding $NaFeCl_4$ which acts as a chlorination agent for the Fe-Nb-Ta alloy producing pentachlorides which are then separated by distillation.

The liquid-liquid extraction method is a modification of the historical fractional crystallization process found by Marignac in 1866. In the Marignac's method, niobium and tantalum oxides were recovered from mineral ores and tin slags by decomposition with hydrofluoric acid followed by addition of potassium hydroxide or carbonate. This produces a solution of potassium niobium oxyfluoride (K_2NbOF_5) and potassium fluorotantalate (K_2TaF_7), which was then partially cooled to crystallize K_2TaF_7. The product was then separated from the solution by decantation. The more soluble K_2NbOF_5 was then recovered from solution by the addition of ammonia to precipitate niobium oxide. The series of reaction steps involved in the Marignac's process are summarized in the flow chart in **Figure 1.8**. One of the main drawbacks of the Marignac's process was the co-precipitation of impurities such as Ti(up to 100 ppm), Si(up to 3000 ppm), and Fe(up to 2000 ppm) that were found in niobium pentoxide obtained by this method.

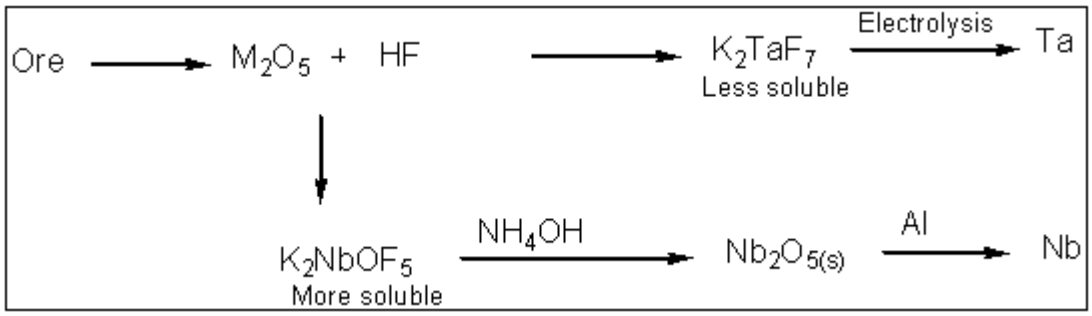


Figure 1.8: Flow chart of the Nb and Ta production using HF

The modern production method for these metals follows a slightly different process. The raw material is first digested by a mixture of HF and other strong mineral acids such as H_2SO_4 or fluoride salts such as NH_4F in HF or other concentrated mineral acids. The solution is then processed by liquid-liquid (solvent) extraction which is based on the extraction of the different ions into either an organic or aqueous phase according to the complex ion structure which in turn depends on the acidity of the aqueous solution. At higher acidity levels, tantalum and niobium ions are extracted into the organic phase leaving other impurities in the aqueous phase. Lower acidity levels are then used to strip niobium and tantalum ions from the organic phase back into the aqueous solution. The separation of niobium and tantalum in this step is achieved by the fact that niobium complexes require higher levels of acidity in the aqueous phase to be extracted into the organic solution and lower levels of acidity to be stripped into the aqueous solution compared to the tantalum complexes. Numerous solvents can be used in the liquid-liquid extraction, but the most frequently used extractants are methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), cyclohexanone and fatty alcohols such as 2-octanol.

The products obtained from this solvent extraction process are i) tantalum strip solution, ii) niobium strip solution and iii) liquid wastes containing impurities as well as residual acids. In the next step of the purification process, niobium hydroxide is then precipitated from the niobium-containing strip solution by the addition of ammonia. Niobium oxide is finally obtained after the washing, the drying and calcinations of niobium hydroxide.

Several methods are used to reduce Nb_2O_5 to metallic niobium. The one method involves the conversion of Nb_2O_5 to NbF_5 followed by the reduction of the NbF_5 with sodium metal. Another method involves the reaction of Nb_2O_5 with a mixture of iron oxide and aluminium as indicated in Equation **1.15**.

$$3Nb_2O_5 + Fe_2O_3 + 12Al \longrightarrow 6Nb + 2Fe + 6Al_2O_3 \qquad \textbf{1.15}$$

Another modification that was reported suggested that the lowering of partial pressure of HF by the H_2SO_4 reduces volatilization loses as well as acid consumption and enhances the digestion process, improving Nb-Ta recovery. The mechanism of the interaction between the tantalite ore and sulphuric acid was investigated by Akimov and Cheryak[1] who suggested a two step process (Equations **1.16** and **1.17**):

I. Formation of iron and manganese sulphate and of tantalum and niobium hydroxides.

$$(Fe, Mn)(Ta, Nb)_2O_6 + H_2SO_4 \longrightarrow (Fe, Mn)SO_4 + (Ta, Nb)_2O_5.H_2O \qquad \textbf{1.16}$$

II. Conversion of tantalum and niobium hydroxides into oxysulphate compounds.

$$2(Ta, Nb)_2O_5.H_2O + H_2SO_4 \longrightarrow H_2O + 2(Ta, Nb)_2O_3(SO_4)_2 \qquad \textbf{1.17}$$

According to the reaction in Equation **1.16**, the decomposition of tantalite or columbite by sulphuric acid results in the formation of niobium and tantalum hydroxides which are further converted into oxysulphate as indicated in Equation **1.17**. However, it is reported that the hydroxides which are produced in the first step form a shell around the tantalite mineral making the further reaction between sulphuric acid and the mineral difficult and thus decreasing the efficiency of this process.[1] A possible solution to this problem is by particle size reduction as

suggested by Welham[22] who found that a powder milled for 50 hours exhibits a dissolution rate 4500 times higher than a powder milled for only 2 hours. This showed that the dissolution rate of the mineral depends both on its surface area and strongly on its crystalline size. Welham recommended the use of a strong acid or hydrofluoric acid since it dissolves columbite-tantalite at a reasonable rate based on the above findings.

1.4 MOTIVATION FOR THIS STUDY

Increasing world demand for Nb and its compounds has prompted several research projects. In one of these projects niobium metal will be at the frontier of future scientific applications. In June 2007, the German Minister of Education, Dr. Annette Schavan, announced the development of the European's largest X-ray laser at the German Electron Synchrotron.[23] The XFEL (X-ray free-electron laser) opens up new areas of application in the unseen world of molecules and tiny structures which will for example allow scientists to observe chemical reactions in real time. High-purity niobium will be used to manufacture the superconducting cavity resonators which will be at the heart of the XFEL. The good machinability at room temperature and high ductility makes niobium ideal for use in this billion Euro venture. Niobium is also recognised in industry as the metal that is used for the production of super-steel, displaying properties such massive strength and endurance as well as corrosion and cracking resistance at high temperatures.[24] The combination of its high mechanical strength, high melting point, resistance to chemical attack and low neutron absorption cross-section, renders it as an ideal metal to be used in the nuclear industry, especially in the construction of reactors in the space-powder system programme. [7]

[22] Welham, N.J. *Canadian Metallurgical Quarterly*. 2001. **40** (2). pp143-154

[23] http://corporate.heraeus.com/media/webmedia_local/media/presse/pressemitteilungen/archiv2007/High-purity_niobium_for_cutting_edge_European_research_11092007.pdf

[24] http://www.tanb.org/niobium1.html

The production of high quality niobium metal and other compounds such as Nb_2O_5, $NbCl_5$ and NbC are always closely associated with quality control steps such as the chemical analysis of these products for impurities. The production of these compounds starts with the chemical manipulation of different ores or minerals (see **Paragraph 1.3**) to separate the niobium from the rest of the minerals. These minerals however differ substantially in chemical composition, even for minerals that are mined in the same country as indicated by the results in **Table 1.8** for tantalites that were mined in Nigeria. These results indicate that the TiO_2 content for example varies between 0 and 33%, Ta_2O_5 between 8 and 60% and Nb_2O_5 between 19 and 38%.

The current importance of Nb in industrial applications, as well as the continued growth of its applications worldwide, underlines the importance of current and future research on this topic. South Africa does not have substantial reserves of Ta/Nb feedstock minerals, but a most likely source of these minerals is one of its closest neighbours, Mozambique. Tantalite, mangano-tantalite and microlite are currently mined from the Naquissupa open pit mine in the Namama orogenic belt in Namialo, Gilé district, 20 km from the Muiane in Mozambique. Other areas such as Marropino and Monte Morrua located in the north of the Zambezia Province are also known to have Nb containing minerals. The currently available production data for niobium mineral in Mozambique is presented in **Table 1.7**.

Table 1.7: Mozambique production of niobium minerals, 2000 to 2004/ Nb_2O_5 (t)

Year	0re	Nb_2O_5 production
2000	25	7
2001	27	7
2002	47	11
2003	189	49
2004	200	50

An interesting problem associated with the composition of these minerals is the possible inclusion of foreign minerals during the geological process millions years

ago or during the sampling (mining) of the minerals (see **Table 1.8**). The difference in chemical composition of the mineral itself or the possible combinations of different minerals (especially during the pre-concentration of low grade ores) complicate the dissolution process of the minerals to allow for the chemical analysis or the enriching of the niobium content. Practically, it means that dissolution processes need to be developed for different minerals which are extremely tedious, taking into account the number of niobium containing minerals that exist in nature. In addition to this problem, the almost exclusive use of Cl_2, HF and fluorinated compounds in the dissolution process of the minerals for the production of Nb_2O_5 which is used as the starting material in the niobium value chain necessitates the search for new, alternative dissolution processes.

Table 1.8: Example of the variations in the composition of tantalite ore samples from different locations in Nigeria[5]

Oxide	Egbe	Komu	Nassarawa	Agunrege	Baba Ode	Ofiki	Igbo Ijaye	Otu
TiO_2%	-	-	3.81 ±0.42	1.64 ±0.37	2.34 ±0.42	1.05 ±0.33	20.36 ±0.58	33.38 ±0.67
MnO%	4.15 ±0.10	9.03 ±0.17	5.80 ±0.13	6.69 ±0.14	8.62 ±0.17	10.10 ±0.18	3.46 ±0.12	0.74 ±0.09
Fe_2O_3%	7.76 ±0.18	3.51 ±0.14	10.69 ±0.23	7.37 ±0.18	4.69 ±0.16	2.86 ±0.13	9.66 ±0.21	9.70 ±0.20
Ta_2O_5%	59.58 ±0.62	49.57 ±0.54	46.15 ±0.52	45.42 ±0.49	42.00 ±0.46	36.63 ±0.42	23.64 ±0.40	8.00 ±0.17
Nb_2O_5%	19.74 ±0.17	29.18 ±0.23	24.86 ±0.20	31.18 ±0.26	32.90 ±0.26	37.48 ±0.29	28.90 ±0.29	22.43 ±0.17
WO_3%	-	0.38 ±0.13	1.80 ±0.14	-	-	-	0.32 ±0.09	0.17 ±0.05
SnO_2%	-	-	8.43 ±1.97	-	-	-	-	-
Hf%	0.22 ±0.05	0.26 ±0.05	0.31 ±0.05	0.18 ±0.05	0.17 ±0.05	0.11 ±0.04	0.13 ±0.04	-
Zn%	-	0.22 ±0.03	0.09 ±0.03	-	0.09 ±0.03	0.07 ±0.02	-	-
Zr%	0.31 ±0.01	0.12 ±0.01	0.26 ±0.01	0.15 ±0.01	0.22 ±0.01	0.17 ±0.01	0.06 ±0.01	0.06 ±0.01
Pb (ppm)	489 ±146	570 ±146	1720 ±195	-	1010 ±168	720 ±146	-	-
Rb ppm)	-	120 ±47	-	-	-	-	-	-
Y (ppm)	-	-	333 ±51	-	-	-	-	-
ThO_2 %	0.34	0.03	0.15	0.02	0.02	0.05	0.03	0.01
U_3O_8%	0.17	0.37	0.65	0.42	0.94	1.57	0.28	0.27

The chemical analysis of the minerals as well as all the different chemical compounds in the whole value chain is extremely important from a quality control perspective. XRF, ENAA, ICP-OES and ICP-MS have previously been used to quantify the tantalites while radiochemical neutron activation analysis (NAA), AAS and ICP-OES were used (see **Chapter 2**) to analyze Nb metal, Nb_2O_5 and other niobium compounds. It is therefore extremely important to develop the necessary

analytical and other skills and knowledge in order to utilize this important metal in future.

With the above-mentioned in mind, the objectives of this study are to:

- Perform an in-depth literature study on the analytical techniques for the analysis of niobium and its associated impurities.
- Identify and compare the different techniques, concentrating on the most recent and modern technique such as ICP, XRD and AAS.
- Develop a universal applicable and environmentally-friendly digestion method for the wet chemical analysis for all tantalite using different fluxes as well as microwave digestion.
- Develop a procedure for the multi-element analyses of niobium, niobium pentoxide, niobium fluoride and the tantalite ores using commercially available equipment such as ICP-OES.
- The physical evaluation of the most relevant and most promising analytical methods using pure standards in the above- mentioned techniques.

2 DISSOLUTION AND SPECTROMETRIC ANALYSIS OF NIOBIUM CONTAINING MINERALS: LITERATURE SURVEY

2.1 INTRODUCTION

Niobium was discovered in 1801 and at first it was mistakenly identified as tantalum due to the similarities in their chemical properties. It was only in 1846 that the German chemist Heinrich Rose discovered and proved the difference between these two elements. It took another 19 years after this discovery to find an effective method to separate niobium and tantalum.[1] The next period was characterized by a series of scientific findings confirming the difference between niobium and tantalum and it was not until the early 20th century when niobium was used as filaments in incandescent lamp that more attention was given to the chemistry of niobium. The discovery in the early 1920s that niobium improves the strength of steel has led to a renewed stimulus in the search for new and more uses of niobium.[8] It was these commercial applications (see **Chapter 1, Section 1.1**) that prompted more research into the production and processing methods for niobium.

One of the critical steps in the development of new niobium products and their uses is the determination of its purity, as well as the presence of any harmful impurities. A number of different analytical methods can be used to ascertain the quality of the element or compound which include techniques such as spectroscopy, gravimetry etc. In order to develop new methods for the production of niobium and its compounds, it is crucial that sufficient information regarding the currently used methods is collected. In this chapter, a general overview of the research that has been done in the production and the analyses of niobium compounds will be discussed.

2.2 DIGESTION TECHNIQUES

The digestion of niobium and tantalum containing minerals/materials has been a challenging topic to scientists for a long time, mainly due to their strong resistance to chemical oxidation (E^{o}= -0.65 for Nb^{v}/Nb and -0.85 for Ta^{v}/Ta). During the 1856-1925 period flux fusion was the trusted method and different fluxes were tested by different scientists for the digestion of niobium and tantalum minerals. Berzelius and Marignac[25] decomposed the mineral by fusing the ore with potassium hydrogen sulphate in a 3:8 sample to flux ratio. The melt was subsequently dissolved in water producing hydrated $Nb_2O_{5(s)}$ and $Ta_2O_{5(s)}$ which was contaminated with SiO_2, TiO_2, ZrO_2, Fe_2O_3 and W_2O_3. The purification of the Nb_2O_5 and Ta_2O_5 were more involved. Berzelius washed the precipitate with H_2SO_4 + HF to remove the SiO_2, and then added ammonium hydrogen sulphite to remove W_2O_3 and SnO_2. In the next step the Fe_2O_3 was converted to FeS and then dissolved in hot HCl. He managed to remove all other impurities by adding H_2SO_4 and H_2O_2 and then saturating the solution with sulphur dioxide. As an alternative Weiss washed the precipitate with hot HCl to leach the desired products while von John fused the precipitate with NaOH to dissolve SiO_2.[26]

In another method, Sears[27] decomposed the niobium mineral by fusing it with sodium pyrosulphate in a 1:7 sample to flux ratio at 770 ^{o}C and 900 ^{o}C and he then dissolved the melt with H_2SO_4 and HF. His results showed that variations in temperature, flux ratio or time had little influence on the solubility of the mineral. He also demonstrated that concentrated H_2SO_4 is more effective than HF in separating Nb and Ta by dissolving Nb while leaving the Ta undissolved. Sears emphasized that a complete separation can be obtained by heating the sample in the flux mixture to a temperature of 825-875 ^{o}C.

[25] Berzelius, J.J., *Afhand. Nya. Handl.,* 1802. **23**. p180

[26] Weiss, L. and Riedelbauch, R., *Liebig's Ann*. 1907. **355**. p60

[27] Sears, G.W. *J. Amer. Chem. Soc*., 1925. **47**. p922

In 1864 Gibbs[28] decomposed the mineral by fusing it with potassium hydrogen fluoride in a 1:3 sample to flux ratio. The melt was dissolved in hot water and HF. Cooling the solution resulted in the crystallization of potassium oxyfluoroniobate which was then filtered to remove the Nb compound. The solution was subsequently boiled in water producing the earth hydrates (tantalum and niobium hydrates). This method was claimed to be better than potassium hydrosulphate fusion, but Giles emphasized difficulties associated with this process and recommended potassium carbonate as a flux.

Joly[29] decomposed the mineral by fusing it with a mixture of sodium carbonate and sugar charcoal in a 1:5 ratio for 5 to 6 hours. The melt was dissolved in boiling HCl. The undissolved residue was heated in Cl_2 and then reacted further with HCl and finally with water to precipitate mixed earth acids (tantalic and niobic acids). Pennington[30] tried the fusion with borax but poor results were obtained.

In a simplified and possibly more successful method Ekeberg *et al.*, fused the mineral with alkali hydroxides and dissolved the melt in dilute HCl which successfully dissolved all the other impurities leaving Nb_2O_5 and Ta_2O_5 undissolved.[31,32]

The qualitative analysis of the minerals was initially achieved by either the Marignac's, Giles's or Powell and Scheller's tests. Marignac's test involved the crystallization of K_2TaF_7 by the addition of potassium fluoride to the hydrofluoric acid solution of the mineral and the isolation of the tantalum fluoride product. This method was however not very sensitive to small quantities of tantalum. The niobium was

[28] Gibbs, O.W., *Amer. J. Science*., 1864. **37** (2). p355

[29] Joly, A., *Ann. Ecole. Norm.,* 1877. **6** (2). p738

[30] Pennington, M.E., *J. Amer. Chem. Soc.,* 1896. **18**. p40

[31] Mellor, J.W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*. 1947. **IX**. pp840-845.

[32] Wilfred, W., Scott, Sc.D., *Standard Methods of Chemical Analysis 5th ed.,* 1948. **1**. pp332-334

crystallized as K_2NbOF_5 from the same solution after the evaporation of the mixture of solvents.

Giles's method involved the ignition of the precipitate obtained from the mineral digestion with hydrochloric and nitric acids and fusing it with potassium carbonate. The melt was then dissolved with dilute phosphoric acid and heated until a clear solution was obtained. The addition of zinc dust to the hot solution produced a brownish to inky-black colour (depending on the amount of niobium), indicating the presence of niobium while tantalum gave no colouration.

Powell and Scheller's test was based on the fact that oxalotantalic acid solution gives a sulphur-yellow precipitate while oxaloniobic acid solution gives a vermillion precipitate with tannin. The precipitate obtained in the Giles's method was ignited and fused with potassium bisulphate and the melt was dissolved in a hot, saturated ammonium oxalate solution. The titanium free oxalate solution (interferent in this test) was then treated with 0.1 to 0.2 g of tannin in hot water, followed by the dropwise addition of 0.5 N ammonia untill a flocculent precipitate was obtained. A pale to bright yellow precipitate indicated the presence of tantalum while an orange to red indicated the presence of niobium.[32]

Recent studies also demonstrated that extremely harsh conditions such as acid mixtures consisting of HF/HNO_3 and HF/H_2SO_4 are suitable for digesting this kind of materials.[33,34,35,36,37,38] Attempts to accelerate the HF dissolution processes for pure

[33] Qing, C., Shibata, T., Shinotsuka, K., Yoshikawa, M., and Tatsumi, Y., *Frontier research on earth evolution,* 2003. **1**. pp357-362

[34] Conte, R.A., Mermet, J.M., Rodrigues, J.D.A., and Martino, J.L., J*. Anal. Atomic Spectrometry.* 1997. **12**. pp1215-1220

[35] Grebneva, O.N., Kubrakova, I.V., Kudinova, T.F., and Kuz'min, N.M., *Spectrochemica Acta Part B*. 1997. **52**. pp1151-1159

[36] Roy, P. Balaram, V. Bhattacharaya, A. Nasipuri, P., and Satyanarayanan, M., *Research Communications*. *Current science*. 2007.**93**. pp1122-1125

[37] Hall, G. E. M., and Pelchat, J. C., J*. Anal. Atomic Spectrometry.* 1990. **5**. pp339-349

Nb metal and Nb_2O_5 by combining the acid digestion with the microwave technique proved to be very successful with niobium recoveries in the range 95-104%[34] and 95-100%.[35] A decrease in the sample preparation stage to 1 hour was also achieved with this alteration.

Although good results have been obtained[34,35] for the digestion of the niobium and niobium-containing minerals/materials with HF, recent research is focused more on the use of ammonium bifluoride (NH_4HF_2) as the fluoride source in place of the dangerous HF. Research has shown that other fluoride compounds such as NaF, KF and CaF_2 may also be used either alone or combined with NH_4HF_2 in the presence of concentrated sulphuric acid. Results obtained for NH_4HF_2 indicate that dissolution of more than 90% can be achieved with this method.[39]

In an attempt to eliminate volatilization, the subsequent loss of analytes as well as fluorine pollution resulting from digestion using HF and fluoride compounds, the use of concentrated KOH for leaching of low-grade niobium–tantalum ore was proposed by the Institute of Process Engineering, Chinese Academy of Sciences. Experimental results obtained from this research show that the decomposition for low grade niobium-tantalum containing ore is close to 100%.[40] Unfortunately, caustics such as the alkali hydroxides, like hydrofluoric acid, attack the glass nebulizers used in most of the ICP-OES and ICP-MS instruments and destroy them and thus rendering this method unsuitable.[41]

The flux fusion with lithium metaborate/tetraborate and the subsequent digestion with HF mixtures of different compositions achieved 100% decomposition of the beach placers and ferrodiorites containing Ti, Zr, Nb, Hf, Ta, Th, and U.[36] In another study,

[38] Uria, J.E.S., Ortiz, C.G., Garcia, A.M., and Sanz-Medel, A., *Mikrochim. Acta [Wien].* 1987. **2**. pp195-202

[39] United States Patent US 7, 182, 925 B2.

[40] Zhou, H., Yi, D., Zhang, Y., and Zheng, S., *Hydrometallurgy.* 2005. **80**. pp126–131

[41] http://www.ivstandards.com/tech/articles/technical/sample-intro.pdf

Nb_2O_5 was fused with $K_2S_2O_7$ followed by the extraction of Nb with concentrated tartaric acid or oxalic acid. This method ($K_2S_2O_7$ fusion) was found to be successful for the dissolution of pure Nb_2O_5 only and the niobium ore was dissolved with HF.[38] The resulting digestions have been analyzed by an ICP-MS,[33,36,37] ICP-OES,[34,35,38] NAAS,[42] FAAS or GFAAS.[36]

Lately, direct solid sample introduction techniques with the chemical analysis of these minerals and compounds have received greater attention. Techniques such as X-ray fluorescence spectrometry (XRF),[5] laser ablation inductively coupled plasmas mass spectrometry (LA-ICP-MS)[43] and electrothermal atomic absorption spectrometry (ETAAS)[44] were employed to avoid the tedious and time consuming digestion steps as well as the analyte loss and contamination from acid digestion or fusion procedures.

2.3 SPECTROMETRIC TECHNIQUES

2.3.1 Spectrophotometric methods and techniques

The use of spectrophotometric methods in the determination of niobium normally is based on its ability to form coloured complexes with certain ligands such as thiocyanate (SCN^-), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), Bromopyrogallol Red and N-benzoyl-N-phenylhydroxylamine (BPHA).[45] In a study involving the extraction of niobium(V) from sulphuric or hydrochloric acid solutions, (containing an excess of thiocyanate ions with tetraphenylphosphonium (TPP) or tetraphenylarsonium (TPA) chloride) into chloroform, a maximum of 91% and 94%

[42] Dampare, S. B., Nyarko, B. J. B., Osae, S., Akaho, E. H. K., Asiedu, D. K., Serfor-Armah, Y. Nude, P., *Journal of Radioanalytical and Nuclear Chemistry*, 2005. **265** (1). pp53.59

[43] Li, S., Hu, B., and Jiang, Z., *J . Anal. At. Spectrom.* 2004, **19** , pp387 – 391

[44] Huang, D., and Krivan, V., *Fresenius J. Anal Chem*. 2000. **368**. pp227–234

[45] Jarosz, M., and Oszwaldowski, S., *Analytical Sciences*. 1993. **9.** pp285-288

Nb were extracted from the solutions respectively. These results indicate that quantitative extraction (over 99%) of niobium into the chloroform can be achieved only when the chloride ions were in excess. The following reactions for the extraction of niobium are proposed (**Equation 2.1** and **2.2**):[46]

$$[Nb(OH)_2]^{3+} + mCl^- \rightarrow [Nb(OH)_2Cl_4]^- + mH_2O \qquad \textbf{2.1}$$

$$[Nb(OH)_2Cl_4]^- + 2NCS^- \rightarrow [Nb(NCS)_2Cl_4]^- \qquad \textbf{2.2}$$

From Reaction **2.2** it is clear that the first step in the extraction process is the substitution of the hydroxide ions by the thiocyanate. A neutral complex $[(C_6H_5)_4X][Nb(NCS)_2Cl_4]$ is formed in the presence of an excess of TPA or TPP which are then extracted into the chloroform solution and spectrophotometrically determined.[47]

Most of the known spectrophotometric methods used for niobium(V) determination are not very sensitive (linear range: 15 -100 ppm and the lower limit of quantification: 8.4 ppm for Nb-SCN). Even efficient reagents such as thiazolylazo or pyridylazo derivatives such as the red-coloured uranium(VI)-1-(2´-thiazolylazo)-2-naphthol (U(VI)-TAN) complex, which obeys Beer's law over the concentration range 0.4 - 6.4 ppm, do not form sensitive systems with niobium(V). Moreover, the spectrophotometric methods used for niobium determination generally have disadvantages regarding selectivity as well as a rather long time required for full colour development (about 1 h).

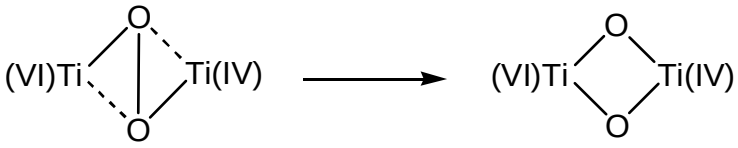
Research indicated that Ti(IV), V(V), Zr(IV), Mo(VI) and Hf(IV) also form complexes with hydrogen peroxide (**Equation 2.3**),[48] in the presence of 5-Br-PADAP thereby interfering with the formation of Nb(V)-H_20_2-5-Br-PADAP complex.[47] The selectivity

[46] Kanzelmeyer, J. H., Rayan, J. and Freund, H., *J. Am. Chem. Soc*. 1956. **78.** pp3020-3023

[47] Tamhina, B. Gojmerac, A. and Bartolin, A., *Croatica Chemica Acta.* 2000. **73**(1). pp57-68

[48] Kuchmii, S.Y., and Kryukov, A.I., *Theoretical and Experimental Chemistry*. 1989. **24** (5). p552.

problem is often overcome by masking the interfering ions with EDTA, cyanite, oxalate or tartrate prior to extraction or the separation of niobium by extraction. The results for the niobium extraction from sulphuric acid solutions with α-benzoin oxime in the presence of a large number of cations (Ti(IV), V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Zr(IV), Mo(VI), Pd(II), Cd(II), Sn(IV), Sb(V), Ta(V), W(VI), Pt(IV), Tl(III), Pb(II) and Bi(III) (100 µg each)) are presented in **Table 2.1**.[45]



2.3

Table 2.1: Spectrophotometric determination of niobium after its extraction from a synthetic mixture of a large number of cations.

