QUANTIFICATION OF TANTALUM IN SERIES OF TANTALUM-CONTAINING COMPOUNDS.

by
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Tommie

“A man should always look for what is, and not for what he thinks should be.”

- Albert Einstein –

Contents

List of abbreviations

Chemicals and other:

AR	Analytical Reagent
CRM	Certified Reference Material
EtOH	ethanol
MeOH	methanol
magn.	magnetic
ppm	parts per million
sol.	solution
vol.	volume
conc.	concentration
ppb	parts per billion

Statistical abbreviations:

conf. int.	confidence interval
LOD	limit of detection
LOQ	limit of quantification
RSD	relative standard deviation

Instrumentation:

ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
AA	Atomic Absorption
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
FAAS	Flame Atomic Absorption Spectroscopy
PIXE	Particle Induced X-ray Emission
EDXRF	Energy Dispersive X-ray Fluorescence
SEM	Scanning Electron Microscope
EDXS	Energy Dispersive X-ray Spectroscopy
UV-vis	Ultra Violet - visible range

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Chapter 1: Introduction

1.1 Basic Information on Tantalum

Tantalum (Ta), the 73rd element in the periodic table, is located in group five, period six. With an atomic weight of 180.95 g/mole, tantalum is regarded as one of the refractory metals because of its high heat resistance (**Table 1-1**).

It is extremely resistant to corrosion and the only acid that readily dissolves metallic tantalum is hydrofluoric acid (HF). The reason for this extreme corrosion resistance is the formation of a thin layer of tantalum oxide (Ta_2O_5), on the surface of the metal that protects the rest of the metal from oxidation. Ta_2O_5, other than most of the other metal oxides, is not degrading to the metal itself, it adheres very well to the metal surface, which therefore adds to the protection of the metal, much like aluminium and its oxide. Ta_2O_5 itself is highly unreactive towards nearly all of the mineral acids.

1.2 The History and Discovery of Tantalum

Tantalum was first discovered in 1802 by a Swedish scientist and mineralogist named Anders Gustav Ekeberg[1] (**Figure 1-1)**. It was widely believed at that stage that tantalum was identical to columbium, previously discovered in 1801 by Mr. Hatchett[2]. This view was held until 1846, when a chemist named Heinrich Rose opposed the fact that columbium and tantalum were identical. Only after much correspondence on this matter between many scientists was the difference between tantalum and columbium accepted and Ekeberg, who had passed away in the meantime, was made the discoverer of tantalum.

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[1] ME Weeks. (May 1932). *Journal of Chemical Education.* Vol. 9. No. 5. pp. 863-884.

[2] WH Wollaston. (Jun 1809). *Philosophical Transactions of the Royal Society of London*. Vol. 99. pp. 246-252.

Table 1-1: Physical properties of tantalum metal[3].

Property	Value
Melting point	2996 ℃
Boiling point	5425 ℃
Specific heat	0.142 J/g℃
Thermal conductivity	54.4 W/m℃
Density	16.9 g/cm^3
Crystal structure	Body centred cubic (bcc)
Electrical resistance (20 ℃) [4]	15.5 µΩ.cm
Dielectric constant	11.6
Coefficient of linear expansion	6.5 x 10^{-6} /℃
Modulus of elasticity (20 ℃)	186 kN/mm^2
Yield stress at:	
20 ℃	179-1060 N/mm^2
500 ℃	44-310 N/mm^2
Tensile strength (20 ℃) :	
Annealed	280-330 N/mm^2
Cold worked	600-1400 N/mm^2
Hardness:	
Annealed	70-110 VPN
Cold worked	180-300 VPN
Ductile/Brittle transition temperature	Below -196 ℃

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[3] CED Rowe. (Jan 1997). *Journal of the Minerals, Metals and Materials Society.* Vol. 49. pp. 26-28.

[4] RC Weast (Editor). (1968-1969). Handbook *of Chemistry and Physics.* 49th Ed. p. E80.

Figure 1-1: Anders Gustav Ekeberg 1767-1813[1].

The element tantalum was named after a Greek god called Tantalus. Tantalus, the son of Zeus and the nymph Plouto, was punished for disclosing godly secrets to the mortals. Tantalus' eternal punishment for this sin was to stand knee deep in water, under a fruit tree. Whenever Tantalus bent down to take a drink of water, the water would recede to below his reach. And whenever he wanted to pick some of the fruit from the low hanging branches of the fruit tree, the branches would lift up to just above his reach, thus forever tantalising him[5].

1.3 Global Occurrence of Tantalite Ore[6]

In nature, tantalum occurs in the form of Ta_2O_5-containing ore, for example tantalite, columbite, tapiolite, microlite, tantite and wodgenite. Of all of the Ta_2O_5-containing ore, tantalite and columbite are the most well-known. These ores have a composition of $[(Fe,Mn)\ (Ta,Nb)_2O_6]$ and are classified as tantalite if the Ta_2O_5 content is 40% or more and similarly, if the Nb_2O_5 content exceeds 40% it is

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[5] Greenwood, N Norman, A Earnshaw. (1997). *Chemistry of the Elements (2nd Ed.)*. Oxford. Butterworth Heinemann. p. 1138.

[6] Roskil Information Services Ltd. (2005). *The Economics of Tantalum*. 9th Ed.

classified as columbium[6]. These ores are relatively rare with an average crustal rock concentration of 1.7 ppm and as little as <0.012 ppb is present in sea water. Tantalum containing minerals occur widely across the earth, usually in concentrated deposits. Countries that have tantalum containing deposits include Australia, Brazil, Canada, Ethiopia, Mozambique, Namibia, Rwanda, South Africa, Uganda and Zimbabwe.

Figure 1-2: A sample of tantalite ore[**7**].

Although many of these countries are actively mining their tantalum deposits, recent statistics[6] indicate that the largest producers, mines and reserves are located in the west of Australia and Brazil.

In South Africa, tantalite is found in pegmatite located in the Northern-Cape, Limpopo and Mpumalanga (**Figure 1-3**). The last recorded production of columbite-tantalite ore from SA was 13.5 tonnes in 1991. Nevertheless, in 2004 a refinement plant was commissioned by Titan Processors Ltd. in Johannesburg to enrich local and imported tantalite ores to high grade Ta_2O_5 with purities as high as 99.5%. This was done by using technology developed by a South African, Dr. Jan Becker[6].

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[7] http://www.commerce-cosmique.org/files/u1/tantalite.jpg. 01 March 2010.

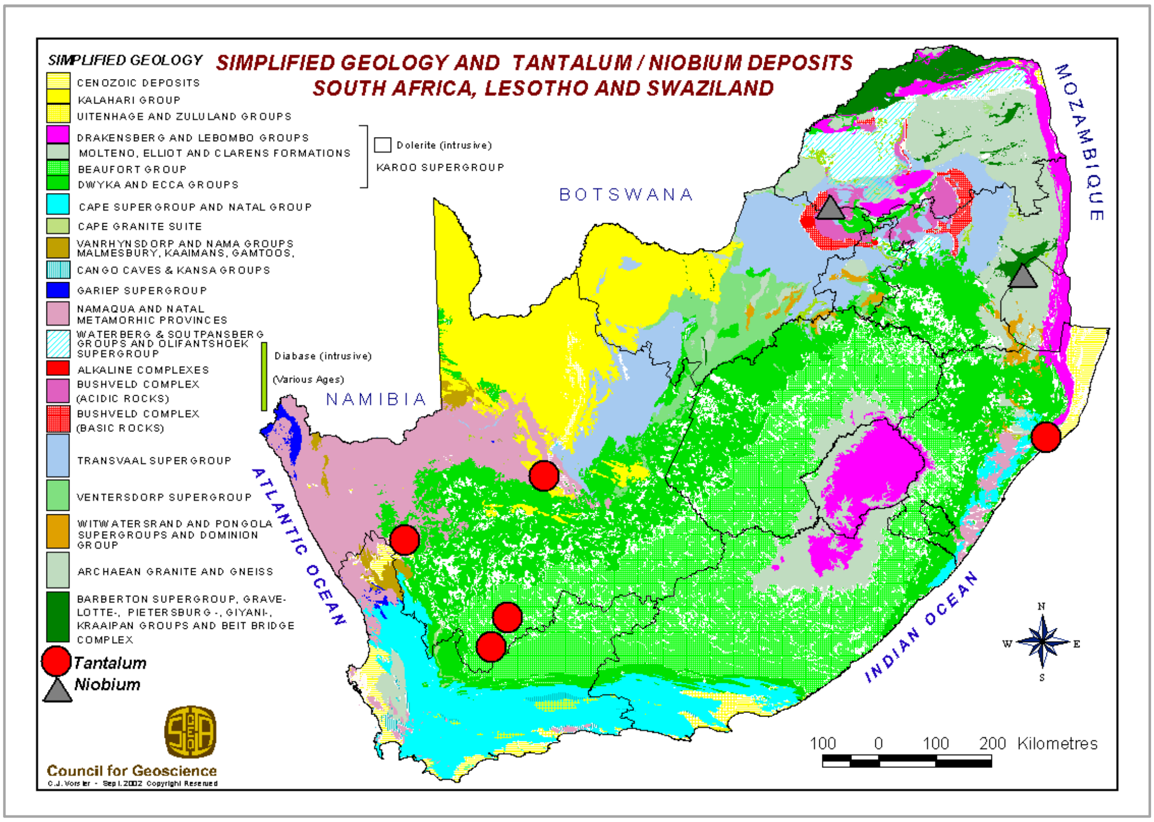

Figure 1-3: Tantalum and niobium deposits in South Africa[8].

There is also a lot of controversy regarding tantalite and columbite ores obtained from central Africa, especially in the Democratic Republic of the Congo (DRC) (**Figure 1-4**). Not unlike the so called “blood-diamonds”, coltan (a local term for an ore that contains both columbite and tantalite, hence the name) is regarded as a “blood-mineral”. It is believed that in many parts of the DRC prisoners of war are being enslaved and forced to illegally mine coltan deposits (**Figure 1-5**). These ores are then supposedly sold on the black market to fund the ongoing civil wars in many of the central African countries. Not all tantalum mines in the DRC are illegal though. There are some established mines like Shamika Resources Inc. as indicated in **Figure 1-4** who legally mine and export these minerals to the rest of the world.

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[8] http://www.geoscience.org.za/images/stories/tantalumniobium.gif. 12 February 2010.

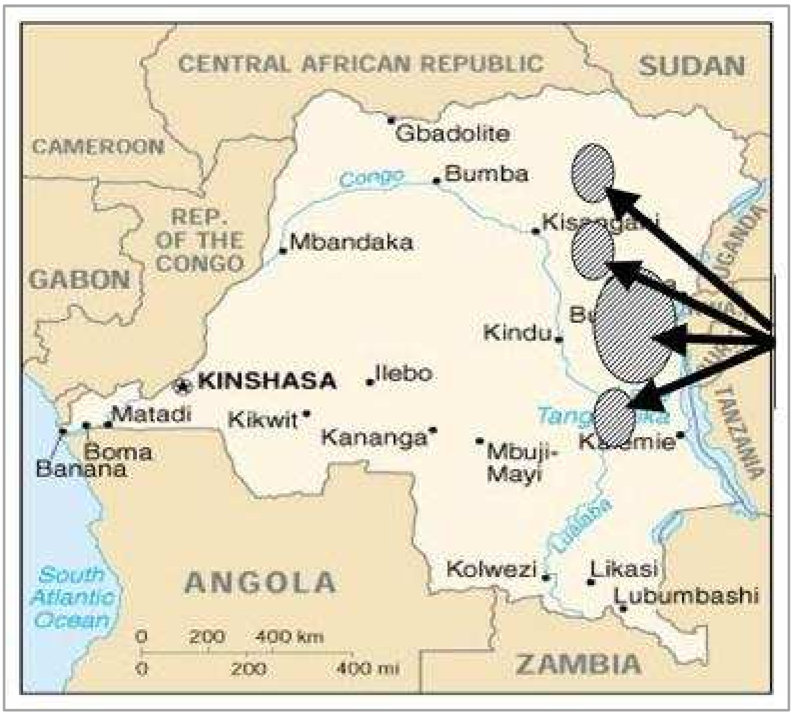

Figure 1-4: Tantalite-columbite deposits in the DRC[9].

Figure 1-5: Informal mining activity in the DRC[10].

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[9] http://www.shamikaresources.com/images/_ar_image3.jpg. 11 February 2010.

[10] http://www.themwambafamilyfoundation.org/mediac/400_0/media/coltan_mines.jpg. 01 March 2010.

1.4 Production and Refinement of Tantalite Ores

Tantalum, unlike some rare metals, is not traded on the metal commodity markets and therefore the price can vary largely. In 2006[11] tantalum concentrate traded at \$15/kg, pure tantalum pentoxide powder at \$500/kg and tantalum metal ingots at \$700/kg. Therefore, as mentioned above, many countries are actively mining columbite-tantalite ores and producing tantalum containing compounds. The largest producer, indicated in **Figure 1-6**, is Australia.

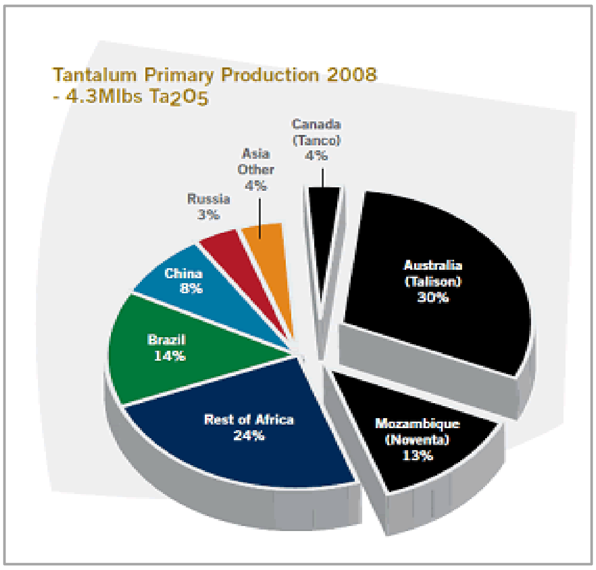

Figure 1-6: Primary Ta_2O_5 production in 2008[12].

Figure 1-7 indicates the amount of raw material mined by the most significant tantalum producers and **Figure 1-8** indicates the amount of Ta_2O_5 processed from the above mentioned raw materials from 2003 to 2007. It can clearly be seen that Australia and Brazil are the two most significant countries in terms of tantalum production over the course of five years. In 2004 Mozambique contributed largely in terms of ore produced, but faded away in the following years.

The first refinement processes for tantalum ores incorporated fluoride chemistry. This involved dissolving tantalum-niobium slurries in HF, after which a stoichiometric amount of KF is added to form potassium fluorotantalate (K_2TaF_7) and potassium oxyfluoroniobate ($K_2NbOF_5 \cdot H_2O$). The former is much less soluble

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[11] http://www.resourceinvestor.com/News/2007/7/Pages/Tantalum--A-Tantalizing-Commodity-Investment.aspx. 10 March 2010.

[12] http://www.marketoracle.co.uk/images/2009/July/Tantalum-21.gif. 01 March 2010.

than the latter and therefore precipitates as fine needles during the first step of the separation process. This method is called fractional crystallisation.

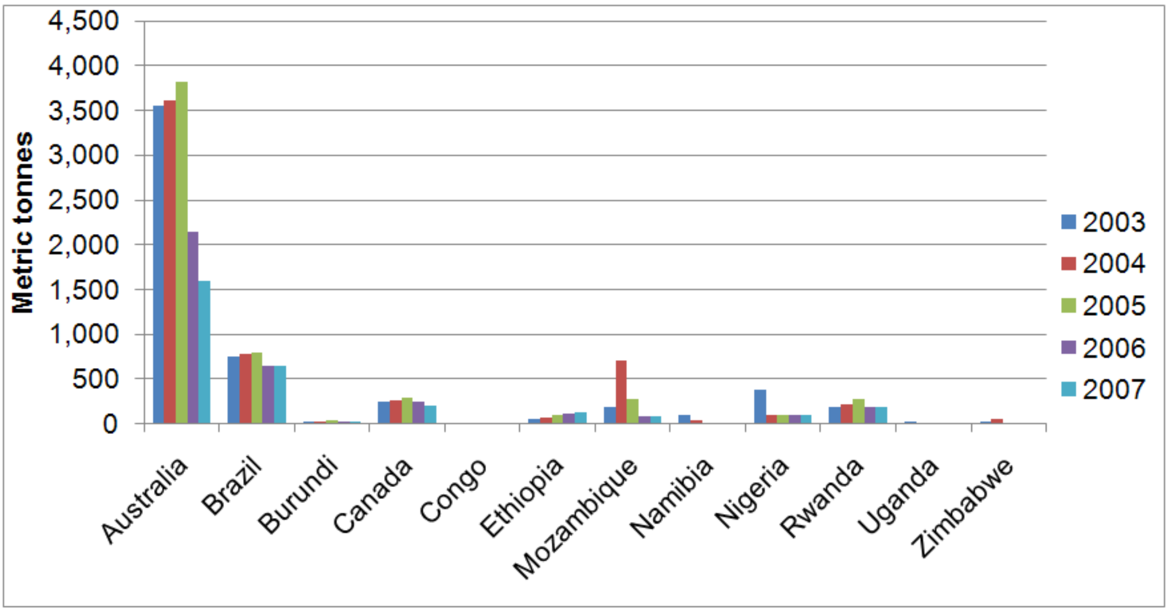

Figure 1-7: Gross mass of columbite-tantalite ore produced by country from 2003 to 2007[13].

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[13] http://www.indexmundi.com/en/commodities/minerals/columbium_(niobium)_and_tantalum/columbium_(niobium)_and_tantalum_t10.html. 01 March 2010.

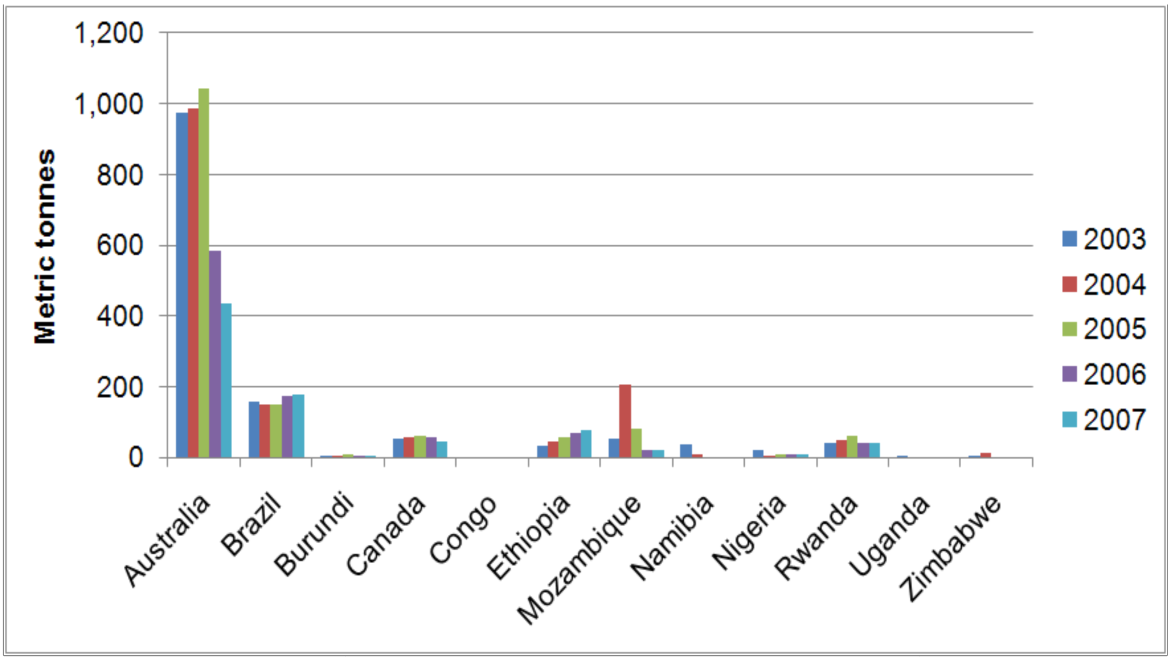

Figure 1-8: Tantalum content from above mentioned ores from 2003 to 2007[13].

Modern day methods use either chlorination of the raw material or liquid-liquid extraction. In the case of chlorination there are two possibilities. The first is a reductive process that occurs between the raw material and chlorine gas in the presence of coal or other similar materials. The second is called chlorination of ferro-alloys ($(Fe,Mn)(Nb,Ta)_2(O)_6$). This is done by melting sodium chloride that contains some iron trichloride ($FeCl_3$), after which chlorine gas is bubbled through the melt giving $NaFeCl_4$ which acts as chlorination agent for the ferro-alloys. Tantalum pentachloride and niobium pentachloride are then obtained through chlorination and can be separated and purified by distillation. The boiling points of the two salts ($TaCl_5$ b.p. = 236℃, $NbCl_5$ b.p. = 248℃) are low enough and far enough apart to enable successful distillation[14]. The liquid-liquid extraction process (described in **Figure 1-9**) is clearly not a simple task. The main steps include digestion, extraction, stripping, crystallisation and filtration. To speed up digestion, the concentrates are first ground. After HF digestion and extraction with an organic solvent like MIBK (methyl isobutyl ketone) or 2-octanol, the solutions are washed with another acid solution to get rid of other metals that may still be present. Finally the solutions are stripped of niobium and tantalum respectively and the so called K-salts (K_2NbOF_5 and K_2TaF_5) are crystallised, filtered and dried.

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[14] A Agulyansky. (2004). *The Chemistry of Tantalum and Niobium Fluoride Compounds.* Amsterdam. Elsevier. Ch. 1.

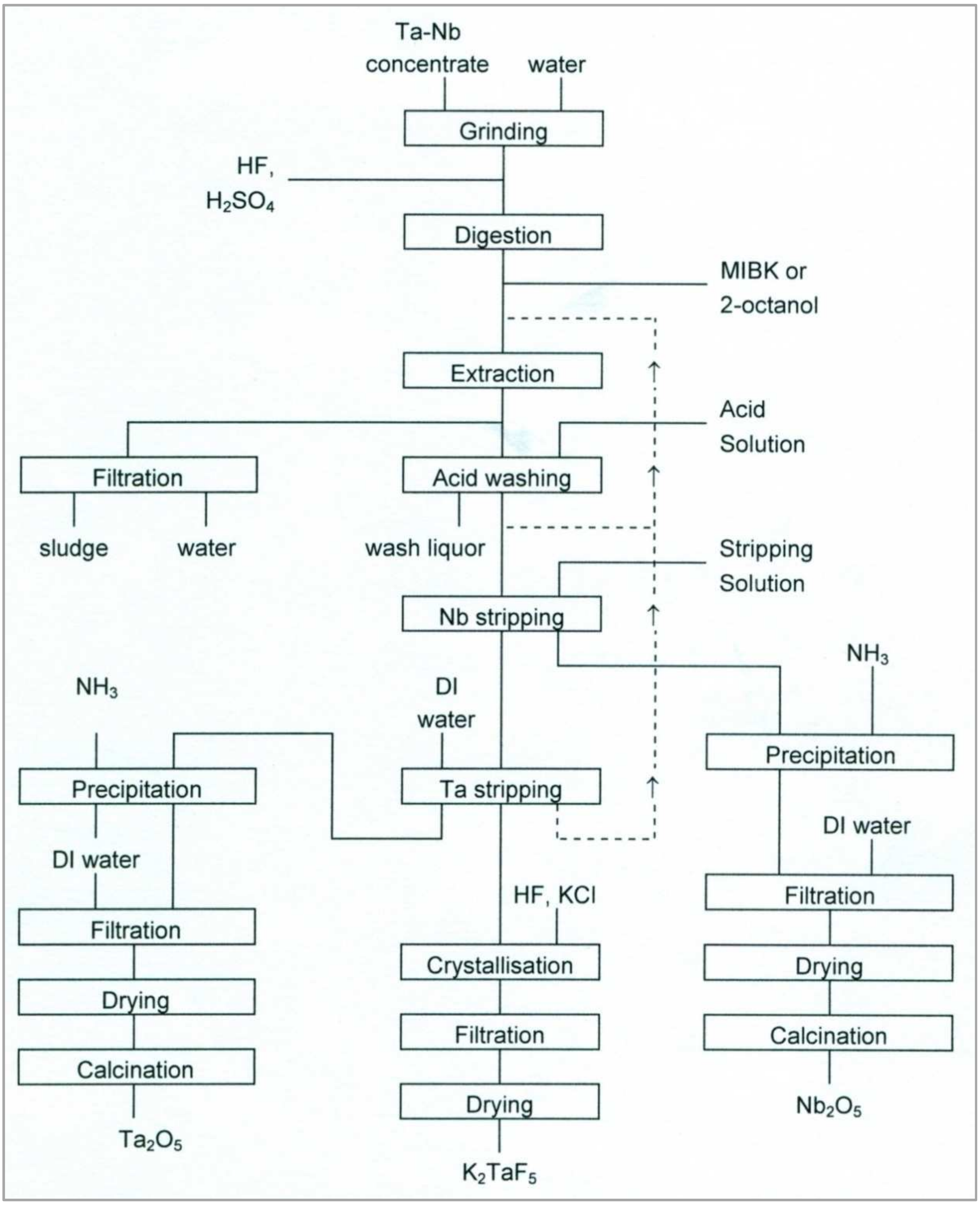

Figure 1-9: Schematic presentation of the liquid-liquid extraction process for separating Ta & Nb[15].

Despite recent mining cutbacks, there are a few future prospects in the tantalum mining and production field. The most prominent of which is a Canadian company called Commerce Resource Corp. that is developing a tantalum mining project

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[15] Roskil Information Services Ltd. (2005). *The Economics of Tantalum*. 9th Ed.

called Blue River Project. Others are Gippsland who is currently busy with a feasibility study for their project in Egypt, Tertiary Metals in Saudi Arabia, and Globe Metals & Mining who is based in Africa[16].

1.5 Applications of Tantalum and Tantalum Products

Tantalum has various applications in everyday life, from the use of Ta_2O_5 in capacitors and highly refractive camera lenses to the use of tantalum metal in medicine and the tooling industry.

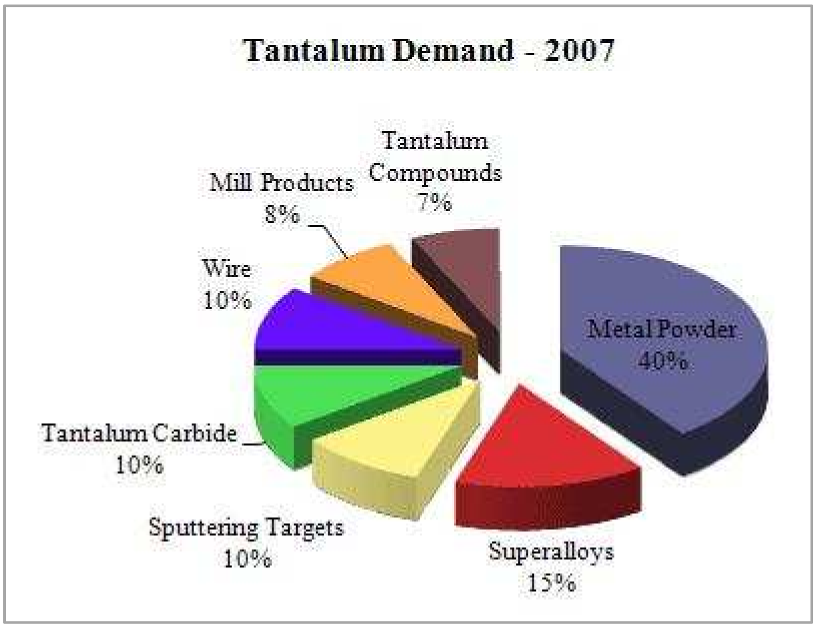

Figure 1-10: Tantalum demand for different applications in 2007[17].

According to statistics, 40% of the tantalum demand in 2007 was in the form of tantalum powder, 15% was for super alloys and the remainder was divided more or less equally between tantalum compounds, mill products, wire, carbides and sputtering targets (**Figure 1-10**). In the medical sector, tantalum is used to make internal prosthetics such as plates, rods, brackets, screws, *etc.* Tantalum is specifically used because of its inertness to all bodily fluids and will therefore not

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[16] http://www.commodityonline.com/news/New-supply-chain-in-tantalum-set-to-emerge-18974-3-1.html. 10 March 2010.

[17] http://www.istockanalyst.com/images/articles/HAI_01132009_Fig2.png2009148679.jpg. 01 March 2010.

have any reaction which can cause infection or inflammation. In a publication[18] by the physicians SH Weeden and RH Schmidt in the Journal of Arthroplasty they report that the use of porous tantalum metal implants in the reconstruction of some of the worst cases of acetabular defects such as Paprosky 3A and 3B (which are medical terms for severe bone deterioration in pelvic and hip joint areas), are very successful. **Figure 1-11** depicts acetabular defects in increasing order of severity (A-F).

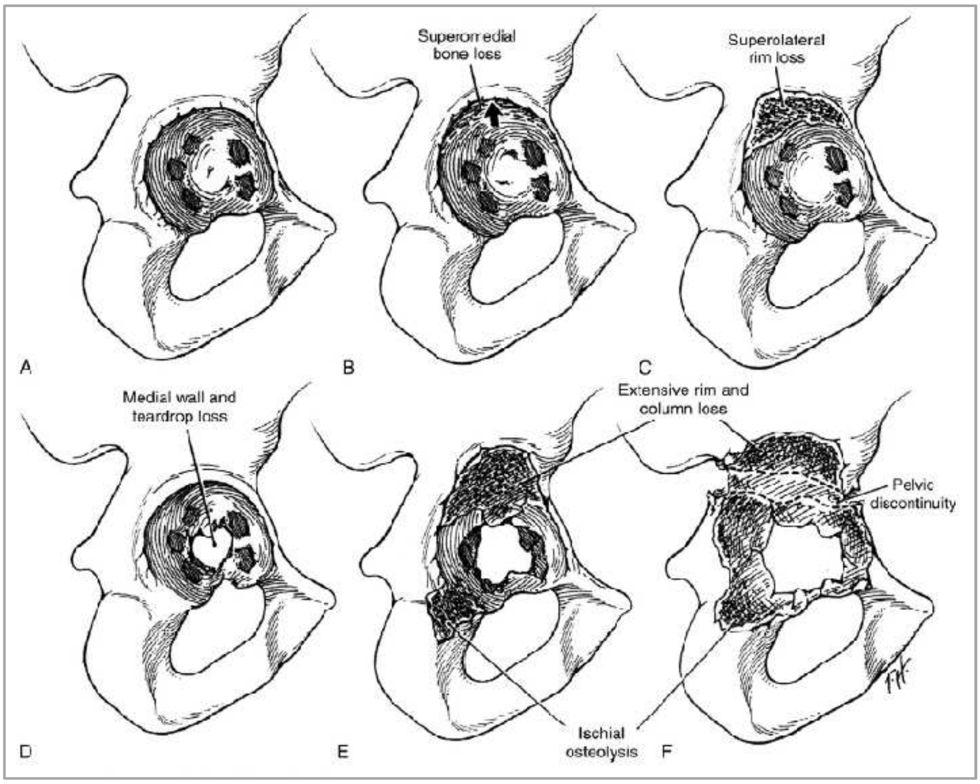

Figure 1-11: A-F depicts various forms of pelvic bone loss in increasing order of severity.

Another study[19] done by BR Levine *et al*. demonstrated the effectiveness of porous tantalum used in implants (**Figure 1-12**). Their results indicated that the porosity of the tantalum allows for excellent fibrous and bony ingrowths, while its tensile strength allows it to be porous yet strong enough. The chemical inertness of tantalum also play a big role in the suitability of this metal for implants because

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[18] SH Weeden, RH Schmidt. (2007). The Use of Tantalum Porous Metal Implants for Paprosky 3A and 3B Defects. *Journal of Arthroplasty.* Vol. 22. No. 6. pp. 151-155.

[19] BR Levine, S Sporer, RA Poggie, CJ Della Valle & JJ Jacobs. (2006). *Biomaterials.* Vol. 27. pp. 4671-4681.

it seldom, if not never, gets rejected by the body nor does it cause infection or inflammation.

