

Separation of Tantalum and Niobium by Solvent Extraction

By

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Summary

Niobium (Nb) and tantalum (Ta) are found in the same group (VB) of the periodic table of elements and therefore have similar chemical properties, which is the reason why they are difficult to separate. They are usually found together in various minerals of which the most important are columbite ((Fe, Mn, Mg)(Nb, Ta)₂O₆) and tantalite ((Fe, Mn)(Nb, Ta)₂O₆).

Several methods have been used to separate Nb and Ta. Most methods use very high concentrations of hydrofluoric acid (HF) and sulphuric acid (H₂SO₄) as the aqueous phase, tributyl phosphate (TBP) as the extractant and methyl isobutyl ketone (MIBK) as the organic phase. High extraction can be achieved, but the reagents used are hazardous. With the increasing demand of both pure Ta and Nb, as well as stricter environmental requirements, a need exists to develop a more efficient and safer technique to separate Ta and Nb.

In this project the focus was on the solvent extraction (SX) of Ta and Nb with the possible application in a membrane-based solvent extraction (MBSX) process. For this purpose, eight different extractants were investigated, namely the cation exchangers di-iso-octyl-phosphinic acid (PA) and di-(2-ethylhexyl)-phosphoric acid (D2EHPA), the neutral solvating extractant 2-thenoyl-trifluoro- acetone (TTA), and the anion exchangers Alamine 336, Aliquat 336, 1-octanol, 2-octanol and 3-octanol. The extractant to metal ratio was varied from 0.1:1 to 10:1, while cyclohexane was used as diluent and 3% v/v 1-octanol was used as modifier for the organic phase. In addition, four different acids, hydrochloric acid (HCl), nitric acid (HNO₃), sulphuric (H₂SO₄) and perchloric acid (HClO₄), were used at different concentrations to determine the best combination for extraction.

First, fluoride salts of Ta and Nb (Ta(Nb)F₅) were tested and the optimum results showed that the highest extraction was obtained with PA and D2EHPA, irrespective of the type of acid used. Similarly, irrespective of the acid used, extraction with PA and D2EHPA increased with increasing acid concentration, followed by Alamine 336, Aliquat 336 and then TTA and the octanols. Extraction values of 97% Ta at 15 mol/dm³ and 85% Nb between 12 and 15 mol/dm³ were obtained. Although extraction of both Ta and Nb was achieved with all the acids tested, only H₂SO₄ showed sufficient separation (log D = 3) of the two metals in the 0 to 2 mol/dm³ acid range and 15 mol/dm³ for PA and D2EHPA, respectively. Precipitation, probably due to hydrolysis of the metals, occurred in the absence of acid when using

Alamine 336, Aliquat 336 and TTA. The octanols showed the least amount of extraction of Ta and Nb, irrespective of the acid investigated. The optimum extraction was achieved with an E/M ratio of 3:1 of PA and D2EHPA as the extractant and 10 mol/dm³ H₂SO₄ in the aqueous phase.

The NH₄Ta(Nb)F₆ salt solution was investigated using the optimum conditions for maximum extraction obtained from the Ta(Nb)F₅ experiments, i.e. 4 mol/dm³ H₂SO₄ with an E/M ratio above 3:1 for the extractant PA and 4 mol/dm³ H₂SO₄ with an E/M ratio of 20:1 for the extractant D2EHPA. Kinetic equilibrium for PA was reached after 10 minutes and for D2EHPA after 20 minutes. The highest extraction of Ta (100%) above 3 mol/dm³ H₂SO₄ and Nb (54%) at 8 mol/dm³ with the highest separation factor of 4.7 with PA was achieved, followed by the 100% extraction of Ta above 5 mol/dm³ and 40% Nb at 10 mol/dm³ with the highest separation factor of 4.9 in D2EHPA. Although the aim of this study was the extraction and separation of Ta and Nb, the recovery or back extraction of the metals from the organic phase, as well as the membrane-based solvent extraction (MBSX) was briefly investigated. From the preliminary results obtained it became apparent that further research into the different aspects, including the type of stripping agent used, stripping agent concentration, effect of Ta to Nb ratio and different sources of Ta and Nb is needed to obtain the optimum conditions for the MBSX process and the subsequent recovery of Ta and Nb.

Keywords: Niobium, Tantalum, Solvent Extraction, Membrane-based Solvent Extraction



opsomming

Niobium (Nb) en tantaal (Ta) word in dieselfde groep (VB) van die periodieke tabel van elemente gevind en het dus ooreenstemmende chemiese eienskappe, wat die rede daarvoor is dat hulle so moeilik is om van mekaar te skei. Hierdie twee metale word saam aangetref in verskeie minerale, waarvan kolumbiet $((\text{Fe}, \text{Mn}, \text{Mg})(\text{Nb}, \text{Ta})_2\text{O}_6)$ en tantaliet $((\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6)$ die belangrikste is.

Etlike metodes is al gebruik om Ta en Nb te skei. Die meeste van die metodes gebruik baie hoë konsentrasies fluorsuur (HF) en swawelsuur (H_2SO_4) in die waterfase, metiel-isobutielketoon (MIBK) as ekstraheermiddel en tri-butielfosfaat (TBP) as die organiese fase. Hoë ekstraksie word verkry, maar die reagentie wat gebruik word is baie gevaarlik. Met die toenemende aanvraag na beide suiwer Ta en Nb, asook strenger omgewingsvereistes, ontstaan 'n aanvraag na die ontwikkeling van meer effektiewe en veiliger tegnieke om Ta en Nb van mekaar te skei.

In hierdie projek word daar gefokus op die vloeistof-vloeistof ekstraksie van Ta en Nb, met die moontlike toepassing in 'n membraangebaseerde ekstraksie proses. Vir hierdie doel is agt verskillende ekstraheermiddels ondersoek, naamlik die kationuitruilers di-iso-oktiel-fosfiensuur (PA) en di-(2-etielheksiel)-fosforsuur (D2EHPA), die neutrale solveringsekstraheermiddel 2-tenoël-trifluor-asetoon (TTA), en die anioonuitruilers Alamine 336, Aliquat 336, 1-oktanol, 2-oktanol en 3-oktanol. Die ekstraheermiddel tot metaal verhouding is gevarieer vanaf 0.1:1 tot 10:1, terwyl sikloheksaan gebruik is as oplosmiddel en 3% v/v 1-oktanol gebruik is as modifiseerder vir die organiese fase. Daarbenewens is vier verskillende sure, soutsuur (HCl), salpetersuur (HNO_3), swawelsuur (H_2SO_4) en perchloorsuur (HClO_4), teen verskillende konsentrasies gebruik om die beste kombinasie vir ekstraksie te bepaal.

Eerstens is die fluoriedsoute van Ta en Nb ($\text{Ta}(\text{Nb})\text{F}_5$) getoets en die optimum resultate het getoon dat die hoogste ekstraksie verkry is in PA en D2EHPA, ongeag die tipe suur wat gebruik is. Soortgelyk, ongeag die suur wat gebruik is, het ekstraksie met PA en D2EHPA toegeneem met toenemende suurkonsentrasie, gevolg deur Alamine 336, Aliquat 336, TTA en die oktane. Ekstraksiewaardes van 97% Ta by 15 mol/dm^3 en 85% Nb tussen 12 en 15 mol/dm^3 is verkry. Alhoewel ekstraksie van beide Ta en Nb verkry is in al die sure wat

getoets is, het slegs H_2SO_4 voldoende skeiding ($\log D = 3$) van die twee metale getoon in die 0 to 2 mol/dm³ suurreeks en 15 mol/dm³ vir onderskeidelik PA en D2EHPA. Presipitasie, waarskynlik as gevolg van die hidrolise van die metaal, het plaasgevind in die afwesigheid van die suur wanneer Alamine, Aliquat 336 en TTA gebruik is. Die oktanol het die minste ekstraksie van Ta en Nb getoon, ongeag van die suur wat ondersoek is. Die optimum ekstraksie is verkry wanneer 'n E/M verhouding van 3:1 PA en D2EHPA en 10 mol/dm³ H_2SO_4 in die waterfase gebruik is.

Die $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ sout oplossing is ondersoek deur die optimum toestande, verkry vanaf die $\text{Ta}(\text{Nb})\text{F}_5$ eksperimente, te gebruik, d.i. 4 mol/dm³ H_2SO_4 met 'n E/M verhouding bo 3:1 vir die ekstraheermiddel PA en 4 mol/dm³ H_2SO_4 met 'n E/M verhouding van 20:1 vir die ekstraheermiddel D2EHPA. Die kinetiese ewewig vir PA is bereik na 10 minute en vir D2EHPA na 20 minute. Ekstraksie van 100% Ta is verkry bo 'n konsentrasie van 3 mol/dm³ en 54% Nb by 8 mol/dm³ met die hoogste skeidingsfaktor van 4.7 met PA, terwyl 100% ekstraksie van Ta bo 5 mol/dm³ en 40% Nb by 10 mol/dm³ verkry is met die hoogste skeidingsfaktor van 4.9 met D2EHPA. Alhoewel die doel van hierdie studie die ekstraksie en skeiding van Ta en Nb was, is die herwinning, oftewel terugwaartse ekstraksie vanaf die organiese fase, asook die membraan-gebaseerde vloeistof-vloeistof ekstraksie kortliks ondersoek. Vanuit die voorlopige resultate het dit duidelik geword dat verdere navorsing oor verskillende aspekte, insluitend die tipe stropingsagent wat gebruik word, die stropingsagent konsentrasie, die effek van die Ta tot Nb verhouding, asook verskillende bronne van Ta en Nb, nodig is om die optimum toestande vir die membraan-gebaseerde vloeistof-vloeistof ekstraksie proses en die daaropvolgende herwinning van Ta en Nb te verkry.