Niobium/µg		RSD % (n=7)	Average at 95% Confidence limit
Added	**Found**		
2.5	2.6	5.3	2.6 ± 0.2
10.0	9.9	2.6	9.9 ± 0.3
20.0	19.6	2.1	19.6 ± 0.4

The results in **Table 2.1** clearly indicate that separation of niobium from a large number of possible interfering elements is very successful and can solve the selectivity problem in the spectrophotometric determination of this metal. In the same study, a comparison was made for the determination of niobium in a certified geological material CTA-AC-1 (apatite) with the niobium content indicated as 4.32 ± 1.24 x 10^{-3}% in the presence of a large amount of calcium. In this study the reaction of calcium and fluoride resulted in the formation of an insoluble calcium fluoride precipitate which interfered with the subsequent extraction of niobium with α-benzoin oxime. **Table 2.2** summarizes the results obtained during the niobium determination in CTA-AC-1 (without matrix separation) using the native sample as well in the presence of additional niobium. The results in column 3 of **Table 2.2** clearly indicate some serious interferences from the elements in solution.[47]

Table 2.2: Determination of niobium in CTA-AC-1. [47]

Sample	Niobium/µg		RSD % (n=7)	Average at 95% Confidence limit
	Added	Found		
0.25	-	8.9	5.6	$3.56 \pm 0.18 X10^{-3}$
0.25	6.0	13.6	-	9.9 ± 0.3

2.3.2 Spectrometric methods and techniques such as ICP (OES or MS)

Spectrometric methods such as inductively coupled plasma optical emission and mass spectrometry (ICP-OES, ICP-MS), neutron activation analysis spectrometry (NAAS), and flame or graphite furnace atomic absorption spectrometry (FAAS or GFAAS) have successfully been used on the wet chemical analysis due to their low detection limits (MS – 1-10 parts per trillion (ppt) or lower, OES – 1-10 parts per billion (ppb)), for the different elements. From the literature[10,33-38,40,44,45,49,50,] it is clear that ICP-MS and ICP-OES are the most widely used techniques for the analysis of niobium and niobium-containing compounds due to their wide linear dynamic range (10^5-10^6 orders of magnitude), good precision, rapid and multi-elemental analysis capabilities. The ICP-MS has an advantage of ensuring much lower detection limits than ICP-OES and FAAS. A disadvantage of ICP-MS is that it is expensive, and there are some problems connected with the choice of suitable analyte isotopes and with background-ion overlap interference and in most cases, this results in increase in the intensity of the analyte and poor accuracy.[35,51]

The most serious problems encountered in the ICP spectrometry (both MS and OES) are the spectral interferences (see **Chapter 3 section 3.3.1**) as well as matrix effects

[49] Sermenov, G.A. and Lopatin, S.L., *Russian Journal of Applied Chemistry.* 2001. **77** (6). pp901-906

[50] Song, X., Duan, T., Guo, P., and Chen, H., *Microchemical Journal*. 2006. **84**. pp22–25

[51] Skoog, A.D., Holler, F.J., Nieman, A.T., *Principles of Instrumental Analysis. 5th ed*. 1998. pp12,265-266

from solvents, acids and concomitant elements.[52] Spectral interferences using both ICP-OES and ICP-MS analyses are very challenging in most niobium matrices requiring the matrix separation prior to analysis.[34,35] High concentrations of concomitant elements (the matrix) and especially the easily ionisable elements such as Ca, Na, Al and Li can lead to analyte/s signal depression or enhancement compared to the calibration standards. In addition, the intensities change with the acid identity and concentrations. It was also found that viscous acids like phosphoric and sulphuric acids require more dilution to improve the spraying efficiency. Furthermore, the spectral interferences from S and P would result in an increase of the intensities of the analytes. [53]

Flame atomic absorption spectrometry has however shown a lack of sensitivity for trace elements in the Nb/Ta matrices. The formation of Nb and Ta refractory compounds even in hot flames such as N_2O-C_2H_2 may explain the poor detection limits (0.6 ppm for Ta and 3.1 ppm for Nb) achieved with FAAS compared to that obtained in ICP-OES analysis (0.009 ppm for Nb when the Nb II 309.41 nm line was used).[38] Although GFAAS is more sensitive and gives relatively low detection limits, its use in analyzing niobium matrices has not been much practiced probably due to the limited number of elements that can be measured at a given time.

In a recent study it was demonstrated that neutron activation analysis (NAAS) is a good analytical technique for analyzing columbite-tantalite minerals due to its accuracy, high selectivity, sensitivity and precision. Epithermal instrumental neutron activation (ENAA) is, however, preferred to conventional NAAS regarding the determination of Ta, Nb, Th and U, as it has the inherent capabilities for sensitive and relatively easy determination of these elements.[42]

[52] McHard, J. A., Foulk, S. J., Nikdel, S., Ullman, A. H., Pollard, B. D., Winefordner, J. D. *Anal. Chem.*, 1979, **51** (11), pp1613–1616

The advantages of the technique relative to the classical neutron activation methods are generally given in terms of the "advantage factor" (AF), a quantity obtained from the ratio of the cadmium or boron (thermal neutron filters) between the interfering nuclide and the desired nuclide. The technique is known to enhance the selectivity of those elements with resonance integrals larger than their thermal-neutron cross sections (I_o/σ_o,>l) in the presence of interfering elements which are strongly activated by thermal neutrons, but have no resonance peaks in the epithermal energy region.[53] The high I_o/σ_o ratio of ^{238}U is responsible for its successful determination in silicate rocks at low levels by ENAA.[54]

2.3.3 Solid sample analytical techniques

Several quantitative analysis studies of niobium compounds which used direct solid sample analytical techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), electrothermal atomic absorption spectrometry (ETAAS) and X-ray fluorescence spectrometry (XRF) have been used and were reported as very successful. [43,44] The detection limits for the analysis of niobium pentoxide were in the range 0.014 to 0.118 ppb for ETAAS and 0.001 to 0.234 ppb for LA-ICP-MS. ETAAS has an advantage of using small sample sizes (about 15 mg). Electrothermal vaporization (ETV) techniques were joined to ICP-OES/MS for direct analysis of solid Nb_2O_5 sample, and the detection limits for ETV-ICP-MS determination of Ta, Ti, Cr, W, Ni, Cu and Mn were in the range of 0.013–0.55 ppb. The limitations of this method are i) it requires specially made equipment for the HF which has been used for the slurry preparation and ii) only a few elements, mainly with high volatility can be determined. [43]

[53] Chisela, F., Gawlik, D., Bratter, P., *Journal of Radioanalytical and Nuclear Chemistry, Articles.* 1987. **112** (2). pp293-308

[54] Steinnes, E., Brunfelt, A.O., *Journal of Radioanalytical and Nuclear Chemistry, Articles.* 1985. **89** (1). pp 28 7-288

XRF is a well-established analytical technique for characterization of ores including tantalite ores,[5] but its application to trace element determination in pure metals and oxides requires a trace-matrix separation step owing to the strong matrix effect caused by the high mass absorptions. Furthermore, both LA-ICP-MS and XRF suffer the lack of enough solid standards with the same composition as the sample in quantities that always incorporate the analyte concentration or intensity within the calibration curve, hence, only semi-quantitative analysis is achieved with these techniques.

2.4 CONCLUSION

The discussions in the above paragraphs clearly indicate that a noticeable amount of work has been done on the analysis of niobium and niobium containing materials. However, very little has been done regarding the search for more environmentally-friendly methods to digest these materials. The introduction of microwave digestion in closed vessels in 1985 has improved the digestion procedures for a large number of samples resulting in reproducibility of the procedures and reducing digestion times. However, the potential of microwave as a heat source in the wet analyses of niobium has not been sufficiently explored and is considerably less documented. This leaves the possibility to investigate the new or alternative methods of digestion and analysis of niobium minerals and other niobium containing material.

3 SELECTION OF ANALYTICAL TECHNIQUES

3.1 INTRODUCTION

An in-depth literature study on the possible analytical techniques for the analysis of niobium and its associated impurities was performed prior to the commencement of the experimental work. The advantages and disadvantages of the analytical techniques were weighed against each other before the final method was selected for use during this study (see **Chapter 2, section 2.2**).

The preferred or most ideal digestion method for the high purity niobium metal, niobium pentafluoride, niobium pentoxide and the three mineral samples is the one that is capable of completely dissolving the sample with no or minimal volatilization or adsorption losses and side contamination of the sample from the reagents. Additionally, the method should be rapid and not harmful to the analyst or to the equipment used for digestion and analysis of the samples.

The spectrometric methods were chosen on the bases of their: i) detection limits with the instrument offering the lowest detection limits being the most preferred, ii) capabilities to simultaneously identify and quantify all the elements in the sample matrix and iii) ability to withstand any interference problems. However, the choice of techniques was also limited by its availability for use in this study. In this chapter the analytical methods that are most likely to be used for this study are discussed in detail.

3.2 DIGESTION TECHNIQUES

3.2.1 Flux fusions

A large number of inorganic samples such as soils, sludges, silicates and some inorganic materials such as metal oxides are highly insoluble and cannot even be dissolved with strong mineral acids. Fusions with an acidic or basic flux to produce the molten salt at high temperature are employed to render them soluble.[55,56] The flux converts the chemical components in the sample into a form that is soluble in acids, bases or water due to a combination of oxidation reaction and acid /base dissolutions which takes place between the flux and inorganic sample at these high temperatures. For example, sodium carbonate reacts with the metal silicates and converts them into sodium silicates that are soluble in hydrochloric acid as indicated in **Equations 3.1** and **3.2**.

$$MSiO_3 + Na_2CO_3 \xrightarrow[10 \text{ to } 30 \text{ minutes}]{900 \text{ to } 1000\ ^oC} Na_2SiO_3 + MCO_3 \qquad \textbf{3.1}$$

$$Na_2SiO_3 + MCO_3 + 4HCl + xH_2O \longrightarrow H_2SiO_3.xH_2O + MCl_2 + CO_2 + H_2O + 2NaCl \qquad \textbf{3.2}$$

Where M = metal

This dissolution process involves the mixing of the sample with an appropriate flux (sometimes ten times in excess) and heating the mixture at a temperature higher than the melting point of the flux to produce a clear melt.[18] Melting during the heating process of a solid results in an inherent loss of crystal cohesion and an increase in

[55] Christian,G.D., *Analytical Chemistry 5th ed*., 1994. p670

[56] Bassette, J., Denney, R.C., Jeffery, G.H., Mendham, J., *Vogel's Textbook of Quantitative Inorganic Analysis. 4th ed.,* 1978. pp105-106

reactivity of the lattice components. This is due to the breaking down of the regular structural, stabilizing, and bonding forces together with the enhancement of stereochemical freedom that permits a wider range of chemical interactions in the melt.[57] In this way, the molten-salt (flux salt), is used as a solvent or reaction species for the chemical reaction. Since the diffusion rates of the components in molten-salts are much higher than those in a solid-state reaction,[58] high reaction kinetics (either chemical or electrochemical reactions) are observed in molten salts.[59] **Table 3.1** categorizes some commonly used fluxes and the sample type with which a particular flux is active.

The clear melt from this reaction must then be cooled to room temperature before dissolving it in dilute acid or water. The acid or acid mixture used to dissolve the melt depends on the analyte/s under investigation. Niobium and tantalum may precipitate even in the presence of more concentrated acids causing a co-precipitation of other analytes. In order to avoid this precipitation, concentrated sulphuric acid, tartaric acid, ammonium oxalate, hydrogen peroxide or hydrofluoric acid can be used. [57]

[57] http://www.geochem.sgs.com/analysis_of_tantalum_bearing_materials_geochem

[58] http://csep10.phys.utk.edu/astr162/lect/light/spectrum.html

[59] http://hyperphysics.phy-astr.gsu.edu/hbase/ems2.html#c4

Table 3.1: The most commonly used fluxes

Flux	***Sample type Decomposed***	***Notes***
Sodium Carbonate	Silicates, refractory oxides, quartz, insoluble phosphates and sulphates.	Na_2CO_3 generally is used because of its lower melting point. K_2CO_3 is preferred for Nb and Ta analyses because the resulting potassium salts are soluble.
Sodium pyrosulphate or potassium pyrosulphate	Basic materials, insoluble oxides and oxide-containing samples.	
Sodium hydroxide or potassium hydroxide	Acidic materials, silicates, oxides, phosphates, and fluorides.	NaOH is used because of its low melting point, rapid, melts dissolve in water and losses to volatility are reduced.
Lithium metaborate	Acidic oxides such as silica and TiO_2 and nearly all minerals.	
Lithium tetraborate	Basic oxides and some resistant silicates.	
Sodium peroxide	Sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals.	

Fusion methods can be used on a wide range of samples and can for example be used to substitute the environmentally harmful hydrofluoric acid. [58] However, for a fusion to be successful the sample must contain chemically bound oxygen as in oxides, carbonates, and silicates. Samples with no chemically bound oxygen, such as sulfides, metals and organics, must be oxidized before the fusion process. Additionally, fusion techniques result in the build up of impurities and side contaminations. Other disadvantages of fusion include longer sample preparation times and possible losses of analytes due to volatilization. [57]

3.2.2 Microwave digestion

Microwaves are defined as electromagnetic radiation with frequency between 300 MHz and 300 GHz and wavelength from 0.1 cm to 100 cm and are situated between the infrared and radio spectra in electromagnetic wave spectrum (**Figure 3.1**).

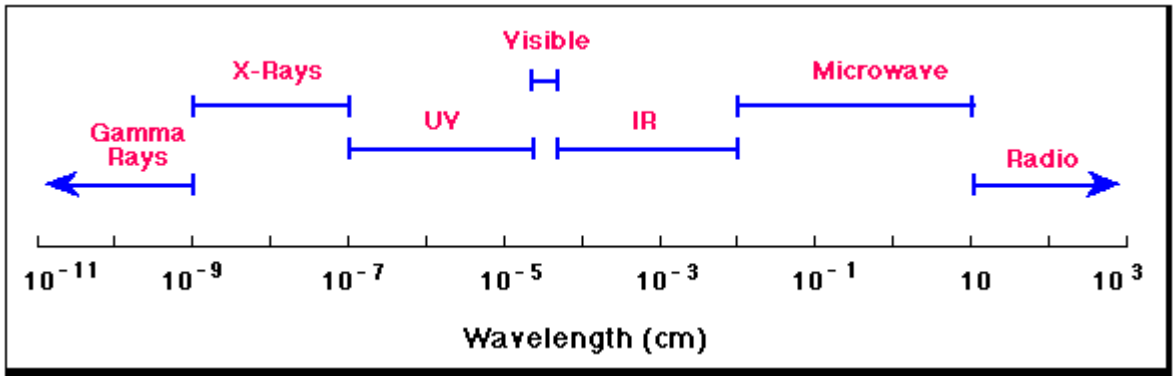


Figure 3.1: Diagram of wavelength of electromagnetic spectrum[59]

The microwave radiation is produced by a magnetron (**Figure 3.2**) before being channelled into a microwave cavity in which the microwaves are distributed by a combination of a mode stirrer, a circulator and a turntable in order to ensure the homogeneous heating of the sample. [60]

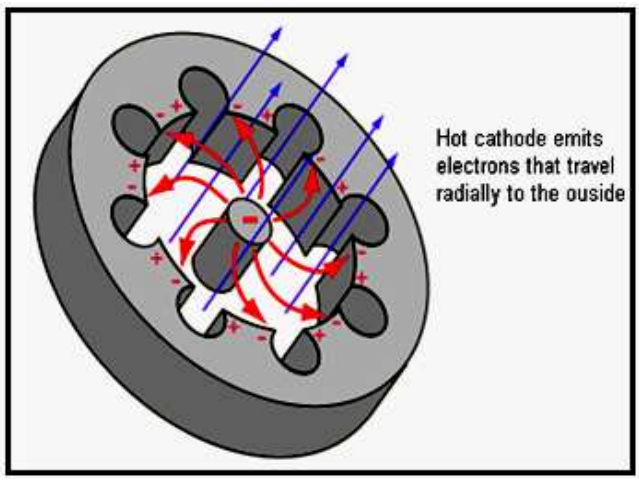


Figure 3.2: Microwave magnetron

The unique combination of the rapid heating ability of microwave energy in closed digestion vessels allows high temperatures to be attained, using minor quantities of simple reagent mixtures in a limited area, and ensures no or little contamination of the sample.[35] Some of the disadvantages associated with the use the microwave technique are restraints in relation to small sample sizes that are digested per run and the vessel cleaning time which can prolong the sample preparation duration for hours.[60] Further more, lack of knowledge of the chemical composition of the sample can make a choice of the solvent (acid) difficult and vessel explosions may result. For example, perchloric and nitric acid can react explosively with organic substance resulting in the loss of the sample as well as damaging the system.[61,62]

3.2.3 Hydrofluoric acid digestion

Hydrofluoric acid is one of the most commonly used acids in digestion methods due to its ability to dissolve silica and other silicates (**see Equation 3.3**). [57]

$$SiO_{2(s)} + 6HF_{(aq)} \longrightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)} \qquad \textbf{3.3}$$

The resulting fluorosilicic acid dissociates into gaseous silicon tetrafluoride and hydrogen fluoride upon heating as indicated in **Equation 3.4**.

$$H_2SiF_{6(aq)} \xrightarrow[\Delta]{} SiF_{4(g)} + 2HF_{(g)} \qquad \textbf{3.4}$$

[60] http://www.milestonesci.com/digres-lit.php

[61] http//www.soton.ac.uk.htm (working with concentrated acids)

[62] http//www.sampleprep/duq/edu.dir/mwavechap16/mwave.htm (Chemical)

Hydrofluoric acid is also used due to its complexing properties that are of great importance in the separation of Nb and Ta as it was indicated in **Chapter 1** (see **Figure 1.8**).[1]

The main drawbacks of HF digestion are the non-biodegradable and dangerous nature of HF to the environment, the large number of operations, and the need for corrosion-resistant equipment. Exposure of the eyes to HF may result in blindness or permanent eye damage. Skin exposure to high concentrated HF (approximately 50% or greater) results in serious and painful destruction of the soft tissue and bone decalcification and also to death.[63] If released into the environment in sufficient concentrations, the fluoride ions can be washed into the water bodies and become toxic to the surrounding plants and animals. Airborne HF in a vapour cloud could burn both plant and animal tissue (inhaling HF vapours can seriously damage the lungs).[64]

3.3 SPECTROMETRIC TECHNIQUES

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

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) is an analytical technique that uses the plasma (6000 to 10000 K) to excite the atoms, elemental ions and molecules in the nebulised spray containing the analyte sample. ICP-OES measurement relies on the emission of a characteristic light at specific wavelength from excited atoms and/or ions which are all characteristic and unique to each element.[51]

[63] http://www.epa.gov/oem/docs/chem/hydro.pdf

[64] http://www.fap.pdx.edu/safety/hydrofluoric_acid/

The basic set up of the torch of an ICP-OES consists of three concentric tubes, namely the outer loop, intermediate loop, and inner loop which collectively make up the torch of the ICP. The torch is surrounded by a water-cooled induction coil (see **Figure 3.3**) of a radio frequency (RF) generator. The coil is energized by an RF generator and creates a changing magnetic-field in the flowing gas in the coil and this induces a circulating eddy current in the electrically conductive gas.

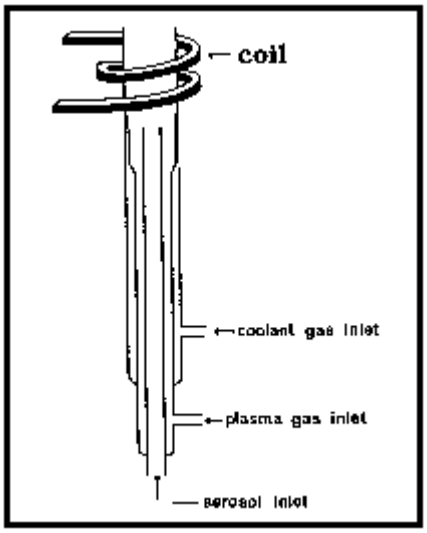


Figure 3.3: Diagram of an ICP-OES torch[65]

The possibility of short-circuiting as well as meltdown from the high temperature plasma is prevented by insulating the instrument with a constant flow of gasses through the system namely the outer gas, intermediate gas, and inner or carrier gas. The plasma is initiated by a spark from a Tesla coil. The outer gas which is typically argon or nitrogen is ionized by the high frequency and power of the RF generator (**Equation 3.5**) and their associated electrons interact with the fluctuating magnetic field produced through induction. The high plasma temperature is produced by friction between the ions and the electrons as they move in the closed annular paths.

[65] http://www.cee.vt.edu/ewr/environmental/teach/smprimer/icp/icp.html

The ions serve in maintaining the plasma, stabilizing the position of the plasma and thermally isolating the plasma from the outer tube.

$$Ar + Energy \longrightarrow Ar^{+} + e^{-} \qquad \textbf{3.5}$$

The sample introduction system consists of a peristaltic pump connected to a nebuliser (see **Figure 3.4**). 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. In the spray chamber three processes dominate, namely collisions with the walls, droplet-droplet collisions and evaporation from the droplets and the walls. The droplet collisions are a result of a low sample uptake from the spray chamber to the plasma. Evaporation from the walls may cause matrix effects if the walls are not conditioned with the sample prior to the analysis.[66]

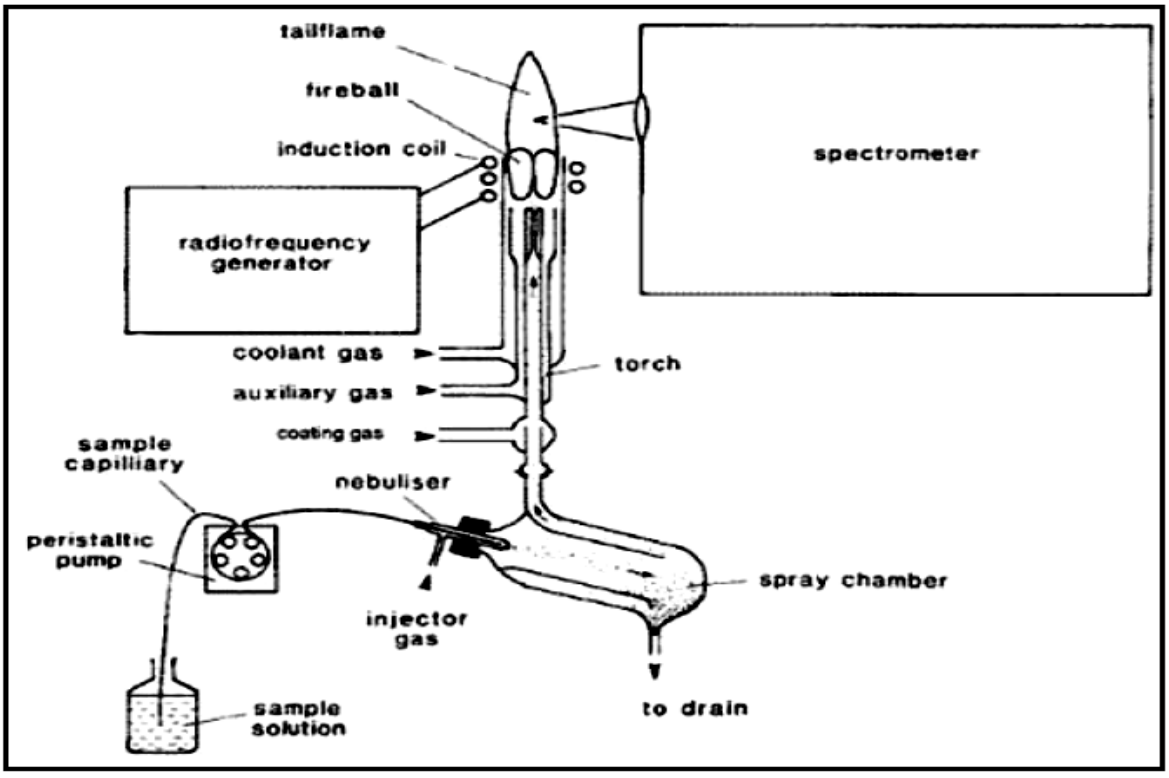


Figure 3.4: Schematic representation of the ICP-OES components

[66] http://www.risoe.dtu.dk/rispubl/NUK/nukpdf/ris-r-1548.pdf

Argon is commonly used for both the intermediate gas and as the carrier gas, as such it carries the sample into the plasma. All elements become thermally excited in the extremely high temperature plasma and emit light at their characteristic wavelengths. This light is collected by the spectrometer and passes through a diffraction grating that serves to resolve the light into a spectrum of its constituent wavelengths. Within the spectrometer, this diffracted light is then collected by a monochromator and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with calibration standards.[51]

The ICP-OES has several advantages that make it a very convenient instrumental technique for elemental analysis in many matrices. These include a wide linear dynamic range (10^5-10^6 orders of magnitude), low detection limits (1-10 ppb range), easy and rapid qualitative analysis, simultaneous multi-element analysis (more than 70 elements including refractories and some non-metals), high sensitivity, good precision (RSD values: 0.5 - 2%) and minimal chemical interference due to the high temperature used. Furthermore, line rich spectra permit the use of several spectral lines for each element to be determined.[67]

The major disadvantage of using ICP spectrometry is that the sample to be analysed must be in solution, preferably in an aqueous solution. Although the ICP-OES does not suffer from chemical interferences, it is affected by the matrix effects and spectral interferences due to the line rich spectra of most elements. The matrix effects become serious at high concentrations of the concomitant elements. Although line intensity enhancements are sometimes observed, matrix effects usually cause the reduction in the analyte signal through the absorption of the light emitted by the analyte. The matrix effects can be minimized by the purification of the sample prior to analysis to remove the offending species from the analyte solution or by using dilute solutions. Another way of reducing the matrix effects is matching the matrix in the

[67] http://aix-lin.upol.cz/~milde/APAS-Comparison.pdf

blank and standard solutions with that in the sample solution or using the standard addition method.

Spectral interferences observed in ICP spectrometry can take several forms, but the most common problem observed is background and line overlap or wing overlap. Sometimes the entire background intensity is elevated (**Figure 3.5**) in the region where the analyte emission occurs. This type of interference can be caused by a large concentration of another element in the solution. The correction for this type of background radiation is typically made by first selecting background points or regions and then a correction mode (**see Figure 3.6**).

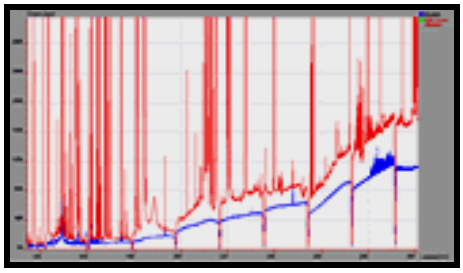


Figure 3.5: Spectrum of 6% Ca solution vs. nitric acid blank

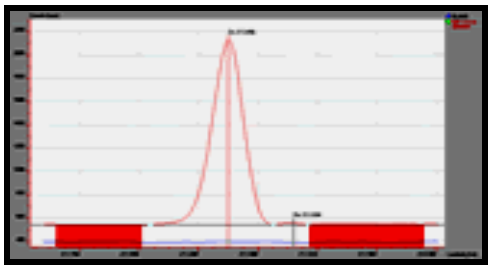


Figure 3.6: Flat background correction

Another form of background spectral interference is that in which an analyte peak occur in a sloping background spectrum. The correction in this case is achieved by selecting the background points at equal distance from the peak center in order to make an accurate correction (**Figure 3.7**). The background intensities are then taken at set wavelengths, averaged and subtracted from the analyte peak intensity. Curved background is encountered when the analytical peak is near a high intensity peak, affecting the background on one side of the analyte peak more than the other. In this case the correction is made by selecting the background points on the affected side of the analyte peak (**Figure 3.8**).[68]

[68] http://www.inorganicventures.com/tech/reliability/part15.asp

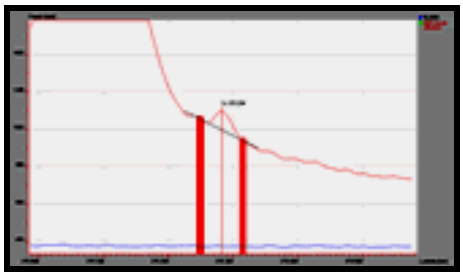


Figure 3.7: Sloping background correction

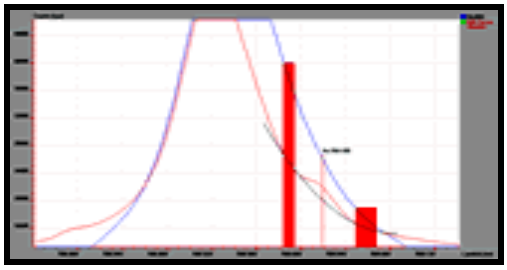


Figure 3.8: Curved background correction

A kind of interferences that is observed and which is difficult to correct for in ICP-OES is the spectral overlap whereby another element present in the solution emits at the same wavelength as the analyte (**Figure 3.9**) (or so close to the wavelength of the analyte (Figure **3.10**) resulting in a wing overlap of the analyte spectrum). This type of a problem is best corrected by choosing another wavelength for the analyte.

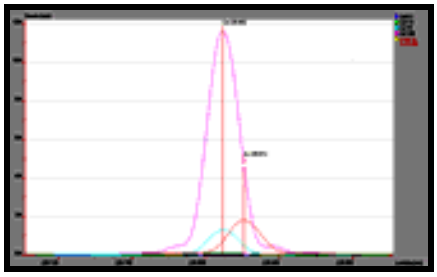


Figure 3.9: Overlapping spectra

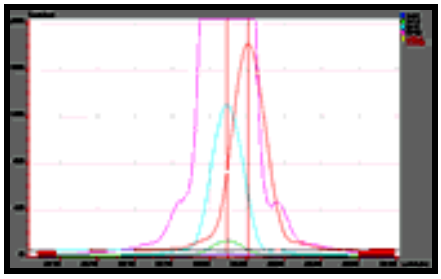


Figure 3.10: Wing overlapping of analyte spectrum

3.3.2 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry technique is based on the fact that ground state metals absorb light at specific wavelengths. Like an ICP-OES, AAS requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 ^{o}C depending on oxidant/fuel mixture and the metal ions in a solution are converted to their atomic state by the flame.

During the combustion, atoms of the element in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths. [68]

A cathode lamp (**Figure 3.11**), made from the element which is to be analysed, is a stable light source which is necessary to emit the sharp characteristic spectrum of the element to be determined. A different cathode lamp is needed for each element, although there are some lamps that can be used to determine three or four different elements if the cathode contains all of them. Each time a lamp is changed, proper alignment is needed in order to get as much light as possible through the flame, where the analyte is being atomized, and into the monochromator.