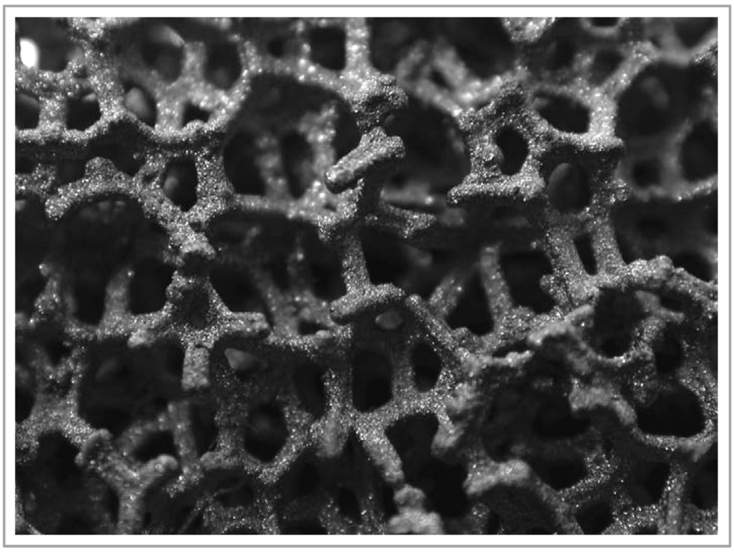

Figure 1-12: Microstructure of porous tantalum[19].

In the electronics field, Ta_2O_5 is used as the dielectric medium in the manufacture of capacitors, like the ones pictured in **Figure 1-13**. In 2005 as much as 60% of all tantalite that was mined got channelled towards capacitor manufacture[20]. These electronic components are used in almost all high-tech electronic appliances from cell phones and computers to office equipment, automotive parts and aerospace technology.

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[20] Roskil Information Services Ltd. (2005). *The Economics of Tantalum.* 9th Ed. Sect. 1.

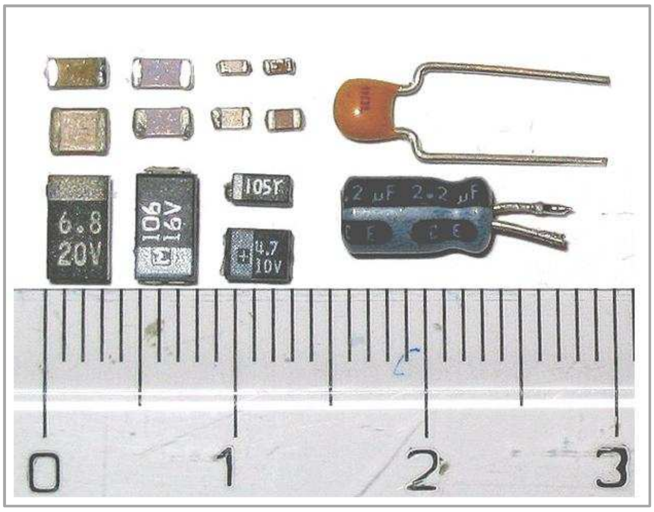

Figure 1-13: Capacitors compared to a centimetre scale[21].

There are two important characteristics that determine the efficiency of the material used to act as a capacitor dielectric. They are the dielectric constant and the dielectric strength. The dielectric constants and dielectric strengths for Ta_2O_5 and other dielectric media used in capacitors are listed in **Table 1-2**. Because tantalum and its oxide have such good dielectric constants they are often the material of choice when it comes to capacitor construction. This is because less of the dielectric medium is needed to achieve the same capacitance compared to a material with a smaller dielectric constant. Therefore, in order to manufacture smaller electronic devices very small capacitors are needed, which in turn requires a dielectric medium that has a high dielectric constant and a high dielectric strength such as tantalum pentoxide.

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[21] http://en.wikipedia.org/wiki/File:Photo-SMDcapacitors.jpg. 08 February 2010.

Table 1-2: Comparison of characteristics of different capacitor dielectrics.

Dielectric medium	Dielectric constant[22]	Dielectric strength[23] (MV.m^{-1})
Vacuum	1.0	3.0
Paper	2.0 – 6.0	14 – 16
Porcelain	5.1 – 5.9	4.0 – 12
Al_2O_3 [24]	9.0	6.0
SiO_2 [25]	3.8	800
Ta_2O_5 [25]	26.0	600

Tantalum metal has also found various uses in the chemical and tooling industry. The chemical inertness of the tantalum metal allows it to be used as lining material in chemical reactors, in the construction of heaters used for chemical production (**Figure 1-14**) and for heat exchangers, to mention a few.

Figure 1-14: Tantalum bayonet-type heater**[26]**.

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[22] http://www.itiomar.it/pubblica/Telecomunicaz/lezioni/3_anno/Cap-Ta-1.pdf. 09 February 2010.

[23] http://physics.info/dielectrics/. 09 February 2010.

[24] DR Askeland. (1996). *The Science and Engineering of Materials.* 3rd S.I. Ed. p656.

[25] Y Li, *et al*. (2008). Anodic Ta_2O_5 for CMOS compatible low voltage electrowetting-on-dielectric device fabrication. *Solid-State Electronics.* p1382-1387.

[26] http://www.apexep.com/user/cimage/Tantalum-Bayonet-Heater.jpg. 09 February 2010.

Making these pieces of equipment however creates unique challenges. Welding tantalum needs to take place in an inert gas atmosphere since the presence of any oxidative compounds cause the formation a protective layer of tantalum pentoxide which in turn affects the weld quality. Special welding chambers must be used when manufacturing these pieces of equipment. Some parts are also machined from a solid billet of tantalum (**Figure 1-15**). This is expensive and wasteful, but necessary in some cases. Tantalum metal, and especially some of its alloys, are very hard and make excellent cutting, grinding and milling tools with tantalum-carbide and tantalum-tungstenate being some of the hardest known alloys currently used in industry.

Figure 1-15: Machined tantalum pump impellers[27].

1.6 Chemistry of Tantalum[28]

Tantalum and niobium are like “inseparable twins”, they nearly always occur together in deposits, they are located in the same group in the periodic table and they have nearly identical chemistries with only a few minor differences here and there. Similarities in chemical and physical properties are the reason for the

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[27] http://www.plantautomation-technology.com/contractor_images/tantaline/pump.jpg, 09 February 2010.

[28] FA Cotton, G Wilkinson. (1966). *Advanced Inorganic Chemistry A Comprehensive Text 2nd Ed*. London. Interscience Publishers. pp. 919-930.

difficult separation of the two elements during the processing of tantalum and niobium containing minerals.

Tantalum and niobium's electron configurations are [Xe] $4f^{14}$ $5d^3$ $6s^2$ and [Kr] $4d^4$ $5s^1$ respectively. Thus, the number of electrons that can be lost from tantalum's valence orbitals are anything from two to five, therefore making its possible oxidation states either 2+, 3+, 4+ or 5+. The most stable oxidation state however is that of 5+ or Ta(V) because when the outer five electrons are lost, it has a fully filled valence electron shell resulting in a [Kr] electron configuration. This, along with the fact that σ- and π-donating ligands like O^{2-} and halides stabilise high oxidation states, is the reason why some of the most stable tantalum compounds are tantalum pentoxide (Ta_2O_5) and tantalum pentahalides (TaX_5 with X = F, Cl, Br).

The oxides are formed by dehydrating tantalic acid ($Ta_2O_5 \bullet nH_2O$) in the presence of elements that can be removed as gasses under an oxygen atmosphere, like sulphur and carbon. If the starting material is tantalum metal, heating it above 200℃ in oxygen will yield tantalum pentoxide.

$TaCl_5$ is obtained by reacting $SOCl_2$ with the hydrous oxide of tantalum ($Ta_2O_5 \bullet nH_2O$), the product then has a dimeric structure in the crystalline form, as shown in **Figure 1-16**. The same procedure applies for niobium as well.

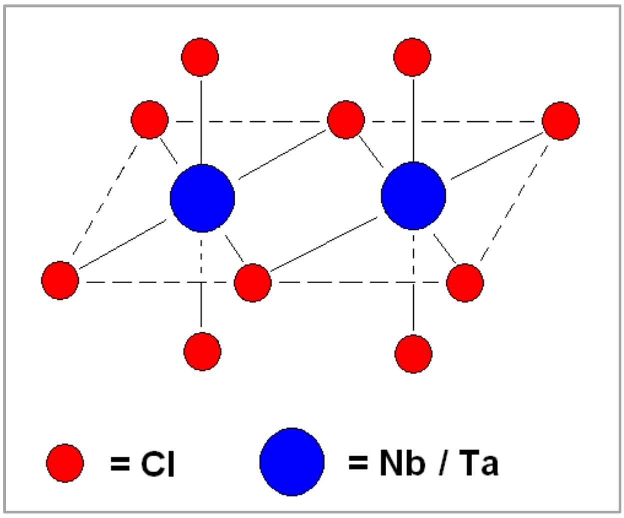

Figure 1-16: Dimeric structure of tantalum/niobium pentachloride in crystalline form[29].

The metals, the pentoxides as well as the pentachlorides of both tantalum and niobium are directly fluorinated to obtain the pentafluoride salt[30]. The pentafluorides of tantalum and niobium form tetrameric structures as indicated in **Figure 1-17**. Fluorination is obtained by simply dissolving the above mentioned starting materials in aqueous HF as given by **Eq. 1-1 to 1-3**.

$$TaCl_5 + 5HF_{(aq)} \rightarrow TaF_5 + 5HCl_{(aq)} \qquad \textbf{Eq. 1-1}$$

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[29] FA Cotton, G Wilkinson. (1966). *Advanced Inorganic Chemistry A Comprehensive Text 2nd Ed.* London. Interscience Publishers. p. 924.

[30] FA Cotton, G Wilkinson. (1966). *Advanced Inorganic Chemistry A Comprehensive Text 2nd Ed.* London. Interscience Publishers. p. 921.

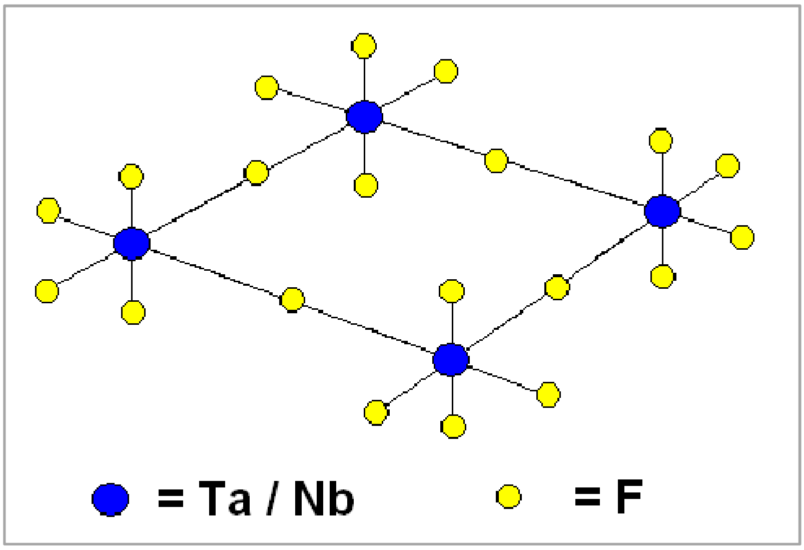

Figure 1-17: Tetrameric structure of tantalum/niobium pentafluoride[31].

Although a lot less than the 5+ oxidation state, these two metals also show lower oxidation state chemistry. Niobium and tantalum dioxides (NbO_2 and TaO_2) for example have the metals in the 4+ oxidation state (Ta(IV) and Nb(IV)). TaO_2 is prepared by reducing Ta_2O_5 at high temperature in the presence of carbon. Tantalum also forms tetrahalides with Cl^-, Br^- and I^- to form $TaCl_4$, $TaBr_4$ and TaI_4 in which the tantalum is Ta(IV). Ta(II) is known to exist as $TaCl_{2.33}$ or Ta_6Cl_{14}. This compound consists of $Ta_6Cl_{12}^{2-}$ ions that are bridged by Cl^- ions[32]. Ta(I) and Ta(-I) are only present in CO and π-C_5H_5 complexes such as $[Ta(CO)_6]^-$ and $[\pi$-$C_5H_5Ta(CO)_4]$ respectively[33].

There are also a few organometallic compounds included in the lower oxidation state chemistry of tantalum. An example is $[Ta((Me_2PCH_2CH_2PMe_2)_2 Cl_4)]$ which has the structure of [M(bidentate)$_2$ (unidentate)$_4$] where the metal is also Ta(IV). This compound has a square antiprism structure as shown in **Figure 1-18**[34] where the positions of the bidentate ligands are indicated by the white spots and the monodentate ligands by the dark spots.

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[31] FA Cotton, G Wilkinson. (1966). *Advanced Inorganic Chemistry A Comprehensive Text 2nd Edition*. London. Interscience Publishers. p. 922.

[32] FA Cotton, G Wilkinson. (1966). *Advanced Inorganic Chemistry A Comprehensive Text 2nd Edition*. London. Interscience Publishers. p. 926.

[33] FA Cotton, G Wilkinson. (1966). *Advanced Inorganic Chemistry A Comprehensive Text 2nd Edition*. London. Interscience Publishers. p. 930.

[34] G Wilkinson, RD Gillard & JA McCleverty (Editors). (1987). *Comprehensive Coordination Chemistry.* Oxford. Pergamon Press. Vol. 1. p. 88.

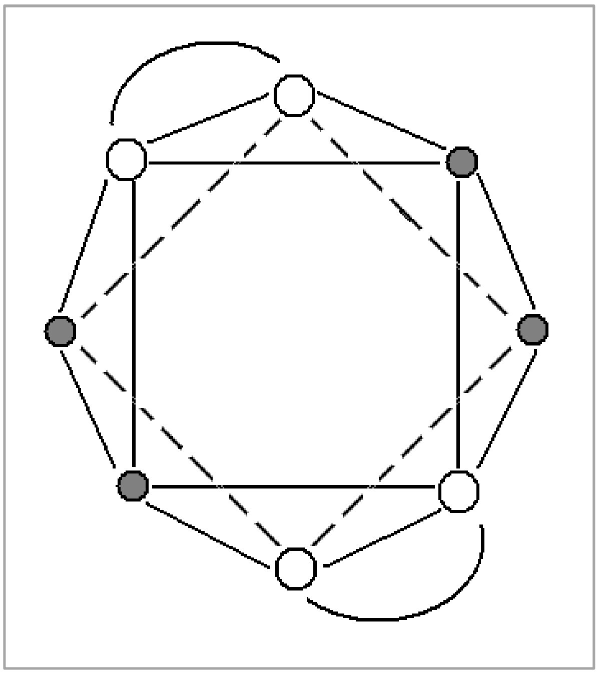

Figure 1-18: The square antiprism structure of $[Ta((Me_2PCH_2CH_2PMe_2)_2Cl_4)]$**[35]**.

Another organometallic compound is the polymeric phosphine complex, $[Ta(OPPh_2O)_2\ (OH)_3]_n$[36], that is used as a filler in special high temperature laminates and can produce materials with remarkably high flexural strengths. The oxidation state of the metal centre in this complex is again Ta(V).

1.7 Aims of This Study

As new applications for tantalum are being developed, the demand for the metal and its compounds increases and the trend towards portable electronics is a major driving force in the need for miniaturization of electronic components. Tantalum capacitors became a product of first choice where high electrical and mechanical stability, along with long service life and volumetric efficiency, are demanded. The use of tantalum metal or its oxides as capacitors and gate terminals in the electronic industry, as well as in optical glass, necessitates the use of extremely pure materials. However, many impurities present in original tantalum ore, even in trace amounts, can adversely affect the properties and therefore the performance

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[35] G Wilkinson, RD Gillard & JA McCleverty (Editors). (1987). *Comprehensive Coordination Chemistry.* Oxford. Pergamon Press. Vol. 1. p. 88.

[36] Gillman et al. (1977). *Chemical Abstracts.* Vol. 87. 54 043.

of the final tantalum product which is used as capacitors and in optical glass[37]. Typical tantalum powder impurities include carbon, iron, nickel, chromium, sodium, potassium and magnesium[38]. The reduction of these impurities in the final powders were heavily pursued in the last few years which led to the reduction of iron from approximately 40 to 20 ppm/m^2 for the period 2004 to 2008, nickel from 50 to 15 and sodium from 8 to 1 ppm/m^2 [39].

Tantalum and tantalum pentoxide are very difficult, if not impossible, to dissolve by simply using any of the mineral acids. The only acid known to readily dissolve both tantalum and tantalum pentoxide is HF (**Eq.1-2 & Eq.1-3**)[40]. This works well, but has two major disadvantages, namely its extreme toxicity towards humans and the issue of disposing of HF-containing waste in an environmentally friendly manner. Despite this, HF dissolution is still a part of every industrial tantalum/niobium refining process.

$$Ta_{(s)} + 6HF \rightarrow HTaF_6 + 2.5H_{2(g)}$$ **Eq. 1-2**

$$Ta_2O_5 + 12HF \rightarrow 2HTaF_6 + 5H_2O$$ **Eq. 1-3**

The separation, isolation and purification of tantalum from its ores and the strict specifications of the metal that is used in some industries necessitates the ability to analyse not only the main element during the enrichment processes, but also the impurities at ng/g levels in the ultra pure metals and oxides. This calls for more effective, more efficient and more accurate sample analysis on various sample matrices and therefore it seemed necessary to develop additional dissolution and quantification procedures and validate these procedures in

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[37] G Anil, MRP Reddy, TL Prakash. (2005). *Journal of Analytical Chemistry.* Vol. 61. No. 7. pp. 641-643.

[38] S Kozono, R Takashi, H Haraguchi. (1999). *Analytical Sciences.* Vol. 16. pp. 69-74.

[39] I Horacek *et al.* High *CV capacitors – challenges and limitations.* http://www.avx.com/docs/techinfo/highcvtant.pdf. 15 March 2010.

[40] A Agulyansky. (2004). *The Chemistry of Tantalum and Niobium Fluoride Compounds.* Amsterdam. Elsevier. p. 13.

accordance with the criteria of the International Standards Organisation (ISO 17025).

The aims of this study were as follows:

- To find an alternative, but effective dissolution method for tantalum metal, tantalum pentoxide, tantalum pentachloride, tantalum pentafluoride and a few different samples of naturally occurring tantalum containing ores without the use of HF.
- To analyse the resulting solutions by means of ICP-OES and obtain analytically correct, accurate and reproducible results.
- Perform method validation on these analytical processes.
- Determine LOD/LOQ of tantalum, and some possible impurities, for the ICP.
- Attempt mechanical separation and analyse separated components to see if separation improves Ta content.

Chapter 2: Analytical techniques for dissolution and analysis of tantalum containing compounds: A literature study

2.1 Introduction

A number of different methods for analysing and refining tantalum from raw materials such as ores, tin slag and recycled products have been developed since its discovery in 1802. Currently the most common method for processing tantalum ore involves the use of HF[41] and, as mentioned before, this acid is extremely harmful and excessive exposure to it can be fatal. One of the main goals of this project was to develop an alternative dissolution method for tantalum and its ores that specifically excludes the use of HF and to develop an analytical technique to quantify tantalum and it's impurities in accordance with ISO 17025.

2.2 Methods of dissolution and analysis in literature

According to a study done by H Zhou, S Zheng and Y Zhang[42], the tantalum (and niobium) in low grade tantalum ore can be leached by highly concentrated KOH. They obtained results of as high as 95.6 % and 98.7 % recoveries for tantalum and niobium respectively with ICP spectrometry. Five parameters were varied in order to optimise the leaching efficiency. This includes particle size, KOH concentration, leaching temperature and time as well as ore to KOH-solution mass ratio. The most effective combination in terms of digestion was found to be finely ground ore (max. 52 µm particle size) mixed with 85 % w/w KOH solution in a mass ratio of 1:7 respectively, stirred at 300 ℃ for 60 min.

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[41] http://tanb.org/tantalum. 24 March 2010

[42] H Zhou, S Zheng and Y Zhang. (2005). *Hydrometallurgy.* Vol. 80. pp. 83-89.

Zhou *et al.* also conducted a study with Yi[43] on the dissolution behaviour of Nb- and Ta-oxides in highly concentrated KOH solutions. It was found that the concentrated KOH initialized two reactions[44] (**Eq. 2-1** and **Eq. 2-2**); one forming water soluble $K_8Nb_6O_{19}$•$n$$H_2O$ and the other forming $KNbO_3$ which is insoluble in water.

$$\boldsymbol{3(Nb,Ta)_2O_5 + 8KOH + (n-4)H_2O \rightarrow K_8(Nb,Ta)_6O_{19} \cdot nH_2O} \qquad \textbf{Eq. 2-1}$$

$$\boldsymbol{K_8(Nb,Ta)_6O_{19} \cdot nH_2O \rightleftharpoons 6K(Nb,Ta)O_3 + 2KOH + (n-1)H_2O} \qquad \textbf{Eq. 2-2}$$

By varying temperature, KOH concentration and the Nb_2O_5/KOH ratio the total reaction could be driven to form the majority of soluble $K_8Nb_6O_{19}$•$n$$H_2O$ and as much as 92.8 % of the available Nb(V) was obtained in solution. However, the same did not apply for Ta_2O_5, as almost all of this oxide was converted to the insoluble $KTaO_3$ form, a maximum of 1.6 % of available Ta(V) was obtained in solution. All quantitative analyses were performed on the ICP-OES.

Premadas *et al.*[45] reported a simple and efficient method for digesting columbite-tantalite minerals for a 32 element analyses. The digestion was done by the fusion of 0.6 g of mineral sample with a flux made of KHF_2 and NaF in a 3:1 mass ratio. The cooled melt was then dissolved in oxalic acid (120 ml, 0.2 M) and boiled for 2-5 min with 0.5 ml H_2O_2. The analyses were carried out on ICP-OES and flame atomic absorption spectrometry (FAAS). Their results indicated >98% tantalum recovery and also indicated fairly good precision and accuracy. However, because of the use of this specific type of flux mixture, the fluoride content had to be removed first by sulphuric acid before being dissolved in oxalic acid to prevent the *in situ* formation of extremely dangerous HF.

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[43] H Zhou, D Yi, Y Zhang and S Zheng. (2005). *Hydrometallurgy.* Vol. 80. pp. 126-131.

[44] MA Orekhov, AH Zelikman, (1963). Tsvetn. Metall. 5. pp. 99–107.

[45] A Premadas, VV Hanuman, VN Dwivedi. (2004). *Atomic Spectroscopy.* Vol. 25. Issue 2. pp. 70-78.

A health and safety study was done to determine the effects on workers at a tantalum processing plant who inhale aerosol-like ore particles (diameter < 2.5 µm). Lima[46] reported that a number of Ta-containing mineral particles such as columbite, columbite-tantalite and pyrochlore can be completely or partially dissolved by SLF (simulated lung fluid). Quantitative analyses were done by PIXE (Particle Induced X-ray Emission) and show dissolutions of 21.5 %, 13.5 % and 2.5 % in terms of tantalum recovery for columbite, pyrochlore and columbite-tantalite respectively. From this, one can clearly see the dissolution resistance of tantalum pentoxide, the primary constituent of tantalite.

In a recent study performed by Mahanta[47] *et al.,* they report a new flux dissolution method for tantalum-containing minerals. The flux they used consisted of a 1:1 mass ratio of Na_2HPO_4 and $NaH_2PO_4{\bullet}H_2O$. They digested *ca.* 0.5 g of mineral sample with *ca.* 8.0 g of flux, dissolved the melt in distilled water and performed quantitative analyses with ICP-OES. The results in **Table 2-1** show complete dissolution and good tantalum recoveries from five different ore samples.

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[46] C Lima *et al.* (2007). *Water, Air and Soil Pollution.* Vol. 186. No. 1-4. pp. 365-371.

[47] PL Mahanta *et al*. (2008). *Atomic Spectroscopy.* Vol. 29. No. 5. pp. 172-179.

Table 2-1: Tantalum pentoxide content results.

Sample	Ta_2O_5 content (mass %)		
	Proposed method	**$KHSO_4$ method**	**NaF+KHF_2 method**
Cb-1	12.20	11.90	11.80
Cb-2	16.70	16.50	16.00
Cb-3	25.70	25.50	26.00
Ta-1	47.60	48.00	47.40
Ta-2	51.20	50.90	50.50

The validity of their method was confirmed by two CRMs and three synthetically prepared samples (see **Table 2-2**).

Table 2-2: CRM and synthetic mixture results.

Sample	Content (mass %)			
	Ta_2O_5		**Nb_2O_5**	
	Certified	**Obtained**	**Certified**	**Obtained**
IGS-33	5.52	5.10	68.71	69.00
IGS-34	49.80	49.70	27.45	26.90
SYN-1	5.1	5.0	9.8	10.0
SYN-2	9.9	10.0	4.1	4.0
SYN-3	2.9	3.0	1.9	2.0

Coedo[48] *et al.* reported a method for separating niobium, tantalum, tungsten, zirconium and hafnium from highly pure iron samples. The separation is done by means of a strong basic anion resin column and quantification was done by ICP-MS. The iron samples are reportedly dissolved by using an acid mixture consisting of nitric, hydrochloric and hydrofluoric acid. These solutions are then passed through a self manufactured resin column containing Dowex 1X8 (50 - 100 mesh) and the eluant is analysed. Recoveries of more than 97 % for all elements

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[48] AG Coedo, TD López, F Alguacil. (1995). *Analytica Chimica Acta.* Vol. 315. pp. 331-338.

present in the CRM 098-1 reference material are reported in **Table 2-3** and a RSD of less than 3 % indicates the method's good precision. Unfortunately, the method still makes use of the undesired HF.

Table 2-3: Recoveries from CRM-098.

Element	Sample conc. (ppm)	Mass recovery (%)
Nb	0.032	102
Ta	0.21	97
Zr	0.060	104
Hf	<0.010	110
W	0.250	99

In an article by Friese and Krivan[49], a solid sampling method is reported for analysing trace elements in high purity tantalum powder. This method makes use of an AA spectrometer modified to analyse solid samples. The high furnace temperature of the AA and the refractory properties of tantalum allow all the elements with a lower boiling point than tantalum to be atomised and were then analysed. The results they obtained from analysing three high purity tantalum powder samples with four different techniques are tabulated in **Table 2-4**. Judging by their results it can be seen that for a given impurity, quantification using the four different methods fall in the same order of magnitude, but the precision is not so good. Although, taken into account that the impurities fall in the ng.g^{-1} range, the results can be seen as fairly good.

It is reported by Obiajunwa[50] that analysis of a solid mineral ore sample by energy-dispersive X-ray fluorescence (EDXRF) is "quite adequate". They report Ta content of 6.94 - 10.55 % in Nigerian mineral ore samples with RSD <10 %. There is, however, no report of tantalum recovery from the reference material analysed and therefore it cannot be said that this method is entirely suited for accurate analysis of tantalum in mineral ores.

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[49] KC Friese, V Krivan, (1998), *Spectrochimica Acta.* Part B 53. pp. 1069-1078.

[50] EI Obiajunwa. (2001). *Nuclear Instruments and Methods in Physics Research.* Vol. 184. pp. 437-440.

Table 2-4: Excerpt from the results by Friese on the element content in three tantalum materials using four different analysis techniques.[49]

Element	**Sample**	**Concentration (ng.g^{-1})**			
		Solid-sampling			**Liquid-sampling**
		AAS 5 EA	**Grün SMI**	**ETV-ICP-AES**	**ETAAS**
Cu	Ta-1	87±4	96±9	100±40	110±20
	Ta-2	68±12	73±5	65±7	77±9
	Ta-3	46±4	50±4	53±8	45±4
Fe	Ta-1	11400±1000	14100±2400	17000±3000	15900±1100
	Ta-2	9100±400	9800±1100	9000±1500	9500±300
	Ta-3	6200±750	7400±700	5900±1000	6300±400
Na	Ta-1	2800±150	2200±100	1500±300	4300±300
	Ta-2	88±14	94±30	120±40	130±30
	Ta-3	350±25	330±40	260±100	450±50

A study conducted by Welham[51] showed remarkable dissolution results following a certain method of mineral preparation. It was found that by extensive dry milling (2 – 50 h) of tantalite/columbite concentrates prior to HF dissolution, one can increase the solubility rate by as much as 300 times. Both dry and wet milling were studied and although wet milling delivered a product of much higher surface area, it was found that dry milling caused the crystalline structure of the mineral to be more amorphous whereas wet milling yielded a more crystalline form. Therefore the dry milled product had a greater and more efficient dissolution rate due to its amorphous nature.

In a related study by Nete[52], an alternative dissolution method was found for niobium and its ores. Niobium metal, Nb_2O_5 and some tantalite ore samples were successfully dissolved by making use of microwave assisted sulphuric acid

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[51] NJ Welham. (2001). *International Journal of Mineral Processing.* Vol. 61. pp. 145-154.

[52] M Nete. (2009). *Dissolution and analytical characterization of tantalite ore, niobium metal and other niobium compounds.* M.Sc. thesis. Bloemfontein: University of the Free State.

digestion. The niobium recoveries were >97 % for the metal and the oxide and *ca.* 95 % for the mineral ore (see **Table 2-5**). He also indicated the success of a flux method that involved the oxide or the mineral being fluxed with lithium tetraborate (LTB) and dissolved in sulphuric acid. These Nb recoveries ranged from 98 – 102 % depending on the samples and conditions. Quantitative and qualitative analyses were mainly done by ICP-OES, but XRF and XRD was also used.

Table 2-5: Results for different samples by either microwave- or flux digestion[52].

Sample	Method	Nb recovery (%)	RSD (%)
Nb	Microwave asst. sulphuric acid digestion	99.78	0.81
	Bench top sulphuric acid digestion	0.36	0.41×10^{-3}
Nb_2O_5	Microwave asst. sulphuric acid digestion	97.49	0.25
	LTB flux and sulphuric acid dissolution	102.76	---
Tantalite ore	Microwave asst. sulphuric acid digestion	95.03	---
	LTB flux	98.54	---

Birks and Brooks[53] reported an accurate method for analysing tantalum in columbium. This method makes use of X-ray fluorescence (XRF). They reported that the K-series spectrum of tantalum overlaps slightly with the L-series spectrum of columbium, but also give two solutions to this problem. The first solution was to compare the integrated intensity of an unresolved columbium-tantalum doublet with the integrated intensity if a resolved columbium line. The second solution involved lowering the X-ray tube voltage in order to excite the tantalum L-spectrum without exciting the niobium K-spectrum. Tantalum content of as low as 0.1 % can be detected and quantitative results with accuracies of *ca.* 4 % can be obtained.

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[53] LS Birks, EJ Brooks. (1950). *Journal of Analytical Chemistry (U.S.).* Vol. 22. No. 8. pp. 1017-1020.

In a study done by Mortimore[54] *et al.* an X-ray spectrographic method was developed for analysing tantalum and niobium in mineral ores. What distinguishes this method from the XRF method developed by Birks and Brooks[53] is that Mortimore used internal standards to obtain more accurate intensity readings instead of making use of physical means like Birks and Brooks. The result was a method able to quantify tantalum and niobium contents at lower limits of 0.2 and 0.05 % respectively with standard deviations of less than 5 %.

Research was done on the dissolution kinetics of ferrocolumbite in HF medium by Rodrigues[55] *et al.* The samples in question were obtained from the Las Cuevas mine in Argentinia and contained about 36.8 % w/w of Ta_2O_5 according to ICP-OES and XRF analyses. It was found that the optimum dissolution, which turned out to be *ca.* 83 % of the original sample mass added to the reaction, was reached in 90 min. at 220 ℃ in a 9 % v/v HF solution.

Another study done by Rodrigues and Ruiz, in collaboration with Rivarola[56], investigated the effect that the addition of carboxylic acids had on the leaching of ferrocolumbite ore by HF. They found that a mixture of tartaric acid (15 % w/v) and HF (15 % v/v) gave a 91 % of tantalum recovery from the ore. However, the use of oxalic acid, under certain conditions, proved to be much more useful because of the formation of an insoluble Fe(II) oxalate while still yielding a 90 % recovery of tantalum from the ore. Characterisation and quantification were performed on SEM (scanning electron microscopy), EDXS (energy dispersive X-ray spectroscopy), XRD and XRF. Some results are tabulated in **Table 2-6**.

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[54] DM Mortimore, PA Romans, JL Tews. (1954). Society for Applied Spectroscopy. Vol. 8. Issue 1. pp. 24-28.

[55] M Rodrigues, O Quiroga, M del C. Ruiz. (2006). *Hydrometallurgy.* Vol. 85. pp. 87-94.

[56] M Rodrigues, J Rivarola, M del C. Ruiz. (2004). *Hydrometallurgy.* Vol. 74. pp. 39-46.

Table 2-6: Tantalum pentoxide recoveries from acid leaching at 220 ℃.

Leaching solution	**Recovery (%)**	
	Ta_2O_5	**Nb_2O_5**
HF (9%)	79	87
HF (9%) + tartaric acid (15%)	86	92
HF (9%) + citric acid (15%)	85	91
HF (9%) + formic acid (15%)	83	89

2.3 Comparison and selection of analytical techniques

2.3.1 X-ray spectrometry

All X-ray spectrometry techniques are based on the fact that each element has its own characteristic X-ray emission spectrum[57], therefore both XRD and XRF are excellent techniques for qualification, especially when it comes to solid samples. The fact that X-ray techniques work as well with solid samples as with liquid samples is a major advantage compared to other techniques such as AA, UV-vis and ICP-OES where the samples have to be in solution.