Sleutel woorde: Niobium, Tantaal, Vloeistof-vloeistof ekstraksie, Membraan-gebaseerde Vloeistof-vloeistof ekstraksie

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Chapter 1

Introduction

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1.1 Background

The capacitor production industry is currently the major consumer of tantalum (Ta)^[1], using about 60% of the total amount of Ta currently produced. Furthermore, Ta is investigated for use as a salting material in nuclear weapons instead of Co, which is currently used. The ^{180m}Ta isotope is the rarest isotope in the Universe.^[2,3] Ta has advantageous properties like its high melting point, high strength and inertness and thus is used in aircraft and missiles and because of its high resistance towards corrosion, it is used to line reactors.^[2] On the other hand, Nb is resistant to corrosion and is a shock absorber and is thus used with alloys to produce dies, cutting tools and high-strength structural steel. It is also used in the construction of nuclear reactor cores, because it does not chemically react to uranium.^[4] Thus, Ta and Nb are needed in pure form for a wide variety of applications, especially for their uses by companies like Necsa for the production of nuclear energy.

Niobium (Nb) and tantalum (Ta) are found in the same group (VB) of the periodic table of elements and therefore have the same chemical properties which are the reason why they are difficult to separate.^[3] In addition, Ta and Nb are usually found together in nature, necessitating their separation. These metals are found in various minerals of which the most important are columbite ((Fe, Mn, Mg)(Nb, Ta)₂O₆) and tantalite ((Fe, Mn)(Nb, Ta)₂O₆).^[2,3]

Although Nb was discovered in 1801 and Ta in 1802, the first metallic form was only produced in 1864 by De Marignac.^[2,3] Several methods have been used to separate Nb and Ta. Currently, most methods use high concentrations of hydrofluoric acid (HF) and sulphuric acid (H₂SO₄) at high temperatures.^[5] Traditionally two processes are used for the separation of Ta and Nb. The first method entails the chlorination of the raw mineral, thereby producing the pentachlorides TaCl₅ and NbCl₅, after which a distillation process is used to separate and purify the metals. This process produces a large amount of by-products, while being a lengthy and costly process for separation. The second process entails the fluorination of the raw mineral. In this process, concentrated HF or a mixture of concentrated HF and H₂SO₄ are used. The dissolved fluoride metals are firstly filtrated and then separated with fractional crystallisation. Disadvantages of this process include the formation of soluble fluoride impurities, which could contaminate the end product and the effect of these chemicals on the environment. A more recent technology that has been used successfully for the separation of various other metals entails solvent extraction (SX).

SX is a method by which two or more compounds are separated based on the relative solubility into two immiscible or partly immiscible liquids. The two phases usually consist of an aqueous phase (containing an acid and a dissolved metal salt) and an organic phase

(containing an extractant and a solvent). The organic phase contains the extractants, of which tributyl phosphate (TBP), methyl isobutyl ketone (MIBK), cyclohexanone and fatty alcohols are best known. The disadvantages of these traditional extractants include their high solubility into the aqueous phase, high flash points, formation of third phases and emulsions, contamination of the final products and low selectivity.

1.2 Problem Statement

Currently, two methods exist for the extraction of Ta and Nb from the raw mineral, but because the required chemicals are so dangerous and the processes so laborious, new, safer and more effective techniques are needed to separate the metals. In view of the numerous advantages of SX^[6,7], it will be the process of choice for this study. A current constraint of SX, i.e. the often dangerous and unsuitable extractants used, has necessitated the search for alternative extractants. In terms of environmental issues, a possible reduction in the amount of acid that has to be added to the aqueous phase would also be beneficial. Thus, this study will entail the extraction and separation of Ta and Nb by SX with the purpose to optimise the subsequent membrane-based solvent extraction (MBSX).

1.3 Aims and Objectives

The aim of this project was to find the best extractant and acid combination for the extraction and separation of Ta and Nb using solvent extraction.

The objectives were as follows:

- In the first stage, Ta(Nb)F₅ salts were used in the aqueous phase to find the optimum conditions in terms of acid and extractant concentrations for extraction. Eight different extractants were investigated, namely the cation exchangers di-iso-octyl-phosphinic acid (PA) and di-(2-ethylhexyl)-phosphoric acid (D2EHPA), the neutral solvating extractant 2-thenoyl-trifluoro- acetone (TTA), and the anion exchangers Alamine 336, Aliquat 336, 1-octanol, 2-octanol and 3-octanol.
- Four different acids, hydrochloric acid (HCl), nitric acid (HNO₃), sulphuric acid (H₂SO₄) and perchloric acid (HClO₄), were investigated to determine the most suitable acid-extractant combination for extraction.
- In the second stage, the extraction conditions of Stage 1 were evaluated using NH₄Ta(Nb)F₆, which is the compound currently used by Necsa. This section entailed

a study on the effect of acid concentration, effect on extractant to metal ratio and the effect that contact time has on extraction.

- In Stage 3, recovery of the metal from the organic phase as well as the application of the above findings in a MBSX process will be briefly investigated.

1.4 Outline of Thesis

In this study on the separation of Nb and Ta, this chapter (1) consists of a short background on Ta and Nb, a problem statement, as well as a section stating the aims and objectives of this study, ending with the outline of the thesis.

Chapter 2 entails a literature survey on Ta and Nb. Firstly, an introduction and background on the metals, including the chemical properties and applications are provided. The next section describes the mining and production of the Ta/Nb containing minerals and current separation techniques of Ta and Nb. In the last two sections, solvent extraction and pertraction are discussed, including their principles and a discussion on possible choices for solvents and extractants.

In Chapter 3 the materials used in this study are listed by a detailed description of the methods that were used to optimise the SX of both Ta(Nb)F_5 and $\text{NH}_4\text{Ta(Nb)F}_6$. Various variables, including the acid and acid concentration, the extractant and extractant concentration, the extractant to metal (E/M) ratio as well as the contact time were optimised. Finally, the methods used to evaluate the recovery and possible application of the optimised variables for MBSX are presented.

Chapter 4 entails the results and discussion of this study. The first section is on the SX of Ta and Nb from Ta(Nb)F_5 , including the study on the effect of acid and extractant, as well as the study of the extractant to metal (E/M) ratio. The second section in this chapter entails the SX of $\text{NH}_4\text{Ta(Nb)F}_6$, including the effect of sulphuric acid concentration, the effect of E/M ratio and the optimum contact time for the extraction of Ta and Nb. The last section includes a brief recovery study of Ta and Nb as well as an MBSX experiment.

Chapter 5 entails the evaluation of this study in accordance to the aims and objectives set out in Chapter 1, as well as recommendations on the future study for the separation of Ta and Nb by SX.

Chapter 2

Literature Survey

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2.1 Introduction

In view of the focus of this study, which deals with the separation of Ta and Nb, some introductory background on Nb and Ta will be provided, before discussing the production of Ta and Nb. The remainder of this section will deal with existing separation techniques, including solvent extraction (SX) and pertraction.

Tantalum (Ta), which is almost always found in the presence of Nb, was named after Tantalus, king of Lydia, son of Zeus in Greek mythology, while niobium (Nb) was named after his daughter Niobe. In central Africa, the term coltan is used to refer to niobium (COLumbium- and TANTalum-) containing minerals. Since Nb is the primary element present, the 'col' term is used before the 'tan' term.^[8]

While Nb is approximately the 32nd most abundant element^[3], Ta is approximately the 53rd most abundant element in the earth's crust.^[2] Nb and Ta are found in various minerals of which the most important are columbite ((Fe, Mn, Mg)(Nb, Ta)₂O₆) and tantalite ((Fe, Mn)(Nb, Ta)₂O₆), where the name depends on which element predominates. In Table 1 the chemical compositions of the most important minerals are presented.^[9,10,11]

Table 1 - Chemical composition of the most important Ta/Nb minerals ^[9,10,11]

Mineral	Nominal composition	Ta ₂ O ₅ , wt. %	Nb ₂ O ₅ , wt. %
Tantalite	(Fe, Mn)(Nb, Ta) ₂ O ₆	42 – 84	1 – 40
Columbite	(Fe, Mn)(Nb, Ta) ₂ O ₆	1 – 40	40 – 75
Pyrochlore	(Ce,Ca,Y) ₂ (Nb,Ta) ₂ O ₆ (OH,F)	0 – 6	37 – 66
Microlite	(Na, Ca)(Ta, Nb) ₂ O ₆ F	68 – 77	0 – 7
Wodginite	(Ta,Nb,Sn,Mn,Fe,Mn) ₁₆ O ₃₂	45 – 56	3 – 15
Yttrotantalite	(Y,U,Ca)(Ta,Nb,Fe ³⁺) ₂ O ₆	14 – 27	41 – 56
Strüverite	(Ti,Ta,Nb,Fe ³⁺) ₃ O ₆	6 – 13	9 – 14
Fergusonite	(Re ³⁺)(Nb,Ta)O ₄	4 – 43	14 – 46
Tapiolite	(Fe,Mn)(Nb,Ta,Ti) ₂ O ₆	40 – 85	8 – 15
Euxenite	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆	1 – 47	4 – 47
Samarskite	(Fe,Ca,U,Y,Ce) ₂ (Ta,Nb) ₂ O ₆	15 – 30	40 – 55

Loparite	$(\text{Ce,Na,Ca})(\text{Ti,Nb,Ta})_2\text{O}_6$	Trace – 3	5 – 20
Simpsonite	$\text{Al}_4(\text{Ta,Nb})_3\text{O}_{13}(\text{OH})$	60 – 80	0.3 – 6
Thoreaulite	SnTa_2O_6	73 – 77	–

While Table 1 gives the most common Ta/Nb minerals, more than 70 different Ta containing minerals have been identified, of which tantalite, microlite and wodginite are economically most important, while pyrochlore is the primary mineral from which Nb is obtained.^[12]

2.2 Background

Nb was discovered in 1801 by the English chemist Charles Hatchett (1765 – 1847)^[13], who named this element columbium, in reference to its American source.^[10] A year later, Ta was discovered by the Swedish chemist, Anders Gustaf Ekeberg (1767-1813)^[14], who named the element tantalum and the mineral tantalite due to the materials' 'tantalizing' resistance to the attack by mineral acids.^[10]