Figure 3.11: A Hollow cathode lamp for Nb[69]

Atomic absorption spectroscopy has several advantages namely high specificity, low detection limits, high sensitivity, good precision (RSD values: FAAS 0.3-1%, GFAAS 1-1.5%), easy to use, and possible interferences and methods of their elimination are

[69] http://www.labhut.com/products/lamps/hollow_cathode/lamps.php?e=Nb

well documented. Unlike an ICP-OES and XRF, simultaneous elemental analysis is impossible and the qualitative analysis is impractical with AAS. One element is determined in a series of samples and the instrumental parameters are optimized for the next element and the series is repeated. In addition, AAS has a disadvantage in that a dangerous mixture of gases is often used. Another disadvantage is that the low temperature of the flame (compared to ICP) is insufficient to completely atomize the highly refractory elements such as oxides and this can lead to low intensities of such elements. [68]

3.3.3 X-Ray Fluorescence Spectrometry (XRF)

X-ray fluorescence spectroscopy is a method based on measuring the X-rays emitted from the elements in a sample upon irradiation with higher-energy X-rays (either from an X-ray tube or radioactive source). The X-rays in the equipment are produce by the electrical heating of the tungsten filament with a low voltage power supply in an evacuated X-ray tube. The electrons produced from the filament are accelerated across the vacuum to the anode, which is at ground state, and bombard it with a high energy. The produced X-rays escape the tube through a beryllium window. Upon interaction with the sample atoms, an inner shell electron of the atom is ejected by an incident photon in the X-ray region[70] causing the higher-energy outer-shell electrons to give up their potential energy by filling the resulting holes and releasing energy in the form of X-rays[51] as indicated in **Figure 3.12**.[71]

[70] Jenkins, R., *X-Ray Fluorescence Spectrometry*. 1988. pp465-487

[71] http://www.horiba.com/scientific/products/x-ray-fluorescence-analysis/resource/xrf-tutorial/x-ray-fluorescence-the-basic-process/

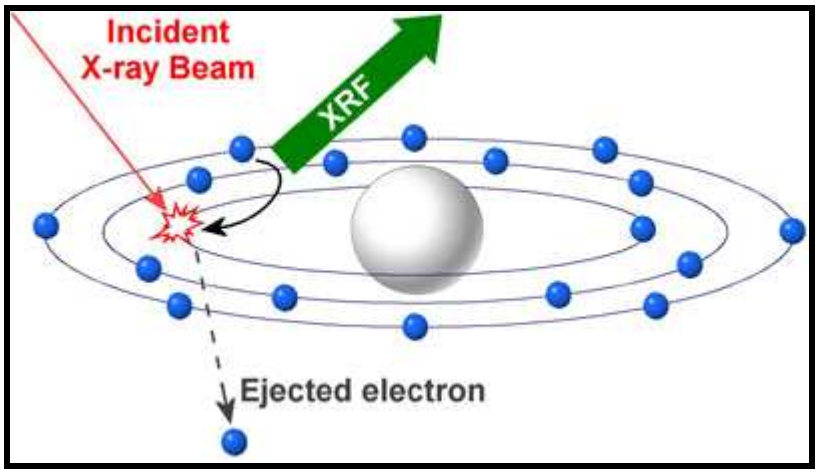


Figure 3.12: X-ray fluorescence

The energy difference between the shells appears as an X-ray emitted by the atom. The energy (or wavelength) of the X-rays is different for each element (qualitative analysis) and the number of X-rays of a certain element is proportional to its concentration (quantitative analysis). However, the number of X-rays entering and leaving the sample is also affected by the physical properties of the sample such as its ability to absorb the X-rays. The heavier elements such as lead absorb X-rays more than the lighter elements like aluminium and the secondary X-rays emitted by a heavier element are sufficiently energetic to stimulate additional secondary emission from a lighter element. The latter can lead to enhancement of the intensity and hence problems with the quantitative analysis of a sample.

The absorption problem is usually corrected by including the mass absorption coefficient (μ_M) in the direct proportional relationship between the intensity (number of X-rays) and the concentration as indicated in **Equation 3.6**.

$$C_i = \frac{I}{\mu_i} \qquad \textbf{3.6}$$

Where I is the intensity (counts/100s), C_i the concentration ($\mu g/m^3$) and μ_i is the sensitivity ($\mu g/cm^2$). The enhancement effects can also be modeled, and corrections can be made provided that the full matrix composition can be deduced. [73]

Compared to other spectrometric methods, such as AAS, ICPS and NAAS, XRF has advantages of being non-destructive, multi-elemental, fast and requiring less sample preparation. **Figure 3.13** summarizes the steps involved during the sample preparation process for the XRF analysis of the pressed pellets. A main disadvantage of the XRF is that analyses are restricted to elements heavier than fluorine.[68] Furthermore, the accuracy of analysis depends strongly on the homogeneity of the particles of the analyte and impurities. These requirements cannot always be fulfilled especially when the amount of sample is very small (<10%). [35]

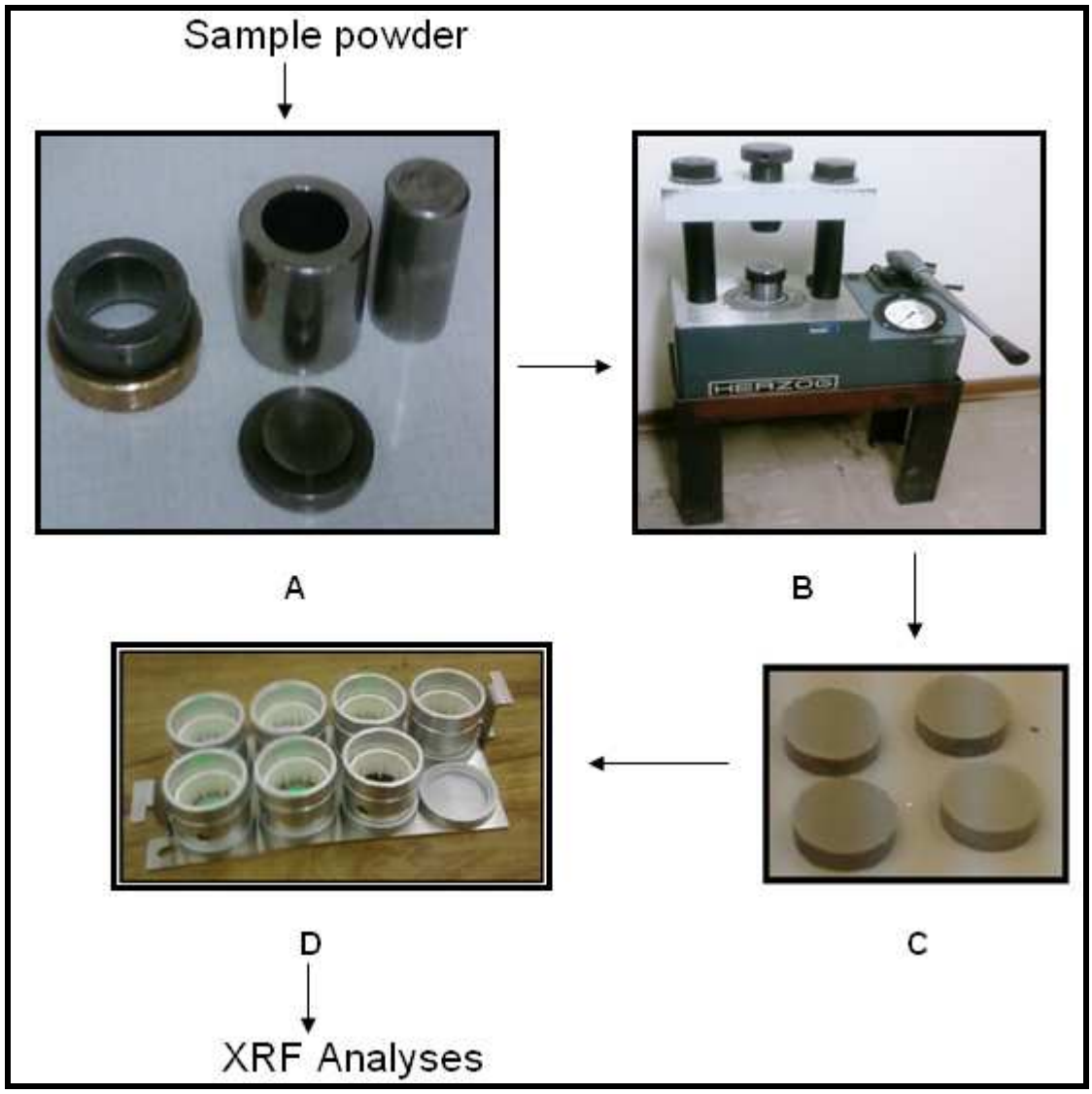


Figure 3.13: Series of steps involved in sample preparation for XRF analysis

A = Sample poured in the dies
B = Pressing instrument
C = Pressed pellets
D = Sample holders

3.3.4 X-Ray Diffraction Spectroscopy (XRD)

The X-ray diffraction is a result of scattering of X-rays as they move through a crystalline material. When an X-ray beam strikes a crystal surface at an angle θ, a portion of this beam is scattered by the layer of atoms at the surface and the

unscattered portion penetrates to the second layer where further scattering takes place and the process continues to the inner layers. [68] The fundamental equation of XRD that relates the scattering angle (2θ), the wavelength of the radiation (λ) and the spacing of the diffracting planes in the material (*d*) is that given by Bragg's law (**Equation 3.7**):[73]

$$\mathbf{n}\lambda = 2d\sin\theta \qquad \textbf{3.7}$$

The XRD shares with XRF the advantages of easy sample preparation procedures and being non-destructive.[74] The sample preparation for the XRD analysis involves pouring a powdered sample into a sample holder shown in **Figure 3.14** and making the surface flat and smooth with a smooth object such as glass slide. Additionally, X-ray powder diffraction is unique in that it is the only analytical technique capable of providing both qualitative and quantitative information about the compounds present in the solid sample without the use of the standard calibration curve. The qualitative analysis is based on the fact that an X-ray diffraction pattern is unique for each crystalline substance and a positive identification of an unknown sample can be made by matching its diffraction pattern with the standard samples. The quantitative analysis is accomplished by measuring the intensity of the diffraction lines and then comparing them with the standards. [68] The technique is mostly used for vitamins, mineralogical, steroids and antibiotics analyses.

Figure 3.14: Sample holder for XRD analysis[72]

The disadvantages of XRD are that a positive identification becomes complex if the sample contains mixtures of crystalline compounds such as in geological samples.

3.3.5 UV-VIS Spectrophotometric Methods

Spectrophotometric methods are based on the measurement of the amount of light transmitted or absorbed by the sample contained in a transparent cell of path length l (cm). According to Beer's law (**Equation 3.8**), the amount of light absorbed or transmitted is directly proportional to the concentration of the analyte. [55,68]

$$A = -\log T = \log \frac{P_0}{P} = \in lc \qquad \textbf{3.8}$$

Where A = absorbance, T = transmittance, P_0 = power of incident radiation, P = power of transmitted radiation, $\in$ = molar extinction coefficient, l = is the path length (cell length) and *c* = concentration of the analyte.

[72] http://microlab.berkeley.edu/labmanual/chap8/8.44.html

The spectrophotometric instruments such as UV/VIS have an advantage of being very easy to operate. UV/VIS spectroscopy shares with the AAS methods the same disadvantages of analyzing one element at a time and suffering from possible chemical interferences. However, different from other spectrometric methods, spectrophotometry has a much shorter linear range. Additionally, it is difficult to synthesize the coloured complexes required for the analysis by this method from the solution of mineral ores due to the harsh conditions (such highly concentrated acids) used to dissolve the samples. Other elements present in the solution may also produce the coloured complexes with the reagent used to complex the analyte and this can lead to false readings. Furthermore, the scattering of radiation by the molecules in the solution can result in disobedience of the Beer's law.

3.4 CONCLUSION

In this study, the ICP-OES method was chosen for the analysis of all the niobium samples. X-ray fluorescence was chosen for comparison of the ICP-OES results of the mineral ore analysis. The mineralogical identification of the minerals was accomplished by XRD analysis.

From the different digestion techniques discussed, it was decided to investigate the microwave-assisted acid digestion with mineral acids other than hydrofluoric acid. It was also decided that the use of perchloric acid should be avoided due to the potential for explosions that may result during the microwave digestion reactions which could lead to destruction of the microwave system. The effectiveness of the different fluxes on niobium oxide and mineral ore digestion were also investigated.

4 SAMPLE PREPARATION METHODS FOR NIOBIUM MINERALS, NIOBIUM AND ITS COMPOUNDS

4.1 INTRODUCTION

The purpose of sample preparation is to convert the original sample into a form that is compatible with the equipment that is being used for laboratory analysis. Usually the sample preparation is considered successful when the sample is in one homogeneous phase, such as a solution or a homogeneous powder.[84] When the analytical method requires dissolution of the sample, sample preparation is the analysis step with the greatest effect on the uncertainty of the final results.[85] An effective sample digestion method is one that completely decomposes the sample matrix, which releases and dissolves all the elements in the sample and allow for the quantitative analysis of these compounds.[86] Factors such as contamination from the atmosphere, apparatus and reagents as well as losses caused by volatilization or incomplete transfers of the sample between the containers can greatly affect the quality of the results and must be seriously considered in any analytical procedure.

The various compositions of geological and metallurgical samples require a variety of procedures to digest them. Dissolution method development involves the selection of parameters that best exploit the chemistry of the sample matrix and the dissolution-enhancing conditions of the sample and reagents. By selecting the appropriate parameters such as digestion vessels, acid mixtures, microwave power and digestion time for example, can be useful in the development of successful methods for the

[84] Knapp, G., *Trends Analyt. Chem.,*1984. **3**. p182

[85] Filgueiras, A. V.; Lavilla, J.; Bendicho, C., *J. Environ. Monitor*., 2002. **4** (6). pp823-857

[86] Rönkkömäki, H., Pöykiö, R., Nurmesniemi, H., Popov, K., Merisalu, E., Tuomi, T., Välimäki, I., *International Journal of Environmental Science and Technology*., 2008. **5** (4). pp485-494

dissolution of metals and minerals, for example by microwave assisted acid digestion and other methods.[61]

In order to achieve a complete analysis of niobium and niobium containing compounds and minerals using ICP-OES, samples were treated with various reagents under different conditions to determine the optimum conditions for effective dissolution of each sample. **Table 4.1** summarises the dissolution methods that were investigated in this study. The success of each digestion technique was evaluated firstly by visual inspection of the dissolution or disappearance of the solid sample and secondly by the extent of dissolution that was quantitatively determined as an analyte percentage recovery from ICP-OES analysis which will be discussed in **Chapter 5**.

Table 4.1: The dissolution methods for selected Nb containing samples

Sample identity	Method of dissolution tested		
	Acid dissolution	Microwave-assisted dissolution	Fusion dissolution
Nb_2O_5	Yes	Yes	Yes
NbF_5	Yes	Yes	No
Nb	Yes	Yes	No
Tantalite A	No	Yes	Yes
Tantalite B	No	Yes	Yes
Sample 1	No	Yes	Yes

4.2 SAMPLE PREPARATION EQUIPMENT AND REAGENTS

An Anton Paar Perkin-Elmer MULTIWAVE 3000 microwave reaction system equipped with an 8SXF100 rotor and eight polytetrafluoroethylene (PTFE) reaction vessels was used for the acid dissolution of samples. Flux fusions were performed in

a high temperature oven supplied by Labequip. Grade B volumetric flasks and glassware bought from Merck were used in this study.

The mineral samples were ground to a fine powder (see **Figure 4.2** for original particle sizes) of less than 12 µm (see **Section 4.3.9**) by means of a vibration grinding mill in a steel milling vessel at the Geology department at the University of the Free State. Sample holders shown in **Figure 3.14** were used to transfer the sample to the XRD instrument for analyses (See **Chapter 5, Section 5.2.3**).

Plastic bottles (tablet containers) were used for weighing and mixing the samples and binder material and/or silica. A vibrating flask shaker was used for homogenous mixing of samples in the bottles. Dies and a pressing instrument were used to produce the pellets (see **Figure 3.13**). The pellets were presented to the XRF instrument (see **Chapter 5, Section 5.2.3**) using sample holders shown in **Figure 3.13**.

The high purity niobium foil (99.8%, 0.127 mm thick), niobium (V) oxide powder (99.99%) and niobium (V) fluoride powder (98%) were bought from Sigma-Aldrich. Three niobium containing minerals, Tantalite A (Naquissupa, Mozambique), Tantalite B (Naquissupa, Mozambique) and Sample 1 were supplied by the South African Nuclear Energy Corporation Limited (Necsa).

The minerals were found to contain some traces of radioactive materials. The respective mineral samples as well as the U and Th calibration samples were stored in closed containers, wrapped in sheets of lead foil and kept locked in cabinets to prevent any unauthorized access. The cabinets were placed approximately 5 m from the working area in the laboratory to reduce the radiation dose. The time set for the analyses of these minerals was a month to avoid a long exposure to the radiation from the radioactive samples. Disposable gloves were used when handling the chemicals to avoid accidental ingestion and measurements were made in the fume

hood to avoid inhalation of the mineral samples' dust. All the minerals, uranium and thorium waste solutions were kept in labelled polyethylene bottles.

All the acids (95-98% sulphuric acid A.C.S. reagent bought from Sigma-Aldrich, 32% hydrochloric acid, 65% nitric acid and 85% orthophosphoric acid bought from Merck) used in this study were of analytical grade. Lithium tetraborate was bought from Johnson Matthey Materials Technology, lithium metaborate (98+%) A.C.S. reagent was bought from Sigma-Aldirch and potassium pyrosulphate and sodium hydroxide were bought from Merck.

4.3 DISSOLUTION PROCEDURES FOR HIGH PURITY Nb SAMPLES

The combination of analytical processes and samples which were used in this study are shown in the flow chart (**Figure 4.1**) and they can be classified into nine categories namely i) particle size reduction and homogenization of ore samples, ii) mineralogical identification of the mineral ores by XRD, iii) determination of major and trace elements in minerals by XRF, iv) acid assisted microwave digestion of mineral for ICP-OES analysis, v) flux fusion digestion of mineral for ICP-OES analysis, vi) flux fusion digestion of Nb_2O_5 for ICP-OES analysis, vii) acid assisted microwave digestion of Nb_2O_5 for ICP-OES analysis, viii) acid assisted microwave digestion of Nb for ICP-OES analysis and ix) acid assisted microwave digestion of NbF_5 for ICP-OES analysis.

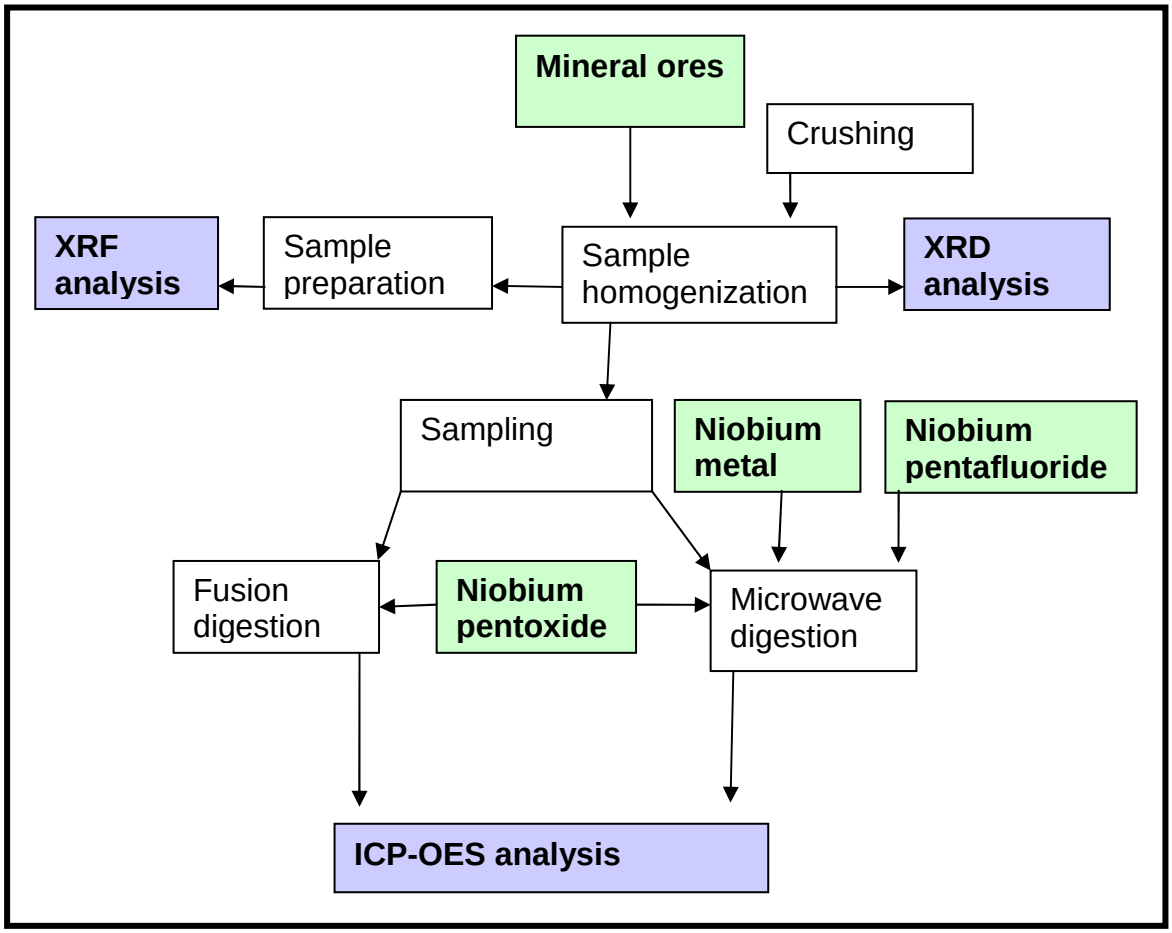


Figure 4.1: Flow chart indicating the different steps followed in the dissolution and quantification of the different samples.

4.3.1 Acid dissolution of high purity Nb_2O_5

Samples of approximately 0.1 g of Nb_2O_5 were accurately weighed to 0.1 mg in five 100 ml beakers. To these were added 20.00 ml of the different acids namely HCl, HNO_3, H_2SO_4, H_3PO_4 and aqua regia. The mixtures were boiled for 1 hour on a hot plate. Visual inspection clearly indicated that not all the sample was dissolved. The remaining solid was removed by filtration while the solution was quantitatively transferred to a 100.00 ml volumetric flask which was then filled to the mark with distilled water. Ten millilitres of this solution was transferred to another 100.00 ml

volumetric flask and diluted to the mark with distilled water for ICP-OES analysis. The ICP-OES results are given in **Table 5.4**.

4.3.2 General microwave-assisted acid dissolution procedure

The polytetrafluorethylene (PTFE) reaction vessels used for this digestion were cleaned by steaming the vessels with 8 ml of 55% nitric acid in microwave-heated sealed vessels for 15 minutes followed by rinsing several times with double distilled water and drying of the vessels before use. Niobium samples accurately weighed (to 0.1 mg) in vials were quantitatively transferred into each pre-cleaned vessel and 10.00 ml analytical grade acids were pipetted into each reacting vessel. The vessels were then placed into the ceramic jackets and placed inside a rotor of the microwave digestion system, sealed, tightened and finally taken to the microwave oven. The microwave parameters shown in **Table 4.2** were kept constant for all the digestions of the niobium samples varying only the heating period where necessary.

Table 4.2: Microwave operating conditions used for the acid assisted digestion

Power	1200 W
Pressure	60 bar (maximum)
Temperature	280 ^{o}C (maximum)
Acid volume	10 ml
Heating period	Varying

4.3.3 Microwave-assisted acid dissolution of Nb_2O_5

4.3.3.1 Determination of the effect of different acids

Aliquots of approximately 0.15 g of Nb_2O_5 powder were accurately weighed (to 0.1 mg) into the dry glass vials and quantitatively transferred into a PTFE vessel of the microwave. Ten-millilitres of concentrated nitric, aqua regia, hydrochloric, sulphuric

and ortho-phosphoric acids were added to the vessels. The samples were digested for 30 minutes in the microwave system under the conditions in **Table 4.2**.

After the 30 minutes digestion some of the solid sample remained undissolved in the vessels containing HCl, HNO_3 and aqua regia solutions. The solid was removed by filtration into a 100.00 ml volumetric flask and the vessels were rinsed four times with distilled water to quantitatively transfer the contents into the volumetric flasks. The solutions were then filled to the mark with distilled water. Visual inspection indicated that in H_2SO_4 and H_3PO_4 solutions no solid remained after this digestion step. The contents were quantitatively transferred to the 100.00 ml volumetric flasks and filled to the mark with distilled water. The solutions were allowed to stand overnight and the ICP-OES measurements were made the following day. **Table 5.5** summarises the results obtained by ICP-OES analysis. The Nb recoveries from HNO_3, HCl and aqua regia were below 3% while the results obtained for the H_2SO_4 and H_3PO_4 indicated that Nb intensities were above the calibration range.

It was decided to use different amounts of Nb_2O_5 varying between 0.02 g to 0.10 g (accurately weighed to 0.1 mg) with constant H_2SO_4 volume (to avoid excessive use of acid that would otherwise increase the viscosity of the solutions as well as damaging the ICP tubes) and under constant microwave conditions to determine the amount of Nb_2O_5 dissolved and to determine the effect of acid volume. After the 30 minutes digestion period all the solids were visually dissolved and the vessel contents were transferred as mentioned above. **Table 5.6** shows the ICP-OES results of the digestion of Nb_2O_5 in H_2SO_4 and H_3PO_4. The ICP-OES analysis results in **Table 5.6** showed that only up to 91.46% of the sample went into solution in H_2SO_4 under the microwave conditions used and that H_3PO_4 was also very successful in the dissolution of the Nb_2O_5. In the next step, it was then decided to investigate the effect of heating period using H_2SO_4 as acid.

4.3.3.2 Determination of the effect of microwave heating period

Sample sizes in the range 0.0801 to 0.1078 g were accurately weighed (to 0.1 mg) into the vials and quantitatively transferred to the microwave PTFE vessels. Ten millilitres of concentrated H_2SO_4 were added and digestion times were increased to 45 minute and 60 minute periods to try to increase the amount of Nb_2O_5 that could be dissolved. No solid remained undissolved after both heating periods. The solutions were transferred and prepared for ICP-OES analysis as mentioned above. The ICP-OES results are shown in **Table 5.7**.

4.3.4 Dissolution of niobium metal (Nb)

4.3.4.1 Acid dissolution of Nb metal

The niobium metal foil was cut with a pair of scissors into small pieces. About 0.15 to 0.99 g of the metal pieces were accurately weighed to 0.1 mg in the five 100 ml beakers. Then 20 ml of concentrated HCl, HNO_3, H_2SO_4, H_3PO_4 and aqua regia were added to the metal cuttings in the beakers. The mixtures were boiled on a hot plate for an hour. Visual inspection indicated that the appearance of the metal pieces was the same as initially after an hour of heating. After this, the solutions were allowed to cool and the pieces were removed by filtration and the filtrate was quantitatively transferred to 100.00 ml volumetric flasks. The metal pieces were washed three times with distilled water to ensure a quantitative transfer of any possible Nb that was dissolved in this step. Ten millilitres of the solution were pipetted into another 100.00 ml volumetric flask and diluted to the mark with distilled water. The solutions were left to stand overnight to attain stable temperature conditions for ICP-OES analysis. The ICP-OES results are given in **Table 5.8**.

4.3.4.2 Microwave-assisted acid dissolution of Nb metal

High purity niobium metal (99.9% purity) foil of 0.125 mm thickness was cut with a pair of scissors and the pieces were accurately weighed (to 0.1 mg) in clean vials (in the range 0.04 to 0.070 g, see **Table 5.9** for actual weights) and then placed in clean

PTFE vessels. Ten millilitres of concentrated H_2SO_4 were added and the vessels sealed as indicated in **Section 4.3.2**. The amount of Nb metal was also varied, keeping the amount of H_2SO_4 constant, to determine a cut-off mass for dissolution. The digestion was done for 45 minutes in the microwave. Visual inspection indicated that all the niobium foil was dissolved after 45 minutes of microwave digestion. The solutions were then quantitatively transferred to the 100.00 ml volumetric flasks and diluted to the mark with distilled water for ICP-OES analysis. The %Nb recoveries obtained on analysis by ICP-OES are reported in **Table 5.9**.

4.3.5 Dissolution of niobium pentafluoride (NbF_5)

The dissolution of high purity NbF_5 was investigated using concentrated sulphuric acid, double distilled water at room temperature and pressure (r.t.p.) as well as sulphuric acid microwave-assisted dissolution. Four NbF_5 samples of about 0.1 g mass were accurately weight (to 0.1 mg) in four vials. Ten millilitres of distilled water were added and the solution was stirred for 10 minutes on a hot plate with a magnetic stirrer. After the initial 10 minutes stirring period the solid was virtually dissolved. A further stirring was done for another 10 minutes during which no more dissolution was observed. The remaining solid was removed by filtration and the filtrate was quantitatively transferred to the 100.00 ml volumetric flasks. The vials were rinsed three times with water to ensure a quantitative transfer of the contents. Ten millilitres of concentrated sulphuric acid were then added to the filtrate to match the standard solutions' matrix and to keep the niobium ions in solution. The solution was then filled to the mark of the volumetric flask.

Ten millilitres of concentrated H_2SO_4 was added to another sample of approximately the same amount of NbF_5 and stirred for 10 minutes. Visual inspection indicated that the entire sample had dissolved after the 10 minute period of constant stirring. The solution was quantitatively transferred to a 100.00 ml volumetric flask and diluted to the mark with distilled water.

The third and fourth samples of NbF_5 were quantitatively transferred from the vials to the PTFE vessels. Ten millilitres of concentrated sulphuric acid were then added. The microwave digestion was done for 45 minutes under the conditions given in **Table 4.2**. Clear solutions were obtained from the microwave digestion and they were quantitatively transferred to the 100.00 ml volumetric flasks and filled to the mark for ICP-OES analysis. The ICP-OES measurements were made the following day and the results are given in **Table 5.11**.

4.3.6 Determination of impurities in Nb_2O_5, Nb metal and NbF_5

Approximately 0.10 g each of Nb_2O_5, Nb metal and NbF_5 were accurately weight (to 0.1 mg) in the vials and quantitatively transferred to the PTFE reactions vessels. Ten millilitres of concentrated H_2SO_4 were added to the vessels. The microwave digestion was done for 45 minutes under the microwave conditions given in **Table 4.2.** Visual inspection indicated that all the samples were completely dissolved after this period. The solutions were quantitatively transferred to 100.00 ml volumetric flasks and diluted to the mark with distilled water. The solutions were allowed to stand overnight and ICP-OES measurements were made the following day. **Table 5.12** summarises the qualitative and subsequent quantitative results of all the impurities present in the above-mentioned samples and which were obtained by the ICP-OES analyses.