One drawback, however, of X-ray spectrometry has to do with sample preparation, specifically for powder samples. Samples in solution have a much better homogeneity than samples in solid form. For this reason, solid state samples for X-ray spectrometry have to be meticulously prepared to ensure proper homogeneity. If this is not the case, results will be inaccurate. Therefore, seeing that a large part of this project involves dissolution, it would be better to employ an analytical method that specialises in the analyses of liquid samples *e.g.* AA or ICP-OES.

Furthermore, while X-ray spectrometry is very useful, simple and convenient for qualification work, it is not the case with quantification. Again, the quality of sample preparation for the calibration standards and the samples greatly

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[57] R Jenkins. (1976). *An Introduction to X-Ray Spectrometry.* New York, USA. Heyden & Son Ltd. p. 120.

influences the accuracy of the results.[58] Other factors that can affect the results include line overlapping due to interference from other constituents, secondary absorption and the third-element effect. Also, although there are X-ray spectrometers that are capable of detecting analytes in very low concentrations such as in the ppm range[59], in general X-ray spectrometry does not have the same sensitivity that for example ICP-OES and ICP-MS have (ppm to ppb).

2.3.2 UV-vis

In order to make use of UV-vis as a quantitative analytical technique, one has to find a ligand or complexing agent that forms some kind of coloured complex upon reaction with the analyte. Since it is already a difficult task getting tantalum into solution, it would seem like unnecessary trouble to try and find a complexing agent that results in a coloured solution just for quantification. Especially when there are methods that can analyse for tantalum in dissolved samples without having to complex, like AA, ICP-MS and ICP-OES. In addition to the above, if one takes into account Beer's law and low concentration levels *e.g.* ppm to ppb, another limitation sets in; the nonlinear behaviour of light in the overlapping of absorbance maxima due to other elements present in solution.

2.3.3 Atomic absorption[60]

Like the name suggests, atomic absorption (AA) depends on the absorption of an analyte's characteristic wavelength instead of its emission, like with ICP-OES. The characteristic wavelengths are produced by a light source called a hollow-cathode lamp, which is made of the analyte material (see **Figure 2-1**). Like ICP-OES, AA is able to detect analyte concentrations in the parts per million to parts per billion range and even lower, with the use of a graphite furnace. However, the use of AA, compared to ICP-OES, has two major drawbacks, both involving the light source. The first is that with AA only about 70 of the elements in the periodic

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[58] R Jenkins. (1976). *An Introduction to X-Ray Spectrometry.* New York, USA. Heyden & Son Ltd. p. 115.

[59] R Jenkins. (1976). *An Introduction to X-Ray Spectrometry.* New York, USA. Heyden & Son Ltd. p. 6.

[60] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed.* Belmont, USA. Brooks/Cole. pp. 840-864.

table can be analysed because the cathode in the lamp has to be made of or coated with the analyte material. The second being that one is only able to analyse for one element at a time due to the fact that each element requires its own light source. This drastically reduces speed and sample throughput and is more suited for routine analyses than for an ever changing research environment.

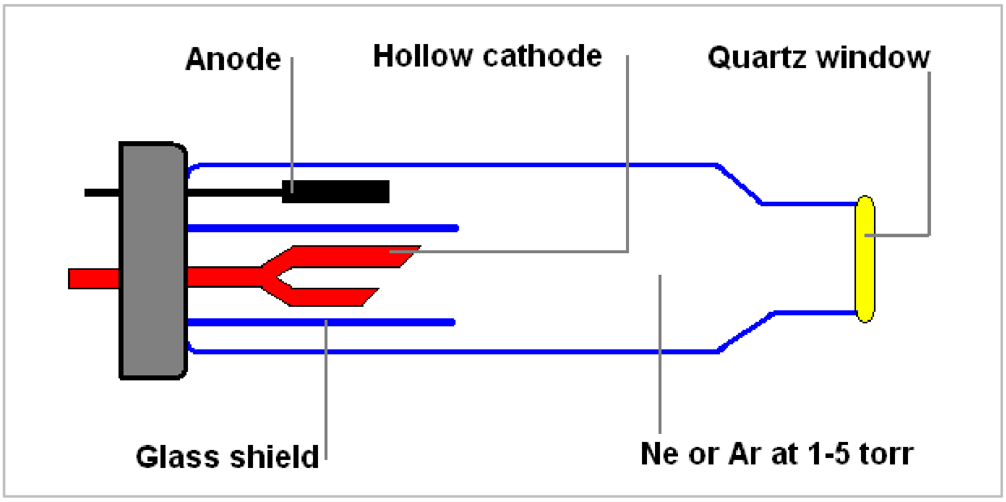

Figure 2-1: Diagram of a hollow-cathode lamp for use in an AA.[61]

2.3.4 ICP-OES

Since the aim of this study was to develop alternative dissolution methods for a number of tantalum containing samples, it would be logical and very convenient to make use of an analytical technique that is suitable for liquid sample analysis. In this case there are many options, but the one that stood out the most prominent was ICP-OES. In addition, ICP-OES is extremely versatile in the analytical lab because of its multi element qualification capabilities, its sample throughput speed, its ease of operation and ease of calibration and the simple interpretation of data. In the following paragraph the working of the ICP-OES will be explained, as well as its benefits.

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[61] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed.* Belmont, USA. Brooks/Cole. p. 860.

2.4 ICP-OES explained

2.4.1 Basic operation of ICP-OES

ICP-OES is an acronym for Inductively Coupled Plasma Optical Emission Spectrometry and is an analytical spectroscopic tool. It works on the principle of the excitation of atoms. The plasma flame of the ICP excites the electrons surrounding the atoms to a certain energy level. When these electrons fall back to their original state, photons are emitted that can be measured by the optics of the equipment. Each element gets excited differently due to the energy difference of the vacant orbitals for the respective elements, and emits at certain wavelengths, therefore this is called the optical emission spectrum (OES). The intensity and wavelength of the emission enable scientists to collect quantitative and qualitative data respectively. **Figure 2-2** displays the basic setup of any ICP. A liquid sample is pumped steadily through a nebuliser together with an inert gas (usually argon), this turns the sample solution into extremely fine droplets. The nebulised mixture then enters a cyclonic spray chamber that forces the larger droplets against the side of the spray chamber. Only appropriately sized droplets enter the plasma flame. The plasma flame, of approximately 6000 ℃, is generated with the help of a radio frequency coil that generates a magnetic field that helps sustain the plasma. The plasma flame vaporises the sample and excites it into the optical emission range. The light emission is then detected by the optics of the equipment and is sent through a series of diffraction gratings to take readings at each of the element’s characteristic emission wavelengths.

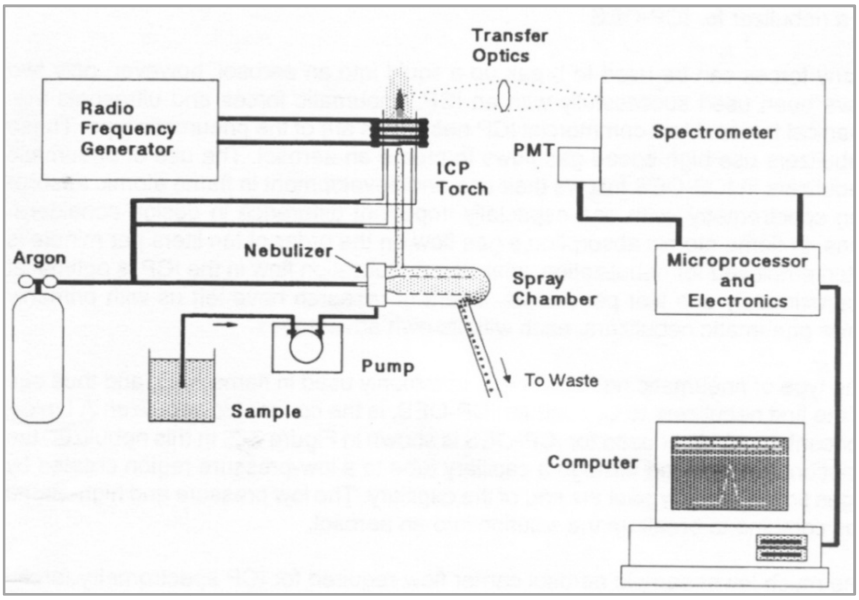

Figure 2-2: Basic schematic representation of an ICP setup.[62]

2.4.2 Components and how they function

2.4.2.1 Nebuliser and spray chamber

The nebuliser is basically a tube that tapers significantly towards one end, ending in an extremely small opening (**Figure 2-3**). An argon gas flow as well as an external constant-flow pump forces the sample through the nebuliser, which results in an extremely fine mist of sample particles.

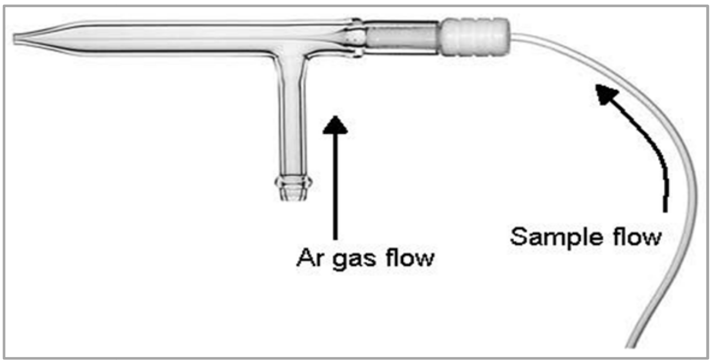

Figure 2-3: Representation of a concentric nebuliser.[63]

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[62] CB Boss, KJ Fredeen. (2004). Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry. *Perkin Elmer Inc*. p. 3-1.

[63] http://www.precisionglassblowing.com/catalog/images/500-70QD.jpg. 06 May 2010.

This mist ends up in the spray chamber (**Figure 2-4**) and is swirled into a circular motion by the pressure of the argon gas flow from the nebuliser that is mounted in a tangent position. The circular motion forces the larger droplets to collide with the side of the chamber and drain out at the bottom. All the droplets of appropriate size get blown into the torch.

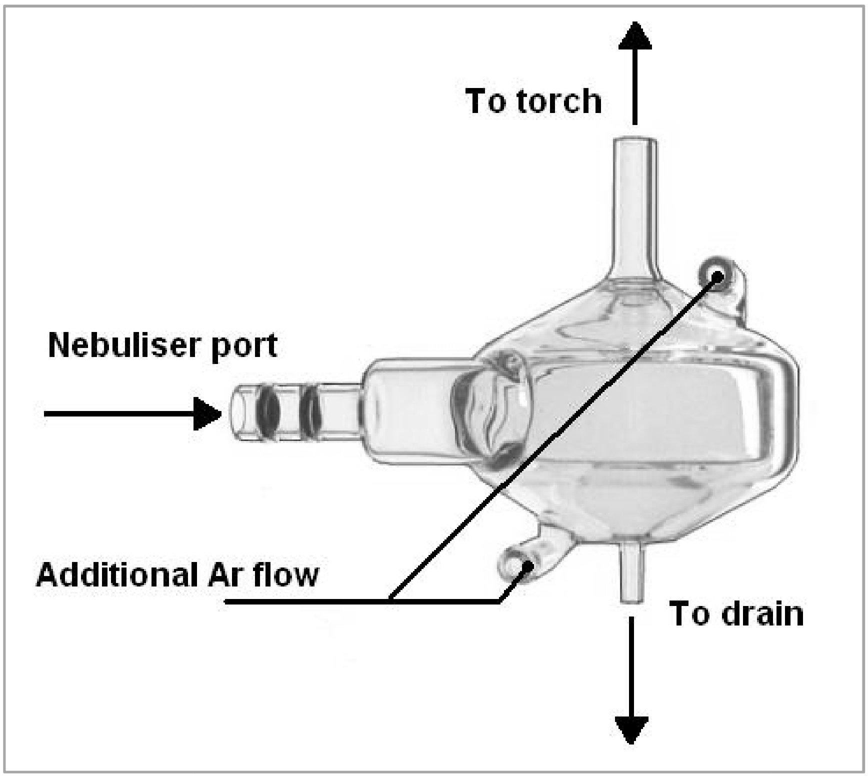

Figure 2-4: Side view of a cyclonic spray chamber.[64]

2.4.2.2 Torch and RF coil

The torch consists of three concentric quartz tubes (**Figure 2-5**). The outer tube guides the plasma gas, the middle tube guides the auxiliary gas and the centre tube has the carrier gas that contains the sample.

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[64] http://www.spray-chamber.com/images/cover_pic.jpg. 06 May 2010.

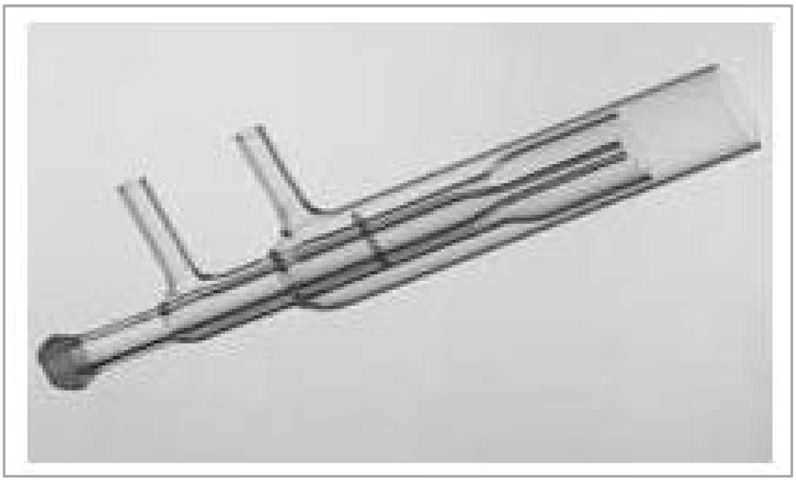

Figure 2-5: ICP torch of which the three concentric tubes are clearly visible.[65]

At the top of the torch is a copper coil, called the the RF coil or the load coil (**Figure 2-6**).[66] When an alternating electric current is passed through this coil, electric and magnetic fields are generated.

Figure 2-6: Copper load coil / RF coil.[67]

An initial spark dissociates an electron from an argon atom according to the following reaction; $Ar \rightarrow Ar^+ + e^-$. This electron gets caught up in the electric and magnetic fields and is also accelerated by them. The high energy electrons then dislodges even more electrons from the argon gas and a plasma is formed and maintained by the constant flow of argon as well as the oscillating RF coil. The

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[65] http://www.spectro.co.th/images_profiles/banner39257.jpg. 7 May 2010.

[66] CB Boss, KJ Fredeen. (2004). Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry. *Perkin Elmer Inc*. p. 3-13 to 3-16.

[67] http://las.perkinelmer.com/Content/Images/smallImages/WE021816.jpg. 11 May 2010.

use of the coil to add energy to the electrons is called inductive coupling, hence the name Inductively Coupled Plasma (ICP).

2.4.2.3 Optics

The optical setup (**Figure 2-7**) of the average ICP consists of a series of lenses and/or mirrors, some form of differentiation of the emission radiation and a detection device. Probably the most crucial part is the differentiation component of which diffraction gratings are by far the most common.

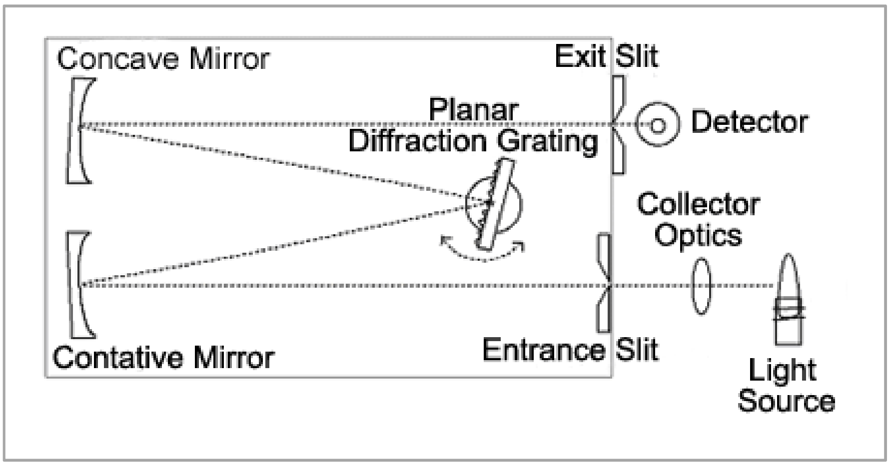

Figure 2-7: Basic schematic representation of an ICP's optical setup.[68]

Two factors influence the angle of diffraction and those are the wavelength of the incident light and the line density. As a rule of thumb, higher wavelengths and higher line densities result in bigger diffraction angles. Line densities on most ICP-OES's vary between 600 and 4200 lines per millimetre.

The diffraction grating forms part of an optical setup called a spectrometer. The spectrometer allows the incident light to be broken up into its monochromatic components and by rotating the diffraction grating it can direct and focus these components on the detectors. With all of this information (intensity, diffraction angle, wavelength *etc.*) the user interface can do calculations and give results in the form of qualitative and quantitative data.

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[68] http://www.siint.com/en/products/icp/tec_descriptions/descriptions1_e.html. 03 May 2010.

2.4.2.4 User interface

The user interface is basically a programmed electronic device that converts wavelength and intensity results to digital format and then sends it to a computer so that the user can manipulate and use the data.

2.4.3 Interferences and choosing wavelengths

As mentioned in **Section 2.4**, each element has a characteristic emission spectrum, but some elements may have certain lines or wavelengths that overlap. This overlapping causes spectral interferences that result in inaccurate measurements. Therefore, care must be taken when choosing a wavelength at which the intensities will be measured. Literature[69] provides a wealth of spectral information on all the elements that can be used to select the most suitable wavelength for any analysis.

2.4.4 Sample preparation

One drawback of using ICP-OES for analyses is that the samples have to be in liquid form. In other words, any solid sample must first be digested and/or dissolved before it can be analysed by the ICP. Dissolution is not the only problem one faces with preparing samples for the ICP. Another critical aspect is called matrix-matching; this requires the standards that are used for a specific analysis to be of as close as possible match to the sample matrix. Properties such as density and viscosity affect the nebulisation of the sample that in turn affects how the flame burns with the sample and in effect, the light it emits. **Table 2-7** gives the spectral interference data for tantalum. Some ICP instruments are capable of analysing samples in slurry form, for this a completely different sample introduction setup is required especially regarding the nebuliser, spray chamber and torch.

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[69] RK Winge, VA Fassel, VJ Peterson & MA Floyd. (1985). *Inductively Coupled Plasma - Atomic Emission Spectroscopy; An Atlas of Spectral Information.* Ames. Elsevier. p. 281.

Table 2-7: Spectral interference data for Ta[69].

Order	Wavelength (nm)	Conc. (ppm)	Estimated detection limit (ppm)	Possible interferences
II	226.230	10<0.01	0.025	Al, Fe
II	240.063	10<0.01	0.028	Cr, Cu, Fe, V
II	268.511	10<0.01	0.030	Cr, Fe, Mn, V
II	233.198	10<0.01	0.031	Fe, Ni
II	228.916	10<0.01	0.031	-
II	263.558	10<0.01	0.034	-
II	238.706	10<0.01	0.037	-
II	223.948	10<0.01	0.043	-
II	267.590	10<0.01	0.044	-
-	205.908	10<0.01	0.044	-
II	219.603	10<0.01	0.051	-
II	260.349	10<0.01	0.055	-
II	248.870	10<0.01	0.055	-
II	284.446	10<0.01	0.057	-
II	269.452	10<0.01	0.060	-
II	296.513	10<0.01	0.060	-

- = None/unknown

Spectral interference is also a side effect of poor matrix matching. Elements that are present in some of the solutions and absent in the others will cause spectral interferences that can only be corrected for by matrix matching. In principle, all the solutions must contain the same amounts of each chemical, except for the amount of analyte, which will vary in the set of standard solutions and be unknown in the sample.

2.5 The microwave digester

Conventional heating makes use of the conductive properties of the container to conduct heat and heat up the contents. The diffusion of heat in this manner is called convection; it is not very uniform and takes some time to develop. Making use of the microwave digester, on the other hand, eliminates conductive heating and convection, heats uniformly and saves time because of quick heat generation. With the combination of microwaves and reaction vessels that can handle a moderate amount of pressure, applications become even more. Previously, to obtain high temperatures and pressures, instrumentation like autoclaves and reaction-bombs had to be used. Modern day microwave digesters can be equipped with temperature and pressure probes to accurately measure these parameters and make controlling them a lot easier.

Microwaves are a form of electromagnetic radiation, categorised between frequencies of 300 and 300 000 MHz, of which a frequency of 2450 MHz is most commonly used in all microwaves appliances.[70] Microwaves have the ability to heat any substance that consists of dipole molecules and/or ions, with water probably being the most obvious example. As microwaves pass through a dipole containing substance the molecules start rotating/vibrating as they attempt to align their dipole moment with the alternating electric field, and it is this movement that generates heat. For more even heat distribution, the instrument is fitted with an electrical motor that rotates the samples and is usually called the rotor or sample carousel. Most plastics and ceramics do not absorb microwave radiation and can therefore be successfully used as containers and/or reaction vessels in microwave ovens. The microwave instrumentation used in this project is pictured in **Figure 2-8**.

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[70] HM Kingston, LB Jassie. (1988). *Introduction to Microwave Sample Preparation Theory and Practice*. USA. American Chemical Society. p. 8.

Figure 2-8: (a) Front view of microwave reactor, (b) open view of microwave reactor with carousel visible.

Probably the most distinct feature that differentiates the chemical microwave reactor from its household cousin is its carrousel or rotor. This rotor is usually designed to hold multiple reaction vessels and different rotors hold different reaction vessels which, in turn, are used for different reaction conditions. These reaction vessels are usually designed in such a way to be able to handle relatively high temperatures and high pressures. Some are fitted with pressure release valves that activate (or break) above certain pressures. Temperature and pressure probes can also be installed on these rotors to actively monitor reaction conditions inside the vessels. **Figure 2-9** illustrates a basic low pressure PTFE reactor.

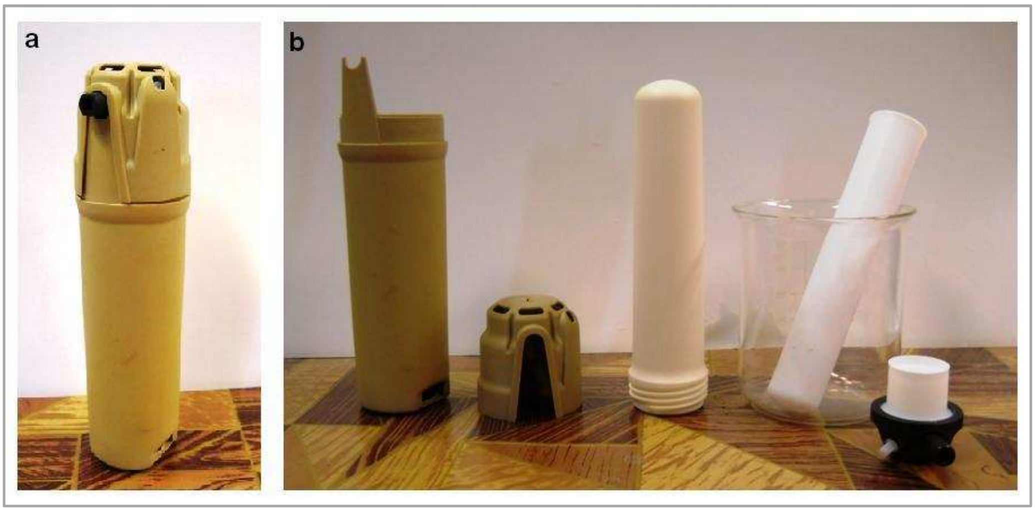

Figure 2-9: (a) Assembled PTFE reactor vessel (b) disassembled PTFE reactor vessel.

The picture in (a) is of an assembled reaction vessel while (b) shows its components. Second from the right in (b) is the PTFE reaction tube that fits into a thick walled ceramic housing (just to the left of the tube). The black and white cap on the far right seals off the tube, everything fits into the holder and cap on the left and is mounted on the carousel (**Figure 2-10**).

Figure 2-10: Carousel with mounting slots for eight reaction vessels.

2.6 The high temperature furnace

High temperature furnaces can typically reach temperatures of well over 1000 ℃ that is beyond conventional methods of heating, while electronically controlled furnaces can also maintain those temperatures very precisely. An alternative to using a high temperature furnace is to use an oxy-acetylene blow torch. This method, however, does not work that well when samples have to stay at such high temperatures for extended periods, nor can the temperature be accurately controlled.

A high temperature furnace (**Figure 2-11**) is basically an oven that is insulated well enough to attain temperatures of above 1000 ℃. In modern times, nearly all of these devices are electrically powered and therefore makes use of electrical heating elements to reach such high temperatures.

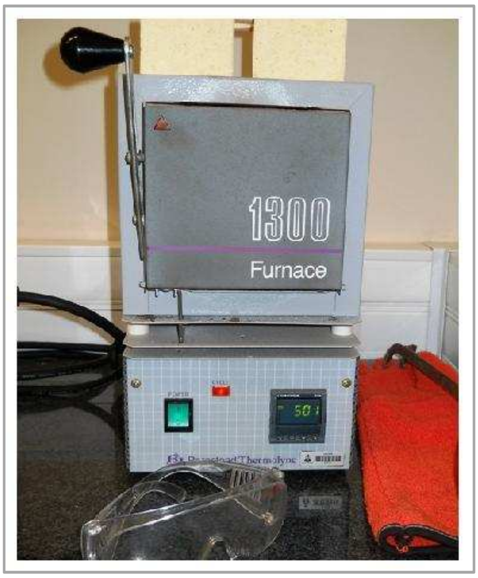

Figure 2-11: High temperature furnace.

Glass fibre is generally used as insulation for these furnaces. The inside cavity is usually made of a very porous and brittle ceramic that makes it extremely resistant to cracking and breaking due to the high temperatures, but also makes it very prone to mechanical damage.

2.7 Analytical techniques

In general, most elements can directly be analysed by external calibration, but when external calibration is not sufficient, analytical techniques such as standard addition and the internal standard method can also be used.[71] Factors that determine which analytical techniques can be used are; the element being analysed, concentration of the element, interfering species and the sample matrix.

External calibration is when an external standard is used to set up a calibration curve against which the specific element will be measured. A set of standard solutions are made up by accurately diluting a certified ICP standard, as well as a blank solution to account for matrix effects. A normal calibration curve is then obtained by the ICP-OES and the samples are then measured against it.

The standard addition technique is usually (but not exclusively) used when working with very low limits of quantification. A set of standards is also made up (just like with the external addition method) but to each standard solution is added the same, known quantity of sample. The resulting intensity *vs.* standard concentration graph will then yield a straight line that intercepts the positive part of the y-axis and the negative part of the x-axis. The concentration of the sample in each of the standard solutions is then simply the absolute value of the intercept of the straight line with the x-axis.

The internal standard technique is a bit more complex than standard addition. An internal standard is an element that is physically and chemically similar to the analyte. As with standard addition, the same, known amount of internal standard is added to all the standard solutions, the samples as well as the blank. The intensities of both the internal standard and the analyte are then measured. Instead of plotting a calibration curve of analyte intensity *vs.* concentration, the ratio between the analyte intensity and internal standard intensity is plotted against concentration ($I_{Analyte}/I_{IS}$ *vs.* $conc_{Analyte}$). With simple mathematical manipulations the concentration of the analyte in the sample can then be determined.

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[71] DA Skoog, DM West, FJ Holler & SR Crouch. (2004). *Fundamentals of analytical chemistry 8th Ed*. USA. Thomson Brooks/Cole. pp. 210-212.

Fortunately, due to the few interfering species of tantalum (**Table 2-7**) and the relatively simple solution matrices (**Chapter 4.2**), it was mostly unnecessary to use any of the two addition methods. Direct calibration was sufficient enough to analyse for tantalum in all samples during this study.

2.8 Method validation

As with any proper analytical research, method validation had to be done. The process of method validation can be divided into nine categories:

- Linearity
- Working range
- Limit of detection (LOD)
- Limit of quantification (LOQ)
- Specificity
- Accuracy
- Precision
- Robustness
- Stability

2.8.1 Linearity

Linearity is a quality measure of the calibration of a method. In analytical chemistry linear calibration curves are generally used as far as possible because of their simplicity and ease of interpretation.[72] It is also an indication that there is a direct relationship between the concentration and the physical property that is measured. To obtain a straight line through a series of data points on a graph of response signal *vs.* analyte concentration, one has to do a linear regression, usually using the least squares method. The least squares method is based on two assumptions:

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[72] ME Swartz, IS Krull. (1997). *Analytical Method Development and Validation.* New York, USA. Marcel Dekker Inc. p. 54.

- That a linear relationship exists between the response signal (*y*) and the standard analyte concentrations (*x*).
- That the error in each point is due to the measurement, *i.e.* there are no errors in the *x*-values of the points.

The whole procedure of linear regression is a complicated process involving multiple steps of calculations, all of which is described in Skoog *et al*.[73] After all the calculations, however, the value of the coefficient of determination (R^2) can be obtained. The closer this value is to one, the better the data points fit on a straight line. Statistically speaking, a calibration curve with an R^2 value close to unity will give more accurate results than one with a lower value. In this project all calibration curves that had R^2 values of less than 0.997 were considered poor quality.

2.8.2 Range[74]

The range (or linear dynamic rage) of a method is classified as the concentration range that can be accurately analysed for on a calibration curve, it is largely dependent on the set of standards. The lower limit of the range is the same as the LOD, while the upper limit is determined by the first data point in the calibration curve that deviates by more than 5 % from the suggested linear regression as illustrated by **Figure 2-12**.

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[73] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed*. Belmont, USA. Brooks/Cole. pp. 194-200.

[74] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed*. Belmont, USA. Brooks/Cole. p. 215.

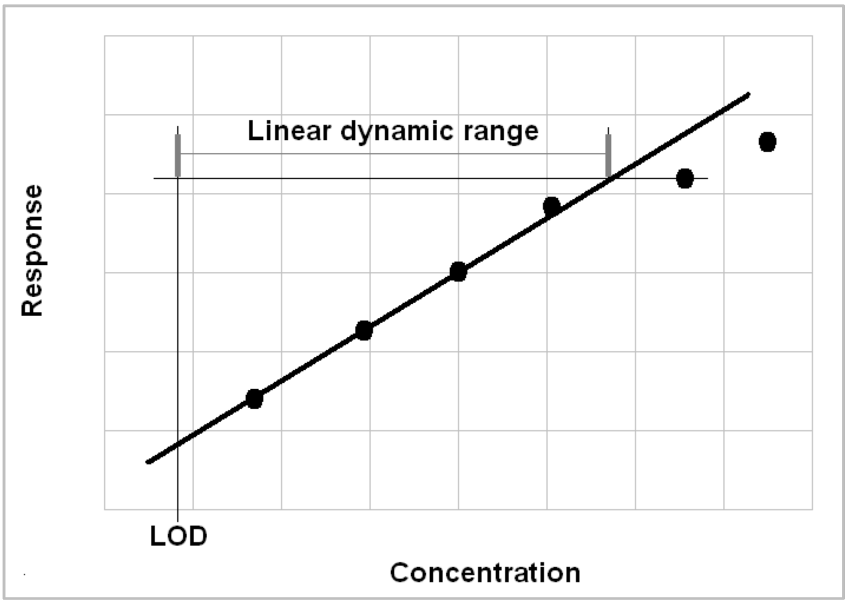

Figure 2-12: Calibration curve illustrating the upper and lower limits of a linear dynamic range[74].

2.8.3 LOD[75]

The limit of detection (LOD), or in some cases detection limit (DL), is described as the smallest analyte concentration that can be detected by the method of analysis. The LOD can be calculated by **Eq. 2-3** where s_b is the standard deviation of the blank solution and m is the slope or sensitivity of the calibration curve.

$$LOD = \frac{ks_b}{m} \qquad \textbf{Eq. 2-3}$$

The constant k is a factor of confidence level, $k=2$ corresponds to a confidence interval of 92.1 % and $k=3$ to one of 98.3 %.

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[75] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed.* Belmont, USA. Brooks/Cole. p. 214.

2.8.4 LOQ

The limit of quantification refers to the lowest concentration of analyte that can be accurately quantified within a particular confidence level. The LOQ is generally calculated as ten times the LOD, *i.e.* LOQ = LOD x 10.