A few years after their discovery (1809), the English chemist William Hyde Wollaston compared the oxides derived from both columbite and tantalite with different densities (5.918 g/cm³ and 7.935 g/cm³, respectively) and concluded that the two oxides, despite their difference in measured density, were identical in terms of their other chemical and physical properties. He decided to call them both tantalum.^[15] The German chemist, Heinrich Rose, disputed this conclusion in 1864 and argued that there were two additional elements in the tantalite sample, columbium and ilmenium, which later turned out to be a mixture of Nb and Ta oxides.^[16]

In 1864 Christian Wilhelm Blomstrand^[17] and Henri Etienne Sainte-Claire Deville showed the differences between Ta and Nb, while the empirical formulas of some of their compounds were determined by Louis J. Troost in 1865.^[18] The Swiss chemist, Jean-Charles Galissard de Marignac^[19] finally confirmed in 1866 that there were only two elements, namely Nb and Ta, in these minerals.^[20]

2.2.1 Chemical Properties

Nb and Ta are found in the same group (VB) of the periodic table of elements and are therefore, chemically and physically similar (Table 2), which is also the reason why they are difficult to separate.^[2,3]

Table 2: Properties of Nb and Ta ^[2,3]

Properties	Niobium	Tantalum
Atomic number	41	73
Atomic mass	92.92 g/mol	180.95 g/mol
Density	8.4 g/cm ³ at 20 °C	16.69 g/cm ³ at 20 °C
Melting point	2410 °C	2850 °C
Boiling point	5100 °C	6000 °C
Van der Waals radius	0.143 nm	0.1425 nm
Ionic radius	0.070 nm (+5) ; 0.069 nm (+4)	0.070 nm (+5)
Electronic shell	[Kr] 4d ⁴ 5s ¹	[Xe] 4f ¹⁴ 5d ³ 6s ²
Energy of first ionisation	652 kJ/mol	674.2 kJ/mol

Nb and Ta can exist in several valences such as +5, +4, +3, +2 and +1, but only Nb(V) and Ta(V) are stable compounds in solution. The reduction of Ta(V) to its lower valence state cannot be achieved even with strong reducing agents, including aluminium (Al), zinc (Zn), cadmium (Cd) and amalgam. Nb(V) is more reactive and can be reduced in acidic solutions to its lower valence state of Nb (III). Nb(III) can exist in concentrated solutions of hydrochloric acid (HCl) or sulphuric acid (H₂SO₄), where complex anions (NbCl₆)³⁻ or (Nb(SO₄)₃)³⁻ are formed. Reduced Nb is unstable and is readily oxidized to Nb(V) by atmospheric oxygen.^[3] In a neutral to acidic solutions range, Nb and Ta hydrolyse to form hydrophilic colloids.

The distribution of soluble chemical species of Nb and Ta in acidic solutions is shown in Figure 1.^[21] Lines 1 and 3 present the hydrolysis of Nb. When the pH level is low (< -1), the cationic form (Nb(OH)₄⁺) has a high relative content (> 80%). As the pH level increases, the amount in the cationic form decreases, resulting in an increase in neutral Nb (Nb(OH)₅). At pH -0.6, the cationic and neutral Nb complexes are at equilibrium. At a pH above 1, only the neutral Nb compound is present. Similar data have been obtained for Ta, but at higher pH

levels. Lines 2 and 4 represent the neutral (Ta(OH)_5) and cationic form (Ta(OH)_4^+) of Ta, respectively. When the pH level is below 1, the relative content of the cationic Ta is high while when the pH is above 1, the neutral Ta compound is present. Thus at pH 1, the two complexes are in equilibrium and at pH values greater than 3, only the neutral Ta complex is present.

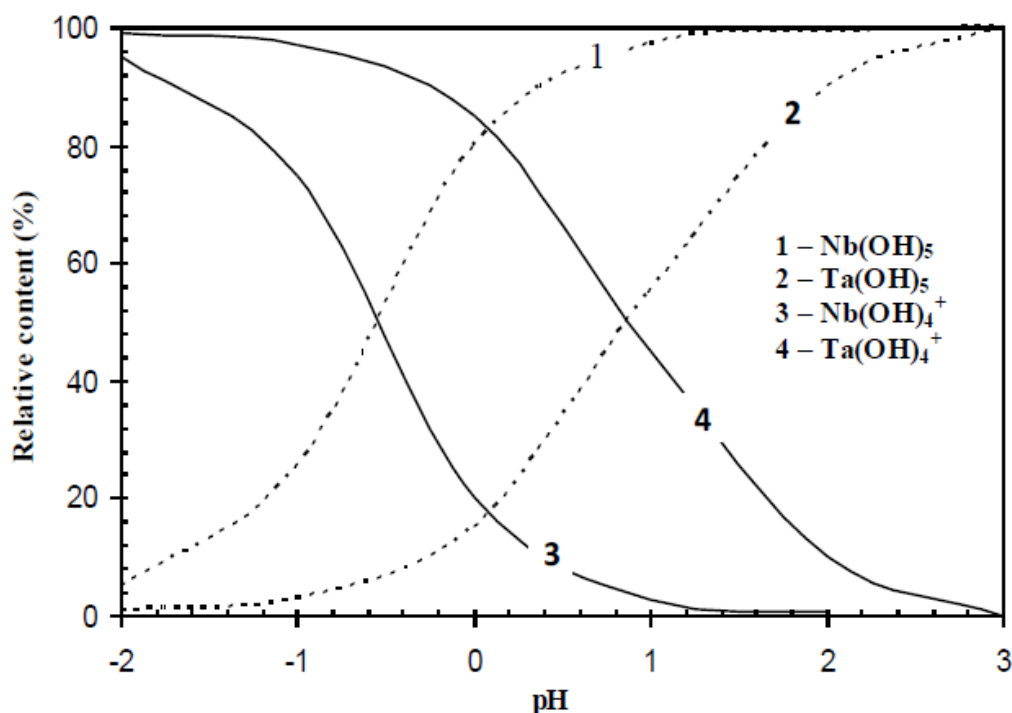


Figure 1 - Distribution of hydrolysed Nb and Ta species in acidic solutions ^[2,21]

However, apart from the above explained species distribution as a function of pH, the use and understanding of speciation data, specifically in the SX processes, are restricted. To date, it has also been shown that the speciation of mass transfer complexes does not always correspond to those governing distribution, for example the effect of pH. ^[22]

2.2.2 Commercial Applications

Ta is more resistant to corrosive agents like hydrofluoric acid (HF) and H_2SO_4 than platinum (Pt), and is therefore frequently used as a replacement for Pt in standard weights and in laboratory ware.^[2] It is further used in a variety of applications including capacitors in electronic circuits, rectifiers, pins used to fix broken bones in the human body, surgical and

dental instruments and in chemical heat exchangers.^[2] The capacitor production industry (which uses about 60% of the total amount of Ta currently produced) is currently the major consumer of Ta.^[23] Furthermore, Ta is investigated for the use as a salting material in nuclear weapons instead of Co, which is currently used. However the ^{180m}Ta isotope is the rarest isotope found in the Universe.^[2]

Nb, on the other hand, is important for its use in micro-alloyed steels, referring to the small amounts of alloying elements used. These micro-alloyed steels are used in the manufacturing of HSLA (high-strength, low-alloy) steels. Nb containing HSLA steels are used in airplanes, automobiles, oil and gas pipelines, as shown in Figure 2, where the global usage of Nb at the end of 2008 is presented.^[24] Due to its structural properties, Nb is mostly used for structural purposes (~30%) including buildings and bridges, followed by automobile applications (~24%), including railroad tracks and ships, pipes (~22%), stainless steel (~10%) and other usages including camera lenses, ceramic capacitors, high energy particle accelerators and MRI solenoid magnets.^[24, 25]

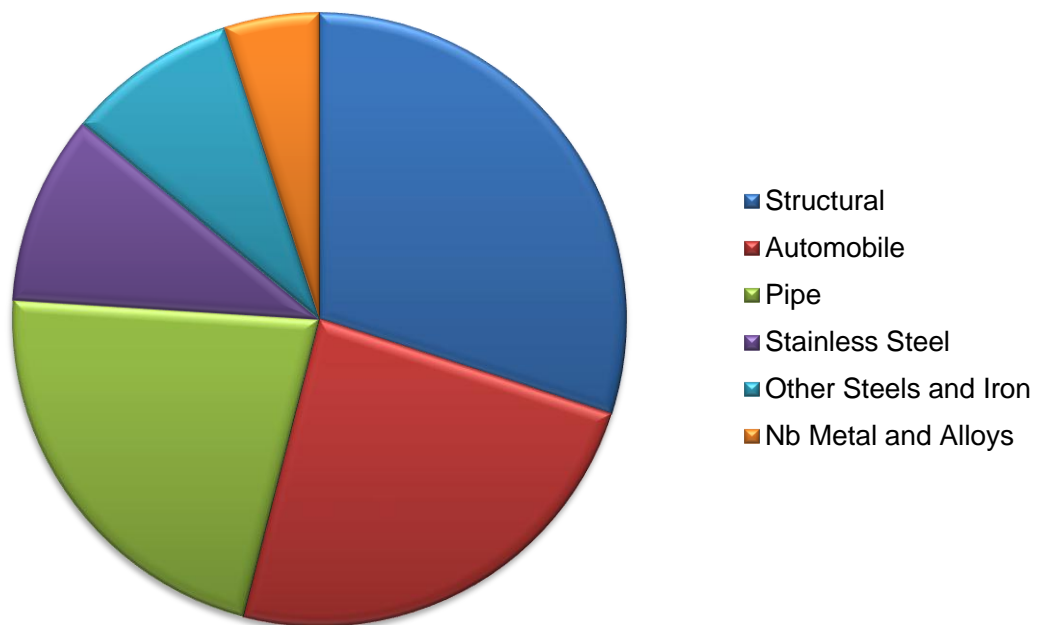


Figure 2: Niobium usage at the end of 2008 ^[24]