4.3.7 Flux fusion digestion of Nb_2O_5

Lithium tetraborate and lithium metaborate fluxes were separately mixed with the Nb_2O_5 samples in a 1 : 20 ratio. Approximately 0.1 g of Nb_2O_5 sample was (accurately weighed to 0.1 mg in a platinum crucible) thoroughly mixed with approximately 2.0 g of the fluxing reagent. The mixture was placed in the high temperature oven set to 1100 ^oC for 30 minutes. A clear melt was obtained for both fluxes and the hot crucible was immediately placed in a cold water bath to crack the glassy melt to speed up the dissolution process. Thirty millilitres of 3.25% HNO_3 were

added to the cold melt and the contents were stirred on a hot plate with a magnetic stirrer until all the melt had dissolved. A white precipitate was obtained after this melting and dissolution processes. The precipitate was removed by filtration and the filtrate was quantitatively transferred to the 100 ml volumetric flask. Five millilitres of 65% HNO_3 were added to each of the volumetric flask and these were filled to the mark with distilled water.

In another fusion method, sodium hydroxide was used as a fluxing agent. Approximately 0.1 g Nb_2O_5 was accurately weight (to 0.1 mg) in a nickel crucible and 2.0 g NaOH mixture was added and thoroughly mixed with Nb_2O_5. This mixture was placed in the high temperature oven set to 600 ^oC until a clear melt was observed (about 55 minutes). The melt was cracked in a cold water bath and then cooled to room temperature. The cold melt was dissolved in 30 ml of distilled water. A white precipitate formed during this dissolution and was removed by filtration and the filtrate was quantitatively transferred to a 100.00 ml volumetric flask. The solution was diluted to the mark with distilled water. The ICP-OES results are presented in **Table 5.13**.

4.3.7.1 Effect of different acids on $Nb_2O_5/Li_2B_4O_7$ melt dissolution

Dilute hydrochloric, nitric and sulphuric acids were tested for the dissolution of the $Nb_2O_5/Li_2B_4O_7$ melt which was fused at 1100 ^oC for 30 minutes. Three fusions were made. In the first fusion 5% sulphuric acid solution was added to the cracked melt (as mentioned above). The contents were stirred until all the glassy melt was no longer visually observed. A white precipitate formed during this dissolution step. The precipitate was removed by filtration and the filtrate was quantitatively transferred to a 100.00 ml volumetric flask. Five millilitres of 95-98% H_2SO_4 were added and the solution was then filled to the mark with distilled water.

In the second melt 5% HCl solution was added to the melt and the contents stirred as above. A white precipitate formed during this process and was also removed by filtration. The filtrate was quantitatively transferred to a 100.00 ml volumetric flask.

Five millilitres of 32% HCl were then pipetted into the solution and the volumetric flask filled to the 100.00 ml mark with distilled water. In the third fusion melt, the melt was dissolved in 3.25% HNO_3 solution. The same white precipitate was obtained as in the HCl and H_2SO_4 cases and was removed by filtration. The filtrate was quantitatively transferred to a 100.00 ml volumetric flask. Five millilitres of 65% HNO_3 were pipetted into the solution and the volumetric flask was filled to the 100.00 ml mark. **Table 5.14** gives the ICP-OES results of the recoveries obtained. In all the solvents (acids) the %Nb recoveries were below 50%.

4.3.7.2 Determination of the effect of HNO_3 concentration on the melt dissolution

The precipitation of the $Nb_2O_5/Li_2B_4O_7$ melt and low %Nb recoveries could be due to i) the chemical instability of niobium in the dilute acid solutions resulting in the formation of an insoluble compound (possibly niobium hydroxide), ii) a precipitation of boric acid resulting in a co-precipitation of niobium or iii) volatilization losses during the fusion or a combination of all these processes. The ICP-OES results in **Table 5.14** indicated that more Nb_2O_5 had dissolved in HNO_3 than in HCl and H_2SO_4. These results prompted an investigation into the effect of the concentration of this acid (HNO_3) on the possible dissolution and subsequent recovery of Nb.

Concentrations of 0.26, 3.25, 16.25, and 32.5% HNO_3 were prepared in 100.00 ml volumetric flasks by dilution from the 65% HNO_3 stock solution. These solutions were added to different $Nb_2O_5/Li_2B_4O_7$ melts obtained as indicated in **Section 4.3.7.1**. Visual inspection indicated that the white precipitate formed in all the solutions. The precipitate was removed by filtration and the filtrate was quantitatively transferred to 100.00 ml volumetric flasks and 5.00 ml of 65% HNO_3 were pipetted into all the solutions. The volumetric flasks were then filled to the mark with distilled water.

The ICP-OES results indicated that there was an increase of %Nb recovery (from 0.70 to 37.39%) with increasing concentration (0.26 to 65%) of HNO_3 (**Table 5.15** and **Figure 5.2**). It was then decided to use concentrated HNO_3 and H_2SO_4 and eliminate

the possibility of the co-precipitation with boric acid by converting the boric acid generated *in situ* into a volatile methyl ester as indicated in **Equation 4.1**.

$$B(OH)_3 + 3CH_3OH \longrightarrow B(OCH_3)_3\uparrow + H_2O \qquad \textbf{4.1}$$

The same procedure of fusion as indicated above was repeated to obtain $Nb_2O_5/Li_2B_4O_7$ melt. Two fusions were made to test dissolution with HNO_3 and H_2SO_4. In the first melt 10 ml of 65% HNO_3 was added to the cold melt followed by immediate slow addition of approximately 30 ml methanol. The solution was stirred on a hot plate with a magnetic stirrer until all the glassy melt dissolved. A milky solution was obtained. The precipitate was removed by filtration and the filtrate was quantitatively transferred to a 100.00 ml volumetric flask. Five millilitres of 65% HNO_3 were added and the volumetric flask was filled to the mark with distilled water.

In the second melt, 10 ml of 95-98% H_2SO_4 were added followed immediately by slow and cautious addition of methanol. The solution was stirred until all the glassy melt was dissolved. A clear solution was obtained and transferred quantitatively to the 100 ml volumetric flask. Five millilitres of 95-98% H_2SO_4 were added and the volumetric flask was filled to the mark with distilled water. The solutions were prepared for ICP-OES analysis by standard addition method as indicated in **Chapter 5**, **Section 5.2.4.2**. The ICP-OES results are give in **Table 5.16**.

4.3.8 Sample preparation procedures for Nb containing mineral ores

In this study three niobium containing minerals were used. The minerals were labelled Tantalite Naquissupa A, Tantalite Naquissupa B and Furiso Sample 1 but for the sake of consistency these minerals will be called Tantalite A, Tantalite B and Sample 1 in this study. Two of these minerals labelled Naquissupa A and B were found to be variations of the tantalite mineral with the chemical compositions given in

Table 4.3 which was analysed by Alfred H Knight. The identity and composition of Sample 1 (**Figure 4.2**) was not known which formed one of the aims in this study.

Figure 4.2: Different niobium containing mineral ores studied

Table 4.3: Chemical analyses of the tantalite minerals by Alfred H Knight analytical laboratories

Sample:	**Minerals**	
Marks	**Tantalite**	**Tantalite**
Description	**Naquissupa A**	**Naquissupa B**
Lab No.:	**80517/1**	**80517/2**
Analysis:		
	%	**%**
Ta_2O_5	27.71	32.69
Nb_2O_5	27.41	15.94
ThO_2	0.65	0.49
U_3O_8	2.83	0.98
Al_2O_3	1.85	3.44
SiO_2	5.73	11.9
WO_3	1.61	1.01
TiO_2	2.68	5.13
Mn_3O_4	8.03	7.09
Fe_2O_3	8.29	7.72
SnO_2	1.41	2.82

4.3.9 Microwave-assisted digestion of the mineral by different acids

The microwave conditions that provide a complete dissolution for the high purity niobium samples were tested for the digestion of the niobium containing minerals. Aliquots of approximately 0.10 g of the mineral samples were accurately weighed (to 0.1 mg) in the vials and quantitatively transferred to the PTFE reaction vessels. Ten millilitres of concentrated H_2SO_4 were added to the vessels. The vessels were sealed and the rotor was tightened. The digestion was done for 45 minutes under the microwave condition given in **Table 4.2**. Visual inspection of the samples after digestion indicated that some solid samples remained undissolved under the conditions used.

The solids were removed by filtration and the filtrate was quantitatively transferred to the 100.00 ml volumetric flasks. The volumetric flasks were filled to the mark with distilled water and the ICP-OES measurements were made the following day. The ICP-OES results are give in **Table 5.17**. The ICP-OES measurements produced non-reproducible results that were far below the target values (maximum Nb_2O_5: 62.96% of the target value). The low recoveries and non-reproducibility of the results for all the analytes was attributed to the large and uneven particles sizes that make the interaction between the sample and the acid difficult.

Before repeating the above procedure, it was decided to visually select the same particle size (small particles chosen, see **Figure 4.2** for the original sample particle size) in each sample and use different amounts of sample with constant H_2SO_4 volume to also determine the effect of acid volume in the digestion of the minerals. The microwave digestion period was also increased to 60 minutes to determine the time dependence of the dissolution process as well as to increase the amount of elements dissolved. Some of the solid samples remained undissolved after this 60 minutes digestion period and the solids were removed by filtration. The filtrate was quantitatively transferred to 100.00 ml volumetric flasks and filled to the mark for ICP-

OES quantitatively analysis. The ICP-OES results are given in **Table 5.19**. Maximum recovery of Nb_2O_5 was increased to 96.75% (that is 26.52%) of the target value of 27.41%. The results were however still not reproducible which made it necessary to grind the samples to smaller and homogeneous particle sizes.

The samples were ground to a fine powder to an average particle size (d_{50} - value) of 9.8 µm (Tantalite A), 9.5 µm (Tantalite B) and 11.1 µm (Sample 1) using a vibration grinding mill in a steel milling vessel at the Geology department at the University of the Free State. Subsamples of the powder mineral ores were sent to Necsa for sample size measurements (see **Figures 5.3 - 5.5**). Other portions of these fine powdered samples were used in the wet digestion for ICP-OES analyses, XRF analyses and XRD analyses.

4.3.9.1 Determination of the effect of different acids

Aqua regia, nitric acid, hydrochloric acid, sulphuric acid and orthophosphoric acid were tested for the digestion of the mineral ores. Accurate measurements of approximately 0.08 g (to 0.1 mg) of the Tantalite A mineral sample were made in vials. The samples were quantitatively transferred to the PTFE vessels. Ten millilitres of concentrated HCl (32%), HNO_3 (65%), H_3PO_4 (85%), aqua regia, and H_2SO_4 (95-98%) were added to the vessels. The vessels were sealed and placed in the rotor, tightened and transferred to the microwave for digestion. Digestion was made under the microwave conditions given in **Table 4.2** for 45 minutes. Visual inspection indicated that mineral solid remained in all the vessels after this time.

The residue was removed by filtration and the filtrate was quantitatively transferred to the 100.00 ml volumetric flasks. The vessel was washed three times with distilled water to ensure a quantitative transfer. The solutions were then diluted to the mark with distilled water. The solutions were left to stand overnight and the qualitative and quantitative analysis was accomplished by ICP-OES. The quantities for the different elements present in the minerals were determined using an external calibration method (see **Chapter 5, Section 5.2.4.1**). **Table 5.20** shows the results obtained

from the acids tested. The ICP-OES results in **Table 5.20** showed that H_2SO_4 and H_3PO_4 dissolved the minerals up to 80% of the target values (see **Table 4.3**). It was then decided to increase the digestion time to get the optimum conditions for a possible 100% dissolution of the mineral samples.

4.3.9.2 Determination of the effect of heating time with H_2SO_4

Aliquots of approximately 0.10 g of the mineral samples were accurately weighed (0.1 mg) in the vials and quantitatively transferred to the PTFE vessels. Ten millilitres of 95-98% H_2SO_4 were added to the vessels and digestion times were varied between 1.5 and 2.5 hours. Even after these periods undissolved solids were still observed in the vessels. The residues were removed by filtration and the filtrate was quantitatively transferred to 100.00 ml volumetric flasks and diluted to the mark with distilled water. The results obtained by ICP-OES analyses are presented in **Table 5.22**. For both digestion times the dissolution had increased up to 90% for all the minerals and the results were very reproducible.

4.3.10 Fusion digestion and standard addition methods on the different mineral samples

4.3.10.1 Determination of the effect of different fluxes

Approximately 0.10 g of the mineral samples was weighed accurately to 0.1 mg and placed in a platinum crucible. To this was added approximately 2.0 g of lithium tetraborate fluxing reagent and thoroughly mixed before heating. The platinum crucible was placed in the high temperature oven set to 1100 ^oC for 30 minutes to produce a glassy melt. The melt was cracked by placing the hot crucible in a cold water bath. Ten millimetres of 95-98% H_2SO_4 were pipetted into the cold melt followed by cautious addition of approximately 30 ml methanol. The crucible was then heated on a hot plate while the contents were constantly stirred with a magnetic stirrer. When all the melt had dissolved, a clear solution was transferred to a 100.00

ml volumetric flask and diluted to the mark with distilled water. Exactly the same procedure was repeated with 32.5% HNO_3 instead of H_2SO_4 for Tantalite A. Different from H_2SO_4, a white precipitate formed during the dissolution with HNO_3 and methanol. The precipitate was filtered and the filtrate was quantitatively transferred to the 100 ml volumetric flask and diluted to the mark with distilled water. The sample preparation for the standard addition method was then followed (see **Chapter 5, Section 5.2.4.2**). The solutions were left to stand overnight to attain a stable temperature before the analyses by ICP-OES.

Another method that makes use of $K_2S_2O_7$ as a fluxing agent[38] was tested. Approximately 0.1 g of Tantalite A was accurately weighed (to 0.1 mg) in a platinum crucible and then about 2.0 g of the $K_2S_2O_7$ flux reagent was added. The contents were thoroughly mixed and then placed in a high temperature oven set to 1000 ^oC for 30 minutes. The clear melt obtained from this fusion was cracked in a cold water bath and then dissolved in 10 ml of the mixture solution of 10% H_2SO_4 and 10% tartaric acids. The dissolution resulted in a white precipitate forming. The precipitate was removed by filtration and the filtrate was quantitatively transferred to a 100.00 ml volumetric flask and the solution was diluted to the mark with the same mixture (10% H_2SO_4 and 10% tartaric acid). The solutions were left to stand overnight and the ICP-OES measurements were made the following day. The ICP-OES results gave the weight percentages as indicated in **Tables 5.23** and **5.24.**

4.3.11 Sample preparation procedure for XRD analysis

The powdered samples were placed in sample holders. The surfaces of the samples were flattened and smoothed by rubbing with a glass slide. The samples were then presented to the X-ray diffractometer (**Chapter 5, Section 5.2.3**) for measurements. **Figures 5.9, 5.10 and 5.11** represent the defractogrammes obtained in this analysis.

4.3.12 Sample preparation procedure for XRF analysis

A failure to get standard reference materials for this study, lead to the use of direct solid analysis by a wavelength dispersive X-Ray fluorescence (WDXRF) for comparison of dissolution results by ICP-OES. Approximately 8.0 g of the sample was mixed with 3.0 g Hoechst wax (binder material) and shaken to obtain a homogeneous mixture (~11.0 g) which is an important step in the sample preparation procedure. The mixture was then poured into the dies and manually pressed up to 30 tons pressure to obtain a flat disc of 30 mm diameter and 9 mm thickness. Due to the low concentrations in the standards for the niobium containing mineral concentrates, standards of the compositions indicated in **Table 4.4** were prepared by mixing high-purity Ta_2O_5/Nb_2O_5 with SiO_2 to calibrate the instrument. The pellets were placed in the sample holder and then transferred to the XRF for quantitative analysis.

Table 4.4: XRF standards of tantalum and niobium oxides

Ta_2O_5/Nb_2O_5	**SiO_2**
%	**%**
25	75
50	50
75	25
100	0

The analysis was then performed using the “Major pellets Programme” which showed some lack of sensitivity for some analytes. It was then decided to use a more sensitive “Pro-trace Programme” to quantify the elements that could not be accurately determined with the “Major pellets Programme”. The initial results were inconclusive and showed that the instrument responses were above the calibration range under the above mentioned conditions in the “Pro-trace Programme” and that dilution should be performed to get more accurate results. It was decided to dilute the rock samples with SiO_2 in a 1-99% sample **:** silica ratio as indicated in **Table 4.5**. About 3.0 g Hoechst wax (binder material) was added to the mixtures and these

mixtures were shaken by hand and for about 30 minutes by a flask shaker to make sure that a homogeneous mixture was obtained. The results are given in **Table 5.25.**

Table 4.5: Mineral sample dilution with silica

Sample identity	Mineral sample		Silica	
	Mass/g	Percent	Mass/g	Percent
Tantalite A	0.0811	1.01	7.9131	98.91
Tantalite B	0.0799	1.00	7.9261	99.08
Sample 1	0.0814	1.02	7.9215	99.02

4.4 CONCLUSION

The importance of the complete dissolution of the minerals and other chemical compounds to allow for their quantification has been emphasized in the introduction of this chapter. Various methods such as normal acid dissolution, microwave assisted dissolution as well as flux methods were tested on the different compounds to evaluate their effectiveness on the dissolution process. From the results obtained in this study, it is clear that different methods were successful on different samples and clearly not a “one method fits all” solution.

Visual inspection indicated that conventional hot plate heating of the Nb_2O_5 and Nb metal in the acids H_2SO_4, H_3PO_4, HNO_3, HCl and aqua regia was ineffective in dissolving these samples. The ICP-OES results also confirmed a non-quantitative dissolution in all the acids tested. NbF_5 which is the easiest to dissolve among the samples under investigation was found to dissolve in H_2SO_4 and distilled water at room temperature and pressure with a little solid remaining in the water dissolution. The ICP-OES results indicated that a quantitative dissolution was obtained from both the H_2SO_4 and water.

All the niobium samples under investigation were found to dissolve in sulphuric acid under the microwave conditions of 1200 W, 280 ^{o}C and 60 bar at different time periods. Microwave assisted acid digestion using concentrated sulphuric acid may be used as an alternative to HF digestion for niobium and its compounds. However, this method does not provide total dissolution of the mineral samples. A 45 minutes digestion period was found to be a minimum period for the digestion of all the high purity niobium samples. The time had to be increased to 90 minutes for the digestion of the minerals to improve the leaching of the analytes. This longer digestion time (90 minutes) with grinding of the rock samples to an average particle size of 10 µm (d_{50}) improved the dissolution of the samples in the microwave oven by up to 90% for Nb. The eight vessels in a microwave rotor allowed digestion of eight samples at a time and this reduced the sample digestion time with the microwave technique greatly.

Despite the many steps involved in the flux fusion digestion methods, visual inspection and ICP-OES results have shown that the niobium mineral samples should be digested using this technique using lithium tetraborate as a flux and sulphuric acid and methanol as solvents to get complete sample decomposition.

In conclusion, it can be said that the study succeeded in finding successful dissolution methods (in some cases more than one) for all of the samples that were investigated which allowed for the qualitative and quantitative analysis of niobium content as well as type and amount of impurities present in these samples. **Table 4.6** summarises the methods that have been investigated indicating their varying degrees of success.

Table 4.6: Evaluation of various dissolution methods on niobium samples

Sample identity	Method of dissolution tested		
	Acid dissolution	**Microwave-assisted dissolution**	**Fusion dissolution**
Nb_2O_5	**x**	√√	√√
NbF_5	√√	√√	**…**
Nb	**x**	√√	**…**
Tantalite A	**…**	√	√√
Tantalite B	**…**	√	√√
Sample 1	**…**	√	√√

√√**-** successful to above 95%
√**-** successful to about 90%
X- not successful
… not tested

5 ICP-OES, XRF AND XRD ANALYSES OF Nb METAL, Nb_2O_5, NbF_5 AND NIOBIUM CONTAINING MINERALS

5.1 INTRODUCTION

The essence of analytical chemistry is the identification (or qualification) and the accurate determination of the amount (quantification) of the different chemical species present in a sample. It is important to ensure that the chemical composition is not altered during the analytical process in order to obtain a representative result for the sample that is analyzed. Critical conditions to meet during this process is i) proper sampling, ii) the homogenisation of the sample, iii) correct sub-sampling, iv) dissolution of the sample (without contamination by solvents or loss of analyte due to volatilisation), v) accurate determination of concentrations using well-maintained equipment and vi) the mathematical evaluation of the results. These principles were followed and the accuracy of the whole analytical process was evaluated at the end of each study.

In this study three different niobium compounds, with known Nb content (in the absence of a standard reference material, CRM), were studied in order to evaluate both the accuracy and precision that could be obtained with the different dissolution procedures. Knowledge that was obtained from this part of the study was used in the second part of the study to determine the niobium content in two chemically more complicated Tantalite mineral samples with known chemical composition. Finally, a completely new mineral with an unknown chemical composition was investigated for its composition and mineral identification. The dissolution processes of the different samples were discussed in **Chapter 4** and the success of these processes was evaluated in terms of visible sample left (or not) in the sample solution. This is at its best in a semi-quantitative result and the only quantitative measure (accurate determination) of the success of the dissolution procedures can only be obtained with

the quantification of the niobium content (and other elements) using ICP-OES, XRF and XRD (semi-quantitative) and these results will be discussed in this chapter.

The ICP-OES results are compared with results obtained using the direct solid sample analysis using XRF to evaluate the effectiveness of each method to try and identify the most promising analytical method for the samples that were studied. The XRD results for the mineral labelled as Sample 1 will also be discussed in detail. The degree of success of the dissolution procedure was measured as the mass percentage recovery of the analyte/s $\left(\frac{\text{mass obtained}}{\text{mass expected}} \times 100\right)$ in the solution. The % recovery is also a measure of the accuracy of the analytical method used for the samples that were studied. The relative standard deviation $\left(\text{RSD} = \frac{s}{\bar{x}} \times 100\right)$ that was calculated for the different runs are an indication of the precision of the respective analyses.

The sensitivity of an instrument or a method is a measure of its ability to discriminate between small differences in analyte concentration.[51] The limit of detection (LOD) as well as the slope of the calibration curve and the reproducibility or precision (expressed by the correlation coefficient, R^2) are used as a measure of the sensitivity of the instrument to the analyte concentrations while the y-intercept provides an estimate of the variability of the intensity measurements as well as acceptable background corrections (zero intercept for the normal calibration curve) made for each analytical determinations. These parameters will all be used to evaluate the effectiveness (accuracy and precision) of the different analytical determinations that were made in this study. All the calculation results have been expressed in four significant figures with the exception of the percentages (RSD and recovery values) which have been expressed to two decimal places.

5.2 EQUIPMENT AND EXPERIMENTAL CONDITIONS

5.2.1 ICP-OES instrument parameters

The efficiency of inductively coupled plasma optical emission spectroscopy as well as the reliability of the data obtained depends on the instrumental operating conditions as well as the choice of parameters for the analysis. Although, the electronic control can alert the user to potential problems, it is very important that the instrument is properly examined before using it to avoid disruptions during the analysis. Additionally, effective cooling and sufficient argon gas must be ensured as the instrument will turn off on its own if it runs out of gas or becomes too hot. The conditions of the plasma and other parameters such as consistency of nebulisation can greatly influence the measurement results as discussed in detail in **Chapter 3**.

The operating parameters of the instrument were always monitored closely to ensure the maximum performance and reliability of the ICP-OES results. All the analyses were performed 20 to 30 minutes after the spectrometer was turned on to achieve a stable plasma as well as constant and reproducible sample introduction. The emission intensity measurements were made under constant default conditions as indicated in **Table 5.1**. These conditions were chosen since they are optimized for a variety of elements.

Table 5.1: ICP-OES operating conditions

R.F. power	1.2 kW
Coolant gas flow	14.0 l/min
Plasma gas flow	1.2 l/min
Carrier gas flow	0.7 l/min
Sample uptake method	Peristaltic pump
Spray chamber	Glass cyclonic spray chamber with concentric nebulizer

The ICP-OES offers two modes with which to analyze the sample in the plasma, namely the radial mode and the axial mode. In the radial mode, radiation is detected at a 90-degree angle from the axis of the ICP. The radial mode gives excellent detection limits and freedom from interferences for a large number of elements. In the axial mode, radiation is detected along the axis of the ICP. This approach has more interferences than the radial mode, but it is more sensitive due to the fact that the spectrometer is sampling from a larger viewing area.[88] In this study, all the data collection was accomplished in the radial mode only.

5.2.2 ICP-OES instrument and sample introduction configuration

The sample introduction system consists of a peristaltic pump connected to a concentric nebuliser (see **Chapter 3**, **Section 3.3.1**). The nebuliser produces an aerosol that is sprayed into the cyclonic spray chamber, and in the spray chamber the smallest aerosol particles follow the gas flow into the plasma. The inner tube of the nebuliser must constantly be checked for potential blockages before the analytical measurements are made. Blockages in the nebuliser or the peristaltic tube usually lead to low sample uptake and poor (or unusable) calibration curves with reduced intensities.

Solutions containing suspended solids or product as a result of incomplete dissolutions were always filtered before they were introduced into the ICP-OES system to avoid the blockage of the sample inlet system. In the case where the blockages did take place, the problem was solved by removing the nebuliser which was then introduced into a dilute hydrochloric acid solution to dissolve the blocking material or by blowing compressed air into the blocked tube to remove the obstruction. The viscosity of the solutions, especially in sulphuric and ortho-phosphoric acids, was reduced by dilution with double distilled water since it was found that viscosity influences the analytical results substantially.

[88] http://www.wcaslab.com/tech/ICP-OES.htm

5.2.3 Equipment and reagents

A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer controlled by a computer was used for the wet analysis of the samples under investigation. Commercially available ICP standard solutions were used for the preparation of the calibration solutions. Separate standard solutions containing 1000 ppm Th and U were bought from De Bruyn Spectroscopic Solutions while 1000 ppm Nb, 1000 ppm Ta, 1000 ppm W, 1000 ppm Si, 1000 ppm Ti, 1000 ppm Sn and 1000 ppm Y were bought from Merck. The multi-element standard No. XXVI containing 1000 ppm each of Mn, Al, Fe, Ca and other elements (which were not analysed in this study) was also bought from Merck.

Direct solid measurements of the minerals' constituents were made at the Geology Department at the University of the Free State. XRD analyses were made using a Siemens D5000 Diffractometer. Quantitative measurements of the mineral constituents were made using a PANalytical Wavelength Dispersive X-Ray Fluorescence (WDXRF) Spectrometer with a rhodium tube as a radiation source.

5.2.4 Preparation of linear calibration curves

5.2.4.1 External calibration curve for microwave and acid digestion analyses

All the external calibration solutions were prepared by introducing 0.1, 0.2, 0.3, 0.5 and 1.0 ml of the 1000 ppm ICP-OES standard solution/s into five 100.00 ml volumetric flasks using a micro-pipette. To these, 10.00 ml of acid which was used to digest the sample was added. The solutions were then diluted to the mark with distilled water to prepare 1.0, 2.0, 3.0, 5.0, and 10.0 ppm concentrations of the respective elements. The blank solutions were prepared by diluting 10.00 ml of the acid being used to the 100.00 ml mark of the volumetric flask and were used for background correction.

5.2.4.2 Standard addition calibration curve for fusion digestion analysis

The standard addition method was used for the analyses of all the solutions that were obtained by flux fusion digestion methods (see **Chapter 3**, **Section 3.2.1**) to compensate for potential matrix effects. Ten milliliter aliquots of a sample solution were added to the five 100.00 ml volumetric flasks followed by a 5.00 ml addition of the acid or base used to dissolve the melt and then the standard solutions were added to make 0.0, 1.0, 3.0, 5.0 and 10.0 ppm calibration solutions. The solutions were then diluted to the 100.00 ml volumetric flask mark with distilled water.

5.3 RESULTS AND DISCUSSIONS

5.3.1 ICP-OES Instrument Validation

5.3.1.1 Determination of detection limits for selected elements

The first step in the development of an analytical method for the determination of different elements and impurities by ICP-OES is selecting the most appropriate emission lines. The determination of the sensitivity of the different lines (LOD) as well as the composition of the sample was used as a basic criterion. The composition of the sample has to be considered in order to avoid possible interference problems. Five 100 ml standard solutions containing 0.4, 1.0, 3.0, 5.0, and 10.0 ppm of the elements in **Table 5.2** and the blank solutions were prepared in 10 ml H_2SO_4. The intensity measurements were performed at the three most sensitive analytical lines of each element. The intensities used for the calculation of the detection limits are the average of three replicate measurements in the standard solution and ten replicate measurements in the blank solution for each element. The detection limits were calculated according to the definition expressed as indicated in **Equation 5.1**.

$$\mathrm{LOD} = \frac{ks_{bl}}{m} \qquad \textbf{5.1}$$

where k is a numerical factor chosen in accordance with the confidence level (the value of k = 3 which corresponds to a 98.3% confidence level was used), m is the slope of the calibration graph and s_{bl} the standard deviation of the blank responses. Lower limit of quantification (LOQ) is defined as ten times the limit of detection. Results obtained in this part of the study are presented in **Table 5.2**.

Low limits of detection for niobium (0.009 ppm) have been obtained when the Nb 309.418 nm (line order 1) and 316.079 nm (line order 2) lines are used. The same detection limit (0.009 ppm) for Nb 309.418 nm was obtained by Uria *et al*.[38] All the limits of detection in **Table 5.2** are below 1 mg/L, which easily allows for trace level elemental analysis for all the elements that were detected in the respective compounds that were studied. The LOD values for Al, Mn, Fe, Ca, Ti and Mg obtained in this study were found to be very similar to those obtained by S. Lötter in the study of ZrO_2 and PDZ.[89] Two alternative analytical lines with limits of detection of 0.016902 ppm (Nb 319.498 nm) and 0.07904 ppm (Nb 313.079 nm) were chosen due to interferences being apparent at the most sensitive wavelengths with these samples.