2.8.5 Specificity

The term specificity refers to the methods ability to measure and account for only the desired analyte[76]. In essence it is the measurement of the total amount of interference that that can come from impurities, matrix components and so forth. For the ICP analyses of tantalum, interference data was obtained from literature (see **Table 2-7**) and fortunately only a few elements cause interference with it, and many of its characteristic wavelengths are interference free.

2.8.6 Accuracy

Accuracy is a term that describes how close a measured value is to the true or accepted value, in other words, the error in the measured value. There are two types of error values, the absolute error, E, and the relative error, E_r of which the formulas are given in **Eq. 2-4** and **Eq. 2-5**[77] respectively, where x_m is the measured value and x_t the true value.

$$E = x_m - x_t \qquad \textbf{Eq. 2-4}$$

$$E_r = \frac{x_m - x_t}{x_m} \times 100\% \qquad \textbf{Eq. 2-5}$$

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[76] ME Swartz, IS Krull. (1997). *Analytical Method Development and Validation.* New York, USA. Marcel Dekker Inc. p. 60.

[77] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed.* Belmont, USA. Brooks/Cole. pp. 93-94.

The true value is usually only known when the amount of analyte is known, like when using a CRM or a chemically pure sample.

In some research, such as with Zhou *et al.*[43], scientists use purified chemicals obtained from specific chemical distributors. Samples or chemicals can also be synthetically made in order to certify the quantities and contents of such a material and to be of as close as possible composition as a naturally occurring sample. Other research incorporates the use of certified reference materials (CRM). Premadas *et al.*[45] validated their methods by the use of two CRM's called IGS-33 and IGS-34.

In this research chemically pure samples were used as reference materials as well as a CRM. The sample chemicals used were mostly from Sigma Aldrich's high purity chemical range (**Table 2-8**). The CRM, called TAN-1, was obtained from the Canadian Certified Reference Material Project (CCRMP) of the Canada Centre for Mineral and Energy Technology. The contents of this CRM, as given in the certificate, are listed in **Table 2-9**.

Table 2-8: Chemical purities of samples used as reference materials.

Sample chemical	Purity (%)
Ta (powder)	99.99
Ta (foil)	99.90
Ta_2O_5	99.00
$TaCl_5$	99.80
TaF_5	98.00

Table 2-9: Certified tantalum content of TAN-1 CRM.[78]

Element	Certified value (%)
Ta	0.236 ± <0.015
Ta_2O_5	0.288 ± <0.016

2.8.7 Precision[79]

Precision refers to the correlation between a set of measured values, *i.e.* how close the measured values are to each other. The indicative values for this criterion are called the standard deviation (*s*) and the coefficient of variance (CV). The former can be calculated by **Eq. 2-6** and the latter by **Eq. 2-7.**

$$\boldsymbol{s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N - 1}}} \qquad \textbf{Eq. 2-6}$$

$$\boldsymbol{CV = \frac{s}{\bar{x}} \times 100}\% \qquad \textbf{Eq. 2-7}$$

As normal practice has it, *N* represents the number of measurements, x_i is the value of the *i*-th measurement and $\bar{x}$ is the arithmetic average of *N* number of values. As can be seen, the CV value is basically the SD value in percentage form which makes the interpretation of the SD value much easier. The lower these values are, the more precise the set of measurements.

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[78] http://www.nrcan.gc.ca/mms-smm/tect-tech/ccrmp/cer-cer/tan-1-eng.pdf. 09 July 2010.

[79] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed*. Belmont, USA. Brooks/Cole. pp. 115-126.

2.8.8 Robustness

Robustness is a term used to describe how a method is affected by small, deliberate changes in method parameters. Parameters such as pH, amount of solvent, temperature, analyte to reagent ratio *etc.* can be altered and the effect (if any) recorded. If these changes do not cause significant variations in results, the method can be said to be very robust. If, however, the opposite is true the correct parameters must clearly be stated in the method documentation and sufficient caution should be given to maintain them at their specified values.

2.8.9 Stability

Stability, in this case, applies to both reagents and sample solutions. In general, the stability, or an expiry date, will be printed on the label of all commercially available reagents and chemicals. However, to determine the stability of sample solutions one has to perform analyses on the same samples over a certain period and use statistical evaluation to determine to what extent they are stable.

2.9 Conclusion

In light of the journals consulted, the preferred methods of dissolution are either by means of HF or with the use of a flux at high temperatures. Although both these methods have their own pros and cons, the flux path seems to pose the least danger to humans and to be the least environmentally damaging of the two because it specifically excludes the use of HF.

From all the information in this chapter, it can clearly be seen that the most popular and advantageous method of analysis is by means of ICP. Different ICP setups allow for different types of analyses and connecting the ICP to other instrumentation like an MS (mass spectrometer) or OES (optical emission spectrometer) broadens analysis possibilities even more. It can further be deduced that the use of ICP is by far the most versatile method of analysis because it offers excellent limits of detection, it is very user friendly and it can accommodate relatively large sample throughputs. Even when interfering species and matrix effects complicate measurements by ICP-OES, analytical techniques like standard addition and the internal standard method can be applied to overcome these obstacles.

One prerequisite to ICP analysis is the fact that samples have to be in liquid form which necessitates dissolution. This can be difficult and even problematic in some cases, requiring harsher digestion techniques, purer reagents and more stringent methods, but since dissolution is an integral part of this project, it does not pose an additional problem. Also, with the aid of microwave digestion and a high temperature furnace at our disposal, the task of digestion and dissolution becomes less of an obstacle.

In conclusion; the use of ICP-OES for analyses, microwave and furnace techniques for digestion and the evaluation of the above mentioned (**Section 2.8**) validation parameters all prove to be a constructive combination to execute this project successfully and to achieve the aims set for this study.

Chapter 3: Digestion of various Ta containing samples

3.1 Introduction

As can be seen from the title of this dissertation, the aim of the study was to digest, dissolve and analyse a number of tantalum containing compounds. These compounds are:

- Tantalum pentafluoride (TaF_5).
- Tantalum pentachloride ($TaCl_5$).
- Tantalum pentoxide (Ta_2O_5).
- Tantalum-containing CRM.
- Tantalum metal (Ta).
- Tantalum-containing mineral ores.

The purity of all six above mentioned compounds were discussed in **Table 2-8** and although tantalum is the golden thread through all six samples, each of these compounds have its own unique matrix and needed its own method development. What works for one sample does not necessarily work for the other, and this chapter clearly demonstrates this statement.

3.2 General experimental procedures

3.2.1 Equipment and apparatus

Mass balance:

The mass balance used during this study was a Scaltech® digital mass balance with an accuracy of ±<0.011 g. The mass of each and every sample that was digested and/or dissolved was recorded to four decimals.

High temperature furnace and ovenware:

The high temperature furnace used for all fusions was a Thermolyne 1300. The furnace is capable of attaining a maximum temperature of 1100 ℃ and can maintain this temperature for up to three hours. The temperature, which is reached within approximately one hour, is regulated by a thermocouple and is electronically kept constant to within one degree.

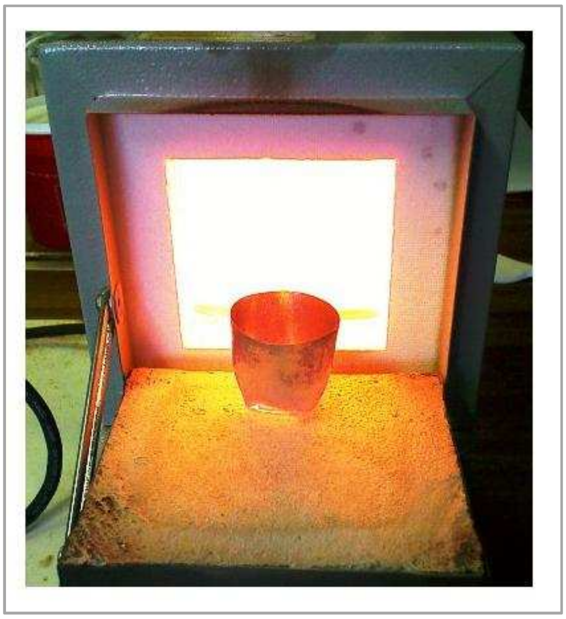

Figure 3-1: Pt crucible in furnace at 1100 °C.

The ovenware consisted mainly of holders and crucibles. The holders were custom manufactured from a high temperature, porous, ceramic brick and were solely used to keep the crucibles from tipping over and spilling their contents.

Two types of crucibles were commonly used in the furnace. The first type is ceramic crucibles of *ca.* 50 ml capacity and can be used up to 600 ℃, the only drawback with these crucibles is that they have to be warmed up and cooled down with the oven in order not to crack when exposed to sudden and harsh temperature changes. This prolongs the experimental time and also affects the ability to accurately control the time and temperature of a fusion. The second type was platinum metal crucibles which were used more often. Two different sizes of these crucibles were used, namely 50 and 30 ml in volume. The platinum crucibles are extremely versatile and were chosen mainly for two reasons. Firstly, the melting point of platinum metal is *ca.* 1772 ℃, well above the working temperature of any experiment performed in this study. Secondly, platinum is inert to any mineral acid, other than *aqua regia*, which makes it the ideal vessel to dissolve melts with a variety of acids. Furthermore, the platinum crucibles can be subjected to sudden and harsh temperature changes without being damaged, unlike the ceramic crucibles. The furnace, at 1100 ℃, as well as the 50 ml platinum crucible just removed from it is shown in **Figure 3-1**.

Microwave oven:

The microwave oven used was a Perkin & Elmer Multiwave 3000. The main advantage of the use of the microwave digester is the possibility of heating sample mixtures in a sealed vessel and thereby reaching much higher temperatures and pressures than what is possible with bench top heating, without evaporation. Only one microwave program was used namely the high-power program of which the parameters are set out in **Table 3-1**.

Table 3-1: Parameters of high-power microwave program.

Max. Power.	Ramp time.	Hold time.	Max. vessel temp.	Max. vessel pressure.	Max. vessel pressure increase.
800 W	15 min	45 min	240 ℃	60 bar	0.5 bar/s

3.2.2 Glassware

All glassware was kept clean by washing each item with a slightly diluted solution of *aqua regia* and rinsing it with distilled water before it was used in an experiment. Glassware was constantly inspected for scratches and cracks as these provide a site for contaminants to accumulate.

3.2.3 Chemicals and reagents

All chemicals and reagents used during the entire study were of known purity and in the case of some experiments, chemicals were of as pure state as possible.

The most common chemicals used during this study and their respective purities are listed in **Table 3-2**.

Table 3-2: Details of chemicals and reagents used in this study.

Chemical	Formula	Purity / grade	Use / purpose
Acids			
Nitric acid	HNO_3	65 % / AR	Analysis
Nitric acid	HNO_3	55 % / TG	Washing
Phosphoric acid	H_3PO_4	85%	Analysis
Sulphuric acid	H_2SO_4	95-98 %	Analysis
Hydrochloric acid	HCl	32 %	Analysis and washing
Reagents			
Lithium tetraborate (LTB)	$Li_2B_4O_7$	99.95 %	Digestion
Potassium hydroxide	KOH	85 %	Digestion
Methanol	CH_3OH	99.5 %	Dissolution
Samples			
Tantalum pentafluoride	TaF_5	98.00 %	Validation
Tantalum pentachloride	$TaCl_5$	99.80 %	Validation
Tantalum pentoxide	Ta_2O_5	99.00 %	Analysis
CRM	TAN-1	See **Table 2-9**	Analysis and validation
Tantalum metal	Ta	99.90	Analysis
Tantalite ore	TAN A	See **Table 4-30**	Analysis

3.3 Experimental procedures and digestion results

3.3.1 Tantalum pentafluoride

Tantalum pentafluoride (TaF_5) is a well documented inorganic compound of which the solubility properties are well known. Literature states that it dissolves readily in water and therefore the dissolution experiments carried out on this compound were done purely to evaluate the method of quantification of tantalum in solution, which was done by ICP-OES. All the dissolution experiments carried out on tantalum pentafluoride started with the dissolution of an accurately weighed sample of tantalum pentafluoride in water before being diluted to 250.0 ml in a volumetric flask. The sample details are given in **Table 3-3** while preparation procedures for ICP-solutions and analysis results are noted in **Section 4.3.1**.

Table 3-3: Sample masses and dissolution results for the water dissolution of TaF_5 samples.

Sample	TaF_5 mass (g)	Days between dissolution and analysis	Average Ta recovery (%)	RSD (%)
1*	0.0696	3	108.32	n/a
2*	0.1251	2	95.88	0.34
3	0.1229	1	96.64	3.55
4	0.1269	0	92.97	1.06
5	0.1388	0	90.96	0.54
6	0.1452	0	90.81	1.45
7**	0.1207	n/a	96.45	1.20
8**	0.1267	n/a	96.12	1.20

* analysed by standard-addition method.

** time trial samples.

Samples 1 and 2 were the very first samples to be dissolved and analysed and gave tantalum recoveries of 108.32 and 95.88 % respectively (**Table 4-2** & **Table 4-3**). To confirm these satisfactory results, Sample 3 was dissolved and analysed giving a lower tantalum recovery, and also a higher RSD value (see **Table 4-3**), therefore the experiment was repeated in triplicate with Samples 4, 5 and 6. Samples 4, 5 and 6 yielded even lower tantalum recoveries as can be seen in **Table 4-5**.

However, it was noted that the samples that were analysed immediately after dissolution gave lower recoveries than those who stood for a few days. This gave reason to conduct a time trial experiment and therefore Sample 7 and 8 were dissolved, prepared as described above, and analysed at certain periods of time to study the effect of time on the tantalum recovery of the two solutions (see

Table 4-7). Sample 8 contained 5.00 ml of nitric acid (AR) in the sample solution to determine if an acidic environment had any effect on the tantalum recoveries. It was found that the fresh solutions gave lower tantalum recoveries and it was therefore beneficial to allow the solution to stand at least three days to stabilise, as can clearly be seen in **Figure 4-1**.

3.3.2 Tantalum pentachloride

The first experiment was simply to try and dissolve tantalum pentachloride in water. The addition of *ca.* 100 ml of water to a 0.1751 g sample of $TaCl_5$ resulted in the crystals being only partially dissolved. This could be seen by visual inspection, while addition of more water did not dissolve the remaining crystals either. The solution was filtered, transferred to a 500.0 ml volumetric flask and diluted to the mark with distilled water. A standard-addition ICP analysis was done on this sample solution and the results (**Section 4.3.3**) confirmed partial dissolution as can be seen from the tantalum recovery of *ca.* 65 %.

After consulting literature[80] on the solubility of tantalum pentachloride, it was found that $TaCl_5$ dissolves readily in some organic solvents. The next solvent investigated was ethanol (CH_3CH_2OH). However, the use of organic solvents in the ICP clogs the torch due to the high carbon content and therefore the solutions that are going to be analysed by the ICP have to contain as little as possible EtOH. This was achieved by dissolving a 0.1726 g tantalum pentachloride sample in *ca.* 3 ml of EtOH before adding *ca.* 100 ml of distilled water to the volumetric flask. The solution was heated to 70 ℃ in order to evaporate the EtOH but an opaque precipitate appeared upon heating. The solution was filtered and diluted with distilled water to 250.0 ml. ICP-solutions were prepared from this sample solution by adding 5.0 ml of nitric acid (65%) and 0.5 ml of sample solution to a 100.0 ml volumetric flask and diluting to the mark with distilled water. A tantalum recovery of *ca.* 88 % suggests that the formation of the opaque precipitate upon heating affected the quantitative dissolution of tantalum pentachloride (see **Table 4-8**).

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[80] RC Weast (Editor). (1968-1969). Handbook *of Chemistry and Physics.* 49th Ed. p. B-253.

The formation of the unwanted precipitate prompted the repeat of the above, but this time without heating. Tantalum pentachloride samples of 0.1069, 0.1071, 0.1560 and 0.1028 g were weighed and dissolved in *ca.* 3 ml of EtOH each, before being transferred to 250.0 ml volumetric flasks and diluted to the mark with distilled water. ICP-solutions were prepared from these sample solutions by adding 5.0 ml of nitric acid and 2.0 ml of the sample solution to a 100.0 ml volumetric flask and diluting to the mark with distilled water. The ICP-solutions were analysed for tantalum content and the results given in **Table 4-9**. It can clearly be seen now that quantitative dissolution of tantalum pentachloride is possible due to tantalum recoveries close to 100 %. However, variations in tantalum recoveries are apparent as time progresses, therefore a proper stability study was undertaken.

The stability study on the EtOH assisted dissolution of tantalum pentachloride was done using the same method used above. Two tantalum pentachloride samples of 0.1317 and 0.1335 g, Samples 1 and 2 respectively, were dissolved in *ca.* 3 ml of EtOH. To the latter sample, *ca.* 5 ml of nitric acid (65%) was added to determine the stability of the sample solution in an acidic medium, compared to the stability of the normal sample solution. Both solutions were diluted to the mark with distilled water in a 250.0 ml volumetric flask. A series of ICP-solutions were made up in the same method described above and analysed at specific time intervals in order to conduct a properly controlled time trial experiment. The details of the ICP analyses and results are listed in **Table 4-11** and in **Figure 4-2**. Results obtained from this study indicate that the freshly prepared ICP-solutions need about a day or two to stabilise and will remain fairly stable for at least one week, regardless of the acidity of the sample solution.

3.3.3 Tantalum pentoxide

3.3.3.1 Acid dissolution of Ta_2O_5

The first dissolution experiments done on tantalum pentoxide were done with microwave assisted acid dissolution. Tantalum pentoxide samples of *ca.* 0.05 g each were added to a set of acids of 10 ml each and were subjected to the same high-power microwave program of which the details are given in **Table 3-1**. The sample details are tabulated in **Table 3-4**.

Table 3-4: Data for microwave assisted acid digestion of tantalum pentoxide.

Sample name	Ta_2O_5 mass (g)	Acid
1	0.0518	HNO_3 (65%)
2	0.0525	H_2SO_4 (95-98%)
3	0.0546	H_3PO_4 (85%)
4	0.0545	*Aqua regia*

Visual inspection indicated incomplete dissolution of tantalum pentoxide in all the reaction vessels. The content of each vessel was filtered into 100.0 ml volumetric flasks and diluted to the mark with distilled water. Quantitative results (see **Table 4-12**) obtained from this study indicated that microwave assisted acid digestion in this media was not very effective on tantalum pentoxide. The inability of microwave digestion to dissolve tantalum pentoxide then prompted the investigation towards flux dissolution techniques.

3.3.3.2 Flux dissolution of Ta_2O_5

Initially, a variety of methods involving different combinations of flux digestions and acid dissolutions were studied in an attempt to find the most effective flux reagent for the complete dissolution of tantalum pentoxide. Results obtained indicated that most fluxes only succeeded in the partial dissolution of tantalum pentoxide. This was done to investigate which flux-acid combination had the potential to completely dissolve tantalum pentoxide.

The first flux used for digesting tantalum pentoxide in this research was pyrosulphate or $K_2S_2O_7$, since it is the flux most commonly used in industry. Not all the parameters of this study were particularly well controlled because the main aim at this stage was to identify a possible flux-acid combination which had the potential for complete dissolution of tantalum pentoxide.

Accurately weighed tantalum pentoxide samples of *ca.* 0.1 g were mixed with the flux in mass ratios of between 1:10 and 1:20 respectively. The first indication of the effectiveness of the digestion of a flux is obtained by visual inspection; if the melt is not clear, it is an indication that the flux was not successful at completely digesting the sample. Visual inspection indicated that none of the melts were completely clear after fusion. Different acids were then employed to dissolve the melts, but none succeeded because of incomplete dissolution. Every sample was filtered before being diluted to 250.0 ml with water in a volumetric flask. Sample details of the experiments are given in **Table 3-5**.

Table 3-5: Sample details of pyrosulphate flux experiments on Ta_2O_5.

Sample number	2	3
Oxide mass (g)	0.1012	0.1142
Oxide : flux mass ratio	1:15	1:18
Fusion time (min)	45	60
Acid	Tartaric (20%)	Fuming sulphuric*
Acid volume (ml)	50	50
Approximate Ta recovery (%)	<1.0	1.5

*20% in SO_3

Due to the poor tantalum recoveries that were obtained after quantitative analyses (see **Section 4.3.4.2**), this method was considered ineffective and further investigation using this flux was ceased.

Based on the work done by Mahanta the next flux that was studied was a 1:1 flux mixture of NaH_2PO_4 and Na_2HPO_4[47] which was reportedly used to digest a sample of tantalite mineral. The only difference was that in this study, KH_2PO_4 was used instead of NaH_2PO_4. An accurately weighed tantalum pentoxide sample of 0.1126 g was placed in a platinum crucible with a 1:18 excess of the phosphate flux mixture and heated at 350 ℃ for 30 minutes. The melt was once again not completely clear and after dissolution with distilled water the solution had to be filtered before being diluted with distilled water to 250.0 ml in a volumetric flask. The standard-addition method was employed and quantitative ICP analysis yielded a tantalum recovery of 1.62 % (See **Section 4.3.4.2**), therefore further investigation of this dissolution method was abandoned.

The third flux that was investigated was KOH. Tantalum oxide samples of approximately 0.1 g were mixed with KOH pellets in ceramic crucibles in mass ratios of about 1:20 before being placed in a furnace for two hours at 600 ℃. Details of the samples are given in **Table 3-6**.

Table 3-6: Sample details of Ta_2O_5 fluxed with KOH.

Parameter	**Sample**	
	1	**2**
Oxide mass (g)	0.1155	0.1405
KOH mass (g)	2.7409	2.2533
Oxide : KOH	1 : 24	1 : 16
Fusion time (min)	120	60
Approx. Ta recovery (%)	78	79

The melts were relatively clear, but upon dissolution with water a residue formed. The solutions were filtered, transferred to 250.0 ml volumetric flasks and diluted to the mark with distilled water, after which they were analysed by ICP-OES. The results indicated good dissolution, but still indicated incomplete recoveries (see **Table 4-13**).

The fourth flux that was used was Na_2CO_3. Tantalum pentoxide samples of approximately 0.1 g were accurately weighed in a platinum crucible before the carbonate salt was added in excess of about 1:20. The crucible was then placed in a pre-heated furnace at 900 ℃ for the durations reported in **Table 3-7**.

Table 3-7: Sample details of Na_2CO_3 fusion with Ta_2O_5.

Sample	Oxide mass (g)	Carbonate mass (g)	Oxide : Na_2CO_3	Fusion time (min)	Volume of sample solution (ml)
1	0.1562	2.2987	1 : 15	80	250.0
2	0.1016	2.0911	1 : 20	90	250.0
3	0.1069	2.5459	1 : 24	105	500.0

The melts, of which none were completely clear after fusion, were dissolved in *ca.* 150 ml water, filtered and diluted to 250.0 ml in volumetric flasks. The quantitative results in **Table 4-15** clearly show incomplete digestion and with recoveries of 66.05 and 64.90 %, no further attention was given to this particular method.

The next flux that was studied for the dissolution of tantalum pentoxide was sodium tetraborate ($Na_2B_4O_7$). A tantalum pentoxide sample of 0.1170 g was weighed, placed in a platinum crucible and an excess of $Na_2B_4O_7$ according to a mass ratio of 1:16 was added. This mixture was then placed in the furnace at 1000 ℃ for 90 min. Immediately after the melt had been removed from the furnace, it was submerged in a solution containing *ca.* 75 ml of phosphoric acid (85%) and 75 ml of distilled water. It was noted that the melt was not completely clear, with a fine white residue still visible. During dissolution the presence of an insoluble fine white powder was noted which indicated either partial digestion of the tantalum pentoxide or the formation of a secondary precipitate. The solution was filtered and diluted with water to 250.0 ml in a volumetric flask. The solutions were analysed by ICP for tantalum content and quantitative analysis yielded a maximum recovery of 83.60 % (see **Table 4-16**) which indicate the ineffectiveness of the method to completely dissolve tantalum pentoxide.

The sixth flux study incorporated the use of lithium tetraborate (LTB) as flux in an attempt to completely digest tantalum pentoxide powder. The first trial on tantalum pentoxide with the LTB-flux was done by adding in a platinum crucible 0.1517 g of tantalum pentoxide to an excess of LTB according to a mass ratio of approximately 1:8. The crucible was then placed in a furnace that was pre-heated to 1100 ℃, shown in **Figure 3-1**, for 90 minutes. Immediately after removing the crucible from the oven, it was submerged in a solution containing 50 ml of nitric acid and *ca.* 100 ml water. The melt was clear after fusion, but during the nitric acid dissolution a white, semi-transparent precipitate appeared in the solution. After complete dissolution of the melt, the solution was filtered into a 500.0 volumetric ml flask and diluted to the mark. ICP-solutions were prepared from this sample solution. From the quantitative results of 24.19 % tantalum recovery in **Section 4.3.4.2** it was decided to use a different acid due to the suspicion that the nitric acid causes a precipitate to form which, in turn, affects the amount of recovery. The reason why nitric acid was regarded the suspected problem, was that in Nete's[52] work, it was the nitric acid that caused a boric acid precipitate to form upon reaction with the borates from the LTB flux.

It was then decided to use phosphoric acid (H_3PO_4) for dissolution of the LTB-melts, also based on Nete's work since he had some success with the acid in the dissolution of niobium pentoxide. The first LTB-phosphoric acid combination was performed by mixing 0.1285 g of the tantalum pentoxide with approximately 1.8 g of the LTB flux in a platinum crucible. This was placed in a furnace at 1100 ℃ for 90 min. The melt was once again clear after fusion and was immediately placed in a solution of 50 ml phosphoric acid and 100 ml water. This time the melt dissolved entirely and without any visible precipitation. The solution was transferred to a 250.0 ml flask and filled to the mark with distilled water. The solution was analysed using the standard-addition method and a large improvement in tantalum recovery, from the previous experiment's 24.19 % to 98.87 and 95.81 %, is shown in the results in **Table 4-17**. These promising results prompted this method to be investigated further.

A number of repetitions were performed using the same method as above. The basic procedure was that an accurately weighed portion of approximately 0.1 g of tantalum pentoxide was mixed with LTB flux in certain mass ratios, all exceeding the 1:10 ratio. The exact amounts and sample details are listed in **Table 3-8**. The flux mixture was then placed in the furnace at 1100 ℃ for a specified amount of time and was then dissolved in a solution that contained 50 ml of phosphoric acid (85 %) in 150 ml of water, and in some cases, 20 ml of methanol. All the melts obtained from this method were clear and so were all the solutions after dissolution of the melts. Thus, by visual inspection, the LTB appeared to have completely digested the tantalum pentoxide samples. The addition of 20 ml of methanol to the acid solution, and extended fusion times from 1.5 to two hours was integrated with the LTB method and the improvement of tantalum recoveries can be seen in the quantitative recovery results in **Table 4-18**. These results were obtained by analysing ICP-solutions, prepared from the sample solutions, on the ICP-OES using the external calibration method (see **Section 4.3.4.2**).

Table 3-8: Sample details for repetitions of dissolution of Ta_2O_5 by LTB flux-phosphoric acid combination method.

Sample	Oxide mass (g)	Oxide : flux mass ratio	Days since preparation of ICP-solution	Fusion time (min)
1	0.1585	1:12	11	90
2	0.1111	1:10	2	90
3	0.1748	1:10	1	90
4*	0.1099	1:10	9	90
5*	0.1154	1:10	7	90
6*	0.1330	1:13	0	120
7*	0.1132	1:15	0	120
8*	0.1080	1:15	1	150

* Methanol assisted dissolution.

3.3.4 Tantalum-containing CRM

3.3.4.1 Alkali dissolution

An alkali solution was prepared by adding *ca.* 3 g of KOH to *ca.* 50 ml of water and heating it to 65 °C. A CRM sample of 5.1602 g was added to this solution. Care was taken that the solution did not evaporate to dryness and was left to stir on the magnetic stirrer for 12 hours. The mixture was still heterogeneous and the effectiveness of the method could only be evaluated after quantitative analyses (see first paragraph of **Section 4.3.5.1**). It was noted that the polymer coating on the stirrer magnet was damaged to such a degree that part of the magnet was already exposed. Since only the CRM and dissolved KOH were present in the mixture, it was concluded that the damage was due to the abrasive nature of the

CRM particles. The mixture was then filtered and the filtrate was diluted with distilled water to 100.0 ml in a volumetric flask. Analysis on the ICP-OES yielded a recovery of 0.02 % for the dissolution process.

3.3.4.2 Alkali flux

In the next step a variation on the alkali experiment was devised. It involved the use of KOH (mp = 420 ℃) as a flux to digest the CRM. Three samples were prepared in graphite crucibles (see **Table 3-9**) and were placed in a pre-heated furnace at 600 ℃ for two hours. Upon inspection after two hours, it was noted that the melt was not clear but appeared to have a milky white colour due to the presence of a solid. It was also found that a substantial amount of sample spilled from the graphite crucibles. By visual inspection the spilled sample appeared to account for less than half the total sample mass. This was most probably due to a vigorous reaction at such high temperature and obviously implied sample loss. Nonetheless, the crucibles were freed from the holder and the remaining content of each crucible was dissolved in *ca.* 50 ml of distilled water containing 5.0 ml of nitric acid. The solutions were filtered and transferred to a 100.0 ml volumetric flask and diluted to the mark with distilled water. The samples were analysed, merely to see if any tantalum went into solution, and the results showed varying tantalum recoveries of *ca.* 11, 8 and 30 % (see **Table 4-20**).

Table 3-9: Sample masses of first KOH-flux experiment on CRM.

No.	CRM mass (g)	KOH mass (g)	Total mass (g)
1	0.2166	1.9273	2.1439
2	0.2010	1.8872	2.0882
3	0.2038	1.9639	2.1677

3.3.4.3 LTB flux

The third series of experiments performed on the CRM was based on the work done by Nete[52] with high temperature fluxes on niobium containing compounds. The basic procedure involved mixing an accurately weighed sample of CRM with a tenfold excess of LTB in a platinum crucible. This mixture was then fused in a furnace at 1100 ℃. The melt was then dissolved in different acids before being prepared for ICP analysis. The preparation for analysis is done when the melt has completely dissolved and requires that the solution be transferred to a 250.0 ml volumetric flask containing 12.5 ml nitric acid and filled to the mark, this is done to match the composition of the standard solutions (see **Section 2.4.4**) and all solutions that are prepared in this manner can therefore be directly analysed by ICP-OES.

A dissolution technique was employed whereby the hot crucible is dipped in water, just deep enough so that the water does not flow into the crucible. This causes the melt to cool down rapidly and crack in the process, due to the sudden change in temperature, which assists greatly with the dissolution process.

Nitric acid:

The common denominator that all the following trials share is the fact that the fusion of the CRM with LTB results in a clear, nearly colourless melt, which indicates that the LTB flux successfully digests the CRM. The first acid used was nitric acid and since it is the same acid present in the prepared ICP standards, each melt was simply dissolved in 12.5 ml of nitric acid and diluted with distilled water to 250.0 ml in a volumetric flask (see **Table 3-10**) and no preparation for ICP analysis was needed. After analysis, the results in **Table 4-21** showed tantalum recoveries averaging *ca.* 75 %.

Table 3-10: Experimental details of nitric acid dissolution of CRM fluxed with LTB for 120 min.

Sample no.	CRM mass (g)	LTB mass (g)
1	0.3868	2.4898
2	0.3697	2.7904
3	0.3141	2.8889
4*	0.3585	3.4337
5*	0.3463	3.1864

* fluxed for 150 min.

Sulphuric acid:

The second acid experimented with was 95-98 % sulphuric acid (H_2SO_4) and each LTB melt was dissolved with 5 ml of concentrated sulphuric acid. Dissolution with sulphuric acid resulted in murky, white solutions which were filtered before being prepared for ICP analysis as described in **Section 4.2**. The quantitative results yielded an average recovery of *ca.* 87 % (**Table 4-22**). Sample masses, fusion times *etc.* for the sulphuric acid trials are given in **Table 3-11**.

Table 3-11: Experimental details of sulphuric acid dissolution of CRM fluxed with LTB for 120 min.

Sample no.	CRM mass (g)	LTB mass (g)
1	0.3152	3.7324
2	0.3271	3.6739
3	0.3458	3.6682
4	0.3353	3.7295
5	0.3301	3.6855
6*	0.3186	5.3328

* fluxed for 150 min.

Phosphoric acid:

The last acid that was employed was 85% phosphoric acid (H_3PO_4). Each melt was dissolved with 5.00 ml of the acid before being prepared for analysis. The sample details are given in **Table 3-12**. All the solutions appeared visually clear, which indicates a preliminary quantitative dissolution, but due to the small amount of tantalum pentoxide present in the CRM, quantitative analysis was conducted on the sample solutions obtained and yielded an average tantalum recovery of *ca.* 90 % (**Table 4-23**).

Table 3-12: Experimental details of phosphoric acid dissolution of CRM fluxed with LTB for 120 min.