2.3 Mining and Production of Ta and Nb

The main Ta ores are located in Brazil, Australia, Canada, Mozambique, Ethiopia, China, Africa, Russia and Southeast Asia. The world demand for Ta is approximately 2300 tonnes

per year. Figure 3 gives the global mined Ta production, according to the latest figures (2009) from the United States Geological Survey.^[24]

There has been a strong growth in the mining and sale of Ta from mines since 1997, which slowed down in 2000, due to the dot com speculation.^[26] The mining had an all-time high in 2000, but took a crash after the 9/11 attacks.^[27] After 2000, the mining recovered slightly, but in 2006 and 2007 the mining again declined because of the American housing market crash. With stabilizing markets, an increase in the mining of Ta is expected. The global recession in 2009 again caused a drop in the production and sale of Ta due to the perceived accompanying uncertainties for the future.^[28]

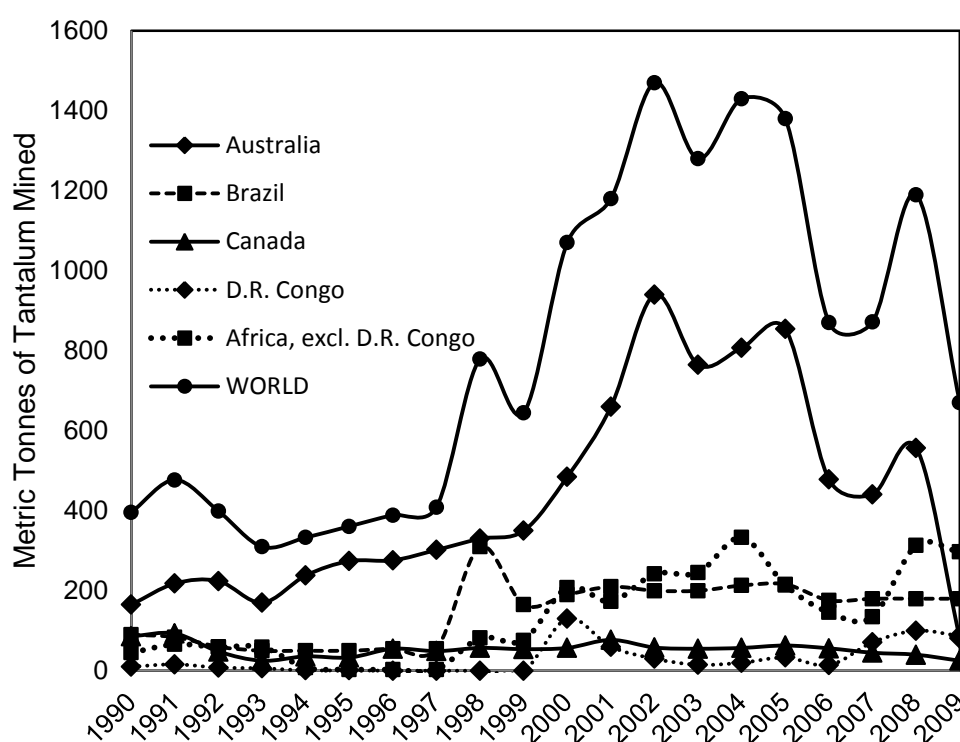


Figure 3: Global mined tantalum production, 1990 – 2009^[24]

The primary Ta chemicals of industrial significance are potassium heptafluoro tantalate (K_2TaF_7), tantalum oxide (Ta_2O_5), tantalum chloride ($TaCl_5$), lithium tantalite ($LiTaO_3$) and tantalum carbide (TaC). K_2TaF_7 , for example, is produced by treating the ores with a mixture of hydrofluoric acid (HF) and sulphuric acid (H_2SO_4) at elevated temperatures. The slurry is filtrated to dispose of the rare earth elements and other elements present and further processing is done via SX using methyl isobutyl ketone (MIBK) and tri-butyl phosphate (TBP). Pure Ta is obtained and converted into K_2TaF_7 or Ta_2O_5 via calcination.^[8,12]

On the other hand, prices for Nb are not fixed as other commodities and are negotiated between the buyers and the sellers. Because Nb is seen as a 'strategic metal' by the US and a 'critical metal' by the EU, the prices have risen each year from R62.21/kg in 2000 to R358.09/kg in 2010.^[29]

The primary mineral source of Nb is pyrochlore ($(\text{Na}_2\text{Ca})_2\text{Nb}_2\text{O}_6(\text{OH},\text{F})$), of which the largest producer is Companhia Brasileira de Metalurgia e Mineração (CBMM) in Araxá, Brazil. The second largest producer is the Boa Vista open pit in Catalão (Brazil) owned by Anglo American Brasil Limitada (Catalão).^[30] Brazil produces more than 85% of the world's Nb, followed by Canada, the Democratic Republic of Congo, Ethiopia, Mozambique, Nigeria, Rwanda and Uganda according to the latest figures (2009) from the United States Geological Survey, with a yearly world production of approximately 61 000 tonnes.^[31] The longevity of these leading producer's mines seems assured, given the extent of their reserves: at local consumption, CBMM has an estimated 400+ years of reserves, Catalão 20+ years and Niobec 18+ years.

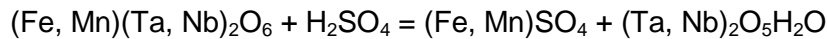
Nb salts produced industrially are $\text{H}_2[\text{NbOF}_5]$ from the reaction of the oxides with HF, the fluorides NbF_5 , NbF_4 , $[\text{NbF}_7]^{2-}$, the chlorides NbCl_5 , NbOCl_3 , $(\text{C}_5\text{H}_5)_2\text{NbCl}_2$, niobium nitrate (NbN) and carbide (NbC).

As stated previously, both Ta and Nb are mined in Africa. For example, at Isithebe, in KwaZulu-Natal, Ta and Nb are recovered from mineral sands originating in Mozambique. The current plant capacity is 90 ton/mineral ore, containing approximately 30% Ta_2O_5 . The ore is leached with concentrated hydrofluoric acid (HF) and the Ta is extracted.^[32] Impurities (such as Si, Fe, Ti, Mg, and Mn) are removed by scrubbing and high-purity (> 99.99%) Ta_2O_5 is currently produced at 360 ton per annum, with the production of high-purity Nb_2O_5 expected to follow shortly.

In industrial processes, the separation and purification of Nb and Ta are all performed in the presence of fluoride, forming fluoro complexes which combine with organic molecules during SX. In Figure 4 a diagram is presented showing the Nb/Ta separation process based on the fluorination route.^[21] The first step is the mining of the mineral ore, then the separation process where other metals are separated from Ta and Nb before the separation of Ta and Nb (discussed in Section 2.4), followed by the production of Ta and Nb in a metallic or salt form.

Akimov and Chernyak^[33] investigated and reported on the mechanism of the interaction between columbite and tantalite and H_2SO_4 for the production of Ta and Nb salts (depicted in

the last section of Figure 4). The said interaction is presented in two steps. In the first step Fe and Mn sulphates and Ta and Nb hydroxides form:



In the second step, Ta and Nb hydroxides are converted into oxy-sulphate compounds:

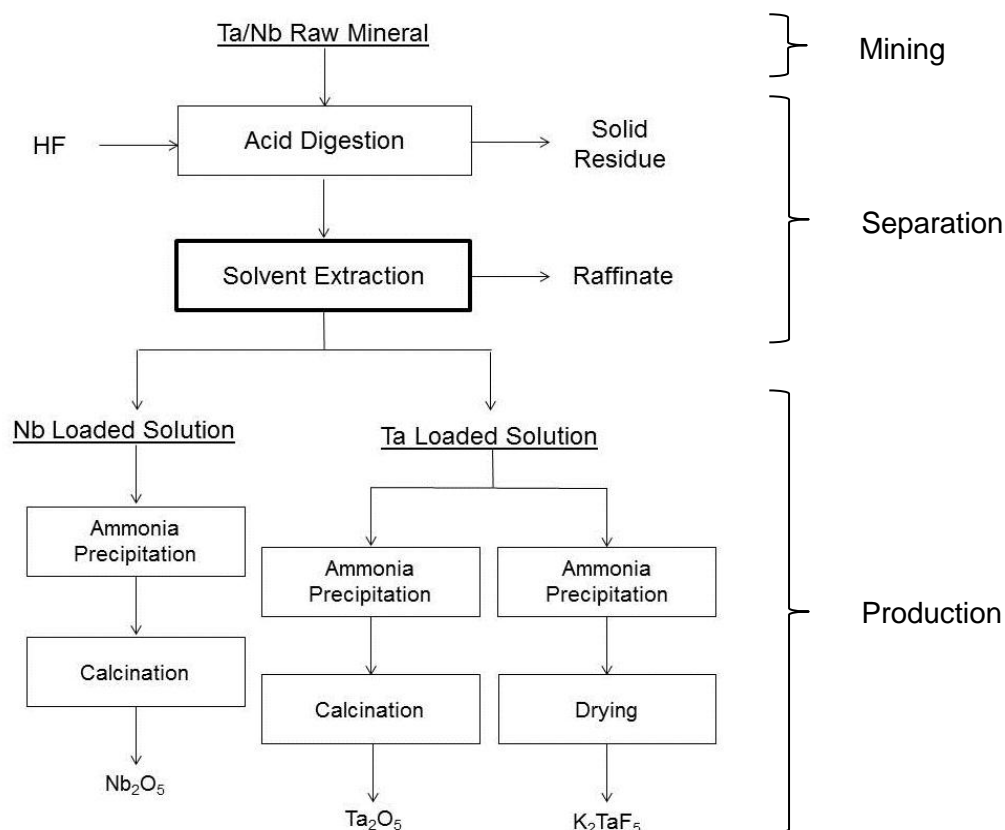
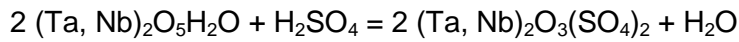


Figure 4 - A schematic flow sheet for Nb and Ta separation and production ^[21]