[89] Lötter, S.J., *Identification and Quantification of Impurities in Zircon, PDZ and other Relevant Zirconium Products. M.Sc. Study, UFS.* 2008. p51.

Table 5.2: Detection limits at three most sensitive line orders

Element	Limits of detection (ppm) at three sensitive wavelengths			Quantification limits (ppm)		
	Line order 1	Line order 2	Line order 3	Line order 1	Line order 2	Line order 3
Nb	0.0094	0.0093	0.010	0.094	0.093	0.10
Ta	0.024	0.0047	0.024	0.24	0.047	0.24
Li	0.00019	0.01	0.0043	0.0019	0.10	0.043
Na	0.0034	0.0066	0.31	0.034	0.066	3.09
Mg	0.00035	0.00024	0.020	0.0035	0.0024	0.20
Al	0.0055	0.0074	0.013	0.055	0.074	0.13
Ca	0.00035	0.0011	0.0025	0.0035	0.011	0.025
Ti	0.0015	0.0015	0.0015	0.015	0.015	0.015
Mn	0.00031	0.00036	0.00071	0.0031	0.0036	0.0070
Fe	0.0035	0.0080	0.0024	0.035	0.080	0.024
Ni	0.0029	0.0083	0.0029	0.029	0.083	0.029
Cu	0.0020	0.0017	0.0058	0.020	0.017	0.058

5.3.1.2 Analytical line selection

The analytical line selection for the analytes under investigation was made on the basis of the above information (**Table 5.2**) and the complexity of the matrix of the niobium sample under investigation. The niobium intensity measurements for the pure niobium sample solutions (Nb_2O_5, Nb metal, and NbF_5) prepared by microwave and acid digestion were made at 309.418 nm (line order 1) while 316.340 nm (line order 2) was used for the three mineral samples and all the solutions prepared by flux digestion. **Table 5.3** displays the different wavelengths selected in this study as well as their experimental and theoretical[90,91] (determined by ICP) detection limits.

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

[91] Optima Simultaneous Spectrometers Wavelength Tables. PerkinElemer Instruments LLC. 2002.

Table 5.3: Selected analytical wavelengths and detection limits for the elements studied

Element	Wavelength (nm)	Measured detection limit (ppm)	Estimated* detection limits (ppm)
Al	394.403	0.0074	0.047
Si	251.612	…	0.012
Ti	336.121	0.0015	0.0053
Mn	257.610	0.00031	0.0014
Fe	259.940	0.0035	0.0062
Ta	268.511	0.024	0.030
Nb	309.418	0.0094	0.036
	316.340	0.0093	0.036
Sn	189.989	…	0.025
W	207.911	…	0.030
Th	374.119	…	0.096
U	367.007	…	0.30
Ca	393.366	0.00035	0.00019

***** Theoretical values

… not measured

5.3.1.3 Calibration curve parameters

Calibration curves showed excellent linearity with slopes greater than 1.0 (sensitivity) and correlation coefficients, $R^2 \geq 0.999$ for all the elements. The obtained y-intercept values (absolute values < 0.1 for all the other elements studied except Fe) indicated good background correction and there was no significant variability observed in the normal (external) calibration data. A note should be taken that for the standard addition method the y-intercept will rightly deviate away from the origin since the

sample (analyte solution) was also added to the 0.0 ppm standard solution (see **Section 5.2.4.2**).

5.3.2 ICP-OES analysis for acid dissolutions of Nb_2O_5

Aliquots of 0.1 g of Nb_2O_5 samples were dissolved in 20.00 ml of five different acids namely HCl, HNO_3, H_2SO_4, H_3PO_4 and aqua-regia. The mixtures were boiled for 1 hour on a hot plate. Visual inspection indicated that not all the sample was dissolved. The remaining solid was filtered and the solutions were quantitatively transferred to a 100.00 ml volumetric flask. Dilutions of the filtrate were made as indicated in **Chapter 4, Section 4.3.1** for the ICP-OES results analyses.

The ICP-OES analysis results for acid dissolutions in **Table 5.4** clearly indicate that it is difficult to quantitatively dissolve Nb_2O_5 by conventional hot plate digestion methods. The quantitative results indicate that H_3PO_4 and H_2SO_4 were the most successful acids from the selected acids, but recoveries of less than 1% were obtained even for these two acids. These results are in total agreement with the natural resistance of Nb compounds to acid attack.

Table 5.4: Dissolution of Nb_2O_5 in different acids using hot plate heat method

	Acid	**H_3PO_4**	**H_2SO_4**	**HCl**	**HNO_3**	**Aqua regia**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.1006	0.1020	0.1068	0.1064	0.1064
	Mean Conc[a]./ppm	0.5994	0.6681	0.01265	0.003160	0.0000
	RSD[b]	0.02	0.01	0.40×10^{-2}	0.01	0.01
	%Nb recovery	0.85	0.94	0.02	0.00	0.00
Calibration curve properties	Slope	1.7081	1.9087	1.8387	1.9319	1.921
	Intercept	-0.0270	-0.0501	-0.0263	-0.0596	-0.0651
	R^2	0.9998	0.99936	0.9999	0.9992	0.999

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

5.3.3 ICP-OES analysis for microwave dissolution of Nb_2O_5

In the next investigation Nb_2O_5 samples were digested with 10.0 ml of the same five acids, but this time the samples were subjected to 30 minutes of microwave digestion under the conditions outlined in **Table 4.2**. Visual inspection indicated that some of the solid sample remained undissolved in the vessels for HCl, HNO_3 and aqua regia solutions while clear solutions were obtained in H_2SO_4 and H_3PO_4. The HCl, HNO_3 and aqua regia solutions were filtered and the filtrate was transferred to 100.00 ml volumetric flasks as indicated in **Chapter 4**, **Section 4.3.3.1**. After the necessary dilutions, solutions were allowed to stand overnight and the ICP-OES measurements were made the following day.

The harsh microwave conditions resulted in improved dissolution of Nb_2O_5 with HCl (2.27% compared to 0.02% for normal acid digestion) but no improvement was evident for HNO_3 and aqua regia (**Table 5.5**) after a 30 minutes digestion period. The relative standard deviations (RSD values < 0.1) in all the acids showed good precision of the measurements.

Table 5.5: Results from using different acids in microwave digestion of Nb_2O_5

	Acids	**H_3PO_4**	**H_2SO_4**	**HCl**	**HNO_3**	**Aqua-regia**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.1581	0.1582	0.1584	0.1584	0.1581
	Mean Conc[a]./ppm	…	…	30.11	0.1217	1.144
	RSD[b]	…	…	0.45	0.04	0.02
	%Nb recovery	…	…	**2.27**	**0.01**	**0.09**
Calibration curve properties	Slope	2.736	0.9620	1.121	0.8260	0.9160
	Intercept	-0.01520	-0.003000	-0.01150	-0.006800	-0.002100
	R^2	0.9999	0.9990	0.9999	0.9995	0.9998

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

The initial results obtained for the H_2SO_4 and H_3PO_4 indicated Nb concentrations which were out of the calibration range which was initially selected under the conditions used at that stage (**Table 5.5**). In order to avoid excessive use of large amounts of standard solutions, the above procedure was repeated using smaller amounts of Nb_2O_5 sample (see **Chapter 4**, **Section 4.3.3.1**). This study was also undertaken to investigate the possible cut-off mass of Nb_2O_5 that can be dissolved in the 10 ml volume of acid which was used to prepare the standard solutions to avoid high viscosity of solutions. The low RSD values obtained in all the acids showed good reproducibility of the measurements.

Visual inspection showed again that all the solid dissolved in both H_2SO_4 and H_3PO_4 solutions. The solutions were transferred to the 100.00 ml volumetric flasks and diluted as indicate in **Chapter 4**, **Section 4.3.3.1** for ICP-OES measurements**. Table 5.6** shows the results of digestion of Nb_2O_5 in H_2SO_4 and H_3PO_4. Improved dissolution of up to 91.46% was obtained with H_2SO_4 (compared to 0.94% in boiling acid). A comparison of the results obtained with the variation of amount of Nb_2O_5 dissolved, showed a recovery of between 84 and 91%. Although, a higher recovery (91.46%) was obtained for the lower amount (0.0207 g) of Nb_2O_5 sample, there is no trend in the sample sizes dissolved on the concentration volume of H_2SO_4 used (**Figure 5.1**).

From **Figure 5.1** it can be seen that the %Nb recovery increased to 91.46% when 0.0207 g of Nb_2O_5 was dissolved (smallest amount of compound) but the recovery drops as the sample masses were increased and then levels off. No further significant decrease or increase of the recovery with the sample amount is observed. The fact that about the same %Nb was recovered for both H_2SO_4 (average 87.29%) and H_3PO_4 (84.28%) indicated that H_3PO_4 could alternatively be used to H_2SO_4. The average Nb recovery of 87.29% during the 30 minutes digestion time with H_2SO_4 also indicated some degree of incomplete digestion or loss to other reactions of Nb_2O_5 even under these conditions. The low RSD values obtained for both acids showed good reproducibility of the measurements but a slight increase of the RSD with an increase in Nb_2O_5 sample sizes in H_2SO_4 was observed.

Table 5.6: Varying mass of Nb_2O_5 sample in H_2SO_4 and H_3PO_4 assisted microwave digestion.

	Acids	**H_2SO_4**	**H_2SO_4**	**H_2SO_4**	**H_2SO_4**	**H_3PO_4**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.0207	0.042	0.0821	0.1077	0.0602
	Mean Conc.[a]/ppm	15.83	29.85	58.90	78.20	42.42
	RSD[b]	0.17	0.27	1.03	1.75	0.50
	%Nb recovery	**91.46**	**85.02**	**85.81**	**86.85**	**84.28**
Calibration curve properties	Slope	1.634				0.9170
	Intercept	0.01750				-0.002300
	R^2	0.9990				0.9998

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

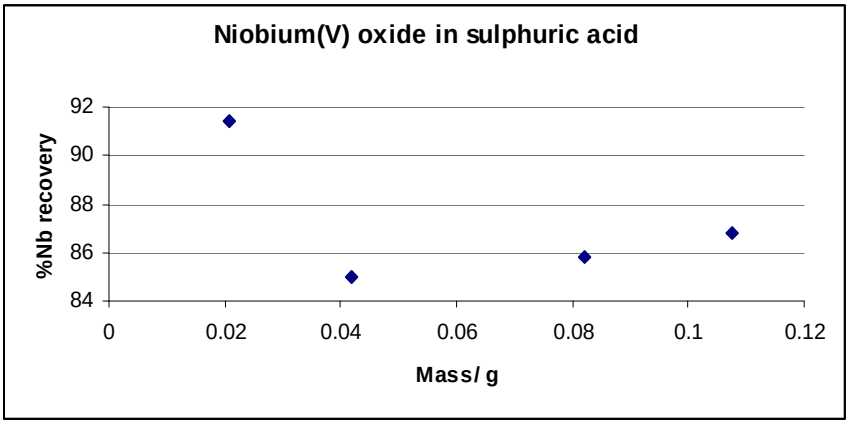


Figure 5.1: Varying mass of sample in 10 ml H_2SO_4

5.3.3.1 Determination of the effect of digestion period

It was then decided to investigate the time dependence of the dissolution of Nb_2O_5 in H_2SO_4 utilising the microwave conditions given in **Table 4.2**. Sample sizes in the range 0.0801 to 0.1078 g were digested in 10.0 ml H_2SO_4 for 45 minutes and 60 minutes. No observable solid remained in the vessels after both irradiation periods. The solutions were transferred and prepared for ICP-OES analysis as indicated in **Chapter 4**, **Section 4.3.3.2**.

The %Nb recoveries of 97.8% and above obtained from this study indicated the complete dissolution of the Nb_2O_5 was accomplished after 45 minutes and no further change was observed on further irradiation (**Table 5.7**) in the 60 minutes digestion period. These results clearly indicate that Nb_2O_5 can be completely dissolved in sulphuric acid under these microwave conditions and thus avoid the use of hydrofluoric acid for its successful digestion/dissolution.

Table 5.7: %Nb recoveries from different digestion periods.

Digestion time/ minutes		**45**				**60**			
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.0801	0.0832	0.0999	0.1057	0.1078	0.1016	0.0822	0.1003
	Mean Conc.[a]/ppm	54.82	57.87	69.06	73.21	74.35	69.24	56.31	69.55
	RSD[b]	0.17	0.27	1.03	1.75	0.41	0.25	0.29	0.92
	%Nb recovery	**97.91**	**99.50**	**98.89**	**99.08**	**98.66**	**97.49**	**98.00**	**99.19**
Calibration curve properties	Slope	1.696							
	Intercept	0.003100							
	R^2	0.9999							

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

5.3.4 ICP-OES analysis for acid dissolution of niobium metal

In this study, the dissolution of Nb metal in different acids was investigated. 0.15 g of the metal pieces were added to concentrated HCl, HNO_3, H_2SO_4, H_3PO_4 and aqua regia and boiled on a hot plate for an hour. Visual inspection indicated no change in the metal appearance after an hour of heating. The metal pieces were removed and the solutions were quantitatively transferred to the 100.00 ml volumetric flasks and diluted as indicated in **Chapter 4**, **Section 4.3.4.1**. The ICP-OES measurements were made the following day.

The quantitative results obtained (**Table 5.8**) from this study indicated a recovery of 0.36% Nb for H_2SO_4 with almost no dissolution using HCl, HNO_3 and aqua regia clearly indicating that Nb metal is highly resistant to H_3PO_4 and H_2SO_4 chemical attack using hot plate heating conditions and even more so for HNO_3, HCl and aqua regia under these conditions. The RSD values obtained indicated that the measurements' reproducibility was good.

Table 5.8: Dissolution of niobium metal in different mineral acids

	Acid	**H_3PO_4**	**H_2SO_4**	**HCl**	**HNO_3**	**Aqua regia**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.1104	0.1144	0.1004	0.1022	0.9914
	Mean Conc.[a]/ppm	0.3473	0.4137	0.00001500	0.00001000	0.00002700
	RSD[b]	0.35×10^{-3}	0.41×10^{-3}	0.14×10^{-2}	0.21×10^{-2}	0.62×10^{-2}
	%Nb recovery	**0.31**	**0.36**	**0.01**	**0.01**	**0.00**
Calibration curve properties	Slope	1.708	1.909	1.839	1.932	1.921
	Intercept	-0.02700	-0.05010	-0.0263	-0.05960	-0.06510
	R^2	0.9998	0.9994	0.9999	0.9992	0.9990

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

5.3.5 ICP-OES analysis for microwave-assisted dissolution of Nb metal in H_2SO_4

Repeating the same procedure that was used in the previous section, the niobium foil was irradiated in the microwave oven for 45 minutes (see **Chapter 4**, **Section 4.3.4.2**) using H_2SO_4 as acid. Visual inspection indicated that all the niobium foil dissolved after 45 minutes of microwave digestion. The solutions were then quantitatively transferred to the 100.00 ml volumetric flasks and diluted to the mark

with distilled water for ICP-OES analysis. The %Nb recoveries obtained on analysis by ICP-OES are reported in **Table 5.9**.

The recovery of 99+% Nb for all the runs indicates that the use of microwave-assisted dissolution is extremely successful for the dissolution of the metal in H_2SO_4. The reproducibility of the measurements (expressed as RSD) was also very good. This method therefore points to an alternative method for Nb metal and avoids the use of HF in the digestion process.

Table 5.9: Microwave-assisted dissolution of niobium foil in H_2SO_4

Sample measurements and calculations	Weighed Mass/g Nb	0.0418	0.049	0.0601	0.0742
	Mean Conc.[a]/ppm	41.77	48.96	60.08	74.03
	RSD[b]	0.70	0.23	1.03	0.81
	%Nb recovery	**99.93**	**99.91**	**99.96**	**99.78**
Calibration curve properties	Slope	1.696			
	Intercept	0.003050			
	R^2	0.9999			

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

During the study it was found that the time between sample preparation and ICP-OES measurement also played a significant role in the final results. The results in **Table 5.10** show that the solutions had to be allowed to stand for some hours to stabilize before ICP-OES measurements were made to avoid over readings. The results obtained from the ICP-OES measurements made 1 hour after the solutions were prepared were in excess of 100% but the results obtained when the same solutions were left to stand for a longer period (minimum of 16 hours) were in the range of 97.91 to 99.93%.

Table 5.10: Nb and Nb_2O_5 solutions measured on different dates

Sample preparation date		**ICP-OES measurements' date**			
24-Jul-08		**24-Jul-08**		**25-Jul-08**	
Sample name	**Weighed Mass/g Nb_2O_5**	**conc. Nb**	**% Nb recovery**	**conc. Nb**	**% Nb recovery**
Nb_2O_5	0.0801	58.94	105.26	54.82	97.91
Nb_2O_5	0.1057	77.22	104.61	73.21	99.08
Nb	0.0418	46.14	110.39	41.77	99.93
Nb	0.0742	80.61	108.64	74.03	99.78

5.3.6 ICP-OES analysis for dissolution of niobium pentafluoride (NbF_5)

The dissolution of high purity NbF_5 was also investigated using concentrated sulphuric acid, double distilled water at room temperature and pressure (r.t.p.) and sulphuric acid microwave assisted dissolution under standard microwave conditions (see also **Chapter 4**, **Section 4.3.5**).

From the results in **Table 5.11** it is clear that the NbF_5 easily dissolves to a large extent in water and sulphuric acid (recoveries of 94 and 95%) at room temperature, but recoveries of about 100% are obtained when microwave digestion was employed. From these results it's apparent that the fluoride compound dissolved much easier than the oxide or the metal foil under milder conditions. Results obtained during this study however indicated that sulphuric acid must be added to the filtrate in the water dissolution procedure immediately after filtration in order to keep Nb in solution which otherwise precipitates (most probably as the hydroxide) in the neutral solution.

Table 5.11: Niobium fluoride dissolution quantification by ICP-OES

Acid		**$H_2SO_{4(micr)}$**	**$H_2SO_{4(micr)}$**	**$H_2SO_{4(conc.)}$ @ r.t.p**	**H_2O @ r.t.p**
Sample measurements and calculations	Weighed Mass/g NbF_5	0.0832	0.0916	0.096	0.0893
	Mean Conc.[a]/ppm	40.70	44.56	444.2	405.4
	RSD[b]	0.26	0.28	0.38	0.34
	%Nb recovery	**100.95**	**100.40**	**95.49**	**93.68**
Calibration curve properties	Slope	1.909			
	Intercept	-0.05010			
	R^2	0.9990			

[a]Measured concentrations were corrected by subtracting the background contributions in the blank
[b]Relative standard deviations are based on *n* = 3 measurements

5.3.7 Trace element determination in high purity Nb samples

Qualitative and quantitative analyses were also performed with the ICP-OES to determine the type and amount of impurities (trace elements) present in the dissolved Nb metal, Nb_2O_5 and NbF_5 solutions. An element was considered as present in the solution if it showed clear emission peaks on at least three of its most sensitive analytical lines. Some of the elements' qualitative data were ambiguous in that peaks at some wavelengths had a lot of noise accompanying them. Quantitative results were used to corroborate the qualitative results.

For some elements it was difficult to make an accurate decision about its presence from the qualitative data due the possible spectral interferences at the sensitive lines of the element. For example, the determination of B at the 249.687 nm analytical line (due to Nb 249.697 nm), Cu at 324.754 nm (due to Nb 324.747 nm), and B at 182.640 nm (due to S 182.037 and 182.625 nm) would be greatly affected by the presence of Nb in the H_2SO_4 matrix. The elements cited in **Table 5.12** were detected in the three different samples (Nb_2O_5, Nb foil and NbF_5) and were subsequently quantified. From the quantitative analyses some elements such as Ti and Ca were verified as absent in all the solutions while other elements such as Ba gave readings

below their detection limits in Nb_2O_5 and Nb metal solutions at the selected emission line (233.527 nm).

Table 5.12: ICP-OES determination of trace elements in niobium metal, niobium oxide and niobium fluoride (%)

Element	Wavelength (nm)	Nb_2O_5	Nb metal	NbF_5
Na	588.995	0.01	-	-
Cu	327.396	0.30	0.38	0.35
Si	251.612	0.68	0.52	1.49
Mo	203.845	-	-	-
Ti	336.121	-	-	-
Ca	396.847	-	-	-
Fe	239.562	0.01	0.01	-
B	208.959	-	-	0.22
Zn	288.215	0.06	0.05	0.06
Ba	233.527	-	-	0.11

The results in **Table 5.12** indicate Cu, Si and Zn to be present in all three samples and that the substance with the highest impurity is NbF_5 with a 1.5% Si content. The rest of the impurities are all below 1% in all the compounds with the least amount of impurities present in the Nb metal. However, the total impurities obtained in all the three samples were above the expected total amounts of impurities with 1.06% total impurity in Nb_2O_5 (purity = 99.99%), 1.04% in Nb metal foil (purity = 99%) and 2.08% NbF_5 (purity = 98%).

5.3.8 ICP-OES analysis for fusion digestion of Nb_2O_5

5.3.8.1 Effect of the different fluxes

Three different fluxes namely $Li_2B_4O_7$, $LiBO_2$ and NaOH were tested for the fusion digestion of high purity Nb_2O_5. The melt that was formed during this process was dissolved, filtered and diluted as indicate in **Chapter 4**, **Section 4.3.7**. Solutions obtained after filtration were prepared for the ICP-OES measurements using the standard addition method procedure as outlined in **Section 5.2.4.2**.

The %Nb recoveries obtained from this study indicated that the Nb dissolution was the highest for $Li_2B_4O_7$ flux and the least for $LiBO_2$ (**Table 5.13**). However, even this high recovery did not provide a satisfactory % recovery. Sodium hydroxide as flux reagent produced Nb recovery that was between the values obtained for the two boron fluxes and therefore did not provide a complete recovery.

Table 5.13: Standard addition and fusion dissolution of Nb_2O_5 in different fluxes (Standard addition method)

Flux / solvent		**$Li_2B_4O_7$/ 3.25% HNO_3**	**$LiBO_2$/ 3.25% HNO_3**	**NaOH/ H_2O**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.1056	0.1057	0.1039
	Conc./ppm	167.3	3.747	66.56
	%Nb recovery	**22.66**	**0.51**	**9.16**
Calibration curve properties	Slope	23.06	21.85	22.62
	Intercept	39.58	0.8189	15.06
	R^2	0.9997	0.9998	0.9998

5.3.8.2 Effect of different acids on Nb_2O_5/$Li_2B_4O_7$ melt dissolution

Dilute hydrochloric, nitric and sulphuric acids were tested for the dissolution of the Nb_2O_5/$Li_2B_4O_7$ melt which was obtained through fusion at 1100 ^oC for 30 minutes.

Three fusions were made and dissolved in 5% H_2SO_4, 5% HCl and 3.25% HNO_3 solutions as indicated in **Chapter 4**, **Section 4.3.7.1**. Solutions obtained after filtration were treated for the ICP-OES measurements following the standard addition method procedure outlined in **Section 5.2.4.2**.

Table 5.14 presents the results obtained from the ICP-OES measurements. The results in Table 5.14 indicate that $Li_2B_4O_7$ as flux reagent and HNO_3 as solvent may be a promising method for the fusion dissolution of Nb_2O_5, but a precipitation formation that occurred during the dissolution step rendered this method unsuccessful. A change from HNO_3 to HCl and H_2SO_4 acids showed no improvement in the recovery of Nb.

Table 5.14: Dissolution of $Nb_2O_5/Li_2B_4O_7$ melt in dilute acids (Standard addition method)

Solvent		**3.25% HNO_3**	**5% HCl**	**5% H_2SO_4**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.0892	0.1104	0.1012
	Conc./ppm	167.3	105.5	66.56
	%Nb recovery	**21.47**	**14.62**	**4.10**
Calibration curve properties	Slope	20.75	4.219	20.98
	Intercept	13.89	4.759	6.090
	R^2	0.9998	0.9998	0.9997

5.3.8.3 Effect of acid concentration on the $Nb_2O_5/Li_2B_4O_7$ melt dissolution

In order to try and increase the dissolution of the melt and therefore the recovery of Nb from the dissolution step it was decided to increase the concentration of the nitric acid as indicated in **Chapter 4**, **Section 4.3.7.2**. Concentrations of 0.26, 3.25, 16.25, 32.5 and 65% HNO_3 were prepared and added to different $Nb_2O_5/Li_2B_4O_7$ melts. The solutions were filtered and Nb content was determined from the filtrate using the standard addition procedure (**Section 5.2.4.2**) for the ICP-OES measurements.

It is evident from these results that the Nb recovery increased with the increase in the HNO_3 concentration as indicated in **Table 5.15** and **Figure 5.2**. This observation indicated that the low Nb recoveries could be due to the trapping of Nb in the melt in dilute solutions and that high acid concentration lead to the release/dissolution of Nb from the melt. However, even at the highest HNO_3 concentration, a complete recovery was still not obtained and this could be attributed to a possible co-precipitation of Nb with boric acid which is present at very high concentrations. The possibility of losses due to volatilization could be ruled out at this stage.

Table 5.15: Effect of HNO_3 concentration (%) on the $Nb_2O_5/Li_2B_4O_7$ melt (standard addition method)

Acid concentration (%HNO_3)		**0.26**	**3.25**	**16.25**	**32.5**	**65**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.1035	0.1056	0.1041	0.1009	0.1006
	Conc./ppm	2.525	71.09	182.3	226.3	263.7
	%Nb recovery	**0.70**	**21.32**	**25.05**	**32.14**	**37.39**
Calibration curve properties	Slope	23.49	20.67	19.61	19.79	18.56
	Intercept	-0.5959	14.69	35.74	43.33	48.94
	R^2	0.9989	0.9999	0.9995	0.9993	0.9981

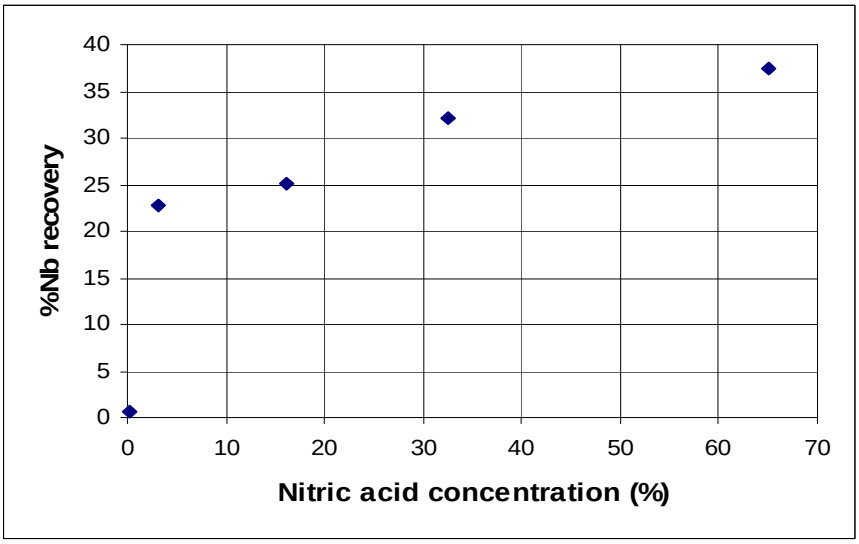


Figure 5.2: %Nb recovery in different HNO_3 concentrations

A modification step to prevent the possible influence of the boric acid on the dissolution of the Nb from the melt was introduced by converting the boron into a volatile ester by addition of methanol (see **Equation 4.1**) was employed. This modification did not produce the expected results for HNO_3 and it was decided to change to H_2SO_4. Excellent Nb recovery was obtained when H_2SO_4 was used as acid rather than HNO_3 (**Table 5.16**).

Table 5.16: The effect of concentrated HNO_3 and H_2SO_4 with methanol on $Li_2B_4O_7/Nb_2O_5$ melt (Standard addition method)

Concentrated acid		**65% HNO_3**	**95-98% H_2SO_4**
Sample measurements and calculations	Weighed Mass/g Nb_2O_5	0.0603	0.0761
	Conc./ppm	25.39	54.67
	%Nb recovery	**36.58**	**102.76**
Calibration curve properties	Slope	0.4333	0.9319
	Intercept	46.35	52.07
	R^2	0.9997	0.9990

5.3.9 ICP-OES analysis for microwave dissolution of niobium containing minerals

Three different niobium containing minerals were also investigated for element content, namely Tantalite A, Tantalite B and Sample 1. Since it was found that digestion of high-purity Nb_2O_5 under microwave conditions of 45 min digestion period, 1200 W, 60 bar pressure and maximum temperature of 280^oC was very successful, producing up to 99.50 %Nb recovery, (see **Table 5.7**) it was decided to use these microwave acid conditions as starting point to study the three mineral ore samples. The samples and digestion conditions were prepared as indicated in **Chapter 4**, **Section 4.3.9** in which visual inspection showed that some solids remained undissolved under these conditions. The solutions were filtered and diluted to the 100.00 ml mark of the volumetric flasks for the ICP-OES measurements. The

% analytes recoveries obtained after the ICP-OES measurements are presented in **Table 5.17**.