Sample no.	CRM mass (g)	LTB mass (g)
1	0.3144	2.2612
2**	0.3184	2.2730
3	0.3445	3.1810
4*	0.3305	3.7655
5	0.3552	3.6332
6	0.3331	3.6707
7	0.3703	3.6577
8	0.3070	4.5960

** fluxed for 150 min. * fluxed for 140 min.

Due to unsatisfactory results obtained, as reported in **Section 4.3.5.3**, it was suspected that spectral interference, due to the complex composition of the CRM, might have a significant effect on the recovery results. Therefore a 0.2105 g sample of the CRM was fused with 2.1536 g of LTB, dissolved in 5.00 ml of phosphoric acid before being diluted to 250.0 ml with distilled water and then subjected to qualitative analysis. The results of the qualitative test are presented in **Table 4-24**.

3.3.5 Tantalum metal

3.3.5.1 Acid digestion

Although well known in literature to be ineffective, the first dissolution trials on the metal samples were bench-top acid dissolutions with a number of different mineral acids. Two different tantalum metal samples, namely powder and foil, of *ca.* 0.1 g of each were initially placed in beakers with 50 ml of HCl, HNO_3, H_2SO_4 and *aqua regia* respectively. The eight samples were left in the acids for 24 hours after which ICP samples were prepared as discussed in **Paragraph 4.3.6.1**. This was, as expected, ineffective as ICP analysis yielded tantalum recoveries of practically 0% for both the foil and the powder samples.

The next attempt to dissolve the metal was to introduce microwave assistance to the acid dissolution. Tantalum powder samples were added to *ca.* 10 ml of the same set of different acids as above and placed in the microwave on the high-power program. The sample details are given in **Table 3-13**.

Table 3-13: Microwave assisted acid digestion of tantalum metal powder.

Sample	Ta mass (g)	Acid
1	0.0546	HNO_3 (65%)
2	0.0533	H_2SO_4 (95-98%)
3	0.0533	H_3PO_4 (85%)
4	0.0517	*Aqua regia*

After the microwave program had finished, roughly the same amounts of tantalum metal powder was still visible. The solutions were filtered and transferred to 100.0 ml volumetric flasks and diluted to the mark with distilled water. From these sample solutions, ICP-solutions were made up and analysed, and as can clearly be seen from **Table 4-25** the tantalum recoveries are very low, and the tantalum recovery for Sample 2 is very different from the rest.

It turned out that the vessel containing sample 2 ruptured by the time the microwave cycle was done and an erratic percentage of recovery was calculated. It was therefore decided to repeat Sample 2 in quadruplicate under identical conditions as above. Four tantalum metal powder samples of 0.0756, 0.0522, 0.0760 and 0.0580 g were weighed and placed in four of the microwave reaction vessels containing 10 ml of H_2SO_4 and then also subjected to the same high-power microwave cycle. After the microwave cycle the same approximate amount of tantalum metal powder was still visible in the reaction vessels. The solutions were filtered into 100.0 ml volumetric flasks and ICP-solutions were prepared from them. Quantitative analysis yielded tantalum recoveries that fell in the same range as the previous results (see **Table 4-26**).

Not bench-top, nor microwave assisted acid dissolution proved to be effective in dissolving tantalum metal powder samples, as is apparent from all the quantitative results (**Table 4-25** and **Table 4-26**), therefore any further investigation on acid dissolution of tantalum metal was ceased.

3.3.5.2 KOH digestion of tantalum metal

Accurately weighed tantalum metal powder samples of *ca.* 0.1 g (see **Table 3-14**) were added to at least a 1:10 excess of KOH dissolved in *ca.* 50 ml of water and left for eight hours on a magnetic stirrer. It was found that at room temperature, no visible reaction occurred. Higher temperatures (*e.g.* 65 ℃) resulted in gas bubbles starting to originate from the metal powder, indicating a reaction and in **Figure 3-2** one can clearly see the “fizz” as the base attacks the metal powder. The end of the reaction was indicated by the fact that no more gas was evolved and all the tantalum powder was dissolved and/or converted to a white precipitate. The solutions were filtered into 250.0 ml volumetric flasks and diluted with distilled water to the mark. These sample solutions were used to prepare ICP-solutions that were quantitatively analysed for tantalum, of which the results showed tantalum recoveries of *ca.* 76 and 62 % for Samples 1 and 2 respectively (**Table 4-27**). The precipitates were washed with distilled water, dried and weighed and their masses reported in **Table 3-14**.

Figure 3-2: Ta metal powder reacting with concentrated KOH solution.

Table 3-14: Details of KOH dissolution of Ta metal powder samples for gravimetric analysis.

Sample	Ta mass (g)	KOH Mass (g)	Precipitate mass (g)	Precipitate mass / initial Ta mass (%)
1	0.1567	17.8660	0.0302	19.27
2	0.1840	11.325	0.0676	36.74

According to basic theory, one can argue that if the precipitate that formed contained tantalum, and if all the tantalum precipitated out, the mass of the precipitate must be more than the mass of the tantalum metal added in the first place. Since the masses of the precipitates are much less than the initial masses of tantalum, it can be assumed that at least a fraction of the initial tantalum mass went into solution. Furthermore, from the precipitate masses in **Table 3-14**, one can see that the more KOH present in the solution, the less precipitate is formed. Therefore, a hotter, more concentrated solution of KOH should result in more tantalum going into solution instead of forming part of the precipitate. Therefore, a series of KOH dissolution experiments were again conducted to determine the amount of tantalum that goes into solution when dissolving tantalum metal powder by using this method.

In the previous experiment done by potassium hydroxide dissolution on tantalum metal it was concluded that a bigger fraction of the metal goes into solution when higher potassium hydroxide concentrations and higher temperatures are used. The following experiments were conducted to determine how much tantalum goes into solution when applying higher concentrations and temperatures to the method used in the previous experiment and also at what parameters an optimum dissolution is achieved.

Tantalum metal samples of 0.1086, 0.1185 and 0.1024 g were added to *ca.* 10 g (approximately a 100 fold excess) of potassium hydroxide in 50 ml of water. The solution was heated to 65 ℃ and left for *ca.* eight hours. The visual result was the same as with the previous experiments, where the metal powder was digested but a white powder precipitated. The mixtures were then filtered, collected in 250.0 ml volumetric flasks and filled to the mark with distilled water. ICP-solutions were prepared from these 250.0 ml sample solutions and quantitative analyses were performed. Quantitative results averaging *ca.* 85 % tantalum recovery (**Table 4-28**) confirmed the suspicion that an increase in KOH concentration increases the amount of tantalum in solution.

A stability study was also conducted to determine the stability of the tantalum containing sample solution obtained by the KOH dissolution method over time. Once again, three tantalum metal samples of 0.2067, 0.2079 and 0.2141 g respectively was each added to a 100 fold excess of KOH and added to *ca.* 100 ml of water. Bigger sample batches were used to minimise the effect of possible sample loss during the transfer and filtration steps of the experiment. The three mixtures were heated to 65 ℃ and the digestion was considered complete by visual inspection after 8 hours. Visual inspection revealed the same results as before, with the complete digestion of the tantalum metal powder, but the appearance of a white precipitate. The solutions were filtered, transferred to 250.0 ml volumetric flasks and diluted to the mark with distilled water. The quantitative results for the stability study (**Table 4-29**) showed an average tantalum recovery of *ca.* 81 % and RSD values that were 1.24 % and lower also indicated that the sample solutions are relatively stable over an eight day period.

3.3.6 Tantalum-containing mineral ores

It was decided to extend the study to a more complicated ore sample to evaluate the effectiveness of the dissolution method as well as the tantalum recovery. It was also decided to investigate the possible magnetic separation of certain elements prior to the dissolution of the minerals as part of the beneficiation of tantalum and niobium from mineral ores. Two tantalite ores, namely Tan-A and Sample 1, were chosen for their relatively high tantalum pentoxide contents of *ca.* 27 and 33 % respectively (see **Section 4.3.7**) as well as for the good ferromagnetic properties of Sample 1.

3.3.6.1 TAN-A

The same method that was effective in dissolving tantalum oxide was applied to the Tan-A mineral ore. Two samples of 0.1019 and 0.1057 g respectively were each added to a 15-fold excess of LTB flux. These samples were placed in platinum crucibles at 1000 °C for three hours. The resulting melts were dark brown in colour, but clear none the less. Each sample was placed in a beaker containing *ca.* 30 ml of phosphoric acid and *ca.* 10 ml of MeOH and was stirred for 3 hours to dissolve. The resulting solutions were clear and free from any precipitate or residue and were transferred to 250.0 ml volumetric flasks and diluted to the mark with distilled water. Comparison of ICP results with those done by Nete[52] (**Section 4.3.7.1**), showed that the method is effective in dissolving both tantalum- and niobium pentoxides present in the ore.

3.3.6.2 Sample 1

In a publication by Mahanta *et al.*[47], a fusion method is described that is extremely efficient at digesting columbite/tantalite ores. This method is very advantageous because of a lower fusing temperature and a shorter fusion time than that used for the LTB flux and also because of the fact that the melt easily dissolves in water at room temperature, eliminating the need for precipitate-causing acids. The flux used in this method is a 1:1 mixture of Na_2HPO_4 and NaH_2PO_4 mixed in excess to the ore in a mass ratio of 16:1. This powder mixture is then placed in the furnace at 900 ° C for 30 minutes. The resulting melt was clear and dissolved easily in distilled water. This method was also tried using the combination of KH_2PO_4 and Na_2HPO_4, but yielded poor results.

A portion of the Sample 1 ore was ground to a fine powder and two samples of 0.1209 and 0.1059 g of this fine ore was digested by the method described above. The resulting solutions were diluted with distilled water to 250.0 ml in volumetric flasks. ICP analyses yielded tantalum pentoxide quantities of *ca.* 30 % (see **Table 4-31**).

Magnetic separation:

A detailed geological investigation and qualitative characterisation of three different pegmatites originating from Mozambique, of which TAN-A and Sample 1 were part of, was reported by Nete[52]. The results clearly indicated that the samples exhibited different degrees of radioactivity and ferromagnetism. The ferromagnetic particles open up the possibility to remove some of the impurities prior to chemical dissolution as well as the identification of the elements associated with the magnetism. A magnetic separation was therefore performed on both textures of the Sample 1 ore. (see **Figure 3-3**). The particle size distribution of the crushed sample varied between *ca.* 5 mm and 1/10th of a mm, while that of the powdered sample varied between 250 µm and 75 µm with a fraction of about 15 % of the powdered sample even smaller than 75 µm.

Figure 3-3: Sample 1 in its two ground forms against a centimetre scale.

Two replicate portions of the ore, still in the crushed form, were subjected to a household permanent magnet to separate the ferromagnetic particles from the rest of the sample. Different portions of Sample 1 were accurately weighed and then spread evenly over a smooth glass surface. A household magnet was held below the glass plate and moved/rotated below the sample to attract and collect the magnetic material. The magnet was subsequently moved to the side of the plate with the collected magnetic material. The magnet was then removed from the plate and returned to the sample to collect the next batch of magnetic material. This procedure was terminated when all the magnetic material, based on visual judgement, were collected. The separated magnetic and non-magnetic portions were then collected, re-weighed and their respective masses are given in **Table 3-15** and **Table 3-16**. Some mass loss, as expected, occurred during this separation process.

Table 3-15: Separated masses of Sample 1 in both ground forms.

Texture	Replicate	Total mass (g)	Non-magnetic mass (g)	Magnetic mass (g)
Crushed	1	15.0815	11.4838	3.5780
Crushed	2	15.0178	11.3610	3.6530
Powdered	1	2.0448	1.8741	0.1513
Powdered	2	2.0471	1.8620	0.1726

The two portions of each replicate, one being ferromagnetic and the other one not, were then ground to a fine powder and samples of each portion (masses in **Table 3-16**) were dissolved by adding each sample to a 16-fold excess of the phosphate flux described above and placed in a platinum crucible at 900 ℃ for 30 min. Afterwards the melts, which were clear and free from any residue or precipitate, were dissolved in water and diluted to 250.0 ml in volumetric flasks. Quantitative ICP-OES analyses were performed on these sample solutions and the results, which are tabulated in **Table 4-32**, showed a good separation of the iron-associated minerals from the ore.

Table 3-16: Sample masses after grinding of the separated portions of Sample 1 in both textures.

Texture	Replicate	Property	Sample mass (g)
Crushed	1	Non-magnetic	0.1159
		Magnetic	0.1047
	2	Non-magnetic	0.1098
		Magnetic	0.1081
Powdered	1	Non-magnetic	0.1095
		Magnetic	0.1035
	2	Non-magnetic	0.1063
		Magnetic	0.1179

The magnetic separation was repeated for the powdered ore and two replicate portions of the ore, this time in the finely ground form, were subjected to a household permanent magnet to separate the ferromagnetic particles from the rest of the sample. The separated masses are tabulated in **Table 3-15**.

Samples of each separated portion (masses in **Table 3-16**) were then dissolved by adding each sample to a 16-fold excess of the phosphate flux described above before being placed at 900 ℃ in a platinum crucible for 30 min. Afterwards the melts, which were clear and free from any residue or precipitate, were dissolved in water and diluted to 250.0 ml in volumetric flasks. Quantitative analysis by ICP-OES revealed an even better separation than with the crushed ore (**Table 4-33**).

The eight solutions obtained after digesting and dissolving the magnetically separated tantalite ore (Sample 1) were analysed by ICP-OES and results showed that the magnetic separation resulted in the separation of iron-associated ores form Sample 1 (see **Section 4.3.7.2**).

3.4 Discussion of dissolution results

The digestion and dissolution results of all the individual samples were mostly satisfactory. Each and every compound was investigated with a number of alternatives until an apparent complete dissolution was obtained. Dissolution was first evaluated visually and if no solids were visible it was assumed that the digestion/dissolution was successful but if some form of solid was visible it was assumed that some of the tantalum might still be present in it. Either way, all the solutions were analysed on the ICP-OES to determine the tantalum recovery, and therefore the extent of dissolution. The compounds, methods investigated and whether they were successful at dissolution are listed in **Table 3-17**.

Table 3-17: Summary of dissolution results for the different tantalum-containing compounds

Compound	Method description	Successful dissolution by visual inspection
TaF_5	Water	✓
$TaCl_5$	Water	×
	Methanol then water	✓
Ta_2O_5	Microwave assisted acid dissolution	×
	Other flux-acid combinations (see **Table 3-18**)	×
	LTB flux dissolved in H_3PO_4 with Methanol assist.	✓
CRM	Low conc. alkali leaching	×
	Alkali flux	×
	LTB flux dissolved in HNO_3	✓
	LTB flux dissolved in H_3PO_4.	✓
	LTB flux dissolved in H_2SO_4.	✓
Ta	Bench-top acid dissolution	×
	Microwave assisted acid dissolution	×
	KOH dissolution	×
Tantalite minerals	LTB flux dissolved in H_3PO_4 with Methanol assist.	✓
	Phosphate flux dissolved in water	✓

Table 3-18: Data for different initial flux digestions on Ta_2O_5.

Nr.	Flux	Mass Ratio Ta_2O_5:Flux	Flux Temp. (℃)	Flux Time (min)	Acid	Vol. acid (ml)	Approximate Recovery (%)
1	$K_2S_2O_7$	1:15	1000	45	Tartaric	50	<1
2	$K_2S_2O_7$	1:18	1000	60	H_2SO_4 (95-98%)	50	1.5
3	1:1 mix KH_2PO_4 : Na_2HPO_4	1:18	350	30	None	-	1.6
4	$Li_2B_4O_7$	1:14	1100	90	H_3PO_4 (85%)	50	76
5	$LiBO_2$	1:10	1100	85	H_3PO_4 (85%)	30	65
6	$Li_2B_4O_7$	1:12	1100	85	HNO_3 (65%)	50	24
7	Na_2CO_3	1:11	900	90	None	-	53
8	$Na_2B_4O_7$	1:16	1000	90	H_3PO_4 (85%)	75	68
9	KOH	1:24	600	120	None	-	68

3.5 Conclusion

In general, the dissolution of the proposed samples was successful seeing that most of the dissolved sample solutions passed visual inspection (*i.e.* no precipitates and/or residues). The dissolution of the two pentahalides proved to be quite easy and their quantitative results will be extremely useful in the validation of the quantification method (see **Chapter 5**). The sample that took the longest to develop a dissolution method for was tantalum pentoxide, but after an effective method was developed, it was implemented with minimal effort and reasonable success on the other tantalum pentoxide containing samples, like the CRM and tantalite ore. The only sample that still falls far short of quantitative dissolution is tantalum metal, this is apparent from the formation of a white precipitate when the metal is dissolved in hot KOH. The characterisation and dissolution of this white precipitate will make for interesting future research.

Chapter 4: Quantification of Ta in different tantalum-containing samples by ICP-OES

4.1 Introduction

Evaluating the efficiency of a dissolution method consists of two basic steps, the first of which is a simple visual inspection. Common sense tells one that if there are any visible particles present in a particular solution, chances are that the analyte in question did not dissolve completely or that some kind of reaction caused the analyte to precipitate from the solution. On the other hand, if the solution is completely clear, one can be relatively sure that the analyte dissolved completely. However, this is not good enough for the analytical chemist and the second step comes into play at this stage. The second step is that of quantification, for only if analyte recoveries of close to 100 % are obtained, can it be said with certainty whether the analyte was completely dissolved or not. This chapter covers exactly that, it will elaborate on the preparation of ICP-solutions, shed light on quantitative results for the sample solutions obtained in **Chapter 3**: and make conclusions accordingly.

(Note: The raw data for all the results in this chapter as well as the calibration curves for each analysis are presented electronically in Appendix A that can be found on the attached CD-ROM labelled “Appendix A”.)

4.2 General experimental procedures

Standard solutions and ICP-solutions:

All sample solutions that were obtained during any experiment done throughout the entire project had to be measured against a set of standard tantalum solutions. A specific set of standard solutions were used until it no longer gave an acceptable calibration curve. The criteria for an acceptable calibration curve were as follows: R^2>0.997 and a y-intercept of as close to zero as possible. The majority of standard solutions were prepared by adding a certain amount of ICP-standard, depending on the desired concentration of the specific standard solution, to 5.0 ml of nitric acid AR (65%) in a 100.0 ml volumetric flask and diluting it to the mark with distilled water. A commercially available ICP-OES 1000 ppm tantalum standard, from Merck, was used to prepare each of the sets of calibration standards. Each set of standards also included a blank solution. This blank solution consisted only of 5.0 ml of nitric acid AR (65%) diluted with distilled water in a 100.0 ml volumetric flask. The calibration data for each set of standard solutions, used for any specific analysis, will be given in Appendix A together with the experimental results for the entire chapter.

Sample preparation is extremely important when using ICP for analysis since it requires matrix matching, which is the most essential part of sample preparation. Matrix matching is when the composition of the sample solution has to be matched as closely as possible to the composition of the standard solutions in order to minimise interference in results obtained from the ICP. Each sample analysed by the ICP-OES had to be prepared for analysis (see **Section 2.4.4**) and, therefore, had to be made up from an original solution of the sample, called a sample solution, by adding 5.0 ml nitric acid AR (65%) to a certain amount of original sample solution (amounts vary due to different experimental circumstances) and diluting to the mark with distilled water in a 100.0 ml volumetric flask. Other ICP-solution volumes were also prepared, but the ratio of 5.0 ml nitric acid in a 100.0 ml solution was always kept constant. Therefore the term “ICP-solution” refers to the matrix-matched sample prepared from the original sample solution, and ICP-solutions that were prepared otherwise will be stated as such and the preparation details given. Since no previous data could be obtained to suggest the best method of analyses between standard-addition and external calibration, both methods were implemented during this experiment. Furthermore, the two most sensitive wavelengths at which tantalum can be analysed for on the ICP-OES is 226.230 and 268.511 nm respectively and all the samples were analysed on both wavelengths to determine which delivers the best results. Coincidentally, these are also the wavelengths at which some of the spectral interferences can occur (see **Table 2-7**), but seeing that the majority of the samples were relatively pure chemicals, this did not cause problems.

Glassware:

The glassware used in this chapter was mainly calibrated volumetric flasks. A variety of volumes were used but it was the 100.0 and 250.0 ml flasks that were utilised most often. All the flasks used throughout the study were B-class flasks and their accuracy is given as ±0.1ml at 20 ℃.

Micro pipettes:

To measure small volumes accurately the use of Brand® Transferpettes® mechanical micro-pipettes were implemented in this study. With the help of a micro-pipette, volumes from 0.1 to 10 ml were easily measured. Two micro-pipettes were used; one had a capacity of 1 to 10 ml with an accuracy of ±0.01 ml and the other one had a capacity of 0.1 to 1 ml with an accuracy of ±0.01 ml.

ICP-OES:

All qualitative and quantitative elemental analyses were done with a Shimadzu® ICPS 7510 inductively coupled plasma optical emission spectrometer (ICP-OES). The ICP software automatically chooses the element's characteristic wavelength with the highest intensity and quantifies for that element at that wavelength by default. The problem with this is the fact that there may be spectral interference (see **Table 2-7**) at that wavelength which the instrument cannot pick up. Fortunately, as mentioned in **Section 2.4.3**, tantalum has virtually no interfering species at the wavelength of maximum intensity and therefore the wavelength to quantify at was chosen to be 226.230 nm.

4.3 Experimental & results

4.3.1 LOD and LOQ

The LOD and LOQ are parameters that are calculated in order to determine what the lowest concentrations of a specific analyte are that the ICP-OES can detect and quantify, in this case the analyte is tantalum. The first set of calibration standards were used to calculate the LOD and LOQ. The set was analysed on the ICP-OES with the same parameters and conditions described in **Section 4.2.**

Table 4-1: Calibration data for calculation of LOD and LOQ for Ta.

Solution	**Vol. of 1000 ppm Merck Ta std. (ml)**	**[Ta] (ppm)**	**Average intensity**	**Number of replicates**	**Standard deviation**
blank	0.0	0.0	0.05335	10	<0.01419
std1	0.10	1.0	0.20070	3	<0.011254
std2	0.20	2.0	0.53929	3	<0.011435
std3	0.50	5.0	1.40677	3	<0.012281
std4	2.00	20.0	5.86936	3	<0.015348
Calibration data		**Slope**			**0.2947**
		Intercept			**-0.0364**
		R^2			**0.9995**
LOD (ppm)					**<0.01427**
LOQ (ppm)					**0.04265**

As described in **Section 2.8.3**, the formula for the LOD is;

$$LOD = \frac{ks_b}{m}$$

Substituting for the appropriate values yields;

$$LOD = \frac{3 \times 0.00419}{0.2947}$$

$$= 0.00427\ ppm$$

The LOQ is then simply ten times the LOD (see **Table 4-1**).

4.3.2 Tantalum pentafluoride

The first experiment was done on tantalum pentafluoride, which is well known to dissolve easily in water as mentioned and proved in **Section 3.3.1**.

For the analysis of Sample 1 a set of standard-addition solutions were prepared in 100.0 ml volumetric flasks by adding 0.100 ml of the sample solution of Sample 1 to a set of standards that would be 0, 2, 5, 8 and 10 ppm in tantalum after dilution. The flasks were then diluted to the mark with distilled water and analysed. Quantitative analysis on the ICP at a wavelength of 226.23 nm yielded a calibration curve with a slope of m = 0.2316, an intercept of c = 0.0229 and an R^2 value of 0.9999. After doing the appropriate calculations a recovery of 108.32 % was obtained.

The analysis of Sample 2 involved that a set of standard-addition solutions were prepared in an identical manner and the only difference was that 0.200 ml of the sample solution of Sample 2 was added to the solutions instead of Sample 1. This set of standard-addition solutions was analysed each day over the course of three days to determine whether a stability study was necessary. **Table 4-2** gives the results for the analysis of Sample 2.

Table 4-2: Quantitative results for TaF_5 dissolution of Sample 2 at λ = 226.230 nm.

Day	**Calibration data**			**Recovery** (%)
	Slope	**Intercept**	**R^2**	
1	0.1604	0.0288	0.9916	26.67*
2	0.1952	0.6157	1	96.11
3	0.2090	0.6561	0.9993	95.65
Average				**95.88**
Standard deviation				**0.33**
RSD (%)				**0.34**

* Not included in statistical evaluation

From the results in **Table 4-2** it appeared that the sample solution was quite unstable immediately after dissolution and to clarify this, the dissolution experiment was repeated and Sample 3 was obtained. This time quantifications were done by external calibration of the ICP with a set of calibration standards that were 1, 2, 5, 10 and 20 ppm in tantalum and were prepared as discussed in **Section 4.2**. On the first day after dissolution of Sample 3 (as described in **Section 3.3.1**), three ICP-solutions (Samples 3.1, 3.2 and 3.3) were prepared from the sample solution of Sample 3 by adding 5.00 ml of nitric acid (AR) to 2.00 ml of the sample solution in 100.0 ml volumetric flasks and diluting to the mark with distilled water. These solutions were analysed by ICP-OES at λ = 226.230 nm, immediately after being prepared and the results tabulated in **Table 4-3**. On the second day after dissolution, two additional ICP-solutions were prepared (Samples 3.4 and 3.5) by adding 5.00 ml of nitric acid (AR) to 2.00 ml of the sample solution of Sample 3 in 100.0 ml volumetric flasks and diluting to the mark with distilled water. These were analysed together with the previous three samples and results are tabulated in **Table 4-4**.

Table 4-3: Quantitative results for sample solution of TaF_5 dissolution of Sample 3 that had been standing for one day.

Sample		Ta Recovery (%)
3.1		100.70
3.2		99.74
3.3		101.46
Average		**100.63**
Standard deviation		**0.86**
RSD (%)		**0.86**
Calibration data	**Slope**	**0.2143**
	Intercept	**-0.0490**
	R^2	**0.9999**

It is apparent from the results in **Table 4-3** and **Table 4-4** that time had an effect on the stability of the sample solution obtained by dissolution of tantalum pentafluoride. The dissolution experiment was repeated in triplicate to study this appearance and the three sample solutions obtained from Samples 4, 5 and 6 were analysed by ICP-OES at $\lambda = 226.230$ nm using external calibration. A set of standards was prepared to be 1, 2, 5, 10 and 20 ppm in tantalum and was used for calibration in the analyses of Samples 4, 5 and 6.

Table 4-4: Quantitative results for sample solution of TaF_5 dissolution of Sample 3 that had been standing for two days.

Sample		**Ta Recovery (%)**
3.1		94.86
3.2		92.65
3.3		95.09
3.4		93.77
3.5		94.86
Average		**94.25**
Standard deviation		**1.03**
RSD (%)		**1.09**
Calibration data	**Slope**	**0.2852**
	Intercept	**-0.0429**
	R^2	**0.9997**

On the same day that the dissolutions in **Section 3.3.1** were performed, ICP-solutions were prepared in duplicate from each of the sample solutions of Samples 4, 5 and 6 by adding 5.00 ml nitric acid (AR) to 2.00 ml of sample solution in 100.0 ml volumetric flasks and diluting them to the mark with distilled water. These were analysed by ICP-OES on the same day as well as one day after dissolution and the results are tabulated in **Table 4-5** and **Table 4-6** respectively.

Table 4-5: Quantitative results at λ = 268.511 nm for sample solutions of TaF_5 dissolution of Samples 4, 5 & 6 immediately after dissolution.

Sample solution		**Ta recovery (%)**
4		92.01
		92.51
5		91.10
		90.27
6		89.40
		90.02
Average		**90.89**
Standard deviation		**1.21**
RSD (%)		**1.33**
Calibration data	**Slope**	**0.2833**
	Intercept	**-0.0568**
	R^2	**0.9999**

Table 4-6: Quantitative results at λ = 268.511 nm for sample solution of TaF_5 dissolution of Sample 4, 5 & 6 one day after dissolution.

Sample solution		Ta recovery (%)
4		94.31
		93.03
5		91.44
		91.03
6		92.20
		91.61
Average		**92.27**
Standard deviation		**1.22**
RSD (%)		**1.32**
Calibration data	**Slope**	**0.3064**
	Intercept	**-0.0575**
	R^2	**0.9998**

It is clear from the results in **Table 4-5** and **Table 4-6** that analysing the solutions immediately after dissolution or one day later did not have a noteworthy effect the tantalum recoveries. The recoveries obtained for Samples 4, 5 and 6 however, were much lower than those obtained for the first three samples. The dissolution experiment was therefore repeated again, this time in the form of a stability study to determine also the stability of the sample solutions over the course of an arbitrary amount of time (seven days).

Two sample solutions were obtained from the dissolution of additional tantalum pentafluoride samples as discussed in **Section 3.3.1**. To the sample solution of Sample 8 was added 5.00 ml of nitric acid (AR) while Sample 7 was simply dissolved in water. The addition of the acid was to determine what effect an acidic environment had on tantalum recoveries. Analyses of these two sample solutions were carried out by external calibration of the ICP-OES at λ = 268.511 nm and a set of calibration standards that were 1, 2, 5, 10 and 20 ppm in tantalum was prepared as discussed in **Section 4.2.**

The analyses were conducted over the course of seven days as opposed to just two as in the previous analyses. Immediately after dissolution, ICP-samples were prepared from each of the sample solutions by adding in a 100.0 ml flask, 5.00 ml of nitric acid (AR) and 2.00 ml of sample solution and then filling it to the mark with distilled water before being analysed on the ICP. The following day, a new set of ICP-solutions were prepared identically to the previous ones. Both sets (*i.e.* four ICP-solutions) were analysed together on the ICP and the results tabulated in **Table 4-7**. This pattern was repeated on the second, third, sixth and seventh day after dissolution.

Table 4-7: Results for stability study of dissolution of TaF_5 with water.

Days since dissolution	**Original**		**Fresh**	
	Sample 7	**Sample 8**	**Sample 7**	**Sample 8**
0	97.24	92.18	---	---
1	96.45	91.92	97.95	95.73
2	97.53	91.97	97.35	97.81
3	95.40	89.79	95.49	95.86
6	94.18	90.42	95.30	94.66
7	95.64	91.72	96.13	96.53
Average	**96.07**	**91.33**	**96.45**	**96.12**
Standard deviation	**1.25**	**0.98**	**1.16**	**1.16**
RSD	**1.30**	**1.08**	**1.20**	**1.20**

The original ICP-solution of Sample 8 showed lower average tantalum recoveries than the other ICP solutions and was therefore considered irrelevant. From **Table 4-7** and more clearly in **Figure 4-1**, one can see that the tantalum pentafluoride solutions are stable over a period of seven days. The slight acidic environment of Sample 8 had no drastic effect on the recovery values, seeing that they are in the same region as those of Sample 7. These results also suggest a slight drop in tantalum recoveries after three days, but the recovery values stayed fairly constant for up to seven days. Furthermore, the results indicate good precision with RSD values of less than 1.3 % but with recoveries of around 96 % the accuracy was less satisfactory.

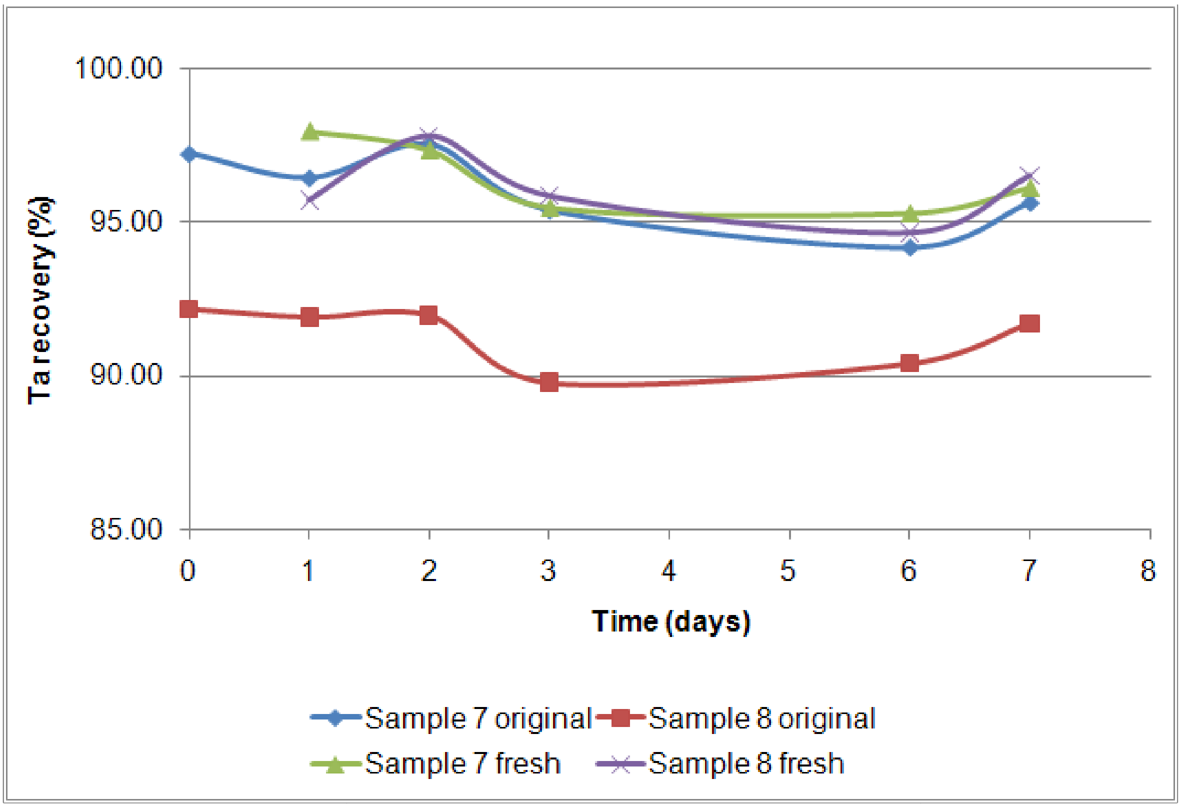

Figure 4-1: Graph of Ta recovery indicating the stability of a TaF_5 solution over a period of seven days.