Thermodynamic analysis^[33] of the interactions in the above equations show that a coherent shell of Ta and Nb hydroxides is formed on the surface of the columbite or tantalite mineral during the interaction with H_2SO_4 . Thus a pseudomorphic structure is formed on the surface of columbite or tantalite minerals, which makes any further interaction thermodynamically disadvantageous. This approach explains that the complete decomposition of columbite or tantalite with H_2SO_4 yielding Nb and Ta hydroxides.^[23]

2.4 Separation of Ta and Nb

2.4.1 Introduction

De Marignac was the first to produce the metallic form of Ta in 1864, by reducing TaCl_5 in a hydrogen atmosphere.^[34] De Marignac also found an effective method for the separation of the two elements when he discovered that the solubility of the potassium heptafluoride salts of Ta and Nb ($\text{K}_2\text{Ta}(\text{Nb})\text{F}_7$) differed, which could be used to separate the two elements. A mixture of niobic and tantalic acid slurries were dissolved in HF and potassium fluoride (KF) was added, producing potassium fluorotantalate, K_2TaF_7 , which precipitates from the solution in the form of fine needles. In the same solution, Nb forms potassium oxyfluoronioate, $\text{K}_2\text{NbF}_5 \cdot \text{H}_2\text{O}$, with a sufficiently high solubility, thus remaining dissolved. The acidity of the solution, however, had to be adjusted in order for K_2NbF_7 to precipitate. This technique, called fractional crystallization, was used as a production process to separate the Nb and Ta until the middle of the 20th century, when solvent extraction (SX) processes replaced fractional crystallization.^[35,36]

Traditionally, two routes are used to separate Ta and Nb, the chlorination route where fractional distillation is used for separation and the fluorination route where SX is used for separation. The two routes will be briefly discussed, followed by a more detailed discussion of SX in Section 2.5.

2.4.2 Chlorination Route

In this process, raw material from a mining site is chlorinated to produce the pentachlorides, TaCl_5 and NbCl_5 , which are separated and purified by distillation.^[11,37] The boiling points of TaCl_5 and NbCl_5 are 236°C and 248°C, respectively, which are low and different enough to make a distillation process feasible.^[23] The mineral ore is blended with coke and chlorinated to separate the resulting Ti-Nb-Ta-oxychlorides from the rare earth elements and most of the thorium (Th). By dropping the temperature of the resulting gas, which also contains the Ti-Nb-Ta-oxychlorides, the Fe, Th and alkali-metal precipitates are removed. The clean Ti-Nb-Ta-oxychlorides gas is cooled to its liquid form and distilled to separate the Nb and Ta from the TiCl_5 . The Nb-Ta-oxychlorides gas is further chlorinated and NbCl_5 and TaCl_5 are produced. The $\text{Nb}(\text{Ta})\text{Cl}_5$ is fractionally distilled, whereafter the NbCl_5 reacts with steam to produce $\text{Nb}(\text{OH})_5$, which is calcinated to Nb_2O_5 . The remaining TaCl_5 reacts with NH_4OH to produce Ta_2O_5 .^[8]

2.4.3 Fluorination Route

The second route for obtaining Ta and Nb is related to Marignac's separation process based on the fluorination of the raw mineral. In the current separation process, the raw mineral is digested at high temperatures, using concentrated HF or a mixture of concentrated HF and H₂SO₄.^[37] The purpose of the digestion is to dissolve the Ta and Nb, producing complex fluoride acids. All other impurities that form soluble fluoride compounds, are also dissolved. The insoluble residual part of the slurry is separated from the solution by filtration. The filtrated solution is processed using SX,^[23] as depicted in the second section of Figure 4.

2.5 Solvent Extraction (SX)

2.5.1 Introduction

After a short introduction, the principles of SX, as well as the role of the solvents and extractants used in SX and the recovery of the metals from the separated phases will be discussed before reviewing pertraction, which is an adaptation of the traditional SX process.

Liquid-liquid extraction, also known as solvent extraction (SX) and partitioning, is a method used to separate two or more compounds based on the relative solubility of the compounds in two immiscible or partly immiscible liquids.^[11] The two liquids or phases are usually water and an organic solvent. Extraction is achieved ideally if one of the compounds is retained in one liquid phase and the other compound(s) is extracted into the other liquid phase. The SX process was developed by Ames Laboratory together with the U.S. Bureau of Mines and has been used since 1957^[38] as an alternative to fractional crystallization (Marignac's method).^[23]

The first major commercial application of SX technology in southern Africa entailed the recovery of uranium (U), a by-product in gold (Au) mining, in the 1950s by Rössing Uranium in Namibia. Since then, southern Africa witnessed the birth of several commercial SX processes in the 1970s, including their use for the recovery of copper (Cu) and precious metals, and for the successful separation of 'problematic' metal pairs such as Nb and Ta, Zr and Hf, Co and Ni. SX is currently used extensively for the separation of rare earth group elements. From the 1980s, SX has been used for the commercial refining of platinum group metals (PGMs) in the North West Province.^[39] More recently, this technology was implemented for other metals, including alkaline metals (Rb, Cs); alkali earths (Be, Mg, Ca); transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg); rare metals (Zr, Hf, Nb, Ta, Mo, W, Tc, Re, Al, Ga, In, Tl, Si, Ge, Sn, As, Bi, Se, Te); precious metals (Au, Ag, Ru, Ir, Pt, Pd, Rh); actinides (U, Th) and lanthanides.^[22,40]

SX for Nb and Ta can be achieved by selective extraction of ions into either the organic or aqueous phase, depending on the complex ion structure. This complex ion structure depends on the solution, for example the acidity of the aqueous solution. At low pH levels ($-2 < \text{pH} < 0$, Figure 2), both Ta and Nb are extracted from the aqueous into the organic phase, while most of the impurities remain in the aqueous phase.^[21] At higher pH levels ($\text{pH} > 2$, Figure 2) Nb and Ta are stripped from the organic solution to the aqueous phase. Nb and Ta can therefore theoretically be separated by SX, because Nb requires a lower pH than Ta to migrate into the organic phase and a higher pH than Ta to be stripped into the aqueous solution.^[23]

The advantages of SX include the effective separation of dissolved components, the production of high-purity products, its relatively low cost, its simplicity of use, the fact that the process can be completely automated and that it does not require excessive labour and service.^[23] Due to its numerous advantages, SX is widely used in various industrial sectors, including:

- the production of vegetable oils and biodiesel,
- the processing of perfumes,
- nuclear reprocessing,
- ore processing and
- the production of fine organic compounds.

2.5.2 Principles

SX methods based on two or three phase systems have been studied widely. Classical SX is based on the partitioning of components between two immiscible or partially miscible phases and is widely used in numerous industrial separation plants. It is mostly used in systems where dispergation of one phase into the second phase occurs.^[41] There are different methods for SX. In this study only batch and continuous extraction will be discussed briefly.^[42,43]

➤ Batchwise single stage extractions

Batchwise single stage extractions are mainly used for small scale laboratory studies, where traditionally a separating funnel is used for separation, as was used in this study (Figure 5).

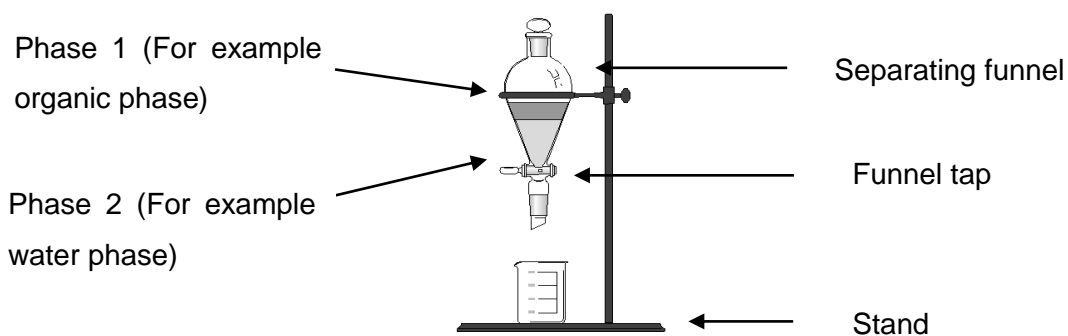


Figure 5 - Separating funnel used for batchwise SX

In this process the organic phase and aqueous phase is contacted in a separating funnel. The densities of the phases differ, making them immiscible or partly miscible in each other. The funnel is carefully shaken and the build-up of possible solvent gasses is released through the tap. The separating funnel is left in order for the phases to separate. The tap is opened and the aqueous phase is selectively poured into a beaker. Subsequently, either the organic or the aqueous phase can be analysed to determine the selectivity attained.

➤ Multistage continuous processes

A continuous process can also be used in industry, especially for the processing of metals, where the separation factor is small, requiring many extraction stages to obtain a satisfactory extraction. The traditional continuous process makes use of mixer-settlers. Alternatively, in a membrane-based solvent extraction (discussed in detail in Section 2.6), a membrane is placed between two phases and a driving force is applied to force a solute to move from one phase to the next. The driving force can be for example temperature (ΔT), pressure (ΔP), concentration (ΔC) or electric potential (ΔE). Figure 6 shows the idealised flow patterns in membrane modules, where Figure 6A shows perfect mixing, Figure 6B the counter-current flow, Figure 6C the co-current flow and Figure 6D the cross flow.