Table 5.17: 45 minutes digestion with H_2SO_4 of non-ground mineral samples

Mineral	**Tantalite A**		**Tantalite B**		**Sample 1**		**Calibration curve properties**		
Analyte	**Mean %**	**RSD[b]**	**Mean %**	**RSD[b]**	**Mean %**	**RSD[b2]**	**Slope**	**Intercept**	**R^2**
Ta_2O_5	7.73	42.98	8.91	9.87	3.46	46.97	0.1448	-0.008800	0.9999
Nb_2O_5	15.61	14.15	6.94	4.77	1.96	81.37	2.219	-0.04350	0.9999
Al_2O_3	0.27	100.84	0.28	8.16	0.10	113.83	0.3253	0.02950	0.9997
SiO_2	0.04	50.25	0.05	14.10	0.10	129.78	0.5281	0.08710	0.9999
TiO_2	0.97	61.12	1.68	13.84	0.52	79.67	19.96	0.03215	0.9998
Mn_3O_4	3.37	24.88	1.95	13.44	0.67	36.09	9.175	-0.01450	0.9997
Fe_2O_3	3.03	25.22	1.72	2.81	0.82	99.60	1.567	0.1292	0.9999
SnO_2	1.65	29.15	1.12	9.04	0.41	96.65	0.07640	-0.02440	1.0000

[b]Relative standard deviations are based on *n* = 3 measurements
[b2]Relative standard deviations are based on *n* = 2 measurements

The microwave digestion of the mineral samples under the above mentioned conditions produced results (**Table 5.17**) that were all below the target percentages (using Alfred H Knight results as a guide, **Table 5.18**). Another feature in **Table 5.17** that is unusual for microwave digestion is the unexpected low precision (repeatability). For example, the relative standard deviation (RSD) for Nb_2O_5 in Tantalite A, Tantalite B and Sample 1 are 14.15, 4.77and 81.37% respectively. This was initially attributed to the unevenness in the particle size which varied between large particles and fine sand as indicated in **Figure 4.2** which led to non-homogeneous samples that were analysed under these conditions.

Table 5.18: Chemical analyses of the tantalite minerals by Alfred H Knight analytical laboratories

Sample:	**Minerals**	
Marks	**Tantalite**	**Tantalite**
Description	**Naquissupa A**	**Naquissupa B**
Lab No.:	**80517/1**	**80517/2**
Analysis:		
	%	**%**
Ta_2O_5	27.71	32.69
Nb_2O_5	27.41	15.94
ThO_2	0.65	0.49
U_3O_8	2.83	0.98
Al_2O_3	1.85	3.44
SiO_2	5.73	11.90
WO_3	1.61	1.01
TiO_2	2.68	5.13
Mn_3O_4	8.03	7.09
Fe_2O_3	8.29	7.72
SnO_2	1.41	2.82

It was then decided to visually select particles with approximately the same dimensions (small particles chosen) for each sample and use different amounts of sample with constant H_2SO_4 volume. The microwave digestion period was increased to 60 minutes to determine the time dependence of the amount of elements recovered with constant acid volume as well as to possibly increase the amount of sample that can be dissolved. The undissolved solid was filtered and the filtrate was prepared as indicated in **Chapter 4**, **Section 4.3.9**. The % analytes obtained from the ICP-OES results are given in **Table 5.19**.

Results obtained from this study (60 minute digestion) clearly indicate an improvement of the dissolution of all the mineral ores. Precision (measured by the RSD) also improved from that obtained in the previous experiment (45 minutes digestion) but the results were still very inaccurate (average: 71.87% Nb recovery).

Table 5.19: 60 minutes digestion with H_2SO_4 of non-ground mineral samples

Mineral	Tantalite A		Tantalite B		Sample 1		Calibration curve properties		
Analyte	Mean %	RSD[b]	Mean %	RSD[b]	Mean %	RSD[b2]	Slope	Intercept	R^2
Ta_2O_5	12.78	11.03	18.62	18.78	6.75	20.65	0.1448	-0.008800	0.9999
Nb_2O_5	19.70	30.91	12.40	16.09	3.85	0.05	2.219	-0.04350	0.9999
Al_2O_3	0.33	41.58	0.62	38.07	0.46	29.62	0.3253	0.02950	0.9997
SiO_2	0.35	102.07	0.59	142.54	0.42	50.28	0.5281	0.08710	0.9999
WO_3	0.72	1.78	0.53	21.88	0.05	36.08	0.1624	-0.01034	1.000
TiO_2	1.33	14.26	3.39	47.58	1.46	36.94	19.96	0.03215	0.9998
Mn_3O_4	5.14	40.38	3.84	12.67	1.15	8.28	9.175	-0.01450	0.9997
Fe_2O_3	3.65	9.48	3.26	22.16	2.26	21.31	1.567	0.1292	0.9999
SnO_2	1.94	7.00	1.96	22.73	1.06	24.94	0.07640	-0.02440	1.000

[b]Relative standard deviations are based on *n* = 3 measurements
[b2]Relative standard deviations are based on *n* = 2 measurements

5.3.10 Particle size determination of the powder mineral samples

At this stage of the study it was decided to try and increase the accuracy and precision of these analyses by reducing the particle size of the minerals to obtain more homogeneous samples and to increase the surface area for possible reactions. After the samples were ground to a fine powder as indicated in **Chapter 4**, **Section 4.3.9**, portions of the samples were sent to Necsa for the determination of the particle sizes. **Figures 5.3**, **5.4** and **5.5** show the particle size distribution determined by a Saturn DigiSizer 5200 V1.12 in the Tantalite A, Tantalite B and Sample 1 respectively. It can be seen from these figures that the particles sizes range from below 0.1 µm to above 100 µm but the maximum particle diameter by volume frequency is approximately 10 µm in all the three mineral samples. The median values for the particle sizes (d_{50} value) were determined as 9.8, 9.5 and 11.1 µm in Tantalite A, Tantalite B and Sample 1 respectively.

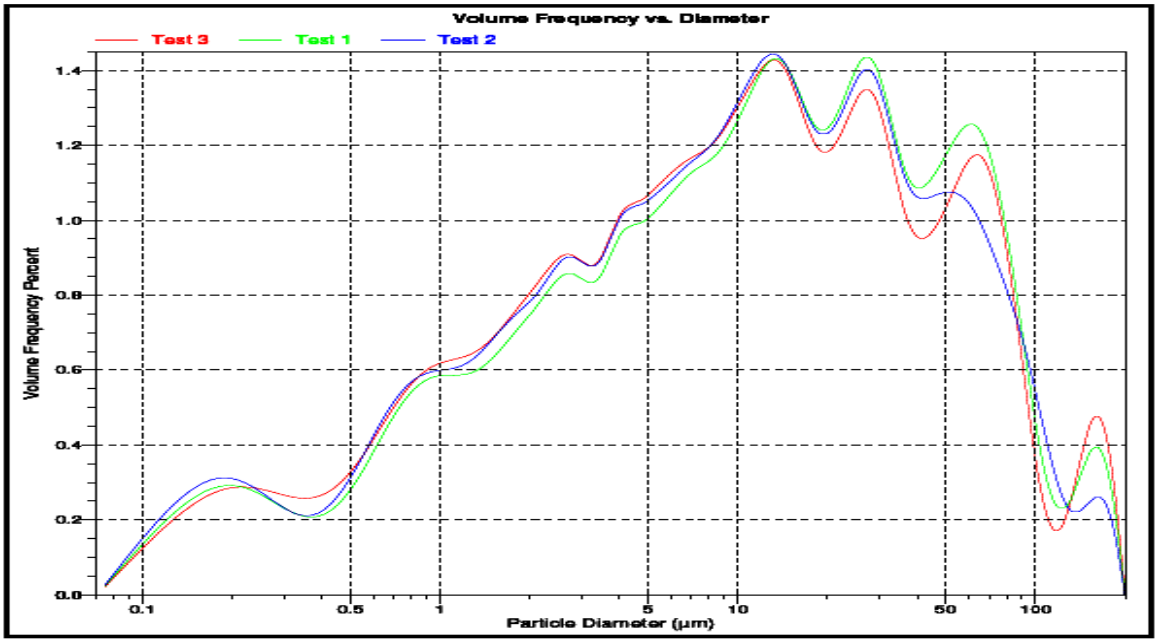


Figure 5.3: Particle size distribution in Tantalite A

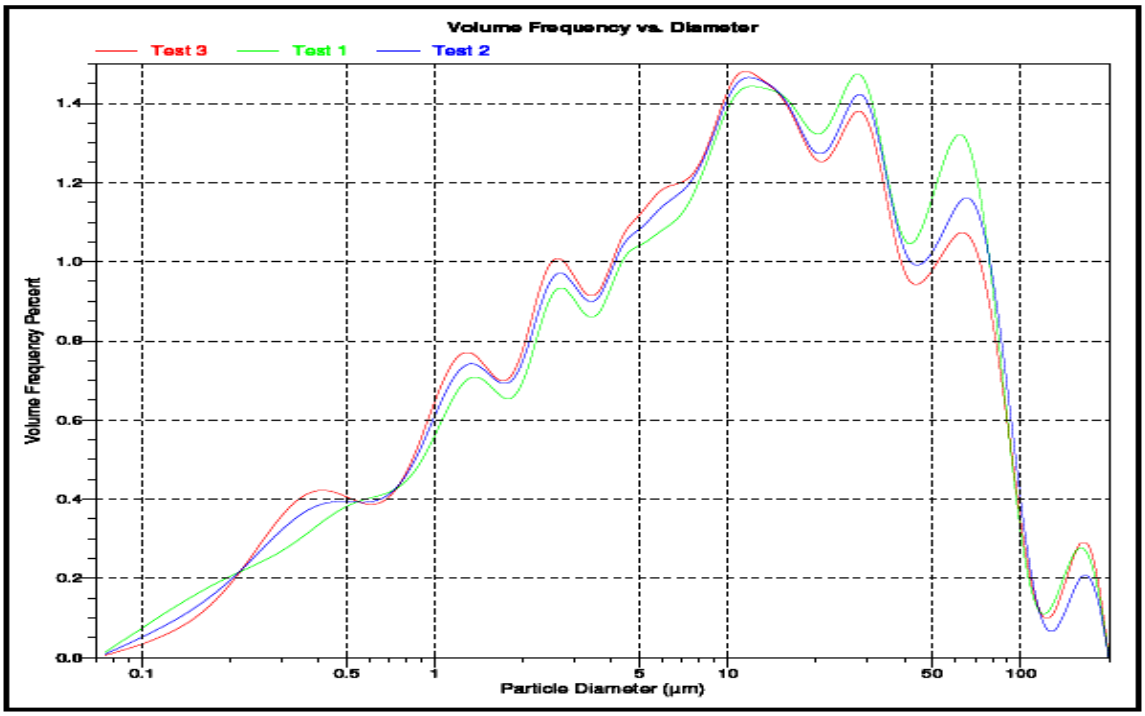


Figure 5.4: Particle size distribution in Tantalite B

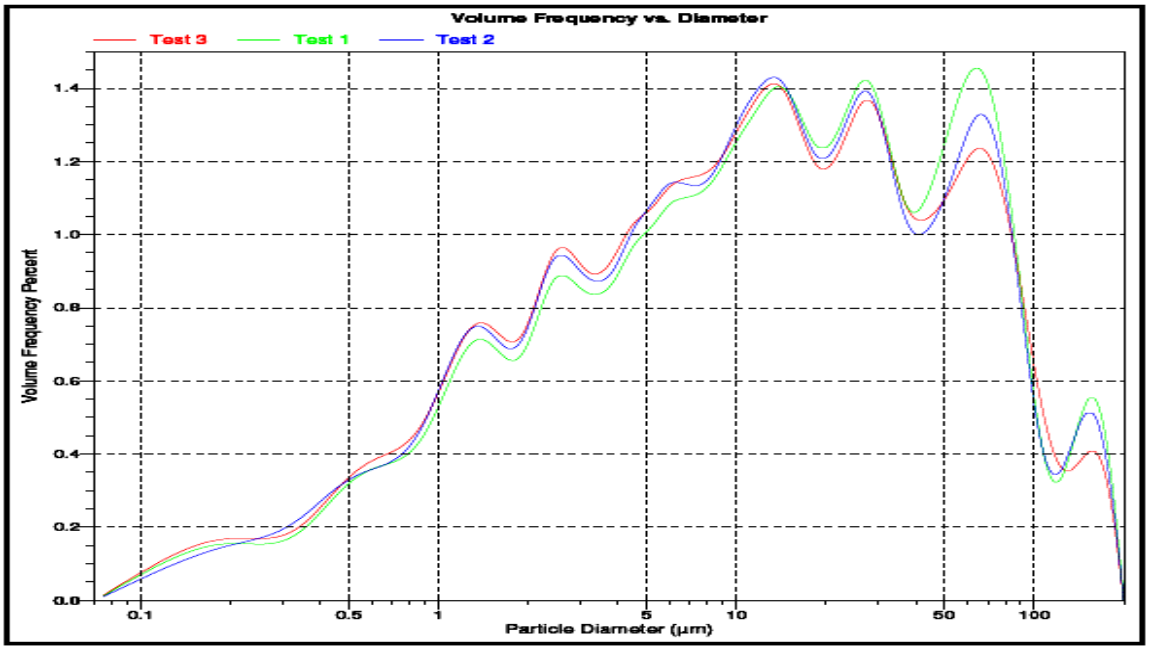


Figure 5.5: Particle size distribution in Sample 1

5.3.11 ICP-OES analysis for microwave dissolution of powder mineral samples

Portions of the milled mineral samples were then used for the microwave digestion tests. The Tantalite A sample was digested in five different acids as indicated in **Table 5.20** for 45 minutes while keeping all other microwave parameters constant at 1200 W, 60 bar and 280 ^{o}C. The results in **Table 5.20** indicate that H_3PO_4 could alternatively be used instead of H_2SO_4. It was observed that H_2SO_4 is more effective for the digestion of Nb_2O_5 than Ta_2O_5 (19.45% Nb_2O_5 versus 6.99% Ta_2O_5) while H_3PO_4 seems to work far better for both Ta_2O_5 and Nb_2O_5 (18.84% Ta_2O_5 and 22.52% Nb_2O_5). The results show that the H_2SO_4 is ineffective in dissolving SiO_2 (0.00% SiO_2).

Although H_3PO_4 and H_2SO_4 produced very promising results for the digestion of Tantalite A, the results in **Table 5.20** were still far below the target values for most of the analytes even after the samples' particle sizes were homogenised. The noteworthy observation in these results is the possibility of a separation method for

Nb and Ta using H_2SO_4 (19.45% Nb_2O_5 versus 6.99% Ta_2O_5) at 45 minutes digestion period. This observation is in agreement with that obtained by Sears results.[27] HCl dissolution results were better than for aqua regia and HNO_3 for most of the elements including Si. However, all the results obtained in this part of the study were inaccurate.

Table 5.20: ICP-OES measurement results after 45 minutes dissolution of tantalite mineral ores in different mineral acids.

Analyte	Tantalite A: % analyte in different acids				
	HNO_3	**HCl**	**Aqua regia**	**H_3PO_4**	**H_2SO_4**
Ta_2O_5	0.02	4.20	0.06	**18.84**	**6.99**
Nb_2O_5	0.08	8.12	1.18	**22.52**	**19.45**
Al_2O_3	1.28	1.43	1.50	1.94	1.43
SiO_2	0.19	1.10	1.26	3.17	0.00
WO_3	0.13	0.82	0.21	1.13	1.06
TiO_2	0.08	1.37	0.49	1.81	2.12
Mn_3O_4	1.13	1.79	1.33	6.96	4.95
Fe_2O_3	1.59	4.56	2.92	6.39	6.58
SnO_2	0.02	0.42	0.16	0.67	0.49
ThO_2	0.26	0.62	0.46	0.61	0.64
U_3O_8	0.20	2.69	1.69	2.76	2.86

5.3.11.1 Effect of digestion time of mineral samples with H_2SO_4 in the microwave

It was decided to increase the irradiation time of samples in the microwave oven to try to improve the recovery of the most important elements in these samples. Aliquots of approximately 0.10 g of the powder mineral samples were digested with H_2SO_4 for 90 minutes in the microwave. The results in **Table 5.21** clearly show a substantial improvement in the amount of elements recovered, as well as an improvement on the reproducibility (decreased RSD values) which reflects the high degree of homogeneity of the sample particle sizes. The precision is good in Tantalite A and B,

with RSD generally below 2.50% and 5.00% respectively except for Si. The deviations from the observed RSD values obtained for SiO_2 can be attributed to the inability of H_2SO_4 to react and digest SiO_2. Higher RSD values were however obtained for the Sample 1 analyses.

Table 5.21: 90 minutes digestion of the milled mineral samples

Mineral	Tantalite A		Tantalite B		Sample 1	
Analyte	**Mean %**	**RSD[b]**	**Mean %**	**RSD[b]**	**Mean %**	**RSD[b]**
Ta_2O_5	24.39	1.34	30.48	3.99	21.18	18.05
Nb_2O_5	24.67	0.53	14.98	1.54	10.40	3.41
Al_2O_3	0.85	1.31	1.00	4.57	0.52	29.65
SiO_2	0.03	113.98	0.00	0.00	0.27	141.42
WO_3	1.33	2.33	0.83	2.31	0.24	11.61
TiO_2	2.43	0.76	5.01	2.11	8.85	0.98
Mn_3O_4	6.76	1.06	5.76	2.93	3.08	3.70
Fe_2O_3	6.12	0.70	5.19	1.81	11.89	7.21
SnO_2	0.79	1.30	1.65	3.47	0.09	8.53
ThO_2	0.60	0.88	0.42	0.41	0.48	0.63
U_3O_8	2.82	0.64	1.06	2.29	0.35	2.33

Although the 90 minutes digestion in H_2SO_4 had improved the dissolution of the most of the analytes, the results were still below target values. It was decided to repeat the above procedure (**Section 5.11.2**) and increase the digestion time to 150 minutes to try and increase the dissolution to 100.00%. However, no further increase of the dissolution was observed with the increase in the time of digestion as indicated by the results in **Table 5.22**. This observation led to the conclusion that maximum dissolution of the analytes was accomplished after a 90 minute digestion period.

Table 5.22: Comparison of digestion times of minerals in the microwave oven

Analyte	Digestion period					
	90 minutes			150 minutes		
	TAN. A	TAN. B	SAM 1	TAN. A	TAN. B	SAM 1
Ta_2O_5	24.39	30.48	21.18	23.63	29.96	24.71
Nb_2O_5	24.67	14.98	10.40	26.05	13.84	10.89
ThO_2	0.60	0.42	0.48	0.62	0.38	0.66
U_3O_8	2.82	1.06	0.36	2.95	0.95	0.37
Al_2O_3	0.85	1.02	0.52	1.06	1.48	0.44
SiO_2	0.03	0.00	0.27	0.00	0.00	0.00
WO_3	1.33	0.84	0.26	1.52	0.77	0.24
TiO_2	2.43	5.07	8.91	2.74	4.91	12.35
Mn_3O_4	6.76	5.86	3.16	5.96	6.78	3.20
Fe_2O_3	6.12	5.25	12.50	6.43	5.46	12.68
SnO_2	0.79	1.68	0.10	0.79	1.40	0.10
Y_2O_3			0.23			0.24
CaO			0.58			0.60

5.3.12 Fusion digestion of minerals with $Li_2B_4O_7$ and $K_2O_7S_2$

In this part of the study the mineral samples were fused with two different fluxes. Approximately 0.10 g of the mineral samples was mixed with approximately 2.0 g of lithium tetraborate fluxing reagent and $K_2S_2O_7$. The mixtures were fused at 1100 ^oC for 30 minutes. The melts were treated as indicated in **Chapter 4**, **Section 4.3.10.1**.

The dissolution of the sample/lithium tetraborate melt in nitric acid was unsuccessful, yielding poor results for most of the analytes (45.79% Nb_2O_5 recovery). Either tantalum hydroxide or niobium hydroxide or both precipitate in the solution causing the possible co-precipitation of other target elements in HNO_3. The addition of methanol to remove boric acid generated *in situ* also could not completely eliminate the precipitation problem. A change from $Li_2B_4O_7$ to $K_2S_2O_7$ as flux reagent had even poorer results indicating that $K_2S_2O_7$ does not work as a flux for any of the tantalite minerals. The results (**Table 5.23**) showed that $Li_2B_4O_7$ is however more successful

as flux compared to $K_2S_2O_7$. From these results it is however observed that WO_3 recovery was higher for the $K_2S_2O_7$ fusion than for $Li_2B_4O_7$ fusion.

Table 5.23: ICP-OES measurement results after fusion dissolution of the Tantalite A sample with $K_2S_2O_7$ and $Li_2B_4O_7$ (Standard addition method)

Method of melt dissolution	Tantalite A	
	$Li_2B_4O_7$: 32.5% HNO_3 + methanol	**$K_2S_2O_7$: 10% H_2SO_4 + 10% tartaric acid**
Analyte	%	%
Ta_2O_5	12.82	0.03
Nb_2O_5	12.55	0.51
Al_2O_3	1.84	0.32
SiO_2	2.09	0.08
WO_3	0.01	1.11
TiO_2	2.00	0.08
Mn_3O_4	9.17	4.29
Fe_2O_3	7.62	0.45
SnO_2	2.97	0.26

Although $Li_2B_4O_7$ fusion and HNO_3/methanol dissolved most of the elements in the different samples, these conditions still did not give satisfactory recoveries. It was decided to investigate the effect of another acid on the mineral/$Li_2B_4O_7$ melt. In this study concentrated H_2SO_4 was used with methanol to dissolve the mineral/$Li_2B_4O_7$ melt. The results in **Table 5.24** show that a change from nitric acid/methanol to sulphuric acid/methanol improved the % analytes recoveries significantly (27.01% compared to 12.55% Nb_2O_5). The fusion with $Li_2B_4O_7$ and the subsequent removal of B from the solution which may form non-soluble boric acid proved to be the most successful dissolution method with best recoveries for all the analytes under investigation.

Table 5.24: ICP-OES measurement results after fusion dissolution of tantalite mineral ores with $Li_2B_4O_7$ and dissolution in H_2SO_4 and methanol (Standard addition method)

Metal oxide	Minerals		
	Tantalite A	**Tantalite B**	**Sample 1**
	%	%	%
Ta_2O_5	30.08	32.63	33.00
Nb_2O_5	27.01	15.72	8.74
ThO_2	0.54	0.41	0.29
U_3O_8	2.81	1.20	0.14
Al_2O_3	2.04	2.55	1.47
SiO_2	3.52	10.99	2.51
WO_3	1.18	0.61	0.16
TiO_2	2.77	6.50	8.19
Mn_3O_4	8.91	7.62	3.13
Fe_2O_3	8.34	7.01	18.71
SnO_2	1.64	2.91	0.15
Y_2O_3	**...**	**...**	0.24
CaO	**...**	**...**	0.52

5.3.13 XRF analyses of the mineral powder samples

In order to confirm the quantitative analyses, it was decided to corroborate the mineral ICP-OES results with solid XRF analyses. The fine powdered samples were mixed with the binder material and pressed to form the pellets that were analysed by the X-ray fluorescence spectrometer (see **Chapter 4**, **Section 4.3.12**). Due to lack of enough calibration standards and other factors such as the sensitivity of the instrument to certain elements, only a semi-quantitative analysis was possible.

The XRF results presented in **Table 5.25** are close to the target results (see **Table 5.18**) for most of the elements. The results obtained from the XRF technique were correlated with the ICP-OES results obtained by the fusion digestion with $Li_2B_4O_7$ and melt dissolved with H_2SO_4/methanol solvent to determine the success of the dissolution method used for the wet analysis.

Table 5.25: XRF analyses results of the mineral samples

Analyte	Tantalite A	Tantalite B	Sample 1
	%	%	%
Nb_2O_5	27.84	17.21	13.12
SnO_2	0.44	3.34	-0.93
Ta_2O_5	24.77	33.88	32.86
WO_3	**11.14**	**9.61**	**8.67**
ThO_2	**2.46**	**1.57**	**0.99**
U_3O_8	3.01	0.87	0.12
Al_2O_3	**4.94**	**4.95**	**5.29**
Fe_2O_3	7.21	6.51	27.33
Mn_3O_4	8.12	7.7	4.41
TiO_2	2.86	5.64	20.5
SiO_2	**9.1**	**10.34**	**16.76**
Y_2O_3	0.01	0.02	0.15
Ca	2.21	1.05	3.03

The semi-quantitative results obtained for WO_3, for example, are unreliable due to the lack of enough calibration standards for W and it was decided that they should be omitted for correlations in **Figure 5.6** to **5.8**. Si and Al calibration curves were also not usable and therefore the SiO_2 and Al_2O_3 results were not included in the correlations. **Figures 5.6** to **5.8** show the correlation between the flux digestion results analysed with ICP-OES and XRF analyses results.

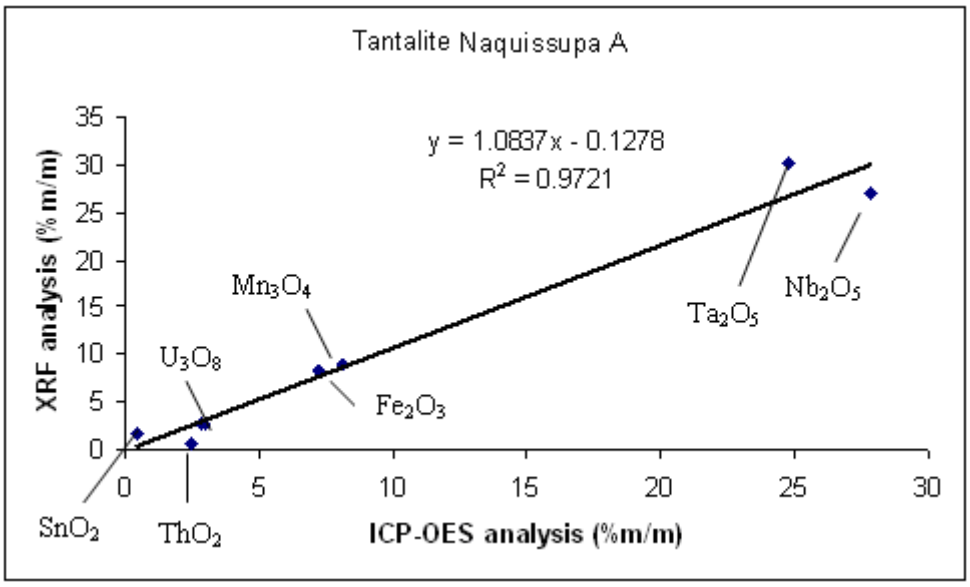


Figure 5.6: Correlation between the results obtained for Tantalite A using ICP-OES and XRF.

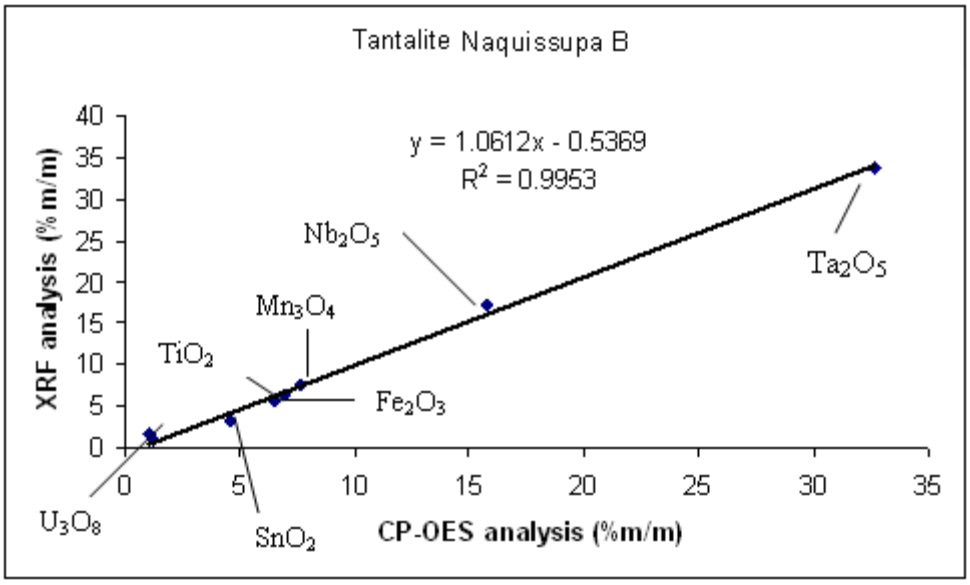


Figure 5.7: Correlation between the results obtained for Tantalite B using ICP-OES and XRF.

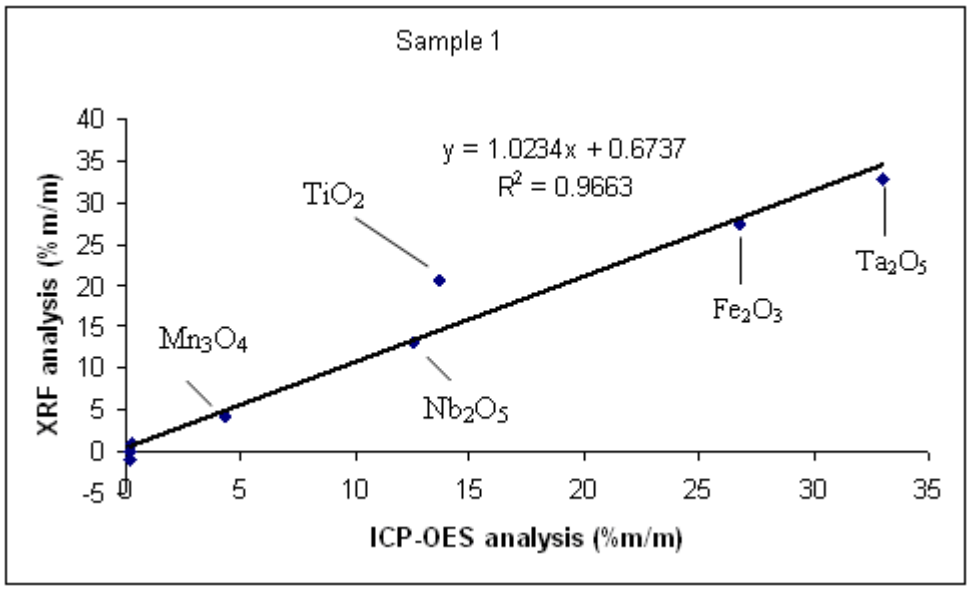


Figure 5.8: Correlation between the results obtained for Sample 1 using ICP-OES and XRF.