4.3.3 Tantalum pentachloride

The first dissolution attempt of tantalum pentachloride was studied using water as the dissolution medium as discussed in **Section 3.3.2**. However, this was not as successful as the water dissolution of tantalum pentafluoride, as some of the tantalum pentachloride still remained undissolved. From the first sample solution obtained by dissolution with water, a set of standard-addition solutions was prepared for analysis in 100.0 ml volumetric flasks by adding 1.00 ml of the sample solution of Sample 1 to a set of standard solutions that would be 2, 4, 6, 8 and 10 ppm in tantalum when diluted and filling them to the mark with distilled water.

ICP analysis of this set of samples at λ = 226.230 nm yielded a linear standard-addition graph with a slope = 0.2294, an intercept = 0.2630 and an R^2 value of 0.9990. After doing the appropriate calculations for the standard-addition method, the tantalum concentration of Sample 1 in the 100.0 ml flasks were found to be 1.146 ppm and because of a 100 times dilution during sample preparation it was 114.6 ppm in the 500.0 ml sample solution. The tantalum concentration in the sample solution converts to 57.32 mg of tantalum and since the initial $TaCl_5$ sample was 175.1 mg, it relates to a 64.81 % tantalum recovery. This low recovery can be ascribed to the fact that the direct addition of water to $TaCl_5$ did not dissolve it completely and therefore decreased the tantalum recovery. Since literature**[80]** states that tantalum pentachloride is readily soluble in ethanol (EtOH), it was thought that the addition of small amounts of EtOH might assist the complete dissolution of tantalum pentachloride yielding an aqueous EtOH solution.

Although not as simple as tantalum pentafluoride, a tantalum pentachloride sample of *ca.* 0.1 g was found to be dissolved fairly easy, initially in *ca.* 3 ml of EtOH and then diluted with distilled water, as mentioned in the second paragraph of **Section 3.3.2**. In an attempt to remove the EtOH, the solution was heated, but after the formation of an opaque precipitate upon heating, the suspicion arose that the tantalum recovery will yet again be compromised.

Analysis of this solution was carried out at λ = 268.511 nm by external calibration of the ICP-OES and a set of calibration standards that were 0.5, 1, 2, 5 and 10 ppm in tantalum was prepared as discussed in **Section 4.2.** An ICP solution was prepared from the sample solution, obtained by filtering and diluting the above solution, by adding in a 100.0 ml flask 5.00 ml of nitric acid (AR), 0.500 ml of the sample solution and diluting to the mark. This solution was analysed the day after the preparation of the ICP solutions and again two weeks later. Suspicions were confirmed after the results in **Table 4-8** were obtained.

Table 4-8: Quantitative results of the first heated ethanol assisted dissolution of $TaCl_5$.

Days after preparation of ICP solution		**Ta recovery (%)**
1		88.02
14		87.34
Average		**87.68**
Standard deviation		**0.48**
RSD (%)		**0.55**
Calibration data	**Slope**	**0.2521**
	Intercept	**-0.0453**
	R^2	**0.9988**

Seeing that the EtOH assisted dissolution of tantalum pentachloride yielded promising results, the experiment was repeated in quadruplicate for further study. Because of precipitate formation due to EtOH evaporation when heated, the four solutions obtained from above dissolutions were not heated and were simply diluted with distilled water to a volume of 250.0 ml as in **Section 3.3.2** and used to prepare a series of ICP-solutions.

These four sample solutions were again analysed at λ = 268.511 nm by the external calibration method using the ICP-OES. A set of standard solutions were prepared in 100.0 ml volumetric flasks by adding 5.00 ml nitric acid (AR) to specific amounts of a 1000 ppm ICP-standard and diluting them with distilled water to obtain standard solutions that were 1, 2, 5, 10 and 20 ppm in tantalum. ICP-solutions were prepared in duplicate from each of the four sample solutions (eight ICP-solutions) by adding 5.00 ml of nitric acid (AR) and 2.00 ml of the sample solution in a 100.0 ml flask and diluting to the mark with water. These eight solutions were analysed immediately after being prepared as well as on the next day and the results tabulated in **Table 4-9** and **Table 4-10** respectively.

Table 4-9: Tantalum recoveries for the ethanol assisted dissolution of $TaCl_5$ analysed immediately after sample preparation.

Sample	**$TaCl_5$ mass (g)**	**Ta recovery (%)**
1	0.1069	102.20
		102.12
2	0.1071	93.96
		96.36
3	0.1560	92.69
		94.80
4	0.1028	97.39
		96.47
Average		**97.00**
Standard deviation		**3.52**
RSD (%)		**3.63**
Calibration data	**Slope**	**0.2833**
	Intercept	**-0.0568**
	R^2	**0.9999**

The results in **Table 4-9** and **Table 4-10** compared to that in **Table 4-8** proved that evaporating the EtOH by heating the solution (see **Section 3.3.2**), did have a negative effect on the tantalum recoveries, which is evident from higher recovery results for the solutions that was not heated. A possibility of solution instability was also noted due to results that varied with time. The results of the solutions analysed after one day showed an average recovery lower than those analysed immediately. Therefore, in order to fully observe the effect that time had on the tantalum recoveries of the dissolution method concerned, a proper stability study was conducted.

Table 4-10: Tantalum recoveries for the ethanol assisted dissolution of $TaCl_5$ analysed one day after sample preparation.

Sample	**$TaCl_5$ mass (g)**	**Ta recovery (%)**
1	0.1069	69.14*
		87.98
2	0.1071	73.43*
		95.61
3	0.1560	92.38
		95.57
4	0.1028	96.63
		94.91
Average		**93.85**
Standard deviation		**3.21**
RSD (%)		**3.42**
Calibration data	**Slope**	**0.3064**
	Intercept	**-0.0575**
	R^2	**0.9998**

* not included in calculation of statistical data.

Together with the stability study, the effect that an acidic environment had on tantalum recoveries was also studied. This was done (as detailed in **Section 3.3.2**) by dissolving two tantalum pentachloride samples (Samples 1 and 2) and adding 5.00 ml of nitric acid (AR) to Sample 2 before diluting them to 250.0 ml in volumetric flasks.

These two sample solutions were analysed on the ICP-OES by the external calibration method at λ = 268.511 nm. A set of standard solutions was prepared in 100.0 ml volumetric flasks by adding 5.00 ml nitric acid (AR) to specific amounts of a 1000 ppm ICP-standard and diluting them with distilled water to obtain standard solutions that were 1, 2, 5, 10 and 20 ppm in tantalum. ICP-solutions were prepared from the sample solutions of Samples 1 and 2 by mixing 5.00 ml of nitric acid (AR) with 2.00 ml of the sample solutions in a 100.0 ml volumetric flask and diluting them to the mark with distilled water. These ICP solutions were analysed immediately on the ICP-OES. One day after dissolution a new set of ICP-solutions was made up identically to those of the previous day and was analysed together with the original set. This pattern was also followed two, three, six and seven days after dissolution. The results are given in **Table 4-11**.

Table 4-11: Results for stability study of the ethanol assisted dissolution of $TaCl_5$.

Days since dissolution	Original		Fresh	
	Sample 1	Sample 2	Sample 1	Sample 2
0	99.39	99.97	-	-
1	100.47	101.01	96.31	103.09
2	100.55	100.55	99.82	100.98
3	100.09	101.15	99.05	98.95
6	101.19	100.69	98.65	100.09
7	100.74	100.79	98.67	99.82
Average	**100.41**	**100.69**	**98.50**	**100.59**
Standard deviation	**0.61**	**0.42**	**1.31**	**1.58**
RSD	**0.61**	**0.41**	**1.33**	**1.57**

From the above results one can draw two conclusions. Firstly, the dissolution method is very effective in quantitatively dissolving tantalum pentachloride, as can be seen from the nearly 100 % tantalum recoveries. Secondly, the method of analysis is very accurate and precise; this can also be seen from the 100 % recoveries and from low RSD values respectively. By looking at **Figure 4-2** one can see that the slight acidic environment of the sample solution of Sample 2 had absolutely no effect on the tantalum recoveries. One can also see from the initial variation in the recovery results that the ICP-solutions are a bit unstable for up to two days after dissolution, after which they stabilise and remain so for up to seven days.

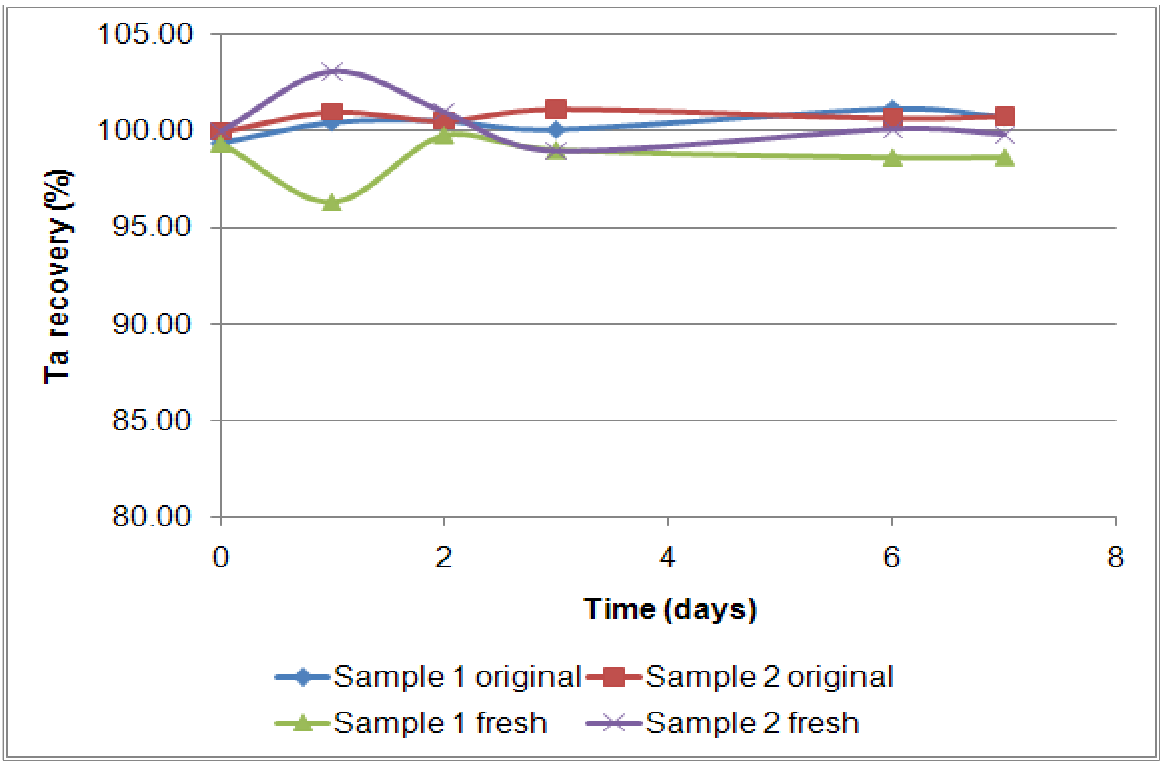

Figure 4-2: Graph of Ta recovery indicating the stability of a $TaCl_5$ solution over a period of seven days.

4.3.4 Tantalum pentoxide

4.3.4.1 Acid dissolution of Ta_2O_5

The first dissolution experiments done on tantalum pentoxide were done with microwave assisted acid dissolution as detailed in **Section 3.3.3.1**. By visual inspection of the samples, it seemed that the microwave assisted acid dissolution of tantalum pentoxide was ineffective. To determine the amount of tantalum that did dissolve, the sample solutions that were obtained thereof were analysed on the ICP-OES by the external calibration method at λ = 226.230 nm.

A set of standard solutions that were 0.5, 1, 2, 5 and 10 ppm in tantalum was prepared in 100.0 ml volumetric flasks by the same method described in **Section 4.3.3**. ICP-solutions were prepared from each of the four sample solutions obtained by adding 5.00 ml of nitric acid to 1.00 ml of each sample solution in 100.0 ml volumetric flasks and diluting to the mark with distilled water.

These ICP-solutions were analysed and the tantalum recoveries were tabulated in **Table 4-12**.

Table 4-12: Tantalum recoveries for microwave assisted acid dissolution of tantalum pentoxide with different acids.

Sample	Acid	Ta recovery (%)
1	HNO_3	4.19
2	H_2SO_4	9.70
3	H_3PO_4	6.91
4	*Aqua regia*	3.88
Calibration data	**Slope**	**0.1776**
	Intercept	**-0.0343**
	R^2	**1**

Although sulphuric acid yielded the best dissolution of tantalum pentoxide, a recovery of 9.70 % can hardly be seen as successful. As expected, acid dissolution of tantalum pentoxide is not a very efficient dissolution method and other means of dissolution needed to be investigated, which led to the experimentation on flux digestion.

4.3.4.2 Flux dissolution of Ta_2O_5

The first flux digestion of tantalum pentoxide was done with pyrosulphate flux, as it is a flux commonly used in industry. The dissolution of the melt obtained after the fusion described in **Section 3.3.3.2**, was performed with tartaric acid and resulted in a murky solution that needed to be filtered. The standard addition method with the ICP-OES was used for analysis of the sample solution obtained after filtration.

The set of standard-addition solutions was prepared in 100.0 ml volumetric flasks with a 1000 ppm tantalum ICP-standard to be 2, 5, 8 and 10 ppm in tantalum when diluted to the mark. Before dilution, 1<0.01 ml of the sample solution was added to each of the standard-addition solutions. ICP analyses at λ = 226.230 nm of the set of solutions gave a linear standard-addition graph with slope = 0.2083, intercept = 0.0471 and an R^2 value of 0.9993.

After doing the appropriate calculations, the tantalum concentration in the standard-addition solutions, due to the sample solution, was 0.2261 ppm and therefore 2.261 ppm in the sample solution. This calculates to 0.5652 mg of tantalum in the 250.0 ml sample solution. An initial amount of 101.2 mg of tantalum pentoxide was used and therefore a mere 0.68% of the tantalum

As mentioned in **Section 3.3.3.2**, the pyrosulphate flux did not yield a completely clear melt but before changing the flux, a more aggressive acid was employed to dissolve the melt, a second flux trial still incorporated pyrosulphate flux, but in combination with fuming sulphuric acid (20% in SO_3) was performed. After the dissolution step, the solution was again not clear and had to be filtered before being diluted to a 250.0 ml sample solution. This sample solution was analysed using the standard-addition method at λ = 226.230 nm by preparing another set of standard-addition solutions in exactly the same way the previous set was prepared. A linear, standard-addition calibration curve was drawn that gave a slope = 0.2329, an intercept = 0.1240 and an R^2 value of 0.9997. After doing the same calculations a tantalum concentration of 0.5345 ppm was obtained in the standard-addition solutions which converted to 5.345ppm in the sample solution. This correlates with 1.336 mg of tantalum in the sample solution. Seeing that 114.2 mg of oxide was weighed, the tantalum recovery turned out to be 1.43%. The results for both digestions using the pyrosulphate flux and different acids were extremely low and the methods were deemed unsuccessful, therefore further experimentation on the pyrosulphate flux was stopped.

After the poor results of the previous experiments, the flux was changed to a 1:1 flux mixture of KH_2PO_4 and Na_2HPO_4 which was based on the work done by Mahanta[47]. Dissolving the melt with water did not yield a clear solution and it had to be filtered before being diluted to a 250.0 ml sample solution.

A set of standard-addition solutions were prepared by adding 1<0.01 ml of the sample solution and 5.00 ml of nitric acid (AR) to 100.0 ml volumetric flasks containing the correct amount of ICP-standard to make solutions that were 2, 5, 8 and 10 ppm in tantalum and diluting with distilled water to the mark. This set was analysed by ICP-OES at λ = 226.230 nm and gave a linear standard-addition graph with a slope = 0.2234, an intercept = 0.1530 and an R^2 value of 0.9989.

Calculations showed that the tantalum concentration in the set of standard-addition samples due to sample solution was 0.6849 ppm. Therefore the concentration of tantalum in the 250.0 ml sample solution was 6.849 ppm, which converts to a mass of 1.712 mg of tantalum in the sample solution. Since an initial mass of 112.6 mg of the oxide was used in the experiment, it resulted in a 1.52 % tantalum recovery.

The low recoveries of the previous flux again prompted a change of flux, this time KOH was used as flux. Although the melts in **Section 3.3.3.2** were clearer than those of the previous three experiments, a slight amount of residue was still visible. ICP-OES analysis was done at λ = 226.230 nm by the external calibration method on samples prepared from the two sample solutions obtained by KOH digestion on the day of digestion and two days afterwards. These ICP-samples were prepared by adding 5.00 ml of nitric acid to 1.00 ml of the sample solution in a 100.0 ml volumetric flask and diluting to the mark with distilled water. These ICP-solutions were analysed and the results are given in **Table 4-13** and **Table 4-14**.

Table 4-13: Recovery results for KOH dissolution of tantalum pentoxide analysed immediately after dissolution.

Sample		**Ta recovery (%)**
1		64.20
2		72.26
Average		**68.23**
Standard deviation		**5.70**
RSD (%)		**8.35**
Calibration data	**Slope**	**0.1794**
	Intercept	**-0.0263**
	R^2	**0.9999**

Table 4-14: Recovery results for KOH dissolution of tantalum pentoxide analysed two days after dissolution.

Sample		Ta recovery (%)
1		77.60
2		79.44
Average		**78.52**
Standard deviation		**1.30**
RSD (%)		**1.66**
Calibration data	**Slope**	**0.1740**
	Intercept	**-0.0466**
	R^2	**0.9982**

The results for the KOH-flux method look much better than any of the fluxes used so far and showed good potential. It was noted, however that the solutions analysed immediately after dissolution gave results of poorer quality suggesting some kind of solution instability. However, with further detailed investigation a method for complete dissolution could be obtained.

Seeing that the KOH-flux yielded promising results, another alkali flux was used, namely Na_2CO_3-flux as described on page 73 in **Section 3.3.3.2**. After fusion, none of the melts appeared clear and were filtered after dissolution. Of the three sample solutions obtained from the digestion experiments, the first (Sample 1) was analysed by the standard addition method, while the external calibration method was used to analyse the other two (Samples 2 and 3) in order to determine which method of analyses would give the best results.

A set of standard-addition solutions were prepared by adding 1.00 ml of the sample solution of Sample 1 and 5.00 ml of nitric acid (AR) to 100.0 ml volumetric flasks containing the correct amount of ICP-standard to make solutions that were 2, 5, 8 and 10 ppm in tantalum, and afterwards diluting with distilled water to the mark. This set was analysed by ICP-OES at λ = 226.230 nm and gave a linear standard-addition graph with a slope = 0.2414, an intercept = 0.4103 and an R^2 value of 0.9988.

Calculating the tantalum concentration, due to the addition sample solution, in the standard-addition solutions yielded a value of 1.699 ppm, and because of a 100-fold dilution in the preparation of the standard-addition solutions it was 169.9 ppm in the sample solution. This corresponds to 42.49 mg of tantalum in the sample solution and since an initial amount of 101.6 mg of tantalum pentoxide was used for the digestion, it correlates with a 51.07 % tantalum recovery.

For the analyses of Samples 2 and 3 the external calibration method was used at λ = 226.230 nm and a set of tantalum calibration standards was prepared (as described in **Section 4.2**) to be 0.5, 1, 2, 5 and 10 ppm in tantalum. For analysis, an ICP solution of Sample 2 was prepared by adding 5.00 ml of nitric acid (AR) to 0.50 ml of the sample solution of Sample 2 in a 100.0 ml volumetric flask and diluting to the mark with distilled water. The ICP-solution for Sample 3 was prepared by adding 5.00 ml of nitric acid (AR) to 1.00 ml of the sample solution of Sample 3 and diluting to 100.0 ml with water in a volumetric flask. After analysis and calculations the results obtained were listed in **Table 4-15**.

Table 4-15: Tantalum recovery and calibration data for the Na_2CO_3-flux digestion method of Sample 2 and 3.

Sample	Ta recovery (%)	Calibration data		
		Slope	Intercept	R^2
2	66.05	0.1778	-0.0357	0.9976
3	64.90	0.2040	0.0387	0.9999

Although the KOH and Na_2CO_3 fluxes seemed to have potential in digesting tantalum pentoxide, none of the melts were completely clear and therefore the search continued for a suitable flux. This led to the use of sodium tetraborate ($Na_2B_4O_7$) as a flux. As mentioned, from visual inspection in **Section 3.3.3.2,** the resulting melt was again not clear and filtration was needed before diluting it to a 250.0 ml sample solution. The external calibration method was again employed for the analysis of the sodium tetraborate flux sample and a set of tantalum calibration standards was prepared (as described in **Section 4.2**) to be 0.5, 1, 2, 5 and 10 ppm in tantalum. From the sample solution obtained in the experiment, an ICP-solution was prepared by mixing 1.00 ml of this solution and 5.00 ml nitric acid in a 100.0 ml volumetric flask and diluting it to the mark with distilled water. This particular ICP-solution was analysed twice, one day after preparation as well as three days afterwards. Qualitative analysis at λ = 226.230 nm revealed the results in **Table 4-16**.

Table 4-16: Tantalum recovery and calibration data for first sample of Ta_2O_5 being fluxed with $Na_2B_4O_7$ and dissolved with H_3PO_4.

Days after dissolution	**Ta recovery (%)**	**Calibration data**		
		Slope	**Intercept**	**R^2**
1	68.77	0.1794	-0.0263	0.9999
3	83.60	0.1740	-0.0466	0.9982

Although the sodium tetraborate flux also proved to be promising, it was still not effective at completely dissolving tantalum pentoxide. However, the use of sodium tetraborate as flux was similar to the work done by Nete[52] on niobium pentoxide with lithium tetraborate (LTB) as flux and led to the next set of experiments. The melts obtained by digestion with LTB flux were clear and were therefore a good indication of the effectiveness of the flux. The only obstacle that remained was to find a suitable dissolution medium for the melts.

The first LTB melt was dissolved with nitric acid (see **Section 3.3.3.2**) and resulted in a precipitate forming. The 500.0 ml sample solution obtained after filtration and dilution was analysed by standard-addition on the ICP-OES. The set of standard-addition solutions were prepared by adding 1.00 ml of the sample solution and 5.00 ml of nitric acid (AR) to 100.0 ml volumetric flasks containing the correct amount of ICP-standard to make solutions that were 2, 5, 8 and 10 ppm in tantalum and afterwards diluting with distilled water to the mark. ICP-OES analysis at λ = 226.230 nm yielded a linear standard-addition graph with a slope = 0.1931, an intercept = 0.1165 and an R^2 value of 0.9985.

Calculations indicated that the tantalum concentration in the standard-addition solutions due to the sample solution was 0.6010 ppm. Because of a 100 fold dilution it had to be 60.10 ppm in the sample solution, which converts to 30.05 mg of tantalum. The initial amount of oxide used was 151.7 mg. This yields a 24.19 % tantalum recovery. It was suspected that the formation of the precipitate due to the use of nitric acid, lowered the recovery substantially and therefore the method was repeated, only with a different acid.

The precipitate formation due to the use of nitric acid, necessitated a repeat of the experiment, but this time phosphoric acid was used to dissolve the melt, instead of nitric acid. This resulted in a relatively clear sample solution without the need for filtration as mentioned on page 75 in **Section 3.3.3.2**. The standard-addition method was again used to quantify tantalum in the sample solution and three sets of standard-addition solutions were prepared from this sample solution in exactly the same way as in the previous analysis. These sets were prepared and analysed on intervals as specified, together with the results in **Table 4-17**.

Table 4-17: Ta recoveries and calibration data at λ = 226.230 nm for the standard-addition analyses of Ta_2O_5 fluxed with LTB and dissolved with H_3PO_4.

Sample	Days since digestion	Ta recovery (%)	Calibration data		
			Slope	Intercept	R^2
1	2	76.92	**0.2146**	**0.6938**	**0.9989**
2	3	98.87	**0.1840**	**0.7658**	**0.9998**
3	3	95.81	**0.1813**	**0.7302**	**0.9998**

This time the recoveries looked extremely good compared to what has been obtained by experimentation with other methods. Further investigation of this method was done by the repetition of a few samples and by varying some parameters like oxide to flux ratio, fusion time and the composition of the solvent solution.

Once again, all the melts obtained by fusing the tantalum pentoxide samples with LTB were clear, as were the sample solutions that were obtained after dissolution with phosphoric acid. Henceforth, every sample solution obtained by fusion with LTB and dissolution with phosphoric acid was analysed on the ICP-OES by using the external calibration method with standard solutions that were prepared in the same fashion as in the previous experiment. The calibration data for each of the analysed samples are given in Appendix A. ICP-solutions were prepared from every sample solution by adding a certain amount of the sample solution to 5.00 ml of nitric acid (AR) and diluting it with water to 100.0 ml in a volumetric flask.

Nete[52] found in his study that lower niobium recoveries were obtained after nitric acid dissolution of the LTB melts. He ascribed this to the formation of a boric acid precipitate that formed during the acid dissolution of the melts obtained by LTB fusion which caused co-precipitation of the niobium. He found that the addition of methanol could be used to prevent this precipitation by converting the boric acid *in situ* to a volatile methyl ester (see **Eq. 4-1**).

This methanol-assisted dissolution was implemented on some of the dissolution experiments described on pages 74-76 in **Section 3.3.3.2**, while other samples were dissolved without the aid of methanol. The quantitative results are given in **Table 4-18**.

Table 4-18: Tantalum recoveries and calibration data from various samples of Ta_2O_5 fluxed with LTB and dissolved with phosphoric acid.

Sample	**Ta recovery (%)**
1	82.80
	55.85
2	56.42
	11.18
3	85.96
4 *	77.31
5 *	83.41
6 **	95.53
	89.71
	96.22
	97.12
	95.31
7 **	97.03
	89.86
	92.49
	93.60
	95.77
Average * **	**94.26**
Standard deviation * **	**2.76**
RSD (%) * **	**2.92**

* Methanol assisted dissolution and 1.5 hrs fusion time.
** Methanol assisted dissolution and 2 hrs fusion time.
*** Only Samples 6 & 7 were used for calculation of statistical data.

$$B(OH)_3 + 3CH_3OH \rightarrow B(OCH_3)_3 \uparrow + H_2O \qquad \textbf{Eq. 4-1}$$

As evident from the results in **Table 4-18**, tantalum recoveries of larger than 90 % were being obtained using the current method combined with methanol assisted dissolution. However, some results seemed to be somewhat random even though the conditions were kept fairly similar. The only parameter that was not kept constant was the time the solutions were left to stand before they were analysed, both before and after preparation. Therefore, a stability study was performed to determine what effect time had on the stability of the sample solutions.

The stability study was performed on a single sample that was digested (see **Table 3-8**), dissolved and diluted to a 250.0 ml sample solution and was done over an arbitrary period of four days. One day after digestion, three ICP-solutions were prepared by adding 5.00 ml of nitric acid (AR) to 2.00 ml of the sample solution in 100.0 ml volumetric flasks and diluting to the mark with distilled water, then immediately analysed. On day two an additional set of three ICP-solutions were prepared and analysed together with the first three. This procedure was repeated on days three and four as well. The details and results are given in **Table 4-19**. The analyses were performed at λ = 268.511 nm.

Table 4-19: Stability study results for Ta recoveries from Ta_2O_5 fluxed with LTB flux and dissolved with phosphoric acid.

Time	Sample	Ta recovery (%)
Day 1	1	95.94
	2	95.37
	3	94.94
Day 2	1	95.36
	2	96.25
	3	96.78
	4	95.92
	5	97.27
	6	97.36
Day 3	1	88.83
	2	96.84
	3	99.65
	7	99.82
	8	101.98
	9	102.66
Day 4*	1	84.43
	2	87.71
	3	89.91
	10	88.89
	11	92.45
	12	92.72
Average		**96.99**
Standard deviation		**3.29**
RSD (%)		**3.39**

***** Recovery results of day 4 not taken into account for statistical calculations due to loss of stability of solution.

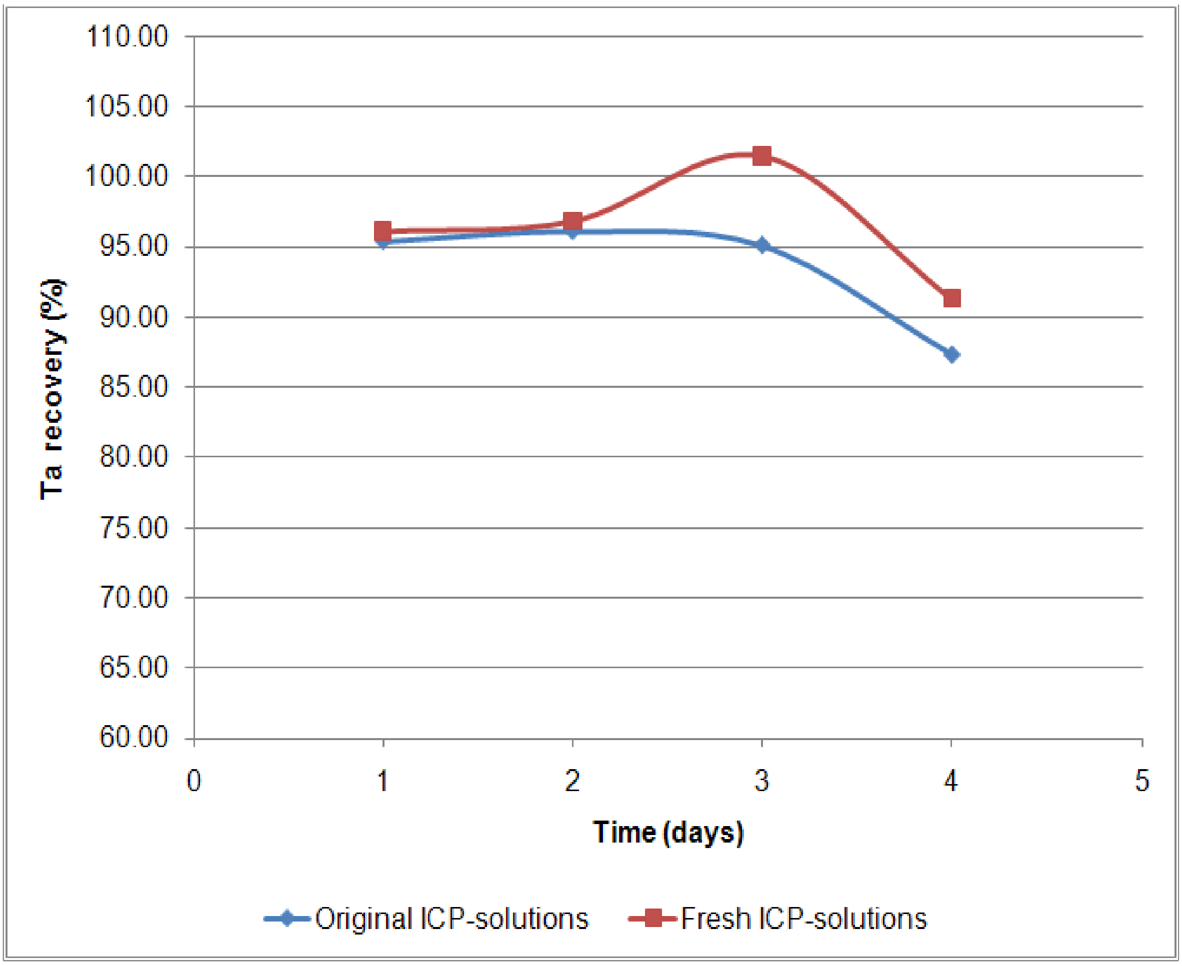

Figure 4-3: Time trial graph of LTB flux-phosphoric acid combination method.