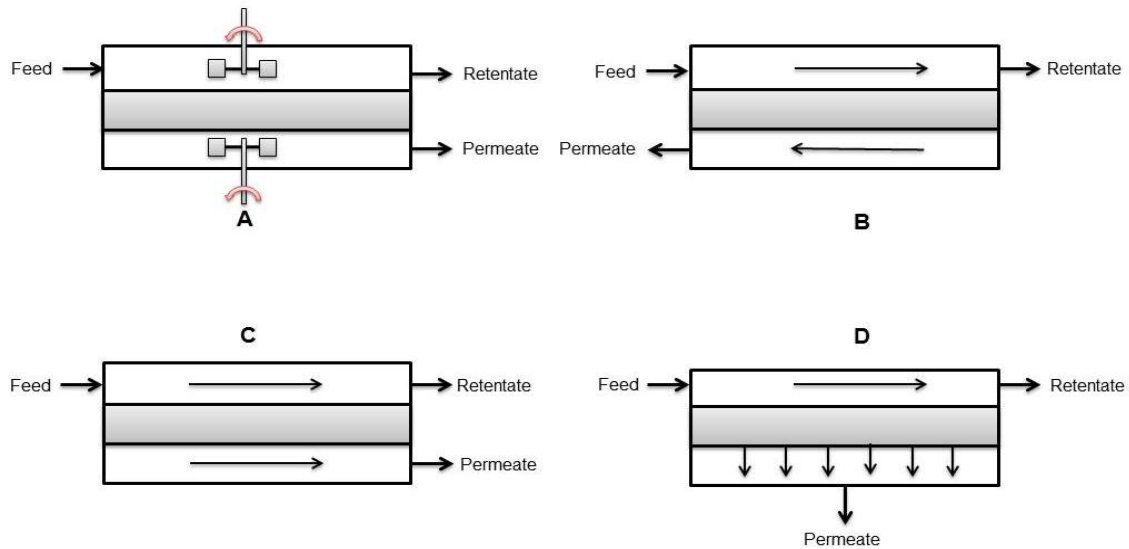


Figure 6 – Single stage membrane processes

Irrespective of the type of process, the most important aspect of SX is that it separates the required component without changing its properties and identity. The principle of separation during SX is based on the varying distribution coefficients of the species between the two phases, where the distribution coefficient is defined as the concentration ratio at equilibrium of the components in the two phases. The extraction rate depends on the mass transport coefficient (K , m/s), the phase contact area (F , m²) and the difference between the initial concentration of the dissolved component and the equilibrium concentration, which is expressed as the driving force (ΔT , ΔP , ΔC or ΔE) of the separation process. The rate of extraction (V , - for example mol/s if the driving force is ΔC , i.e. mol/m³) can therefore be calculated using the following equation: ^[23]

$$V = K \times F \times \Delta C \quad (\text{Eq. 1})$$

According to literature, the most effective way to increase the extraction rate is by increasing the phase contact area (because of its influence on the production capacity of the separation process), ^[23] which can be achieved by the intensive mixing of small drops of one phase into the other phase. Thus, the phase contact area is an important parameter. ^[23]

Figure 7 gives a diagram showing the main components of an SX process for a system containing two dissolved compounds. The initial solution (P) is an aqueous phase (X) containing two dissolved compounds, A and B, with initial concentrations $X_{A,P}$ and $X_{B,P}$, respectively. The extractant (Q) is an organic phase (Y) containing no dissolved compounds in the initial state prior to the interaction between the phases; thus, $Y_{A,Q} = 0$ and $Y_{B,Q} = 0$. ^[23]

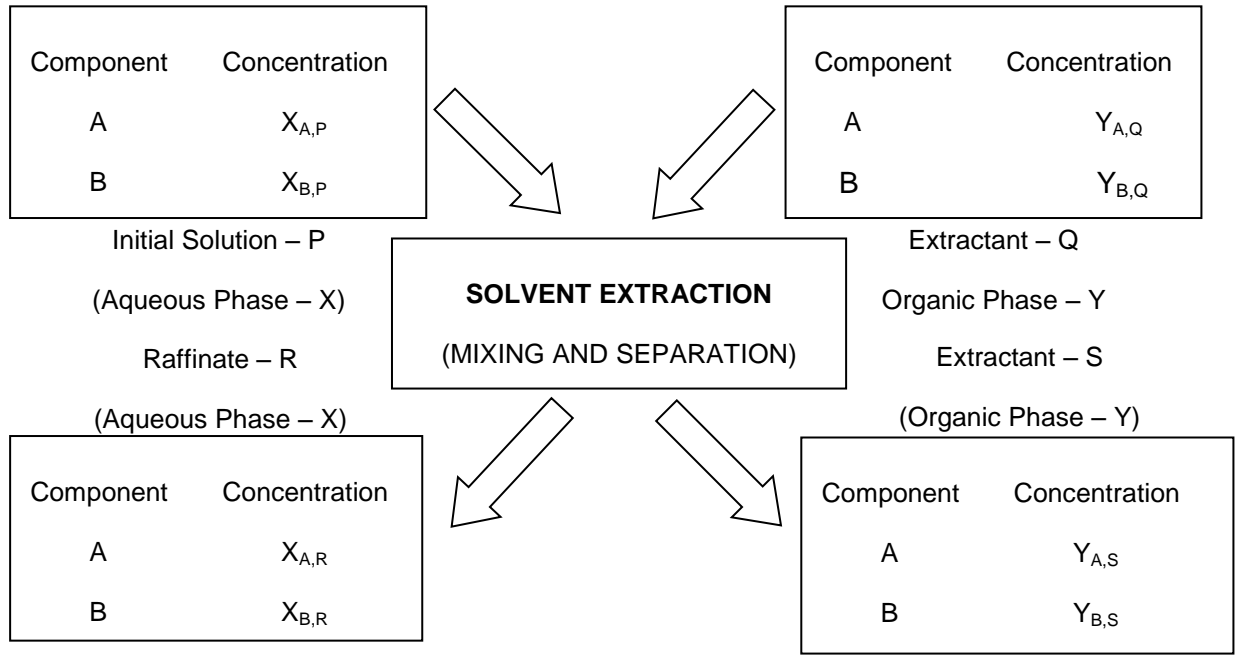


Figure 7 - SX system containing two dissolved components^[23]

During SX the aqueous and organic phases are mixed for a specific period of time, followed by the separation of the two phases. The resultant two phases are again aqueous and organic. The one phase is the raffinate (R), an aqueous phase (X) containing components A and B at concentrations $X_{A,R}$ and $X_{B,R}$, respectively. The second phase is the extract (S), an organic phase (Y) in which the concentrations of components A and B are denoted $Y_{A,S}$ and $Y_{B,S}$.^[23]

The distribution coefficients, α_A and α_B of components A and B, respectively, can be calculated as follows:^[23]

$$\alpha_A = \frac{X_{A,R}}{X_{A,S}} \quad \alpha_B = \frac{X_{B,R}}{X_{B,S}} \quad (\text{Eq. 2a and 2b})$$

where $X_{A,P}$ and $X_{B,P}$ are the concentrations (mol/dm^3) of components A and B, respectively, in the aqueous phase X, with $X_{A,R}$ and $X_{B,R}$ being the concentrations of components A and B, respectively, in the aqueous phase X of the raffinate R.

From this, the separation coefficient, D, is calculated as the ratio between the two distribution coefficients, α_A and α_B :^[23]

$$D = \frac{\alpha_A}{\alpha_B} \quad (\text{Eq. 3})$$

From this, the separation factor, β , (Eq. 4) is defined as the log value of the separation coefficient D:

$$\beta = \log D \quad (\text{Eq. 4})$$

2.5.3 Solvents

The choice of an organic solvent depends on the compounds to be separated. Some of the factors that are important when choosing a solvent include ^[43]:

- One of the components should be more soluble in the solvent than the other component.
- The occurring reaction should be stable and irreversible during extraction but reversible during back extraction. Reversible reactions may produce the previous form, resulting in an unsuccessful extraction.
- The extracted compound and the solvent should be easily separated, so that the solvent can be reused.
- The separation should be cost effective – the running cost should not exceed the profit margin.
- The solvent should not be toxic or corrosive as it can harm the extraction instruments and the environment.
- Temperature and pH of the phases should be regulated as they influence the separation of the compounds.

2.5.4 Extractants

For the extraction of Ta and Nb, numerous solvents have been investigated, but the most frequently used extractants are methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), fatty alcohols ^[44] and amines. Due to the importance of the extractants for separation, the different extractants will be discussed in the next section. ^[23, 45]

2.5.4.1 MIBK

MIBK is most frequently used as an extractant in SX due to its low density (0.802 g/mL), low viscosity (0.58 cP at 20°C), low solubility in H₂O (1.91 g/100mL) and generally high selectivity resulting in the production of high-purity products. It is commercially obtained from an aldol condensation of acetone. However, it is a volatile compound with a low flash point (14°C), which makes the use of MIBK dangerous, requiring special handling conditions.^[46] In addition, MIBK can exist in an aqueous raffinate in concentrations of up to 1.7% wt, which leads to the need for complicated and expensive systems for the recovery of the extractant.^[47]

Gabra^[48] illustrated the use of MIBK as an extractant for the separation of Nb and Ta. For this process, pyrochlore mineral with a high Nb percentage and negligible Ta content was used. The mineral was dissolved in 46 wt% HF and 98% H₂SO₄ resulting in the formation of the fluoro – or oxyfluoro complexes. The composition of the complex depended mainly on the HF concentration (25% HF – HNbF₆, 35% HF – H₂NbOF₅, 95-99% HF - HNbF₆ and H₂NbF₇). The separation of Nb and Ta was achieved using MIBK where 96% Nb was extracted using 2 N HF and 10 N H₂SO₄. The extracted Nb was stripped using distilled water and hydrated Nb₂O₅ was precipitated using ammonium hydroxide at pH 8 before being calcinated at 900°C.

2.5.4.2 TBP

TBP is less soluble (0.606 mL/100 mL water) than MIBK and less dangerous, but has a high density (0.973 g/mL).^[49] This can lead to poor stratification, especially during the stripping process, leading to insufficient separation, while the extractant can cause additional contamination (by phosphorous) of the final products.^[44, 50]

Nishimura et al.^[51] extracted Ta₂O₅ and Nb₂O₅ in the form of fluorotantalates and -niobates from a 1.28N HF-H₂SO₄ solution into TBP (Nb₂O₅ + H₂SO₄ ↔ H₂NbOF₅), diagrammatically presented in Figure 8. The H₂NbOF₅ existing in the aqueous phase is stable in an organic phase as HNbF₆ or H₂NbF₇. Extractability was found to be functions of HF, H₂SO₄, TBP and oxide concentrations, as well as the organic solvent ratio and extraction frequency. Using this method, 98.8% Ta and 98% Nb were extracted.