Agreement between XRF and ICP-OES analysis is in general satisfactory with slopes of 1.08, 1.06 and 1.02 intercepts of -0.12, -0.54 and 0.67 for Tantalite A, Tantalite B and Sample 1 respectively. Correlation coefficients between 0.966 and 0.995 indicate extremely good correlation between the quantitative results obtained with these two analytical methods. Agreement was very good for TiO_2 (RSD value: 2.27%) and Nb_2O_5 (RSD value: 2.13%) in Tantalite A and Ta_2O_5 (RSD value: 2.66%) and Mn_3O_4 (RSD value: 0.70%) in Tantalite B.

The XRF results indicate the successfulness of the flux digestion method and the ICP-OES analyses for tantalite mineral ores. Some disagreements observed between XRF and ICP-OES analyses for some analytes (such as SnO_2 and ThO_2) can be explained by the inhomogeneity of the mass per unit area and the particle size effects for XRF and possible contaminations from the poorly cleaned grinding vessels during sample preparations for XRF and ICP-OES analyses.

5.3.14 Qualitative determination of the composition of the mineral samples

5.3.14.1 X-Ray diffraction analyses of the minerals

It was finally decided to try and identify (qualitative analysis) the sample demarcated as Sample 1. The powdered samples were placed in the sample holders and prepared for the X-ray diffractometer for measurements as indicated in **Chapter 4**, **Section 4.3.11**. **Figures 5.9 – 5.11** show the XRD patterns for the mineral samples that were investigated. The identities of the mineral samples were determined by automated searching and matching the more intensive XRD patterns obtained, with the XRD patterns of known materials at the Geology Department at the University of the Free State.

The XRD patterns for the two Tantalite minerals are identical with some differences in the intensity of some of the main peaks such as the peak at around $2\theta = 30^{o}$ (**Figures 5.9** and **5.10**, see also **Table 5.26**) and were totally different from the XRD pattern of the unknown Sample 1. However, no XRD patterns of the standards were found to exactly match all the peaks in all the three mineral samples investigated in this study. The best XRD match for the two Tantalite minerals (A and B) was obtained with the ferrocolumbite and manganotantalite mineral patterns. Some non-matching peaks were found to match with those of euxenite, microlite (see **Table 1.1**) and quartz. Interesting enough is that most of the peaks in the unknown Sample 1 XRD pattern showed a better match with both the ferrocolumbite and manganotantalite mineral XRD patterns, while some other peaks in its XRD spectrum matched with that of microlite and quartz. The amount of quartz was found to be very high in Sample 1 compared to that present in the Tantalites A and B as indicated by the strong peak at $2\theta = 26.54^{o}$ for Sample 1 which is less intense in the respective Tantalite A and Tantalite B minerals.

Table 5.26: The XRD reflection angles for the mineral samples

Mineral	Angle of reflection (2θ/degrees)														
TAN. A	12.3	14.8	24.4	26.8	28.0	**30.0**	31.3	35.0	35.9	40.8	43.1	51.6	53.2	63.6	67.9
TAN. B	12.4	14.8	24.4	26.7	28.0	**31.0**	31.3	34.4	35.8	40.8	43.1	…	53.2	63.5	67.8
SAM 1	14.7	21.0	24.3	**26.5**	27.9	30.0	32.7	34.7	37.9	52.3	60.0	61.6	63.7	66.8	…

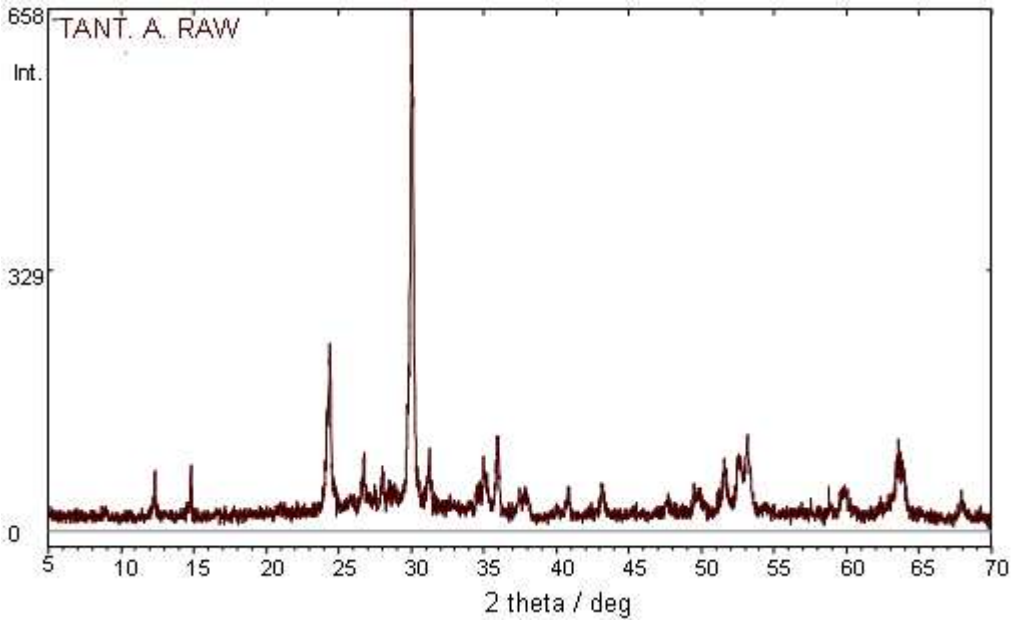


Figure 5.9: XRD pattern of Tantalite Naquissupa A mineral

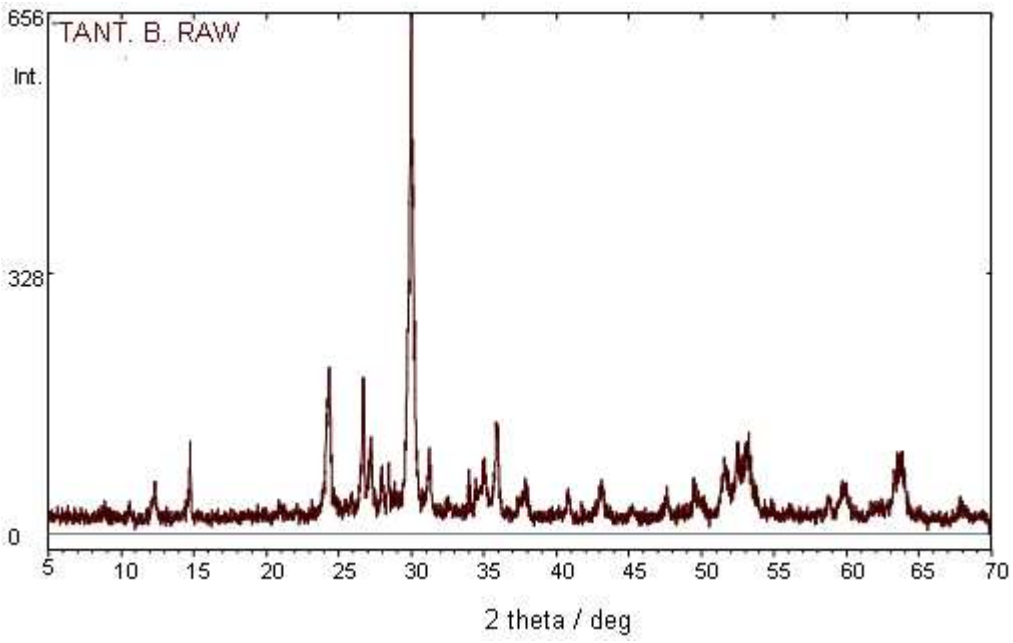


Figure 5.10: XRD pattern of Tantalite Naquissupa B mineral

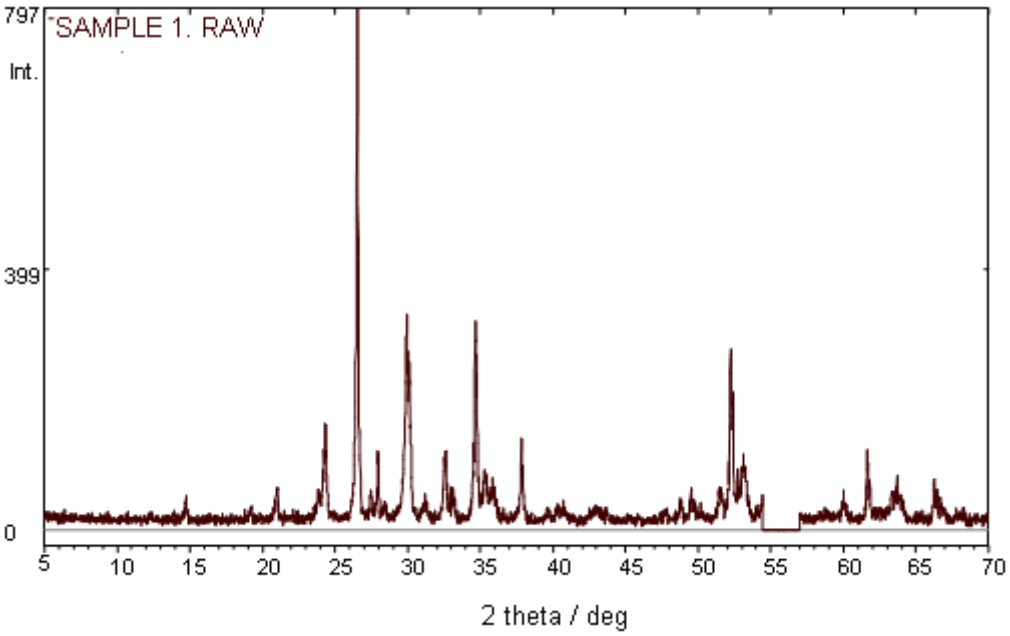


Figure 5.11: XRD pattern of an unknown Sample 1 mineral

5.3.14.2 Magnetism, radioactivity and microscopic properties of the mineral samples

Since the XRD patterns indicated a mixture of minerals in all the mineral samples studied, it was decided to investigate the magnetic as well as the radioactive

properties of these minerals to improve the allocation of the mineral identity of the samples. The samples were poured on a piece of paper and a hand magnet was then moved across the paper to check if the grains were attracted to the magnet. Sample 1 showed the most intense magnetic properties with a large number of its grains/particles that reacted to the magnetic field, followed by Tantalite A (but very few grains were attracted to the magnet) and finally Tantalite B which showed almost no magnetism at all. The high magnetism observed in Sample 1 was attributed to the higher Fe content obtained in this mineral (see **Tables 5.24** and **5.25**) which is higher than in the Tantalite (A and B) minerals.

Radioactivity determinations (qualitative analysis) were accomplished using a Scintillometer which showed that both Tantalite A and Tantalite B contained radioactive materials as confirmed with the presence of U (1.2 to 2.81%) and Th (0.41 to 0.54%). No detectable radioactivity was observed in Sample 1, most probably due to the low U and Th contents as indicated in **Table 5.24**. The radioactivity in these samples (Tantalites A and B) could be due to the presence of microlite and euxenite that were obtained by the XRD analyses since these minerals always contain radioactive elements[92,93] while pure tantalite is not radioactive.[94] Although some of the lines on the XRD pattern for Tantalites A and B correspond rather well to euxenite mineral, this mineral may be present in very small amounts since it is very difficult to determined its crystalline structure from the raw material (without prior heat treatment to induce recrystallization) by the XRD analysis. The identification is prevented by the process called metamictization (self-radiation that destroys the crystalline structure) which is evident in euxenite and which is a radioactive mineral.[95]

[92] http://www.uraniumminerals.com/UTh/Euxenite.htm

[93] http://www.galleries.com/minerals/oxides/microlit/microlit.htm

[94] Baba, A.A., Adekola, F.A., Dele-Ige, O.I., Bale, R.B., *Journal of Minerals & Materials Characterization & Engineering*. 2007. **7** (1). pp 83-95

[95] http://www.hedegaard.com/Minerals/Groups/Radioactives.html

The minerals were also visually inspected under the microscope to possibly identify the grains of the different minerals that were obtained by XRD analyses and possibly to identify any minerals that may exist in very small quantities since their XRD patterns were not well defined in the obtained spectra. Microscopic examination showed grains of ferrocolumbite/manganotantalite, microlite, quartz, muscovite (mica), garnet, tourmaline and a blackish mineral with a conchoidal fracture that resembles euxenite in both the Tantalite A and Tantalite B samples. Microscopic examination of Sample 1 showed the presence of ferrocolumbite/manganotantalite, quartz, mica, and garnet.

From these qualitative results it is clear that the XRD patterns of all the samples closely match that of ferrocolumbite and manganotantalite. However, ICP-OES and XRF results (**Tables 5.24** and **5.25**) showed that all the three minerals studied contain more tantalum than niobium, in which case the mineral is called the (mangano)tantalite (see **Chapter 1**, **Section 1.1**) instead of (ferro)columbite. At this stage, a conclusion was reached that the Tantalites A and B are a variation of manganotantalite (major component) with small amounts of microlite, euxenite, tourmaline, garnet and some quartz and mica impurities while the unknown Sample 1 is possibly a mixture of manganotantalite (major component), microlite and garnet (minor components) with some impurities of quartz and mica. The results of all the tests done in this part are summarised in **Table 5.27**.

Table 5.27: Test results for the composition identification of the mineral samples

Test / Sample	Minerals identified by XRD analysis	Minerals observed under microscope	Radioactivity	Magnetism
Tantalite A	Quartz (accessory), mica (accessory), microlite, manganotantalite, ferrocolumbite, euxenite, hornblend (amphebles)	Quartz (accessory), mica (accessory), microlite, manganotantalite, ferrocolumbite, euxenite, garnet, tourmaline	Radioactive	Very little magnetism
Tantalite B	Quartz (accessory), mica (accessory), microlite, manganotantalite, ferrocolumbite, euxenite, hornblend (amphebles)	Quartz (accessory), mica (accessory), microlite, manganotantalite, ferrocolumbite, euxenite, garnet, tourmaline	Radioactive	Very little to no magnetism
Sample 1	Manganotantalite, ferrocolumbite, quartz, mica, microlite?, hornblend (amphebles)	Manganotantalite, ferrocolumbite, quartz, mica, garnet	Very little radioactivity	Strong magnetism

5.4 CONCLUSION

The final stage of the analysis in this study was to assess the success of the dissolution methods tested with ICP-OES. For accurate and precise qualitative and quantitative determinations by ICP-OES the dissolution method must completely decompose the sample. However, as mentioned earlier in this chapter, reactivity of the analytes (especially Nb and Ta) in solution can affect the method of dissolution. The direct solid analysis by XRF was also employed for comparison with the ICP-OES results.

Good precision was observed in the results of the acid dissolution of the pure Nb_2O_5 and Nb metal by using the hot plate with RSD values of 0.008 and 0.0004, but the results were very inaccurate (0.94% and 0.36% respectively). Good recoveries were also obtained for NbF_5 where 95% and 93% were obtained from the dissolution of this sample in sulphuric acid and water respectively indicating good precision and accuracy.

Microwave-assisted digestion with sulphuric acid dissolves the niobium samples studied to varying degrees. Complete dissolution of up to 100% recoveries for all the high purity niobium samples was obtained after 45 minutes time of heating. The digestion time is the only microwave parameter that was investigated in this study and it was found that the dissolution of some samples in the microwave is time dependent. For Nb_2O_5 dissolution a minimum of 45 minutes is required to obtain recoveries of 99+% Nb. The mineral samples require a minimum of 90 minutes to obtain up to 90% Nb recovery. The fact that microwave-sulphuric acid digestion does not dissolve silica, renders this method less desirable for a complete ICP-OES analysis.

Flux fusion method for Nb_2O_5 and all the mineral samples using $Li_2B_4O_7$ as a flux reagent and concentrated H_2SO_4/methanol mixture as a solvent improved the flux melt dissolution greatly. Recoveries of 108.57% Ta_2O_5, 98.56% Nb_2O_5, 100.56% Fe_2O_3 and 111.00% Mn_3O_4 for the Tantalite A sample and 100.58% Ta_2O_5, 109.59% Nb_2O_5, 99.23% Fe_2O_3 and 101.76% Mn_3O_4 for the Tantalite B sample were obtained. **Table 5.28** summarizes the ICP-OES results of the dissolution methods (see also **Table 4.6**) that were tested in this study. %Nb recoveries have been used as an example to show the accuracy of the results obtained by the different dissolution methods.

Table 5.28: %Nb recovery from different dissolution methods for niobium samples

Sample identity	Maximum %Nb recovery		
	Acid dissolution	Microwave-assisted dissolution	Fusion dissolution
Nb_2O_5	0.94	99.50	102.76
NbF_5	95.49	100.95	…
Nb	0.36	99.93	…
Tantalite A	…	90.00	98.56
Tantalite B	…	93.98	109.59
Sample 1	…	…	…

The agreement between XRF results and ICP-OES results is satisfactory indicating the successfulness of the fusion with $Li_2B_4O_7$ and dissolution of the melt in concentrated H_2SO_4 and methanol. Relative standard deviations (RSD values) were 2.13, 13.70, 6.60 and 10.27 % for Nb_2O_5, Ta_2O_5, Mn_3O_4 and Fe_2O_3 respectively in Tantalite A. For Tantalite B the RSD values were 6.40, 2.66, 0.70 and 5.14% for Nb_2O_5, Ta_2O_5, Mn_3O_4 and Fe_2O_3 respectively. The best agreement was obtained in the Sample 1 analyses where the RSD values were 3.38, 0.31, 1.08 and 1.50% for Nb_2O_5, Ta_2O_5, Mn_3O_4 and Fe_2O_3 respectively.

Comparisons between the Alfred H Knight results and the XRF and ICP-OES analyses results showed that good agreement exists between most of the analytes. Although some percentages were higher than expected for fusion and ICP-OES standard addition method, this technique still proved to be more accurate than the XRF technique (**Table 5.29**).

Table 5.29: Comparison of ICP-OES (standard addition method), XRF and Alfred H Knight results of tantalite minerals' analyses

Analyte	Tantalite A					Tantalite B				
	Knight	ICP-OES	XRF	ICP-OES	XRF	Knight	ICP-OES	XRF	ICP-OES	XRF
	$\%M_xO_y$**	$\%M_xO_y$	$\%M_xO_y$	%rec.	%rec.	$\%M_xO_y$**	$\%M_xO_y$	$\%M_xO_y$	%rec.	%rec.
Ta_2O_5	27.71	30.08	24.77	**108.57**	**89.39**	32.69	32.88	33.9	**100.58**	**103.64**
Nb_2O_5	27.41	27.01	27.84	**98.56**	**101.57**	15.94	17.47	17.2	**109.59**	**107.97**
ThO_2	0.65	0.54	**2.46**	**82.66**	**378.46**	0.49	0.41	**1.57**	**82.85**	**320.41**
U_3O_8	2.83	2.81	3.01	**99.25**	**106.36**	0.98	0.94	0.87	**95.77**	**88.78**
Al_2O_3	1.85	2.04	**4.94**	**110.48**	**267.03**	3.44	2.85	**4.95**	**82.84**	**143.90**
SiO_2	5.73	3.52	**9.1**	**61.38**	**158.81**	11.9	10.20	**10.3**	**85.68**	**86.89**
WO_3	1.61	1.18	**11.14**	**72.99**	**691.93**	1.01	0.84	**9.61**	**82.82**	**951.49**
TiO_2	2.68	2.77	2.86	**103.29**	**106.72**	5.13	5.18	5.64	**101.03**	**109.94**
Mn_3O_4	8.03	8.91	8.12	**111.00**	**101.12**	7.09	7.21	7.7	**101.76**	**108.60**
Fe_2O_3	8.29	8.34	7.21	**100.55**	**86.97**	7.72	7.66	6.51	**99.23**	**84.33**
SnO_2	1.41	1.64	0.44	**116.28**	**31.21**	2.82	2.91	3.34	**103.36**	**118.44**

****** Reference values

In general, the microwave assisted dissolution with H_2SO_4 for high purity Nb metal, Nb_2O_5 and NbF_5 yielded very accurate results and excellent precision was observed in all the analyses. The ICP-OES normal (or external) calibration curves obtained for all the analytes showed good linearity (R^2 values ≥ 0.999) and small y-intercepts which gave an indication of the reliability of the analytical results. A change to an ICP-OES standard addition method for the fusion digestion was also very successful since no significant chemical interferences from the fluxes were observed in the final results. Calibration curves obtained using this method also showed an excellent linearity for all the elements that were analysed in this study.

6 EVALUATION OF THE STUDY AND FUTURE RESEARCH

6.1 DEGREE OF SUCCESS WITH REGARD TO THE SET OBJECTIVES

This chapter evaluates the achievements in this study in terms of the objectives laid out at the beginning of this study. In general this study has been very successful in achieving the objectives as outlined in **Chapter 1**, **Section 1.4**. The literature study undertaken in this study has indicated that a significant amount of work has been done on the dissolution and analysis of niobium compounds but that the dissolution of niobium compounds was normally achieved by the use of the dangerous and difficult to handle hydrofluoric acid. Additionally, limited research has been done on the use of flux fusion and especially microwave-assisted digestion methods for the wet analysis of these compounds. It was also evident that very little work has been done regarding the search for more environmentally-friendly methods to digest niobium containing materials.

In this study, different analytical techniques were considered for the measurements of the major and minor elements in the high purity niobium compound as well as the niobium containing minerals. ICP-OES, solid XRF and XRD were decided upon due to their multi-elemental analyses capabilities. ICP-OES has the advantage of offering rapid measurements for the analysis of the sample solutions obtained from the wet digestion techniques while XRF has an advantage of simple sample preparation but long data collection times. Comparison of the results obtained by standard addition ICP-OES and XRF techniques showed that very similar results were achieved while lithium tetraborate fusion and standard addition ICP-OES yield more accurate results (98.56 to 109.59% Nb recoveries).

The use of microwave assisted digestion was investigated for the dissolution of different niobium compounds in this study. The microwave digestion technique has several advantages that were of great importance in this study, namely reduced sample preparation time and use of closed digestion vessels which prevent the loss of analytes through volatilization and ensure less environmental contamination from the use of smaller volumes of reagents. The latter is especially important for trace element analysis in the high purity niobium metal and niobium compounds studied for which most of the impurity concentrations were very close to the detection limits of the ICP. The microwave assisted digestion with H_2SO_4 in closed PTFE vessels at 1200 W, 60 bar, 280 ^oC for 45 minutes for high purity Nb metal, Nb_2O_5 and NbF_5 produced clear solutions and the ICP-OES analyses confirmed that a total recovery of Nb was achieved in these dissolutions. Good precision and accuracy for all the analyses of the high purity niobium samples' solution were observed. This technique showed some limited ability to digest the mineral sample matrix (especially silica) and therefore required longer digestion time of 90 minutes for a better dissolution of most of the elements in the niobium containing mineral samples. This method completely avoids the use of hydrofluoric acid to dissolve high purity niobium metal, niobium oxide and niobium fluoride.

The use of a fusion digestion method for pure niobium(V) oxide and the three niobium containing minerals was investigated in this study. Different flux reagents namely sodium hydroxide, lithium metaborate, lithium tetraborate and potassium pyrosulphate were tested. Accurate results were obtained with lithium tetraborate digestion and H_2SO_4/methanol mixture for the dissolution of the resulting melt. Calibration curves obtained using both the normal and the standard addition ICP-OES analyses methods also showed good linearity for all the elements that were analyzed in the concentration ranges used in this study.

In conclusion it can be said that not only were all the main objectives achieved in this study, but all the main criteria for proper analytical analyses such as precision, accuracy, linearity of calibration curves and proper background corrections was met and maintained in this study. In addition to the above, the unknown mineral sample was successfully analyzed and identified.

6.2 FUTURE RESEARCH

It was hypothesized in this research that niobium can possibly be separated from tantalum by the adjustment of the microwave parameters such as digestion time in H_2SO_4 assisted microwave digestion. This hypothesis will be investigated further in the next phase of the project. It was also observed that the dissolution of the lithium tetraborate/niobium(V) oxide melt increased with an increase in nitric acid concentration, and this needs to be investigated further with higher concentrations that were used. The use of salts such as sulphate and less harmful fluorides for the dissolution of niobium compounds with the hot plate, microwave oven and fusion methods will be investigated in the next phase of this research.

It was found in this study that some particles/grains of the mineral samples mainly in Sample 1 are magnetic. This finding will be used to physically separate the magnetic grains or minerals as a first step in a separation or purification step of niobium from the minerals. The different properties of the mineral (or minerals) will be investigated with the ICP-OES, XRF and XRD to determine the elements or minerals that have been separated and compare it with results obtained in this study.

7 APPENDIX

7.1 A: Statistical treatment of data

The following equations were used for statistical analysis of data collected from the instrumental measurements in this study.

The average of the set of results was calculated using the formula: $\bar{x} = \frac{\Sigma x_i}{N}$ where $\bar{x}$ is the average, Σx_i is the sum of N replicate results.

The standard deviation between the replicate results was determined using the formula: $s = \sqrt{\frac{\Sigma_{i=1}^{N}\left(x_i = \bar{x}\right)^2}{N-1}}$ where s is the standard deviation, $\Sigma_{i=1}^{N}\left(x_i = \bar{x}\right)^2$ is the sum of the deviations.

Relative standard deviation was calculated as the percentage of the standard deviation relative to the mean (average) as follows: $RSD = \frac{s}{\bar{x}} \times 100$ where RSD is the relative standard deviation.

The mass percentage recovery of the analyte was calculated using the following formula: $\%\,\text{recovery} = \left(\frac{\text{mass obtained (mg)}}{\text{expected mass (mg)}}\right) \times 100$. In the case of wet analyses, **mass obtained** = **conc. (ppm)** $\times$ **V_f (L)** $\times$ **d.f.** $\times$ **coversion factor** where V_f is the total volume of the volumetric flask, d.f. is the dilution factor and the conversion factor relates the element to the compound containing the element. In the case of solid (XRF) analyses, **conc. (ppm)** $\times$ **mass of pellet (Kg)** $\times$ **coversion factor** = **mass obtained**.

The concentration of the analyte was determined from the standard addition calibration curve using the Equation: $c_x = \frac{bc_s}{mV_x}$ where c_x is the unknown analyte concentration, V_x is the constant volume of the analyte solution that was spiked in the standard solutions, c_s is the concentration of the standard stock solution, b is the y-intercept and m is the slope of calibration curve.

The detection limits were calculated according to the following equation: $\mathrm{LOD} = \frac{ks_{bl}}{m}$ where *k* is a numerical factor chosen in accordance with the confidence level (the value of *k* = 3 which corresponds to a 98.3% confidence level was used), *m* is the slope of the calibration graph and s_{bl} the standard deviation of the blank responses. Lower limit of quantification (LOQ) is defined as ten times the detection limit.

The slope, y-intercept and correlation coefficient (R^2) were determined using Microsoft Excel.

7.2 B: Detection limits

Table 7.1: Calibration data for the determination of detection limits at three most sensitive line orders (**Table 5.2**)

	Line order 1											
	Li	Na	Mg	Al	Ca	Ti	Mn	Fe	Ni	Cu	Nb	Ta
	610.364	330.232	383.231	167.079	442.673	337.28	260.569	238.204	221.647	224.7	309.418	226.23
Conc. / ppm	Intensities											
Blank	0.034445	0.013198	0.01043	0.000281	0.0126	0.023509	0.007795	0.01363	0.017757	0.019651	0.030268	0.00282
0.4	0.046554	0.002242	0.01143	0.003321	0.143883	0.326231	0.232959	0.142199	0.096199	0.06144	0.077894	0.01684
1	0.128979	0.00383	0.02957	0.00848	0.363092	0.849651	0.610396	0.371585	0.253968	0.169133	0.211916	0.05251
2	0.264595	0.005599	0.05808	0.016772	0.750962	1.75337	1.22386	0.756358	0.511353	0.34642	0.449816	0.09882
5	0.751021	0.01302	0.15242	0.041326	2.05295	4.54329	3.25817	1.99195	1.33297	0.92809	1.41425	0.28006
10	1.60634	0.024053	0.30111	0.073203	4.13254	9.06937	6.49199	3.96099	2.68213	1.83826	2.85808	0.5797
S_{bl}	0.000233	0.000237	0.0002	0.000032	0.000342	0.000448	0.000154	0.000315	0.000258	0.000358	0.000923	0.00026
m	2.5721	0.9589	3.497	0.1163	19.818	0.8892	1.1863	0.2373	0.1933	0.2788	0.2933	0.0291
	Line order 2											
	Li	Na	Mg	Al	Ca	Ti	Mn	Fe	Ni	Cu	Nb	Ta
	323.261	588.995	280.27	394.403	396.847	336.121	259.373	239.562	341.477	324.754	316.34	240.063
Conc. / ppm	Intensities											
Blank	0.011945	0.196939	0.02148	0.00825	0.323239	0.044038	0.013622	0.025836	0.011919	0.047333	0.01583	0.00107
0.4	.000387r	0.130942	0.51846	1.22433	0.033431	8.07692	0.803747	0.642229	0.172218	0.049776	0.193914	0.04289
1	0.004118	1.47607	3.07995	0.086954	19.3389	2.00552	1.60318	0.444722	0.123095	0.890508	1.42942	0.11679
2	0.008652	3.1597	5.80819	0.16783	37.1978	3.98756	2.97709	0.848098	0.24733	1.77048	3.78118	0.21824
5	0.025164	9.30347	14.4915	0.447934	91.0072	9.84661	7.51228	2.15194	0.639688	4.57732	10.8953	0.58058
10	0.054717	20.0618	27.6542	0.883969	164.044	18.8345	14.453	4.15129	1.24649	8.9182	24.5572	1.16075
S_{bl}	0.00019	0.00448	0.00022	0.000218	0.005955	0.00091	0.000172	0.001102	0.000348	0.000518	0.066981	0.00018
m	0.0057	2.046	2.7523	0.0889	16.118	1.8787	1.4389	0.4147	0.1251	0.8959	0.0558	0.1166
	Line order 3											
	Li	Na	Mg	Al	Ca	Ti	Mn	Fe	Ni	Cu	Nb	Ta
	670.785	589.592	279.553	396.153	393.366	337.28	257.61	259.94	231.604	327.396	269.706	268.511
Conc. / ppm	Intensities											
Blank	0.034914	0.076376	0.01682	0.007269	0.418276	0.023715	0.007253	0.00779	0.013116	0.011008	0.015925	0.00769
0.4	0.726744	0.231939	1.35076	0.038731	9.59679	0.321606	0.421981	0.080843	0.068666	0.09542	0.020929	0.01202
1	2.01071	0.648217	3.57508	0.102604	24.142	0.847164	1.1328	0.218251	0.185099	0.252606	0.251404	0.03024

2	4.28507	1.40277	7.19577	0.208004	46.8563	1.74932	2.25255	0.441587	0.36382	0.508107	0.696507	0.05432
5	12.2991	4.24167	18.4358	0.562036	113.678	4.44839	5.92508	1.16992	0.963971	1.34983	2.02825	0.14524
10	25.2152	9.35752	34.833	1.15026	201.915	8.84796	11.7821	2.35199	1.91978	2.76457	4.55459	0.29091
s_{bl}	0.000164	0.001091	0.00041	0.000212	0.002293	0.000456	0.000122	0.000274	0.000185	0.000189	0.016004	0.00023
m	0.1633	0.0023	0.0303	0.0072	0.4183	0.9131	0.6545	0.3992	0.2699	0.1859	0.2224	0.0291

7.3 C-1: Raw data for the analyses of pure Nb_2O_5

Table 7.2: Dissolution of Nb_2O_5 in different acids on hot plate heat (**Table 5.4**)

Acid	**Mass/g Nb_2O_5**	**Mass/g Nb**	**conc/ppm Nb**	Intensitiy
H3PO4	0.1006	0.070324	0.599442	0.635697
H2SO4	0.102	0.071303	0.66811	0.758715
HCl	0.1068	0.074658	0.01265	0.02165
HNO3	0.1064	0.074379	0.00316	003069r
Aqua regia	0.1064	0.074379	0	0.000521

Table 7.3: Dissolution of Nb_2O_5 in different acids in a microwave oven (**Table 5.5**)

Acid	**Mass/g Nb_2O_5**	**Mass/g Nb**	**Conc. Nb/ppm**	**Intensity**
HNO_3	0.1584	0.11073	0.12168	.003069r
HCl	0.1584	0.11073	30.1129	3.36297
H_2SO_4	0.1582	0.11059	!!!	!!!
Aqua-regia	0.1583	0.11066	1.1444	0.08755
H_3PO_4	0.1581	0.11052	!!!	!!!