One can clearly see from the declining recovery values in **Figure 4-3** that the concentration starts to drop after about two to three days. Since both the fresh and the original ICP-solutions follow the same trend, one can deduce that the sample solution deteriorates upon standing, and that it is not because of sample preparation that recovery values start to drop. Furthermore, this dissolution method is considered fairly effective because of a relatively good average recovery of *ca.* 97 %. The average recovery value also reflects the accuracy of the analysis method and the RSD value of 3.39 %, which reflects the degree of precision, can also be regarded as fairly good. However, if one only takes into account the results of the solutions that had been standing for two days and less, one can calculate that the average tantalum recovery is 96.06 ±0.86 % with an RSD of 0.89 %. This gives a slightly lower average recovery but a much better degree of precision.

4.3.5 Tantalum CRM

4.3.5.1 Alkali dissolution

The use of KOH to dissolve the tantalum pentoxide in a tantalum containing CRM is described in **Section 3.3.4.1**. The results obtained indicated that no apparent dissolution took place and therefore the filtered solution had to be quantitatively analysed. An ICP-sample was prepared from the sample solution according to the alkali dissolution method by adding 5.00 ml of nitric acid and 2.00 ml of the sample solution to a 100.0 ml volumetric flask and diluting it to the mark with distilled water. This solution was then analysed by means of ICP-OES by the external calibration method and results for the sample solution showed tantalum concentrations in the same order of magnitude as that of the blank solution in the set of standards. Calculations indicated a tantalum recovery of 0.02 %. This result clearly indicates the total ineffectiveness of moderate alkaline solutions to dissolve the CRM to any degree.

4.3.5.2 Alkali flux

Even though KOH, in solution did not dissolve the CRM, it was again used, this time in the solid form as a fluxing agent (see **Section 3.3.4.2**). Unfortunately, slightly less than half the contents of the crucibles in the KOH-flux experiment spilled during fusion and much of the sample was lost. Nonetheless, the remaining sample mass in each crucible was dissolved with 5.00 ml of nitric acid, filtered and diluted with distilled water to 100.0 ml in volumetric flasks. ICP-samples were not prepared from these three sample solutions because the composition of these solutions was already as close as possible match to the composition of the calibration samples (see **Section 4.2** on preparation of ICP-solutions) and they were therefore analysed as they were by the external calibration method on the ICP-OES at λ = 226.230 nm. The solutions were merely analysed to see if any dissolution took place despite significant sample loss. **Table 4-20** gives the tantalum recoveries of the three solutions as well as the calibration data.

Table 4-20: ICP results for the first KOH flux attempt on a CRM sample and corresponding calibration data.

Sample	CRM mass (g)	Ta recovery (%)
1	0.2166	11.17
2	0.2010	8.59
3	0.2038	30.36
Calibration data	**Slope**	**0.2354**
	Intercept	**-0.0781**
	R^2	**0.9999**

Seeing that much less than half the contents were lost, even a tantalum recovery of *ca.* 30 %, as in sample 3, was not sufficient to indicate complete (or near complete) dissolution. Combined with the fact that the melts were not clear after fusion, this method was deemed inefficient at dissolving the CRM.

4.3.5.3 LTB flux

Because of the fact that the use of LTB gave good dissolution and subsequent good tantalum recoveries for tantalum pentoxide, it seemed to be the next logical step in the dissolution of the CRM. LTB fusion and different acids were experimented with to find the most effective combination for complete dissolution.

Nitric acid dissolution:

The first LTB flux trials were done on *ca.* 0.3 g samples of the CRM and the melts were dissolved only with 12.5 ml nitric acid (AR) and transferred to 250.0 ml volumetric flasks as described in **Section 3.3.4.3**. No preparation of ICP-solutions was necessary because these solutions had in effect already been prepared for ICP analysis by dissolving only with nitric acid. They were analysed by the external calibration method on the ICP-OES at λ = 226.230 nm by making use of a set of tantalum standards that were 1, 2, 5, 10 and 20 ppm in tantalum and the analysis results are given in **Table 4-21**.

Table 4-21: Tantalum recoveries for CRM fluxed with LTB and dissolved with nitric acid.

Sample	Ta recovery (%)
1	89.58
	109.39
	101.44
2	83.58
	56.09
	55.45
3	69.14
	73.20
4	55.81
	63.51
5	65.62
Average	**74.80**
Standard deviation	**18.80**
RSD (%)	**25.13%**

The recovery results obtained from all the above experiments seemed to vary randomly and no specific pattern or cause could be identified. The dissolution of the melts with nitric acid was considered ineffective due to the inability to obtain consistent results and therefore the attention was shifted towards other acids.

Sulphuric acid dissolution:

The digestion method was done identically to the previous method, but instead of nitric acid, sulphuric acid was used to dissolve the melt (see page 73 in **Section 3.3.4.3**). The LTB melts were dissolved in 5.00 ml of sulphuric acid before being transferred to 250.0 ml volumetric flasks containing 12.50 ml of nitric acid and being diluted to the mark with distilled water. These solutions were also analysed as they were, because they had already been prepared for ICP analysis.

The ICP-OES analyses were done at λ = 226.230 nm by the external calibration method using a set of tantalum standards identical those used above and the results are given in **Table 4-22**.

The sulphuric acid dissolutions yielded better results than the dissolutions done by nitric acid. This can be seen from a higher average tantalum recovery of *ca.* 87 % compared to the *ca.* 75 % recovery obtained by nitric acid dissolution. Also, and still far from ideal, a lower RSD value of 11.45 % was obtained compared to *ca.* 25 % for nitric acid dissolution. However, both these values were still not satisfactory and experimentation with other acids continued. The time it took before the sulphuric acid solutions were analysed did not appear to have a great affect on the tantalum recoveries, since both fresh and older solutions yielded both lower and higher recoveries.

Table 4-22: Tantalum recoveries for CRM fluxed with LTB and dissolved with sulphuric acid.

Sample	Ta recovery (%)
1	99.69
2	87.62
3	76.21
4	90.62
	95.06
	87.75
	92.70
5	75.08
	66.96
	94.25
6	87.32
Average	**86.66**
Standard deviation	**9.92**
RSD (%)	**11.45**

Phosphoric acid dissolution:

Although the LTB melts were clear after fusion, varying results were obtained with nitric and sulphuric acid dissolution, thus the dissolving acid was once again changed. This time the melts were dissolved with phosphoric acid before being prepared for ICP analysis. In **Section 3.3.4.3** the sample solutions were obtained by dissolving the melts in 5.00 ml of phosphoric acid before adding them to 12.50 ml nitric acid in 250.0 ml volumetric flasks and diluting to the mark with distilled water. These solutions were once again analysed on the ICP-OES as they were by the external calibration method at λ = 226.230 nm because they have in effect been prepared for ICP analyses. For the calibration curve a set of standards that were 1, 2, 5, 10 and 20 ppm in tantalum was prepared as described in **Section 4.2.** The recovery results for each sample are listed in **Table 4-23**.

It was noted that all the tantalum recoveries in **Table 4-23** fell in the same approximate order of magnitude, except for a few (which are indicated by *). Two of these values had one thing in common and that is the fact that they were analysed immediately after preparation. This led to the belief that a freshly prepared solution needed at least one day to stabilise. Although the average recovery was far from satisfactory, the phosphoric acid dissolution yielded results that were more stable than the results of the nitric and sulphuric acid dissolutions and this can clearly be seen in the smaller RSD value of 5.82 % compared to the 25.13 % for nitric acid dissolution and the 11.45 % for sulphuric acid.

Table 4-23: Tantalum recoveries for CRM fluxed with LTB and dissolved with phosphoric acid.

Sample	Ta recovery (%)
1	55.11*
2	102.90
	85.21
	83.61
3	90.82
	87.44
	90.08
4	90.30
	83.76
	90.24
5	88.79
	71.06
	87.98
6	54.09*
	88.61
7	83.43
8	103.00
Average	**89.73**
Standard deviation	**6.17**
RSD (%)	**6.88**

* = not included in statistical evaluation.

Seeing that recoveries were being obtained for the CRM that were not entirely satisfactory, but consistent nonetheless, it was suspected that there might be significant interference from other constituents present in this particular CRM. Therefore an additional qualitative experiment was performed to determine the composition of the CRM, TAN-1. After dissolution (as described in the last part of **Section 3.3.4.3**) a simple qualitative analysis was performed on the sample solution and the results are given in **Table 4-24** while **Figure 4-4** illustrates the relative intensities measured for each element at its most sensitive wavelength.

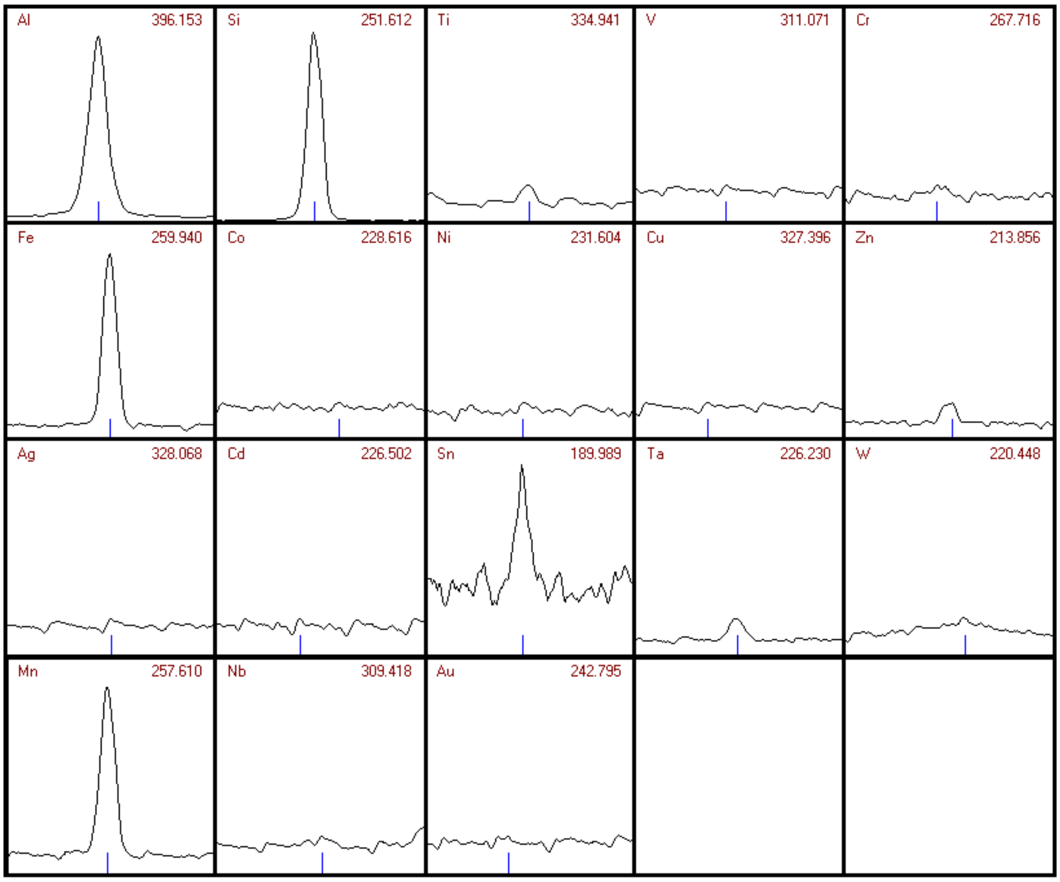

Figure 4-4: Intensity profiles of each element in the CRM at their most sensitive wavelengths.

As one can see from **Table 4-24**, the two most abundant elements in the CRM are silica and aluminium. This can also be seen in **Figure 4-4** from the high relative peak intensities of silica and aluminium. Although the peaks of iron and manganese are also quite large, they are not as intense as silica and aluminium because the ICP-OES is quite sensitive to these elements (among others). One can therefore not rely on the intensity profiles alone, and have to take the approximate concentrations into account as well.

Table 4-24: Approximate elemental composition of the TAN-1 CRM in decreasing order of concentration.

Approximate element concentration	Elements		
>10 ppm	Al	Si	-
>0.1 ppm	W	Fe	Ta
	Sn	Nb	Ti
	Cu	-	-
<0.1 ppm	Ni	Au	Mn
	Ag	Zn	V
	Co	Cr	Cd

As indicated in **Table 2-7**, the elements aluminium and iron can cause spectral interference in the analysis of tantalum and both of these elements are present in the CRM in quantities higher than tantalum. The possibility for interference by the presence of aluminium is therefore large, which could explain the low recovery of tantalum from the CRM. The selection of alternative, interference-free wavelengths can shed light on this problem.

4.3.6 Tantalum metal

4.3.6.1 Microwave assisted acid dissolution of Ta metal

It is well known that tantalum metal is extremely resistant to even some of the most corrosive acidic conditions. Nonetheless, acid dissolution experiments were performed on tantalum metal to determine exactly to what extent it dissolves in certain acids.

After the microwave dissolution of a number of tantalum samples in different acids (**Section 3.3.5.1**), ICP-solutions were prepared by adding 5.00 ml of nitric acid (AR) to 1.00 ml of the sample solutions, obtained by these microwave assisted acid dissolutions, in 100.0 ml volumetric flasks and diluting them to the mark with distilled water.

After microwave digestion, these ICP solutions were analysed on the ICP-OES using the external calibration method at λ = 226.230 nm. The set of tantalum standards used for the calibration curve was prepared by adding 5.00 ml of nitric acid (AR) and a specific amount of 1000 ppm tantalum standard in 100.0 ml volumetric flasks to yield a set of standard solutions that were 0.5, 1, 2, 5 and 10 ppm in tantalum after dilution to the mark with distilled water. The quantitative results and tantalum recoveries for the different acids are given in **Table 4-25**.

Table 4-25: Tantalum recoveries for different microwave assisted acid dissolutions of tantalum metal.

Sample	**Acid**	**Ta recovery (%)**
1	HNO_3 (65%)	4.57
2	H_2SO_4 (95-98%)	28.49
3	HCl (32%)	8.67
4	*Aqua regia*	3.87
Calibration data	**Slope**	**0.1776**
	Intercept	**-0.0343**
	R^2	**1**

As mentioned in the experimental procedure in **Section 3.3.5.1**, the result of Sample 2 was considered incorrect because of possible sample loss and/or contamination due to the failure of the microwave reaction vessel. Therefore this sample was repeated in quadruplicate in an identical manner as the previous experiment to obtain trustworthy results, which are shown in **Table 4-26**. The sample preparation and analysis method were exactly the same as before.

Table 4-26: Tantalum recoveries of the repeat of microwave assisted sulphuric acid digestion of tantalum metal (Sample 2).

Sample		**Ta recovery (%)**
2.1		2.60
2.2		5.00
2.3		3.48
2.4		5.67
Average		**4.19**
Standard deviation		**1.40**
RSD (%)		**33.43**
Calibration data	**Slope**	**0.2040**
	Intercept	**0.0387**
	R^2	**0.9999**

It can clearly be seen from the results and statistical data in **Table 4-25** and **Table 4-26** that neither of these acids is suited for the dissolution of tantalum metal, even with the aid of microwave technology. Therefore, as suspected, acid dissolution of tantalum metal was deemed ineffective and other means of dissolution had to be investigated.

4.3.6.2 KOH dissolution of Ta metal

The experiments done in **Section 3.3.5.2** with the KOH dissolution of tantalum metal powder showed that the more concentrated the KOH solution was, the less precipitate formed, and therefore, by direct assumption, the more tantalum in solution. The sample solutions obtained in these experiments were used to prepare ICP- solutions by adding to a 100.0 ml volumetric flask 5.00 ml of nitric acid, 5.00 ml of sample solution and diluting to the mark with distilled water. ICP analysis was done by the external calibration method at λ = 226.230 nm and a set of tantalum standards that were 0.5, 1, 2, 5 and 10 ppm, was used for the calibration curve. The results are reported in **Table 4-27**.

Table 4-27: Quantitative results of KOH dissolution of Ta metal powder samples.

Sample	Ta mass (g)	KOH Mass (g)	Precipitate / Ta (m/m)	Ta recovery (%)
1	0.1567	17.8660	0.1927	75.85
2	0.1840	11.3250	0.3674	61.77
Calibration data		**Slope**		**0.1778**
		Intercept		**-0.0357**
		R^2		**0.9976**

From the results in **Table 4-27** it appears that an increase in KOH concentration increased the tantalum recoveries in the previous experiment. In order to confirm that an increase in KOH concentration does in fact increase tantalum metal dissolution, three additional tantalum metal powder samples were dissolved, this time using the more concentrated KOH dissolution method as described in **Section 3.3.5.2**.

ICP-solutions were prepared by adding 2.00 ml of each of the sample solutions obtained into 100.0 ml volumetric flasks together with 5.00 ml of nitric acid. The flasks were then filled to the mark with distilled water. The ICP-solutions were analysed by the external calibration method at λ = 268.511 nm and the results are given in **Table 4-28**.

Table 4-28: Quantitative results for dissolution of Ta metal powder samples with approximately 100-fold excess of KOH.

Sample	Ta mass (g)	[Ta] in stock sol. (ppm)	Ta recovery (%)
1	0.1086	372.793	85.82
2	0.1185	387.688	81.79
3	0.1024	353.985	86.42
Average			**84.68**
Standard deviation			**2.52**
RSD			**2.97 %**
Calibration data		**Slope**	**0.3023**
		Intercept	**-0.0605**
		R^2	**0.9999**

Results showed recoveries averaging about 85 %. The results indicated that although a drastic increase in KOH concentration resulted in higher tantalum recoveries, it is still not efficient enough to dissolve the metal quantitatively, due to the fact that a certain amount (*ca.* 15 %) of the metal is possibly converted to a white precipitate that remained in the reaction mixture after the dissolution step.

A stability study was also done on three new samples by using the same method as discussed in the last paragraph in **Section 3.3.5.2.** The stability study was conducted over a period of eight days. On the first day after dissolution, three ICP-solutions were prepared, one from each of the sample solutions. These solutions were prepared by adding 5.00 ml of nitric acid (AR) to 2.00 ml of the sample solution in 100.0 ml volumetric flasks and diluting to the mark with distilled water. They were analysed immediately on the ICP-OES at λ = 268.511 nm by the external calibration method using an identical set of standards as mentioned above.

On the second day after dissolution an additional set of ICP-solutions were prepared in the same manner as the previous ones and analysed together with the original three solutions. This pattern was repeated three, four, seven and eight days after dissolution. Analysis results are reported according to sample solution number in **Table 4-29**, but for ease of comparison the results are also given in the form of a graph of tantalum recovery *vs.* time in **Figure 4-5**.

Table 4-29: Stability study results for KOH dissolution of Ta metal.

Time (days)	**Sample solution**					
	1		**2**		**3**	
	Original	**Fresh**	**Original**	**Fresh**	**Original**	**Fresh**
1	78.49	78.49	82.27	82.27	82.40	82.40
2	78.13	77.37	81.61	80.07	81.68	81.67
3	78.17	78.87	82.05	81.27	81.98	83.17
4	78.60	78.52	81.94	81.07	84.60	83.88
7	78.95	79.05	82.38	81.51	82.75	82.22
8	78.90	79.41	82.48	82.20	82.77	83.60
Average	**78.54**	**78.62**	**82.12**	**81.40**	**82.70**	**82.82**
Std Dev	**0.35**	**0.70**	**0.32**	**0.82**	**1.03**	**0.86**
RSD	**0.44%**	**0.89%**	**0.39%**	**1.00%**	**1.24%**	**1.04%**

From **Figure 4-5**, as well as from the results in **Table 4-29**, one can clearly see that the tantalum solutions obtained by the KOH dissolution method are relatively stable, only small variations in tantalum recovery occurred during the course of eight days. Also, no major recovery differences are apparent between the original ICP-solutions and the fresh ones, which indicate that the preparation of ICP-solutions has no effect on tantalum recoveries. However, the KOH dissolution of tantalum metal is still not completely effective because of the formation of the white precipitate.

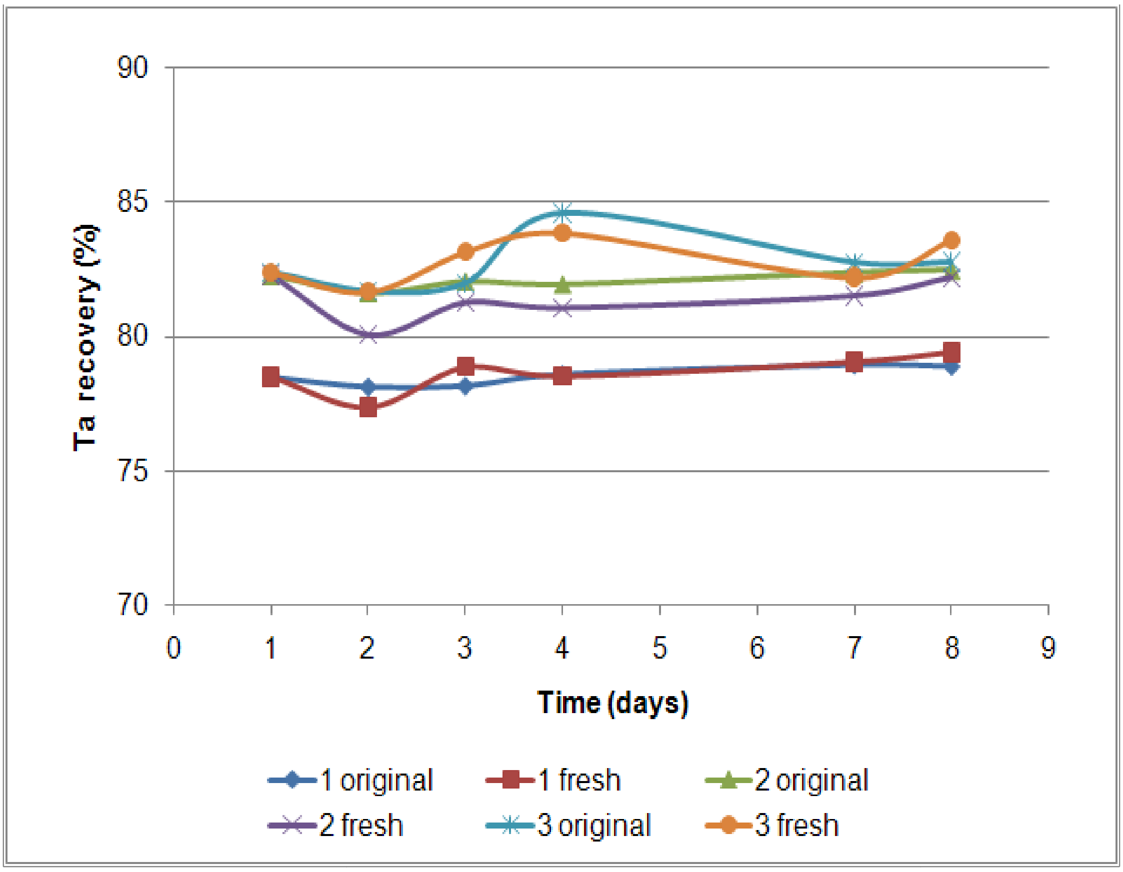

Figure 4-5: Ta recovery plotted against time for time trial experiment of KOH digestion of Ta metal.

4.3.7 Tantalum containing ore

4.3.7.1 Tan-A:

From the sample solution obtained in **Section 3.3.6.1,** an ICP-solution was prepared in a 100.0 ml volumetric flask by adding 5.00 ml of the sample solution to 5.00 ml nitric acid and diluting with distilled water to the mark. Analysis of this sample was done on the ICP-OES with the external calibration method. The set of standards used was a multi-element standard that consisted of the following elements: Ta, Nb, Th, U, Al, Si, W, Ti, Mn, Fe and Sn. The standard solutions were prepared by adding 5.00 ml nitric acid in each 100.0 ml volumetric flask to just enough of each ICP-standard to make a set of solutions that would be 1, 2, 4, 6 and 8 ppm in each of the 11 elements after dilution with distilled water. The quantitative results obtained are given in **Table 4-30**, together with those obtained by AH Knight[81] for comparative purposes.

Table 4-30: Comparison between quantitative results from AH Knight and quantitative results for the methanol-assisted phosphoric acid dissolution of Tan-A ore fluxed with LTB.

Constituent	**Wavelength (nm)**	**Quantity (%)**			
		This results			**AH Knight***
		1	**2**	**Average**	
Ta_2O_5	268.511	28.14	27.23	27.69	27.71
Nb_2O_5	316.340	31.07	29.94	30.51	27.41
ThO_2	374.119	0.40	0.64	0.52	0.65
U_3O_8	367.007	2.78	3.16	2.97	2.83
Al_2O_3	394.403	<0.01	0.50	0.25	1.85
SiO_2	251.612	<0.01	5.70	2.85	5.73
WO_3	207.911	0.14	0.04	0.09	1.61
TiO_2	336.121	2.92	2.78	2.85	2.68
Mn_3O_4	257.610	7.31	6.85	7.08	8.03
Fe_2O_3	259.940	7.66	7.04	7.35	8.29
SnO_2	189.989	<0.01	<0.01	<0.01	1.41
Mass balance (%)		**80.42**	**83.88**	**82.15**	**88.20**

* Results obtained by AH Knight Laboratories

The tantalum results obtained by this method agree extremely well with that obtained by Knight, as does the results for thorium, uranium, titanium, iron and manganese. The other results might deviate slightly due to the use of a different method than the one used by Knight, which might not be best suited for the dissolution of those particular elements.

It was also noted that both sets of results only accounted for *ca.* 80 to 88 % of the sample; this could be the result of at least two things. First, the assumption is

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[81] Alfred H Knight Analytical Laboratories. Unit 1, 24 Jones Road, Jet Park, Johannesburg, 1459.

made that all the metals are present in their oxide forms which might not be entirely true. The metals can also be present in their sulphide forms or even as both. Secondly, volatile substances can be present in the ore, like water molecules attached to the metal compounds in the form of crystal water, which would obviously evaporate upon fusion.

4.3.7.2 Sample 1:

The phosphate flux mixture used for the digestion of Sample 1 in **Section 3.3.6.2** proved to be very efficient at completely digesting the ore sample, as was apparent from the fact that the melt was clear and absent of any residues or precipitates. The sample solutions obtained from the digestion and dissolution of duplicate samples of Sample 1 was analysed on the ICP-OES by the external calibration method.

Two ICP-solutions were prepared from the two sample solutions obtained in **Section 3.3.6.2** by adding in each 100.0 ml volumetric flask, 5.00 ml of nitric acid (AR) and 5.00 ml of the sample solutions before diluting to the mark with distilled water. The set of standards was also a multi-element set, but this time containing only 9 elements namely, Ta, Nb, Al, Si, W, Ti, Mn, Fe and Sn. The standard solutions were prepared by adding 5.00ml of nitric acid in each 100.0 ml volumetric flask to just enough of each ICP-standard to make a set of solutions that would be 1, 2, 4, 6 and 8 ppm in each of the nine elements after dilution with distilled water. The quantitative results, together with the results obtained from Nete[52], are given in **Table 4-31**.

Table 4-31: Comparison between constituent quantities of Sample 1 obtained in this study and those obtained by Nete.

Constituent	**Quantity (%)**			
	This study			**Nete***
	replicate 1	**replicate 2**	**Average**	
Ta_2O_5	30.35	29.60	29.98	32.99
Nb_2O_5	7.06	7.45	7.26	8.74
Al_2O_3	<0.01	<0.01	<0.01	1.47
SiO_2	6.05	7.07	6.56	2.51
WO_3	1.65	0.71	1.18	0.16
TiO_2	10.34	11.01	10.68	8.19
Mn_3O_4	1.15	0.70	0.93	3.13
Fe_2O_3	18.45	18.51	18.48	18.71
SnO_2	<0.01	<0.01	<0.01	0.15
		Total:	**37.84**	**76.05**

* Dissolution performed by LTB fusion followed by H_2SO_4/MeOH dissolution.

As mentioned in **Section 3.3.6.2**, certain particles of the Sample 1 ore exhibited ferromagnetic behaviour due to the presence of a considerable amount of iron (see **Table 4-31**). This physical characteristic was exploited as a means of mechanical separation of the ore by using household magnets to separate the magnetic particles from the non-magnetic particles in both the crushed and powdered textures. After digesting and dissolving the separated portions of the ore in both the textures, quantitative analyses were conducted to determine the effect of the separation.

The quantitative analyses were conducted on the ICP-OES using the external calibration method. The eight sample solutions obtained by digesting and dissolving the separated portions of the Sample 1 ore were analysed by preparing ICP-solutions from each of them by adding 2.00 ml of the sample solution to 5.00 ml hydrochloric acid and diluting with distilled water to 100.0 ml in volumetric flasks.

The set of standards was again a multi-element set, containing the same nine elements used for the non-separated sample, namely: Ta, Nb, Al, Si, W, Ti, Mn, Fe and Sn. The standard solutions were prepared by adding 5.00 ml of hydrochloric acid in each 100.0 ml volumetric flask to just enough of each ICP-standard to make a set of solutions that would be 1, 2, 3, 5 and 10 ppm in each of the nine elements after dilution with distilled water.

Nitric acid was substituted for hydrochloric acid in this case, specifically because the nitric acid caused precipitation in the multi-element standards rendering them useless after about a day. The standard solutions lasted longer in the hydrochloric acid medium and caused no precipitation whatsoever. The quantitative results are given in **Table 4-32** and **Table 4-33**.

Table 4-32: Comparison of constituent quantities before and after magnetic separation of Sample 1 in the crushed form.

Constituent	**Quantity (%)**						
	Non-separated	**Non-magnetic**			**Magnetic**		
		1	**2**	**average**	**1**	**2**	**average**
Ta_2O_5	29.98	29.73	27.94	28.84	2.10	2.21	2.16
Nb_2O_5	7.26	9.52	8.44	8.98	2.21	1.78	1.99
Al_2O_3	<0.01	0.14	0.16	0.15	<0.01	<0.01	<0.01
SiO_2	6.56	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
WO_3	1.18	2.57	0.43	1.50	0.22	0.02	0.12
TiO_2	10.68	1.48	1.18	1.33	8.42	7.77	8.10
Mn_3O_4	0.93	2.15	1.68	1.92	<0.01	<0.01	<0.01
Fe_2O_3	18.48	8.23	7.37	7.80	13.46	11.42	12.44
SnO_2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total:	**37.84**			**12.56**			**12.45**

From the results in **Table 4-32** and **Table 4-33** one can clearly see that the magnetic separation is very effective in separating iron associated ores from the niobium and tantalum in the Sample 1 ore, as well as titanium associated ores. It was also noted that a better separation was obtained with the Sample 1 in the powdered form compared to the crushed form. This can be an indication that some of the magnetically attracted metal compounds, like the iron- and titanium minerals, can be physically associated with the rest of the minerals and they can be “released” by mechanical grinding.

Table 4-33: Comparison of constituent quantities before and after magnetic separation of Sample 1 in the powdered form.

Constituent	**Quantity (%)**						
	Non-separated	**Separated**					
		Non-magnetic			**Magnetic**		
		1	**2**	**average**	**1**	**2**	**average**
Ta_2O_5	29.98	30.63	27.17	28.90	2.14	2.13	2.14
Nb_2O_5	7.26	8.40	7.34	7.87	1.23	1.21	1.22
Al_2O_3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
SiO_2	6.56	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
WO_3	1.18	<0.01	0.03	0.02	0.01	<0.01	0.01
TiO_2	10.68	1.21	0.45	0.83	11.70	9.14	10.42
Mn_3O_4	0.93	1.34	1.11	1.23	<0.01	<0.01	<0.01
Fe_2O_3	18.48	2.51	0.31	1.41	21.55	17.87	19.71
SnO_2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total:	**37.84**			**3.5**			**19.720**

The fact that nearly all the tantalum and niobium that is recovered is found in the non-magnetic portion supports the assumption that the metals are present in the ore in the pentoxide forms. This phenomenon can easily be explained by the electron configuration of these metals as the oxides of both these metals are in the +5 oxidation state. In the process of oxidation of the metals, of which the electron configurations are $[Kr]4d^4 5s^1$ and $[Xe]4f^{14}5d^3 6s^2$ for niobium and tantalum respectively, the elements lose the valence electrons to yield [Kr] and $[Xe]\ 4f^{14}$ electron configurations with no electrons in the outer orbitals. Both states are then diamagnetic, which explains why they are not attracted to the applied magnetic field during separation[82].

It was also noted that in both cases some of the niobium and tantalum were present in the magnetic portion. A possible explanation is the fact that both metals can also be found in the +3 oxidation state where the electron configurations are $[Kr]4d^25s^1$ and $[Xe]4f^{14}5d^16s^2$ for niobium(III) and tantalum(III) respectively, which are both paramagnetic. The presence of these elements in the magnetic portion can however also be explained in terms of poor separation during the grinding process and that some of the tantalum and niobium were still part of the iron containing portion of the sample.