According to Figure 8, Ta/Nb containing mineral ore is dissolved in high concentrations of HF and H₂SO₄. For the extraction of the metal, the organic phase consists of TBP and the aqueous phase of HF, H₂SO₄ and dissolved metal. After the two phases have been

separated, only Ta and Nb have been extracted into the organic phase, while all the other metals have remained in the aqueous phase. To strip the organic phase of the metals, aqueous ammonia (NH₄OH) was added as an aqueous phase. The pH of the solution was adjusted with HF and H₂SO₄. The phases were separated, with the organic phase containing the Ta and the aqueous phase containing the Nb.

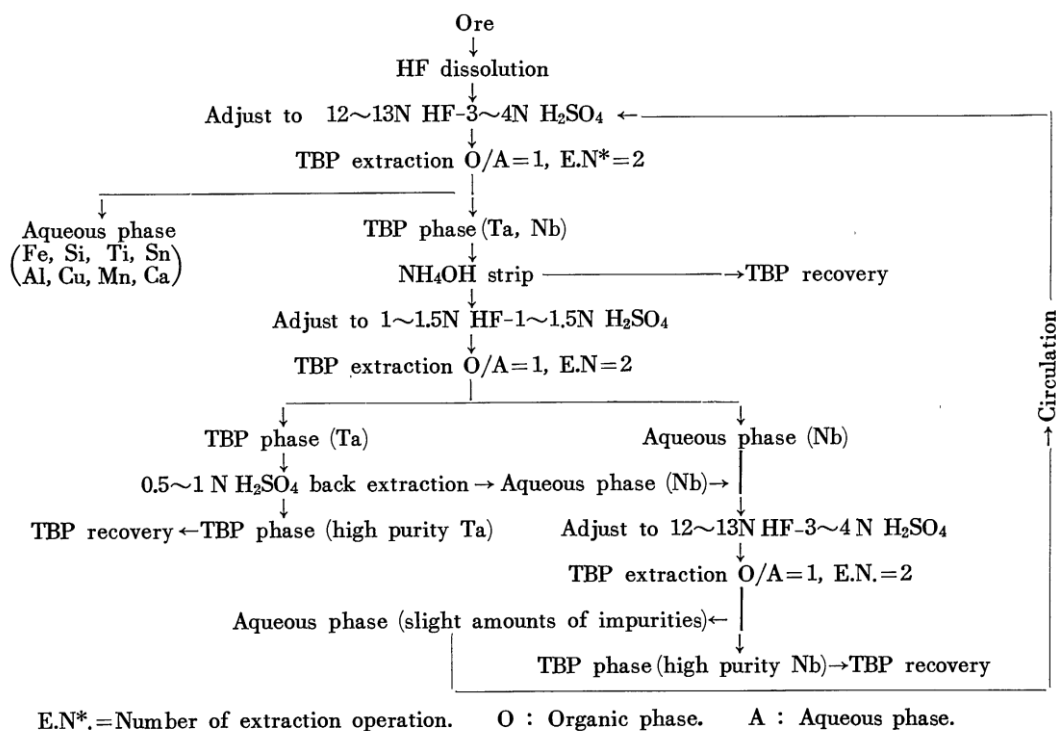


Figure 8 – Flow sheet for the extraction and separation of Ta and Nb with TBP ^[51]

In another method described by Campderrós and Marchese^[52] pure Nb₂O₅ and Ta₂O₅ were used and dissolved in HCl. The organic phase was TBP. They showed that, as the pH of the aqueous phase changes, the metallic species changes, for example at a higher acidic pH (3 to 6 mol/dm³ HCl), the neutral complex Nb(OH)₂Cl₃.TBP(org) was formed. When the acid concentration was increased to 6 to 8 mol/dm³ HCl, the anionic species [Nb(OH)₂Cl₄]⁻TBPH⁺(org) was formed preferentially. At a very low pH (≥ 8 mol/dm³ HCl), the cationic species [HNbOCl]⁺Cl⁻TBP(org) was formed. Similarly, they found that the Ta complex is extractable at low HCl concentrations (3 to 6 mol/dm³ HCl) according to the following proposed complexation reaction:



Using this method, a separation factor of 55% in terms of Nb was attained in the organic phase with HCl concentrations ranging between 8 and 10 mol/dm³. The maximum extraction

of 25% Ta was achieved using 2 mol/dm³ HCl. This lower yield was ascribed to the fact that Nb formed more stable complexes in an acid environment.

2.5.4.3 Octanol

Traditionally, octanol is used as a solvent in SX. Due to changing the methods for safer and more effective technology, octanol is now also more widely used as an extractant, due to its main advantages which include its low solubility in water, its sufficiently low volatility and its reduced danger because of its higher flash point (81°C). Notwithstanding its lower extracting ability, octanol has a number of advantages over TBP, such as its higher flash point than that of TBP, making it safer to use in the laboratory. In addition, 1-octanol has a lower viscosity than TBP and octanol is cheaper than TBP. An important characteristic feature of an extractant is its stability on prolonged contact with process solutions. Alcohols with a C8 - C12 chain length have a low solubility in aqueous media and have a particular commercial potential as perspective extractants for Ta and Nb separation.^[23] Particular emphasis has recently been placed on the investigation of Ta and Nb extraction using octanol (C₈H₁₈O) in the forms of 1-octanol and 2-octanol.^[50, 53, 54, 55]

In view of octanol's availability, low cost and safety, Agulyansky et al^[53] used 2-octanol, diluted with kerosene, for the extraction of both Nb and Ta from a feed solution. Tantalite mineral was melted with ammonium hydrofluoride, followed by the digestion of the soluble components with water. H₂SO₄ was added to the solution while keeping the concentration of Ta₂O₅ at 50–60 g/L and that of Nb₂O₅ at 30 g/L. Solutions of 2.5 – 3.5 M H₂SO₄ were found to be optimal for Ta extraction, while extraction of Nb into the organic phase only started at an acidity of > 5 M H₂SO₄ since Nb has a lower molecular weight and is a stronger Lewis acid and thus needs a stronger acid solution to be extracted. This difference makes it possible to separate these two metals via SX. Distribution coefficients obtained ranged from 200 to 250. Figure 9 shows an example of the extraction of Nb and Ta with 2-octanol as a function of the H₂SO₄ concentration.

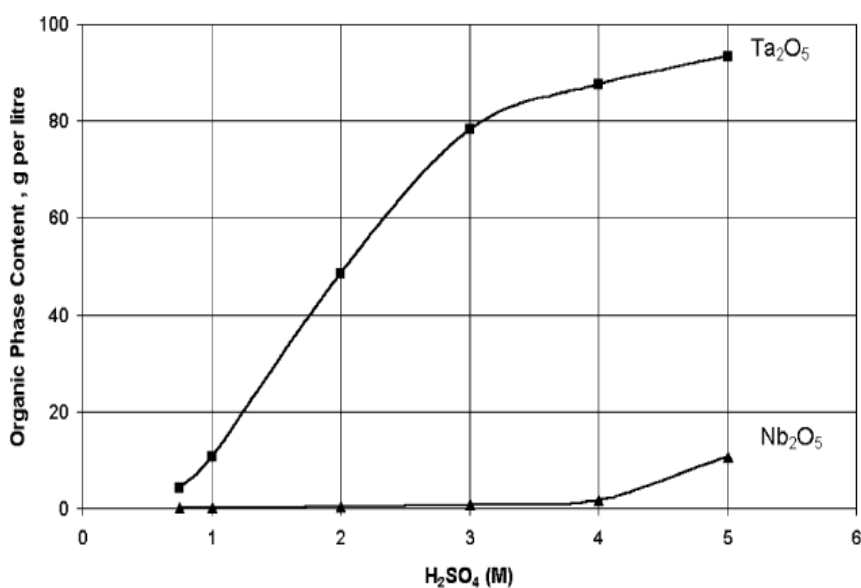


Figure 9 - Extraction of Nb and Ta with 2-octanol ^[53]

El-Hazek et al^[54] also used 2-octanol for the extraction of Ta and Nb from polymineralized ore material from South Gabal El-A'urf. The highly mineralized ore was melted with potassium bisulphate before removing all other elements and impurities from the sulphate leach liquor. A high-purity Ta was obtained by keeping the pH of the leach liquor at 2.0 using 100% 2-octanol. When distilled water was used as a stripping agent, the stripping time was 20 min. The Ta strip solution was neutralized with an ammonia solution and Ta was completely precipitated at pH 4.5 – 5.5. Figure 10 shows the optimum conditions in terms of the H₂SO₄ concentration. After calcination, a relatively pure Ta₂O₅ was obtained.^[54] Since Ta extracted more readily with octanol than with TBP, it could be a cost effective alternative extractant for the separation of Ta and Nb.

With respect to Nb, a pH of 0.7 and 100% 2-octanol was sufficient to extract most of Nb content efficiently. A mixture of 7 M HF and 6 M H₂SO₄ was the most efficient for Nb stripping from the loaded solvent, resulting in a 99.2% stripping efficiency. By neutralizing the Nb strip solution using the ammonia solution, Nb was completely precipitated at pH 6.5 - 7.5. Nb extraction with octanol was lower than with TBP. This result differs from that of Ta, but extraction and separation of both metals were still possible.

Contrary to the previous two papers, Mayorov and Nikolaev^[55] used 1-octanol (C₈H₁₈O) and TBP in their SX experiments. During preliminary studies they found that 1-octanol, as well as other octanol isomers (octanol-2 and 2-ethylhexanol), had similar extracting parameters.