Table 7.4: Varying amounts of Nb_2O_5 in H_2SO_4 and H_3PO_4 in microwave oven (**Table 5.6**)

Acid	**Mass/ g of Nb_2O_5**	**Mass/ g Nb**	**conc/ppm Nb**	**Intensity**
H_2SO_4	0.0207	0.01731	15.8281	3.1625
H_2SO_4	0.042	0.03511	29.8546	6.0248
H_2SO4	0.0821	0.06864	58.9013	11.952
H_2SO4	0.1077	0.09004	78.1959	15.889
H_2SO4	0.1202	0.10049	!!!	!!!
H_3PO_4	0.0602	0.05033	42.4154	11.589

Table 7.5: Effect of digestion period for dissolution of Nb_2O_5 in microwave with H_2SO_4 at 1200 W, 260^oC and 60 bar (**Table 5.7**)

45min heating			**309.418nm**	
Sample	**Mass/ g Nb_2O_5**	**Mass/ g Nb**	**conc/ ppm Nb**	Intensity
10ml H_2SO_4 digestion				
Nb_2O_5	0.0801	0.05599	54.8239	106.6
Nb_2O_5	0.0832	0.05816	57.8719	112.5
Nb_2O_5	0.0999	0.06984	69.0588	142.1
Nb_2O_5	0.1057	0.07389	73.207	156.6
60min heating				
Nb_2O_5	0.1078	0.07536	74.3507	158.2
Nb_2O_5	0.1016	0.07102	69.2438	144.7
Nb_2O5	0.0822	0.05746	56.3139	109.5
Nb_2O_5	0.1003	0.07012	69.5481	143.8

Table 7.6: Analysis of Nb solutions at different times (**Table 5.10)**

24-Jul-08	**1200w power**		**309.418nm**	
10ml H_2SO_4 digestion	**Mass/g Nb_2O_5**	**Mass/g Nb**	**conc/ppm Nb**	**Intensity**
Sample				
Nb_2O_5	0.0801	0.055994	58.9378	112.476
Nb_2O_5	0.1056	0.07382	77.2217	155.52
Nb	0.0418	0.0418	46.1446	100.188
Nb	0.0742	0.0742	80.6094	156.027
25-Jul-08				
10ml H_2SO_4 digestion				
Sample				
Nb_2O_5	0.0801	0.055994	54.8239	106.564
Nb_2O_5	0.0832	0.058161	57.8719	112.474
Nb_2O_5	0.0999	0.069835	69.0588	142.115
Nb_2O_5	0.1057	0.073889	73.207	141.838
Nb	0.0418	0.0418	41.7727	87.7379
Nb	0.049	0.049	48.9573	104.437
Nb	0.0601	0.0601	60.0771	119.479
Nb	0.0742	0.0742	74.0345	141.838

Table 7.7: Fusion dissolution of Nb_2O_5 using different fluxes (**Table 5.13**)

Solvent	**3.25% HNO_3**	**H_2O**	**3.25% HNO_3**
Flux	**$Li_2B_4O_7$**	**NaOH**	**$LiBO_2$**
Volume/ml Nb stock solution	**Intensity Nb**	**Intensity Nb**	**Intensity Nb**
0	39.5742	14.8644	1.01118
0.1	41.8377	17.4099	2.92939
0.2	44.0477	19.6049	5.04961
0.5	51.5015	26.5094	11.721
0.8	57.9124	33.214	
1	62.5788	37.5345	22.7215
Weighed Nb_2O_5 mass/ g	0.1056	0.1039	0.1057
% Nb recovery	**22.66294**	**9.1643864**	**0.507128**

Table 7.8: Dissolution of $Nb_2O_5/Li_2B_4O_7$ melt in different acids (**Table 5.14**)

Flux	**$Li_2B_4O_7$**	**$Li_2B_4O_7$**	**$Li_2B_4O_7$**
Acid	**5% HCl**	**3.25% HNO_3**	**5% H_2SO_4**
Volume/ml Nb stock solution	**Intensity Nb**	**Intensity Nb**	**Intensity Nb**
0	4.63703	13.8595	6.18118
0.1	4.9822	15.9383	8.18047
0.2		17.9716	10.2979
0.5	7.02138	24.4895	16.3265
1	8.95725	34.5465	23.0286
Weighed Nb_2O_5 mass/ g	0.1104	0.0892	0.1012
% Nb recovery	9.555723	21.470987	4.102872

Table 7.9: Effect of HNO_3 concentration (%) on the $Nb_2O_5/Li_2B_4O_7$ melt (**Table 5.15**)

Conc./ ppm Nb	**Nb intensities**				
	0.26%	**3.25%**	**16.25%**	**32.50%**	**65%**
0	.010384r	39.5742	35.9083	9.85954	49.3813
1	1.72626	41.8377	37.7326	10.2368	50.3273
2	4.06362	44.0477	39.356	10.822	52.5651
5	11.0708	51.5015	45.6487	12.1291	58.3303
10	22.5493	62.5788	55.3542	14.3244	67.5116
Weighed sample	0.1035	0.1056	0.1041	0.1006	0.1009

Table 7.10: Concentrated HNO_3 and H_2SO_4 with methanol on $Li_2B_4O_7/Nb_2O_5$ melt (**Table 5.16**)

Conc/ppm	Nb Intensity	
	95-98% H2SO4	65% HNO3
0	52.226	49.3813
1	52.484	50.3273
3	54.9082	52.5651
5	56.5781	58.3303
10	61.4665	67.5116
Weighed sample	0.0761	0.1009

7.4 C-2: Raw data for dissolution of niobium metal foil

Table 7.11: Dissolution of Nb foil in different acid on hot plate heat (**Table 5.8**)

Acid	Mass/g of sample	conc/ppm Nb	Intensitiy
H_3PO_4	0.1104	0.347335	0.15389
H_2SO_4	0.1144	0.41367	0.429152
HCl	0.1004	0.000015	0.000214
HNO_3	0.10215	0.00001	0.001341
Aqua regia	0.9914	0.000027	0.05824

Table 7.12: Microwave-assisted dissolution of niobium foil in H_2SO_4 for 45 minutes digestion (**Table 5.9**)

Acid	Mass/g of sample	conc/ppm Nb	mass/g Nb dissolved	%Nb in solution
Nb	0.0418	41.7727	0.041773	99.93469
Nb	0.049	48.9573	0.048957	99.91286
Nb	0.0601	60.0771	0.060077	99.9619
Nb	0.0742	74.0345	0.074035	99.77695

7.5 C-3: NbF_5 dissolution analysis

Table 7.13: Niobium fluoride dissolution quantification by ICP-OES (**Table 5.11**)

Solvent	Mass/g fluoride sample	Mass/g Fluoride sample	Mass/g Nb	conc/ppm metal	Intensity
$H_2SO_{4(micr)}$	0.0832	0.081536	0.040316	40.6977	77.2685
$H_2SO_{4(micr)}$	0.0916	0.089768	0.044386	44.5623	84.6543
H_2SO_4(conc.)	0.096	0.09408	0.046518	444.214	848.439
H_2O @ r.t.p	0.0893	0.087514	0.043272	405.35	774.166

Table 7.14: Concentrations of the trace elements identified in the pure niobium samples (**Table 5.12**)

Sample	Conc.							
	B	Si	Ti	Cu	Zn	Ba		
NbF_5	2.72612	18.3841		4.05014	7.7978	1.29547		
NbF_5	1.79153	11.9803	0	2.99912	4.053	0.967188		
NbF_5	2.50702	18.0705	0	4.08271	7.9805	1.31076		
NbF_5	2.65042	16.8037	0	4.02583	7.8623	1.29811		
	Na	Si	Ca	Ti	Fe	Cu	Zn	Mo
Nb_2O_5	0.06025	6.7484	0	0	0.05102	2.9862	6.0816	0.01014
Nb_2O_5	0.06215	7.3258	0	0	0.06121	3.2518	6.4081	0.01102
	Na	Si	Ca	Ti	Fe	Cu	Zn	Mo
Nb	0.03884	4.3483	0	0	0.0632	3.0218	4.2038	0.01025
Nb	0.03984	3.8932	0	0	0.0612	3.0115	4.1986	0.01014

7.6 D: Analysis of dissolution of mineral samples

Table 7.15: Metal oxide/ metal ratio

Si	Ti	Mn	Fe	Ta	Nb	Al	Sn	W	Th	U	Y	Ca
2.13929	1.66830	1.38829	1.42973	1.22104	1.43052	1.88943	1.26955	1.26108	1.13790	1.17924	1.26993	1.39920

Table 7.16: Digestion of large particle minerals for 45 minutes, 10 ml H_2SO_4, 1200 W, 260^oC, 60 bar (**Table 5.17**)

Mineral	Element conc/ ppm									
	Mass/g	Si	Ti	Mn	Fe	Ta	Nb	Al	Sn	W
TA 1	0.1185	0.3682	11.602	35.127	32.301	111.621	141.793	3.5838	20.5763	8.8896
TA 2	0.1084	0.16079	4.86407	27.528	20.871	57.3247	126.036	0.4321	12.3429	3.6416
TA 3	0.0886	0.11663	2.73279	15.712	15.159	37.9762	80.972	0.7007	9.14406	2.8842
TB 4	0.1003	0.21006	11.3508	11.891	12.381	66.4519	50.6375	1.3499	8.26864	3.2977
TB 5	0.1182	0.32236	10.13	18.087	13.809	95.2207	54.3416	1.8473	11.4675	2.9368
TB 6	0.1058	0.23673	10.9883	15.758	12.846	76.1693	51.9659	1.6376	8.91386	2.5284
Tun 7	0.1859	0.07099	2.55019	6.6541	3.1509	35.2064	10.8013	0.1898	1.91105	0.3177
Tun 8	0.0908	0.80786	5.82067	7.1481	11.575	44.7602	25.5429	1.1193	6.47747	0.5974

Table 7.17: Digestion of selected particles of minerals for 60 minutes, 10 ml H_2SO_4, 1200 W, 260 ^oC, 60 bar (**Table 5.19**)

Mineral	Mass/g	Element conc./ ppm								
		Si	Ti	Mn	Fe	Ta	Nb	Al	Sn	W
TA 1	0.0164	0.58698	1.2181	8.7772	4.3821	18.024	30.4011	0.1601	2.57424	0.9203
TA 2	0.0537	0.29769	3.8492	13.048	12.204	49.111	55.5139	0.9884	7.54448	3.01326
TA 3	0.1011	0.81123	9.3497	33.705	27.386	113.94	125.853	2.4438	16.2283	5.85016
TB 4	0.0165	1.21082	5.0837	4.6072	4.4762	28.719	15.8275	0.7716	3.06478	0.7455
TB 5	0.0581	0.35812	10.69	18.02	13.919	94.893	54.3215	1.6495	9.35093	2.90089
TB 6	0.1009	0.3716	11.865	24.237	17.4	121.06	71.2862	2.3219	11.7539	3.23191
Tun 7	0.0127	0.16223	1.3975	0.9938	2.3125	5.9989	3.41407	0.3705	1.25122	0.03806
Tun 8	0.0609	1.63619	3.9256	5.3584	8.1846	38.605	16.3833	1.1611	4.20106	0.30756

Table 7.18: Digestion of milled minerals in microwave for 90 minutes (**Tables 5.21 and 5.22**)

Mineral	Mass/g	Element conc./ ppm											
		Si	Ti	Mn	Fe	Ta	Nb	Al	Sn	W	Th	U	Y
TAN. A 1	0.0878	0	12.7588	42.8578	37.7534	172.717	151.826	3.9913	5.3596	9.4801	4.6102	20.8773	
TA N. A2	0.0883	0.2661	12.9732	43.407	37.9877	178.192	152.753	4.0321	5.5276	9.144	4.7186	21.1196	
TAN. A3	0.0859	0.0877	12.4393	41.3558	36.4995	172.434	147.206	3.827	5.3399	8.9276	4.5576	20.6892	
TAN. B 4	0.0825	0	24.8278	35.0285	30.3405	207.983	86.6724	4.3565	11.0046	5.4075	3.0147	7.2484	
TAN. B 5	0.0879	0	25.8275	35.2856	31.2591	209.812	90.4677	4.4645	10.9783	5.691	3.2326	7.8845	
TAN. B 6	0.0832	0.0399	25.5007	34.9015	30.4502	214.811	88.2621	4.6279	10.9634	5.6323	3.0633	7.6509	
SAM. 1a	0.0885	0	46.6387	19.1367	69.8469	133.928	62.8141	1.9101	0.6152	1.5659	3.6962	2.5938	1.5687
SAM. 1b	0.0866	2.216	46.2735	19.7315	75.6874	169.389	64.4988	2.8607	0.6793	1.8064	3.649	2.6232	1.5437

Table 7.19: Dissolution of milled minerals in microwave for 150 minutes (**Table 5.22**)

Mineral	Mass/g	Si	Ti	Mn	Fe	Ta	Nb	Al	Sn	W	Th	U	Y	Ca
TAN. A 1	0.0859	0	14.0979	42.8578	37.7534	166.264	156.405	4.79661	5.37711	10.357	4.6522	21.507		0
TAN. A 2	0.0819	0	13.6839	43.407	37.9877	156.87	151.222	4.70987	5.14918	9.4572				0
TAN. A 3	0.0832	0	13.7075	41.3558	36.4995	153.37	151.69	4.61171	5.03918	9.3092				0
TAN. B 4	0.0893	0	26.3081	35.0285	34.1237	162.829	86.3791	6.98035	9.86655	5.432	2.97534	7.2074		0
TAN. B 5	0.0854	0	27.1583	35.2856	34.5638	158.729	87.6283	6.43736	9.1742	5.4456				0
TAN. B 6	0.0806	0	25.7389	34.9015	33.4788	156.758	84.7178	6.48292	9.30804	5.2773				0
SAM. 1a	0.082		60.69	18.8723	69.8469	118.953	62.4516	1.91988	0.66149	1.5375	4.77086	2.5428	1.5687	3.5054
SAM. 1b	0.0844	0	60.4607	18.3485	75.6874	110.809	62.0135	1.88552	0.63633	1.4968			1.5437	3.6198

Table 7.20: Different acids to dissolve minerals in microwave for 45 minutes (**Table 5.20**)

Acid name	Mass/g	Element conc./ ppm										
		Si	Ti	Mn	Fe	Ta	Nb	Al	Sn	W	Th	U
HNO_3	0.0829	0.7176	0.42	6.737	9.225	0.1290	0.4476	5.616	0.162	0.8517	1.905	1.396
HCl	0.0815	4.1723	6.694	10.49	25.98	28.02	46.254	6.182	2.6725	5.2745	4.433	18.61
Aqua regia	0.0843	4.9625	2.482	8.072	17.24	0.42	6.9548	6.677	1.0343	1.3794	3.391	12.05
H_3PO_4	0.0866	12.819	9.396	43.41	38.7	133.6	136.31	8.91	4.5998	7.7797	4.671	20.28
H_2SO_4	0.0847	0	10.74	30.21	38.96	48.5	115.17	6.392	3.2489	7.1345	4.753	20.53
H_3PO_4	0.0827	15.914	15.76	35.23	32	145.1	73.742	11.98	8.0854	4.1925	2.987	6.89
Aqua regia	0.0855	6.4833	4.01	7.731	15.59	0.18	3.3114	9.176	0.5771	1.1217	2.58	3.333
HCl	0.0845	4.5975	8.38	9.041	20.38	11.27	14.474	8.923	1.6331	2.5393	3.023	5.011

Table 7.21: Fusion digestion of mineral samples with $K_2S_2O_7$ and $Li_2B_4O_7$ (**Table 5.23**)

TAN. A + $k_2S_2O_7$									
Conc./ppm	Al	Si	Ti	Mn	Fe	Nb	Sn	Ta	W
0	0.14214	0.0667	1.6974	55.653	2.0982	1.85036	0.0467	0.00356	0.31335
1	0.45671	0.5692	16.951	63.457	3.6136	3.77019	0.1231	0.15953	0.45888
4	1.4812	2.3992	66.333	89.46	8.276	10.6891	0.3762	0.6283	0.96238
8	2.8654	4.6935	130.89	123.45	14.693	19.7058	0.7368	1.23861	1.62425
10	3.56829	5.8163	161.57	139.32	17.769	24.1007	0.9127	1.53654	1.93633
Mass	0.2132								
Tan A + $Li_2B_4O_7$									
Conc./ppm	Al	Si	Ti	Mn	Fe	Nb	Sn	Ta	W
0	0.7577	1.2859	53.714	123.37	18.084	51.2341	0.3895	4.27702	0.03262
1	0.96976	1.6805	65.362	127.09	18.946	52.4376	0.427	4.3316	0.12044
4	1.70068	2.969	110.45	146.42	22.288	58.4017	0.5848	4.77806	0.40153
8	2.71453	4.7124	169.72	170.1	26.991	66.0482	0.806	5.31881	0.95306
10	3.2145	5.5261	195.47	183.51	28.926	70.0116	0.9151	5.55906	1.20213
Mass/g	0.3047								

Table 7.22: Dissolution of minerals by $Li_2B_4O_7$ fusion and H_2SO_4 and methanol (**Table 5.24**)

Sam											
	Int										
Conc./ppm	Al	Si	Ti	Mn	Fe	Nb	Sn	Ta	W	Th	U
0	0.50664	1.5	113.03	25.346	25.884	20.8467	0.5509	5.10122	0.00158	0.3595	0.0474
1	0.77914	1.9557	123.14	31.936	26.637	22.9465	0.5969	5.20267	0.09982	0.4576	0.2316
4	1.72939	3.5422	161.35	55.179	30.517	29.6571	0.7919	5.60895	0.53121	0.7242	0.87
8	2.98548	5.5735	215.37	85.741	36.018	38.7433	1.0767	6.23959	1.12267	1.0678	1.7405
10	3.61569	6.9747	239.87	100.09	38.522	43.2292	1.2154	6.53222	1.40915	1.2895	2.1471
Tan A											
	Int										
Conc./ppm	Al	Si	Ti	Mn	Fe	Nb	Sn	Ta	W	Th	U
0	0.36145	0.2206	21.831	51.027	8.7098		0.0989		0.16547	0.35	0.5238
1	0.63825	0.5549	31.94	58.15	10.072	46.6766	0.1851	3.61026	0.26758	0.9068	0.7093
2	0.9222	1.0543	44.382	64.765	11.392	48.9592	0.2569	3.7325	0.43832	1.5899	0.9171
3	1.23428	1.6022	56.144	72.774	12.83	50.3847	0.3285	3.86734	0.58589	2.2299	1.1225
5	1.84462	2.5198	79.983	87.007	15.669	55.5775	0.4801	4.13596	0.87928	3.4883	1.5308
Tan B											
	Int										
Conc./ppm	Al	Si	Ti	Mn	Fe	Nb	Sn	Ta	W	Th	U
0	0.63126	2.1216	47.611	45.697	7.8681	25.4804	0.2806	4.80487	0.05304	0.1457	0.1867
1	0.91593	2.4214	47.068	51.989	9.0649	26.9862	0.3479	4.85594	0.18214	0.1621	0.3775
4	1.54049	3.5541	86.558	67.007	11.904	31.5347	0.5068	5.20377	0.46332	0.4493	0.8148
8	2.5607	5.1542	126.41	91.612	16.483	37.7593	0.7482		0.93564	0.8712	1.4598

7.7 E: XRF analyses of powder mineral samples

Table 7.23: XRF results for solid analysis of minerals using major and trace programmes (**Table 5.25**)

Selected archive: Majors-pellets											
Sample	Sum	Al_2O_3	CaO	Fe_2O_3	MnO	MgO	Na_2O	TiO_2	SiO_2		
	of conc.	Al	Ca	Fe	Mn	Mg	Na	Ti	Si		
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)		
TAN-A-1%	109.395	0.135	0.012	0.026	0.045	-0.026	0.082	0.024	109.084		
SAM1-1%	110.786	0.15	0.016	0.241	0.026	-0.018	0.158	0.127	110.074		
TAN-B-1%	108.644	0.145	0.021	0.082	0.047	-0.023	0.004	0.044	108.317		
TAN-A	14.249	1.901	0.292	3.666	4.253	-0.751	0.018	1.246	3.093		
TAN-B	15.52	1.906	0.612	3.314	4.032	-0.885	0.17	2.457	3.516		
SAM-1	33.101	2.035	0.346	13.901	2.311	-0.957	0.741	8.936	5.697		
Selected archive: Vergenoeg-trace											
Sample	Sum	CaO	TiO_2	$Fe2O_3$	Y_2O_3	Nb_2O_5	SnO_2	Ta_2O_5	WO_3	ThO_2	U_3O_8
	of conc.	Ca	Ti	Fe	Y	Nb	Sn	Ta	W	Th	U
	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
SAM-1	84.051	3887.5	104739	118139	1522.6	57144.9	546.18	520035	-263.51	3959.9	1222.9
TAN-A	83.028	3469.8	14449	33488	18248	206161.2	5951.8	454424	8523.9	15646	23079
TAN-B	81.591	7158.4	27804	30878	7411.7	71918.34	19781	581233	4290.22	6928.8	6331.5
TANA-1-99	0.538	208.2	238.56	453.07	164.82	1415.308	25.353	1475.31	642.36	157.24	185.66
TANB-1-99	0.608	341.45	454.07	963.97	73.584	874.862	191.61	2018.11	554.076	100.62	53.866
SAM1-1-99	0.82	308.59	1456.3	2975.3	13.76	667.077	-53.157	1957.15	500.15	63.05	7.356

7.8 F: XRD spectra of pure minerals

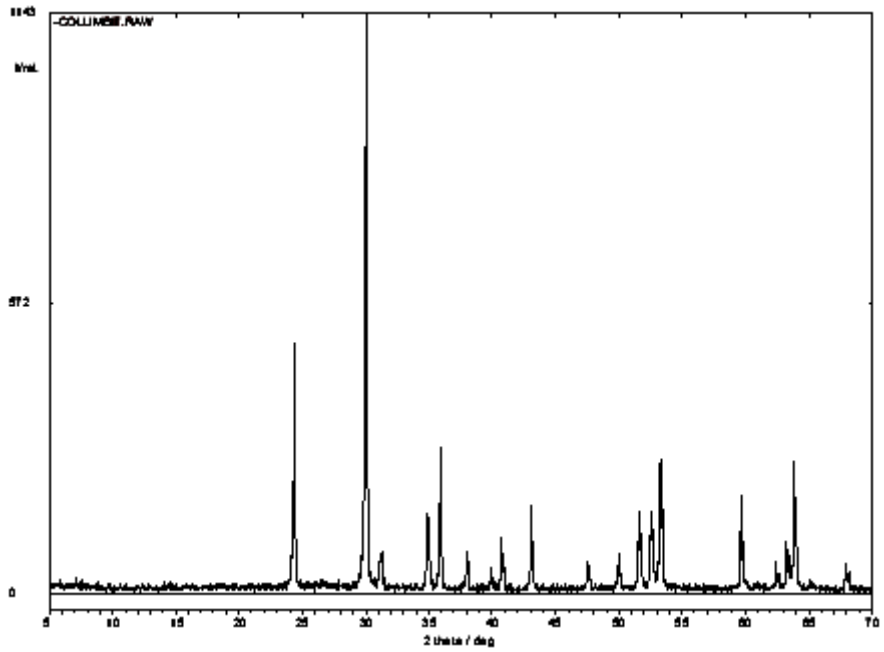


Figure 7.1: XRD spectrum of pure columbite/tantalite

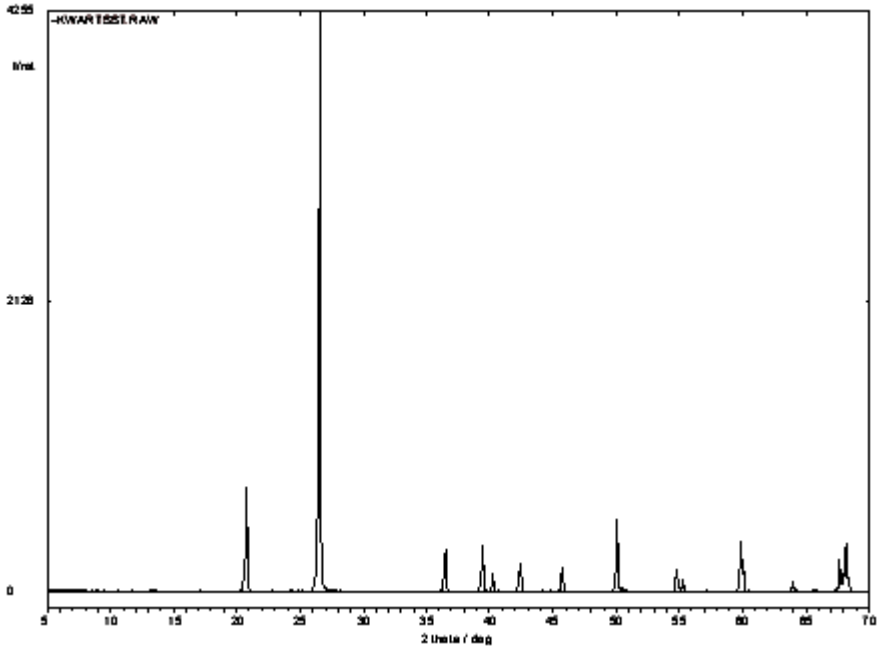


Figure 7.2: XRD spectrum of pure quartz

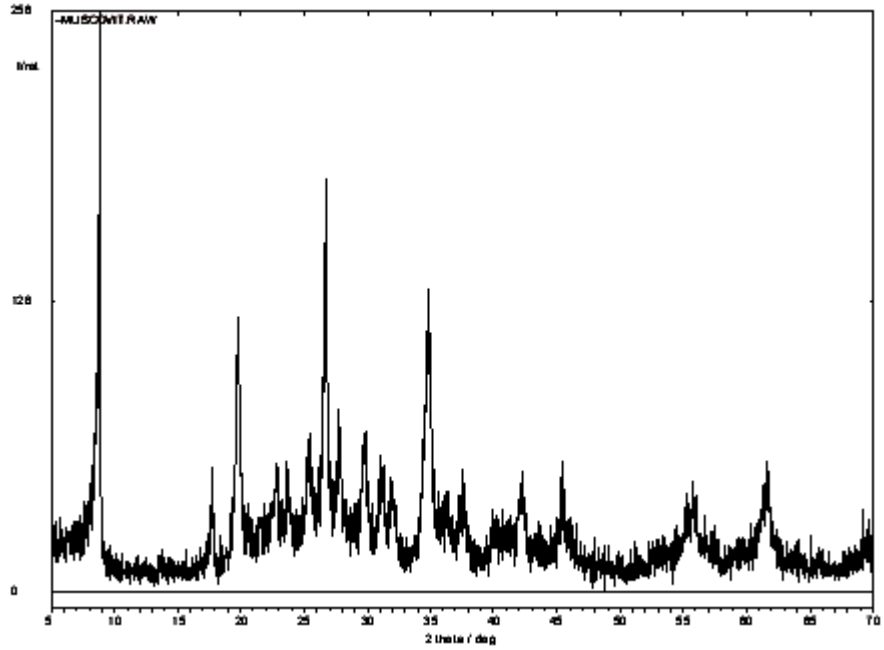


Figure 7.3: XRD spectrum of muscovite