It is very probable that iron is present as Fe (III), in the form of iron oxide (Fe_2O_3), of which the electron configuration is $[Ar]\ 3d^34s^2$ which also makes it paramagnetic. As for titanium, its most preferred oxidation states are Ti (III) and Ti (IV), of which the electron configurations are $[Ar]\ 4s^1$ and [Ar] respectively, and it was assumed to be present in the ore in the latter state. There are two possible explanations for it being present almost exclusively in the magnetic portion of the separation. It can either be present in the Ti (III) oxidation state as Ti_2O_3, which has one unpaired electron in the valence shell, and is therefore also paramagnetic, or it can be associated solely to the iron containing minerals and is not completely separated by the grinding process.

In conclusion, magnetic separation of columbite/tantalite ores (like Sample 1) has its advantages for the mining industry and refining plants in the view that it is both a simple and effective separation method and can be totally mechanised, eliminating the need for costly human labour.

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[82] FA Cotton, G Wilkinson, PL Gaus. (1995). *Basic Inorganic Chemistry* 3*nd* *Ed*. London. John Wiley & Sons, Inc. p. 67.

4.4 Comparison of successful dissolution methods for various Ta an Nb containing compounds.

The work done in this study and the work done by Nete[52] in his thesis showed many similarities. The main focus of this study was the quantitative dissolution of tantalum containing compounds, while the focus of Nete's work was on the dissolution of niobium containing compounds. As discussed in **Section 1.6** the chemistry of tantalum and niobium are very similar, mainly because they belong to the same group in the periodic table. For this reason it was anticipated that the dissolution of certain tantalum compounds would show similarities to the dissolution of their niobium counterparts. However, this was found not to be true in all cases as can be seen from the comparative tables below.

The first of the similar compounds were the pentafluorides, namely tantalum- and niobium pentafluoride. In this study, dilution with water yielded tantalum recoveries of 96 % and higher, while in Nete's work niobium pentafluoride was dissolved with microwave assisted sulphuric acid digestion and 100 % recoveries were obtained (see **Table 4-35**). No mention is made in Nete's work on dissolving niobium pentafluoride in water only. However, the initial table-top sulphuric acid dissolution of niobium pentafluoride (by Nete) yielded results of *ca.* 95 %. Therefore it can be assumed that tantalum pentafluoride is much more soluble in mild conditions such as neutral pH and room temperature than niobium pentafluoride.

Probably the most interesting and noteworthy results were obtained by comparison of the dissolution methods for Ta_2O_5 and Nb_2O_5. As can be seen in **Table 4-34**, Nb_2O_5 can be easily and almost completely dissolved with microwave assisted sulphuric acid dissolution while this same method has a minimal effect on Ta_2O_5. This phenomenon can be explained by comparing the metal-oxygen bond strengths of the two metals. The bond strength for Nb-O is 93 $Kcal.mol^{-1}$ and that for Ta-O is 195 $Kcal.mol^{-1}$, more than double that of Nb-O[83]. This is a handy characteristic that can be exploited in industry for separation and purification.

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[83] RC Weast (Editor). (1968-1969). Handbook *of Chemistry and Physics.* 49th Ed. p. F-158.

Table 4-34: Comparison between results obtained by Nete and in this study for the dissolution of the pentoxides of Ta and Nb.

Dissolution method for M_2O_5	**Metal recovery (%)**	
	M = Ta	**M = Nb***
Microwave assisted dissolution with…		
HCl	n.c.	2.27
H_2SO_4	4.19	99.19
HNO_3	3.31	0.01
H_3PO_4	8.67	84.28
Aqua regia	3.88	0.09
Fusion with LTB and dissolution with…		
HNO_3	24.19	36.58
H_2SO_4	n.c.	102.76
H_3PO_4	94.81	n.c.

* Niobium results obtained by Nete[52].

n.c.: not conducted.

Table 4-35: Comparison between results obtained by Nete and in this study for the dissolution of Ta and Nb metals and their pentafluorides.

Sample type	**Dissolution method**	**Metal recovery (%)**	
		Ta	**Nb***
$(Ta,Nb)F_5$	Dissolution by water (this work)	96.21	n.c.
$(Ta,Nb)F_5$	Microwave assisted sulphuric acid dissolution (Nete)	n.c.	100.68
Ta, Nb	Microwave assisted sulphuric acid digestion	4.18	99.90

* Niobium results obtained by Nete[52].

n.c.: not conducted.

From the results in **Table 4-35** one can see that the same discrimination by sulphuric acid between Ta_2O_5 and Nb_2O_5 is exhibited between tantalum and niobium metals as well. Once again, this can be employed to separate and purify the two metals.

The analyses of the tantalite ore sample, TAN-A, by three different analysts show good correlation, specifically for Ta_2O_5 and Nb_2O_5 content (see **Table 4-30** and **Table 4-36**). There are, however, a few constituents that do not agree quite as well. This is most probably due to the fact that three different methods of dissolution were applied.

Table 4-36: Comparison between results obtained by Nete and in this study for the dissolution of the TAN-A ore sample.

Constituent	**Mass percentage (%)**	
	This study*	**Nete****
Ta_2O_5	27.23	30.08
Nb_2O_5	29.94	27.01
ThO_2	0.64	0.54
U_3O_8	3.16	2.81
Al_2O_3	0.50	2.04
SiO_2	5.70	3.52
WO_3	0.04	1.18
TiO_2	2.78	2.77
Mn_3O_4	6.85	8.91
Fe_2O_3	7.04	8.34
SnO_2	<0.01	1.64

* Dissolution by LTB fusion dissolved with MeOH/H_3PO_4.

**Dissolution by LTB fusion dissolved by MeOH/H_2SO_4 by Nete.

4.5 Discussion and Conclusion

Looking at the results obtained in this study, it appears that the dissolutions were relatively successful even though recoveries of *ca.* 100 % were not always obtained (see **Table 4-37**).

The pentahalides dissolved easily and their good quantitative results indicated complete dissolution. The good results will help with the verification of the effectiveness of the quantification method, which was done by ICP-OES.

Table 4-37: Maximum Ta recoveries for final methods on proposed samples.

Sample	Final method	Max. Ta recovery (%)	RSD (%)
TaF_5	Water dissolution	96.45	1.20
$TaCl_5$	Ethanol assisted water dissolution	100.09	1.31
Ta_2O_5	Methanol assisted phosphoric acid dissolution of LTB melt	94.81	4.98
TAN-1 (CRM)	Methanol assisted phosphoric acid dissolution of LTB melt	88.15	5.82
Ta metal	KOH dissolution	84.68	2.97
Tantalite ore (TAN-A & Sample 1)	Methanol assisted phosphoric acid dissolution of LTB melt	>95*	n/a**
	Phosphate flux dissolved in water	>95*	n/a**

* Recoveries expressed in terms of values obtained by other analysts.

** Statistical data for tantalite ores cannot be evaluated very accurately because it is not a certified sample and constituent quantities vary.

Although the average tantalum recovery for the tantalum pentoxides is *ca.* 95 %, the dissolutions were considered successful because of the fact that the solutions obtained from the dissolution of tantalum pentoxide are not extremely stable and recoveries of closer to 100 % were recorded at certain times.

Although it is commonly accepted that an effective dissolution method for a CRM must yield a recovery of as close to 100 % as possible, this was not exactly the case with TAN-1. As can be seen from the quantitative results for TAN-1, a tantalum recovery of only about 88 % was obtained which can be the result of two things. Firstly, the tantalum pentoxide content is extremely low in TAN-1 (Ta_2O_5 = 0.288 %) and the smallest of sample loss can result in significant differences in recovery. The second reason is the fact that the CRM contains a lot of other constituents (see **Table 4-24**) that can affect the dissolution of the tantalum pentoxide directly, or even the quantification of the tantalum that did go into solution. Further investigation on this particular CRM will need to be done in order to confirm the above theories

Tantalum metal once again proved true to its reputation. Even with KOH dissolution the metal still did not completely dissolve and kept forming a white precipitate. Nevertheless, at least about 85 % of the metal was successfully dissolved by the developed method and the complete dissolution of the metal will make for interesting future research.

Very satisfying results were obtained for the tantalite ore and although the CRM was also a tantalum containing ore, TAN-A was much more compatible with the developed dissolution method because it is a closer match to the ores being mined commercially than the CRM. This can clearly be seen by comparison of the quantitative results from both Nete[52] and Knight[81] with those obtained in this study (**Section 4.3.7**).

The magnetic separation of the Sample 1 ore led to interesting results. By grinding the ore before separation nearly all of the iron-associated minerals can be magnetically removed from Sample 1. Together with the iron, titanium is also separated from the ore (see **Table 4-32** and **Table 4-33**). This results in the enrichment of tantalum and niobium in the non magnetic portion of Sample 1. Further investigation into the magnetic separation of columbite/tantalite ores can yield promising applications for the tantalum mining industry.

Chapter 5: Method Validation

5.1 Introduction

Method validation can be said to be the other half of analytical chemistry, of which the first half is method development of course. As discussed in **Section 2.8**, method validation can be performed by evaluating certain parameters, but it is not limited to these parameters. Method validation is essential for any analytical laboratory and forms part of quality assurance which makes sure that analytical results from chemical laboratories are of a high standard. Organisations such as the International Organisation for Standards (ISO) have sets of standards by which the quality of results are judged. Probably the most well known and widely applied standard in chemical analytical laboratories is the ISO 17025 standard.

Statistical data evaluation forms part of ISO 17025 and one of these statistical values is called the statistical *t*-test. The *t*-value determines if an experimentally obtained value is in fact the same, or different, as the true or accepted value. This is done in conjunction with the null hypothesis which either states that the obtained results are equal to the accepted value or that they are not, *e.g.* H_0: $\bar{x}$ = µ or H_0: $\bar{x}$ ≠ µ. The formula for the statistical t-test is given in **Eq. 5-1.**

$$\boldsymbol{t = \frac{\bar{x} - \mu}{s/\sqrt{N}}} \qquad \textbf{Eq. 5-1}$$

Where $\bar{x}$ is the experimental average obtained by the analyst, *s* is the standard deviation of aforementioned results, μ is the true/accepted value and *N* is the number of replicates. The calculated *t*-value is then compared to statistically determined t_{crit} values that are listed in a table[84] according to confidence intervals and degrees of freedom. If the *t*-value falls outside this range, $\bar{x}$ is statistically not considered to be equal to *µ.*

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[84] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed*. Belmont, USA. Brooks/Cole. p. 147.

5.2 Tantalum pentafluoride

The pentafluoride (purity 98.00 %) dissolved very easily in water, as mentioned in **Section 3.3.1** and by visual inspection, complete dissolution was obtained. Only upon quantitative analysis, it was found to fall slightly short of quantitative dissolution yielding a constant recovery of only *ca.* 96 %. The method validation parameters in **Table 5-1** indicate relative success but the *t*-value of -35.45 indicated the acceptance of the alternative hypothesis i.e. 98.00 % ≠ 96.21 %.

Table 5-1: Validation data for the dissolution and quantification of TaF_5.

Validation criteria	**Parameter**	**Value**
Working range	Range of std. sol.	1 – 20 ppm
Linearity	R^2 value	0.9998
	Y-intercept	0.0653
Sensitivity	Slope of calibration curve	0.2999
Selectivity	Standard deviation of the slope, s_m	<0.0139
Robustness	Soluble in solutions with a variety of neutral to acidic pH	good
Stability	Solutions stable for up to 7 days	moderate
Accuracy	Average Ta recovery	96.21 %
Precision	Standard deviation	0.2020
μ_0	True / accepted Ta-content value.	98.00 %
t-value		-35.45
t_{crit} at 95 % conf. interval		±2.13
Null hypothesis		**reject**

5.3 Tantalum pentachloride

The most effective dissolution method for the tantalum pentachloride was the ethanol assisted water dissolution. This yielded an average recovery of *ca.* 100 % and a *t*-value of far below the t_{crit} at a 95 % confidence interval. The method also passed the other validation criteria very well as can be seen from the validation data in **Table 5-2**.

Table 5-2: Validation data for the dissolution and quantification of $TaCl_5$.

Validation criteria	Parameter	Value
Working range	Range of std. sol.	1 – 20 ppm
Linearity	R^2 value	0.9998
	Y-intercept	0.0653
Sensitivity	Slope of calibration curve	0.2999
Selectivity	Standard deviation of the slope, s_m	<0.0139
Robustness	Incomplete dissolution if water is added directly to salt	moderate
Stability	Solutions stable for up to 7 days	moderate
Accuracy	Average Ta recovery	100.05 %
Precision	Standard deviation	1.2406
μ_0	True / accepted Ta-content value.	99.80 %
t-value		0.95
t_{crit} at 95 % conf. int.		±2.09
Null hypothesis		**accept**

5.4 Tantalum pentoxide

Although the pentoxide was one of the more important samples that were to be studied, it was not a roaring success in terms of complete dissolution and quantification. The developed method did, however, deliver relatively satisfying recoveries of *ca.* 97 %, and the null hypothesis was accepted at a confidence interval of 95 %. **Table 5-3** lists the other validation parameters, of which all support the developed method.

Table 5-3: Validation data for the dissolution and quantification of Ta_2O_5.

Validation criteria	Parameter	Value
Working range	Range of std. sol.	1 – 20 ppm
Linearity	R^2 value	0.9997
	Y-intercept	0.0798
Sensitivity	Slope of calibration curve	0.2667
Selectivity	Standard deviation of the slope, s_m	0.0175
Robustness	Sensitive to change in flux as well as acid	poor
Stability	Solutions destabilise after 2 days	poor
Accuracy	Average Ta recovery	96.99 %
Precision	Standard deviation	3.2880
μ_0	True / accepted Ta-content value.	99.00 %
t-value		-2.80
t_{crit} at 95 % conf. int.		±2.09
Null hypothesis		**accept**

5.5 CRM

The TAN-1 CRM proved to be more of a challenge than initially thought. The maximum recovery that was obtained by the dissolution method described in **Section 3.3.4.3** was *ca.* 89 % of the certified value and as a result, the null hypothesis was rejected at the 95 % confidence interval (see **Table 5-4**).

Table 5-4: Validation data for the dissolution and quantification of the CRM, TAN-1.

Validation criteria	**Parameter**	**Value**
Working range	Range of std. sol.	1 – 20 ppm
Linearity	R^2 value	0.9999
	Y-intercept	0.0534
Sensitivity	Slope of calibration curve	0.2298
Selectivity	Standard deviation of the slope, s_m	0.0278
Robustness	Incomplete dissolution	-
Stability	-	-
Accuracy	Average Ta content	0.2118 %
Precision	Standard deviation	0.0162
μ_0	True / accepted Ta-content value.	0.236 ± <0.015 %
z-value		-18.61
z_{crit} at 95 % conf. int.		±1.96
Null hypothesis		**reject**

- not calculated/evaluated

5.6 Tantalum metal

As expected, the tantalum metal was extremely difficult to dissolve completely without the use of HF. The method that resulted in a maximum dissolution of *ca.* 82 % was a highly concentrated, heated solution of KOH. It can clearly be seen in **Table 5-5** that the *t*-value was extremely far out of range and that the null hypothesis was rejected without a doubt. This, however, is to be expected from an incomplete dissolution. On the other hand, the other validation data indicated that the quantification method was quite precise.

Table 5-5: Validation data for the dissolution and quantification of Ta metal.

Validation criteria	**Parameter**	**Value**
Working range	Range of std. sol.	1 – 20 ppm
Linearity	R^2 value	0.9996
	Y-intercept	0.0665
Sensitivity	Slope of calibration curve	0.3031
Selectivity	Standard deviation of the slope, s_m	0.0102
Robustness	Incomplete dissolution	-
Stability	Most stable 2-8 days after dissolution	moderate
Accuracy	Average Ta recovery	82.26 %
Precision	Standard deviation	0.9529
μ_0	True / accepted Ta-content value.	99.99 %
t-value		-91.15
t_{crit} at 95 % conf. int.		±2.09
Null hypothesis		**reject**

- not calculated/evaluated

5.7 Tantalum containing ore

The method developed for analysing tantalum in Tan-A ore proved to be a success. The recoveries obtained by the AH Knight[81] analytical laboratory was assumed to be the true value and statistical values was calculated accordingly. An average tantalum pentoxide content of 27.69 % was obtained compared to 27.71 % obtained by Knight. The *t*-value calculated for Tan-A fell well within the 95 % confidence interval and the null hypothesis was therefore accepted.

Table 5-6: Validation data for the dissolution and quantification of Ta in the Ta containing mineral ore, Tan-A.

Validation criteria	Parameter	Value
Working range	Range of std. sol.	1 – 8 ppm
Linearity	R^2 value	0.9999
	Intercept	<0.0162
Sensitivity	Slope of calibration curve	0.0294
Selectivity	Standard deviation of the slope, s_m	-
Robustness	Sensitive to changes in flux as well as acid	poor
Stability*	-	-
Accuracy	Average Ta recovery	27.69 %
Precision	Standard deviation	0.6424
μ_0	True / accepted Ta-content value.	27.71 %**
t-value		-0.03
t_{crit} at 95 % conf. int.		±12.7
Null hypothesis		**accept**

*Based on the stability of Ta_2O_5 solutions, samples were analysed within a week.

** Average tantalum pentoxide content obtained by AH Knight Laboratories.

- not calculated/evaluated

In the case of the Sample 1 ore, no true or known value was available, except for the analysis done by Nete. Therefore, at a loss of any certified values, the obtained value can only be statistically compared to Nete's value for the tantalum pentoxide content in Sample 1 by calculating a *t*-value using **Eq. 5-2**[85] instead of **Eq. 5-1**.

$$\boldsymbol{t = \frac{\overline{x}_1 - \overline{x}_2}{s_{pooled}\sqrt{\frac{N_1 + N_2}{N_1 N_2}}}}$$ **Eq. 5-2**

Where the subscripts 1 indicate values of this study and subscripts 2 indicate values obtained by Nete and s_{pooled} can be calculated using the formula in Skoog *et al.*[86]. Bearing this in mind, the validation data in **Table 5-7** indicates that the dissolution and quantification of tantalum in the Sample 1 ore was also successful. The fact that the null hypothesis was rejected at a 95 % confidence interval merely indicated that the two values were not the same values and that the difference between them was not the result of random error.

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[85] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed.* Belmont, USA. Brooks/Cole. pp. 154-155.

[86] DA Skoog, DM West, FJ Holler, SR Crouch. (2004). *Fundamentals of Analytical Chemistry 8th Ed.* Belmont, USA. Brooks/Cole. pp. 124

Table 5-7: Validation data for the dissolution and quantification of Ta in the Ta containing mineral ore, Sample 1.

Validation criteria	**Parameter**	**Value**
Working range	Range of std. sol.	1 - 8 ppm
Linearity	R^2 value	0.9999
	intercept	<0.0136
Sensitivity	Slope of calibration curve	0.1249
Selectivity	Standard deviation of the slope, s_m	-
Robustness	Sensitive to changes in flux as well as acid	poor
Stability*	-	-
Accuracy	Average Ta recovery	29.98 %
Precision	Standard deviation	0.5306
μ_0	True / accepted Ta-content value.	32.99 %**
t-value		-5.38
t_{crit} at 95 % conf. int.		±3.18
Null hypothesis		**reject**

*Based on the stability of Ta_2O_5 solutions, samples were analysed within a week.

** Average tantalum pentoxide content determined by Nete[52].

- not calculated/evaluated

5.8 Conclusion

The method validation done above was considered satisfactory. All calibration curves showed good linearity as can be seen from the excellent R^2-values which were all above 0.997 as discussed in **Section 2.8.1** and their slopes were also fairly constant.

Criteria such as robustness and stability that were generally perceived as moderate to poor is an indication of the complexity of the dissolution methods developed, for example, if tantalum pentoxide dissolved completely in a number of acid-flux combinations, it would not have been considered such a challenge.

As for the general evaluation on precision and accuracy regarding the developed methods, they were considered to be relatively good, but still left some room for improvement. Samples like tantalum pentachloride however, showed with its impeccable precision and accuracy that the ICP can very effectively be used for the quantitative analysis for tantalum.

Many of the developed methods of which the null hypothesis was rejected, was because of incomplete dissolution and the rejection of the hypotheses were expected. Other rejected samples could have the decision ascribed to the fact there are still some refinement to be done to those particular methods. The results obtained by the methods of which the null hypothesis was accepted, are regarded as true and accurate because of thorough method validation.

Chapter 6: Evaluation of this study and possibilities for future research

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6.1 Success of the study with regard to the aims set out

The aims of this study were as follow:

- To find an alternative, but effective dissolution method for tantalum metal, tantalum pentoxide, tantalum pentachloride, tantalum pentafluoride and a few different samples of naturally occurring tantalum containing ores without the use of HF.
- To analyse the resulting solutions by means of ICP-OES and obtain analytically correct, accurate and reproducible results.
- Perform method validation on these analytical processes.
- Determine LOD/LOQ of tantalum, and some possible impurities, for the ICP.
- Attempt mechanical separation and analyse separated components to see if separation improves Ta content.

These aims were largely accomplished, especially with regard to the last three points. Method validation revealed valuable insights to the success of certain methods and also where room for improvement exists in others. The determination of LOD/LOQ on the ICP-OES had shown that tantalum quantities of as low as 40 ppb could be analysed. By far the most interesting find, in terms of real-world applications, was the results obtained by magnetic separation of tantalite ore as discussed in Section **4.3.7.2**.

As set out in **Section 1.7**, the first aim of this project was to find alternative dissolution methods for primarily Ta, Ta_2O_5 and tantalum containing mineral ores that specifically excluded the use of dangerous HF. This aim was largely accomplished as evident in **Table 3-17** and from the quantitative results obtained for these compounds as described in **Chapter 4**:.

The dissolution methods for all the compounds that contain Ta_2O_5 had one thing in common, namely high-temperature fluxing. Although this method, combined with acid dissolution, is quite successful at getting virtually all the tantalum into solution, it is unlikely to become commercially feasible due to high costs that go hand-in-hand with maintaining such high temperatures. It is, however, very useful in a laboratory environment where these types of samples have to be analysed. HF is a very dangerous acid and requires extensive safety precautions and training to be used safely and effectively in an analytical laboratory. The methods developed in this project, however, can be executed under less stringent circumstances and can therefore be of an advantage in the average analytical laboratory.

Other tantalum containing compounds that were dissolved and analysed included tantalum pentafluoride, tantalum pentachloride as well as a CRM. The methods developed for these samples were also largely successful, with the exception of the CRM. The CRM proved to be quite a challenge to dissolve completely as was evident from the low tantalum recoveries obtained. A reason for such low recoveries might have been the fact that aluminium, which is a major constituent of the CRM, interfered with the spectral analyses of tantalum during quantification.

The second major aim was to make use of ICP-OES as analytical tool to quantify the tantalum that went into solution during the developed dissolution methods. ICP-OES proved to be an excellent and indispensable quantification method, especially when analysing tantalum. The greatest hurdle with ICP-OES (and also with other spectroscopic methods) was spectral interferences from other elements and interfering species. Luckily, in this case, the tantalum emission spectrum is not affected by many elements (see

Table 2-7), which allow for more accurate measurements at a number of different wavelengths.

The instrument is simple to use and can be easily calibrated with commercially available standards. This makes measurements easier for the user and minimises mechanical errors. It was noted that the ICP-OES was much more suitable to bulk analyses than for the analysis of one sample at a time due to a warm up period that has to be allowed for at each start up as well as the instrument’s consumption of argon gas. The plasma torch and nebuliser tip also blocks easily if care is not taken to analyse solutions free of suspensions and precipitates.

6.2 Future research

Some of the less successful dissolution methods were those of the CRM and the tantalum metal and also the tantalum pentoxide, to a certain extent. There are also samples that have the potential of unravelling into very interesting future studies such as the ore samples and their magnetic separation.

One of the gaps in this study grew from the inability of the developed methods to completely dissolve the TAN-1 CRM. This could most likely be due to the high content of aluminates and silicates. Further study into the effects of possible spectral interference as well as the utilisation of other digestion methods would definitely shed light onto the matter. Another difficult sample was tantalum metal. Seeing that no single method in this study could be found that completely dissolved the metal, future attention regarding its dissolution might turn to multi-step procedures.

Regarding the tantalum pentoxide samples, it was not found to be unsuccessful, but neither was it particularly successful either. The problem can lie in any of the variables such as the type of flux used, temperature fused at, type of acids used, concentration of acids used, pH, wavelength measured at, time of analysis etc. An insightful study could be done on the effect that variations in these parameters have on the recovery of tantalum from die dissolution of tantalum pentoxide.

Probably the most interesting future study could come from the magnetic separation of tantalite ores. There already appeared to be a tendency for a better separation of iron and titanium with the powdered ore. Other magnetic separation techniques might be explored like using variable electromagnetism to determine what effect the strength of a magnetic field has on the efficiency of the separation. Other techniques such as suspending the powdered ore in water, whilst applying a magnetic field, might also lead to better separation.

6.3 Conclusion

In conclusion, this study is regarded to be mostly successful. By largely achieving the aims initially set out and on the way making interesting finds and creating opportunities for further research into the topic, this study can also be seen as a valuable addition to knowledge in the field of tantalum chemistry.

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Opsomming

Die hoofdoel van hierdie navorsing was eerstens die suksesvolle vertering van ‘n reeks tantaal-bevattende verbindings, met die spesifieke uitsluiting van HF, en tweedens die akkurate kwantifisering van die tantaal met behulp van induktief-gekoppelde plasma optiese-emissie spektrometrie (IGP-OES). Die reeks tantaal-verbindings sluit TaF_5, $TaCl_5$, Ta_2O_5, Ta-metaal, Ta-GVM (gesertifiseerde verwysingsmateriaal), asook twee tipes tantaliet-ertse in.

Die doel van die pentahaliedverbindings se studie was hoofsaaklik om die gebruik van IGP-OES as analiitiese metode ten opsigte van tantaalherwinning te verifieer. Die waterige oplossing en gevolglike kwantifisering van beide die samestellings was baie suksesvol en het herwinningsresultate van 96 % en 100 % vir die fluoried- en chloriedsoute onderskeidelik opgelewer. Validasie van die vertering en kwantifisering vir die pentafluoried was binne aanvaarbare grense, terwyl die oplos- en kwantifiseringsmetodes vir die pentachloried as uiters suksesvol beskou word met ‘n herwinning van 100.05 % en ‘n $t = 0.95$.

Verteringsresultate het getoon dat tantaalpentoksied heelwat moeiliker as die pentahaliede oplos, maar relatiewe goeie resultate is uiteindelik na verskeie verteringsmetodes verkry. Die suksesvolste vertering is met behulp van hoë temperatuur (1100 ℃) litiumtetraboraat smeltmiddel verkry, waarna die pentoksied-monsters met ‘n mengsel van fosforsuur en metanol opgelos is. Tantaalherwinning van ongeveer 97 % is met hierdie metode verkry.

Die studie het ook getoon dat die GVM, asook die tantaalmetaal baie moeilik deur enige van die bekende verteringsmetodes opgelos kan word. Ten spyte van die feit dat die tantaal as Ta_2O_5 (0.236 %) in die GVM teenwoordig is, het die verteringsmetode wat vir die tantaaloksied tydens hierdie studie ontwikkel is, nie daarin geslaag om die GVM volledig op te los nie. ‘n Kwalitatiewe ondersoek van die GVM het getoon dat daar ‘n verskeidenheid van elemente, o.a. Al, Si en Fe in die monster teenwoordig is, waarvan veral Al die potensiaal het om by die gekose golflengte waarby kwantifisering van tantaal uitgevoer is, met die resultate in te meng. Tantaal herwinning van 89.75 % is vir die GVM gekry. Tantaalmetaal is daarvoor bekend dat dit chemies inert in van die mees uiterse chemiese omgewings is. Gevolglik is dit nie ‘n verrassing dat geen verteringsmetode wat tydens hierdie studie ondersoek is volledige vertering kon bewerkstellig nie, en ‘n maksimum tantaalherwinning van slegs 90 % vir die mees suksesvolle metode verkry is.

Van die twee tipes ertse wat ondersoek is, is die beste herwinnig vanaf die Tan-A erts verkry met ‘n gemiddelde berekende tantaalpentoksied inhoud van 27.69 % vergeleke met die gevestigde waarde van 27.71 %. Die Sample 1 erts het ‘n gemiddelde berekende tantaalpentoksiedinhoud van 29.98 % opgelewer en alhoewel hierdie resultaat nie statisties dieselfde as dié wat deur vorige studies verkry is nie, is die verteirng en die gevolglike herwinning as susksevol beskou. Die natuurlike magnetiese eienskappe van die Sample 1 erts is dan ook gebruik om van die onsuiwerhede van die oorspronklike erts voor vertering te probeer skei. Die skeiding word as ‘n reuse sukses beskou en het moontlikhede vir nuwe toekomstige studies aangedui. Die twee hoof komponente wat bykans volledig van die res van die erts geskei is , was die yster- en titaan geassosieerde ertse. Die metaaloksied inhoud van die erts was na skeidng 1.41 % en 0.83 % vir yster- en titaanoksiede onderskeidelik waar dit voor skeiding 18.48 % en 10.68 % was.

Laastens is volledige metode-validasie op al die ontwikkelde oplos- en kwantifiseringsmetodes vir die verskillende tantaalverbindings uitgevoer om effektiwiteit, akkuraatheid en presisie te bepaal om sodoende die doeltreffendheid van elke metode statisties te kan beoordeel. Hierdie validasie het dan ook ‘n paar leemtes in hierdie studie geïdentifiseer, wat uitstekende geleenthede vir interessante en insiggewende studiemoontlikhede in die toekoms aandui.

Summary

The main objective of this research was firstly the successful digestion of a series of tantalum containing compounds, with specific exclusion of HF, and secondly, the accurate quantification of tantalum with the help of inductively-coupled plasma optical-emission spectrometry (ICP-OES). The series of tantalum containing compounds include TaF_5, $TaCl_5$, Ta_2O_5, Ta-metal, Ta-CRM (certified reference material), as well as two types of tantalite-ore.

The goal of the study of the pentahalide compounds was to verify the use of ICP-OES as analytical method in terms of tantalum recovery. The aqueous dissolution and subsequent quantification of both these compounds was very successful and yielded recovery results of 96 % and 100 % for the fluoride and chloride salts respectively. Validation of the dissolution and quantification of the pentafluoride was within an acceptable range, while the dissolution and quantification methods for the pentachloride was considered exceptionally successful with a recovery of 100.05 % and a *t*-value = 0.95.

Digestion results showed that tantalum pentoxide was considerably more difficult to dissolve than the pentahalides, but good results were eventually obtained after experimentation with various digestion methods. The most successful digestion method was obtained with the help of a high temperature (1100 ℃) lithium tetraborate flux, after which the pentoxide melt was dissolved with a mixture of phosphoric acid and methanol. Tantalum recoveries of *ca.* 97 % were obtained with this method.

This study also showed that the CRM and the tantalum metal did not dissolve easily with any of the developed digestion methods. Despite the fact that tantalum is present in the CRM in the form of tantalum pentoxide (0.236 %), the method developed for tantalum pentoxide dissolution did not succeed in completely dissolving the CRM. A qualitative study showed that there are a variety of elements present in the CRM, including Al, Si and Fe, of which especially Al has the potential of interfering with tantalum quantifications at certain chosen wavelengths. Tantalum recoveries of 89.75 % were obtained for the CRM. Tantalum metal is known to be chemically inert in some of the most extreme

chemical environments. Therefore it was no surprise that none of the digestion methods investigated during this study could achieve complete dissolution of the metal, and a maximum recovery of only 90 % was obtained for the most successful method.

Of the two types of ore analysed, Tan-A yielded the best result with a calculated tantalum pentoxide content of 27.69 % compared to the accepted value of 27.17 %. The Sample 1 ore yielded an average tantalum pentoxide content of 29.98 % and although this result was not statistically the same as the results obtained by previous studies, the digestion and subsequent recovery was still considered successful. The natural magnetic characteristics of the Sample 1 ore were used to separate some of the impurities from the original ore before digestion. This magnetic separation was seen as a huge success and indicated possibilities for future studies. The two main components that were almost completely separated from the original ore were the iron- and titanium-associated ores. The metal oxide content after separation was 1.41 % and 0.83 % for iron- and titanium oxides respectively, where it was 18.48 % and 10.68 % before separation.

Lastly, complete method validation was performed on all the developed digestion and quantification methods for all the tantalum containing compounds to determine efficiency, accuracy and precision in order to statistically judge the effectiveness of each method. This validation has also identified a few gaps in this study, which indicated excellent opportunities for interesting and insightful future studies.

Keywords

- Tantalum
- Tantalum pentoxide
- Tantalite
- Dissolution/Digestion
- Fusion
- Separation
- Quantification
- ICP-OES
- Quality assurance
- Method validation