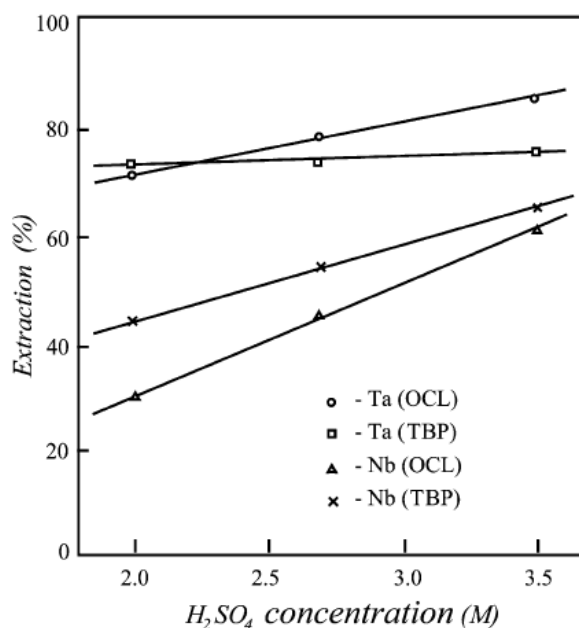


Figure 10 - Extraction of Ta and Nb with 1-octanol ($V_o/V_{aq} = 1.5:1$) and TBP ($V_o/V_{aq} = 0.75:1$) from a solution of 0.45 M Ta, 0.75 M Nb and 6 M free HF ^[55]

2.5.4.4 Amines

Alamine 336 and Aliquat 336 are commercial quaternary amines used for solvent extraction. Both amines are water insoluble, making them ideal for SX. Alamine 336 and Aliquat 336 have high flash points of 179°C and 132°C, respectively, making them safer to use in a laboratory. The disadvantage of these amines is their tendency toward third phase and emulsion formation. As prevention, a modifier, for example 1-octanol, is usually added. Another disadvantage is that these amines are difficult to strip from the extracted metal. ^[56]

One of the first cited separation techniques in 1952 and 1954 already used amines as extractants. The method has been used to demonstrate the first separation of Nb and Ta by SX by Leddicotte ^[57] and Ellenburg ^[58]. The first use of high-molecular weight amines was for the extraction of mineral acids reported in 1948. ^[54] Seeley and Crouse ^[59] expanded on the first experiments and successfully extracted 54 metals using representative primary, secondary, tertiary, and quaternary amines with alkyl-ammonium nitrates and sulphates as extractants in a diethyl-benzene diluent.

Paulus et al ^[60] performed batch extraction experiments for Nb, Ta, and Pa with the quaternary ammonium salt Aliquat 336 in pure HF, HCl, and HBr solutions. Born's theory for the transfer of ions from the aqueous phase into the organic phase was applied ^[61] to predict the extractability of the oxygen containing chloride complexes of Nb, Pa and Db, with the

result that Pa should always show higher partition coefficients than Nb. The opposite was, however, experimentally observed. Due to the presence of fluoride ions in the experiments^[62, 63], multiple charged fluoride or mixed fluoride/chloride complexes might have formed showing a different extraction behaviour. Subsequently, extractions with pure HCl solutions were done.^[61] Extraction was performed using 1 – 12 M HCl with the fluoride salt of Aliquat 336-HF and the bromide salt of Aliquat 336-HBr. Extraction was achieved, except for Ta in the Aliquat 336-HBr system, where no extraction occurred, irrespective of the HBr concentration.

Hussaini and Rice^[64] leached Nb/Ta ore with 10.8 M H₂SO₄. Figure 11 shows the flow sheet used for the processing and extraction of Nb and Ta using Alamine 336 from the leach liquor as the tertiary amine, with kerosene/xylene as diluents and n-decanol as a modifier. The aqueous phase was 30% H₂O₂ at 60 °C and 48% HF at room temperature. The separation factor was higher when using kerosene (1.79 ± 0.074) than xylene (1.13 ± 0.098) as diluent. The extraction of both metals was the highest at an H₂SO₄ concentration of 0.5 M and an HF concentration in the range of 0.2 – 0.5 M for the Nb extraction and 0.1 – 0.2 M for the Ta extraction. 88.2% Nb and 99.3 % Ta, respectively, were stripped from 10% Alamine 336 in kerosene in the presence of 25 g/L ammonium carbonate. The purity of the Nb and Ta products achieved was 91.2% and 92.7%, respectively.

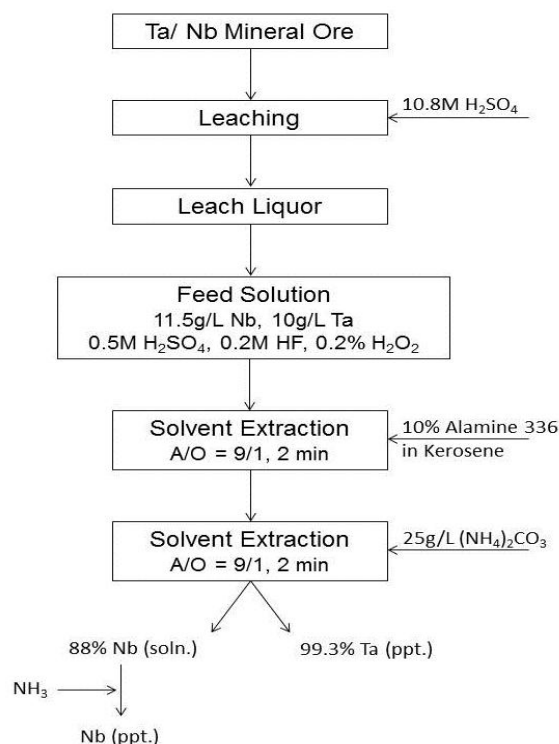


Figure 11 - Flow sheet for extraction and separation of Nb from Ta by Alamine 336 in kerosene^[64]

2.5.5 Recovery

According to literature, common stripping agents used to recover metals from an organic phase include acids (ex. H_2SO_4 and HCl), bases (ex. Na_2CO_3 and NaOH), thiourea with HCl , and water. Although little data is available on the recovery of Ta and Nb, a brief overview of these stripping agents and their uses for various metals are discussed.

2.5.5.1 Acids

Devi et al^[65] suggested that H_2SO_4 concentrations of between 0.001 and 0.12 mol/dm³ are needed for the recovery of manganese after extraction with D2EHPA and sulphate solutions. They further showed that 0.02 mol/dm³ H_2SO_4 gave the best recovery of 97.5%. Mohapatra^[66], Htwe and Lwin^[67] and Zhu and Cheng^[68] used 1 mol/dm³ H_2SO_4 to recover all the Nb from a D2EHPA organic phase.

Although sulphate media was still the most common, there were a surprising number of chloride-based systems.^[22,40] Shen and Xue^[69] investigated 0.1 to 6 mol/dm³ HCl for the recovery of Pd, Au and Pt and showed the best extraction when using 0.1 mol/dm³ HCl for the recovery of Au and 6 mol/dm³ HCl for the recovery of Pd.

2.5.5.2 Bases

Kulkarni et al^[70] proposed using 0.1 to 2 mol/dm³ Na_2CO_3 for the recovery of U after extraction with tri-n-octyl phosphine oxide (TOPO) and water. A 0.5 mol/dm³ solution gave a 90% recovery of U. In another study, Seyfi and Abdi^[71] investigated the extraction of Ti(IV) with TBP in sulphate and nitrate acid mediums, and found that 2 mol/dm³ Na_2CO_3 was most effective by recovering 99% of the Ti. Venkateswaran and Palanivelu^[72] investigated the extraction of Cr(IV) with tributyl ammonium bromide in dichloromethane and stripped the Cr(IV) using 1 mol/dm³ NaOH , yielding a recovery of 98% Cr(IV).

2.5.5.3 Thiourea

Li et al^[73] suggested using 1 mol/dm³ acid thiourea for the recovery of Au while Sun and Lee^[74] used 0.1 to 1 mol/dm³ thiourea with 0.5 mol/dm³ HCl for the recovery of 99% Pd(IV) and less than 8% Pt(IV).

2.5.5.4 Water

El-Hazek et al^[54] used 7 mol/dm³ HF with 6 mol/dm³ H₂SO₄ and octanol for the extraction of Ta and Nb and distilled water for 100% recovery at a pH of 2.0 (buffering with HF).

2.6 Pertraction

2.6.1 Introduction

When two phases are separated by a membrane during SX, the process is called pertraction. Since the membranes are only a physical support for the liquid–liquid interface, it does not function as an active component of a system.^[75] Membranes are already used in various industries as a clean technology, including in the water, textile, tanneries, paper, metal plating, electronics, pharmaceutical, food, metal separation, acid separation and hydrocarbon industries. According to Koltuniewicz and Drioli, clean technologies are defined: “*as any technique, process, product and/or solution developed or adopted, that reduces or even eliminates the amount of pollutants emitted and waste created, energy consumed and noise generated while helping to save raw materials, natural resources and energy to sustain environmental preservation over the long run*”.^[76]

According to some literature, pertraction is also called membrane based solvent extraction (MBSX) and is an alternative to classical SX^[41,77,78,79,80,81,87], where mass-transfer between two immiscible liquids occurs from the liquid-liquid interface immobilized at the mouth of the pores of a microporous wall, which is not wetted by one of the phases in contact. The main aim of this approach is to avoid dispergation of the liquid phase which in many systems is connected with emulsion formation problems and with the entrainment of the solvent droplets and their subsequent loss.^[77] The solvent can be regenerated by membrane based solvent stripping (MBSS) where the solute is re-extracted into the stripping solution.

The main advantages, apart from the dispersion free operation, of using the membrane-based pertraction over the traditional SX are that the pertraction: allows independent variation of the phase flow rates, does not require a density difference between the phases, can handle systems that form emulsions and provides a very high interfacial area per unit volume especially when using hollow-fibre modules. The first paper on MBSE was published by Kim^[82] in 1984.

2.6.2 Principles

A schematic flow sheet of the simultaneous MBSX and membrane-based solvent stripping (MBSS) processes with the closed loop of the solvent is shown in Figure 12. With this process, both the recovery of the solvent and the concentration of the solute can be achieved. Preferable contactors for MBSE and MBSS are hollow fibre contactors due to the high membrane areas provided.^[77]

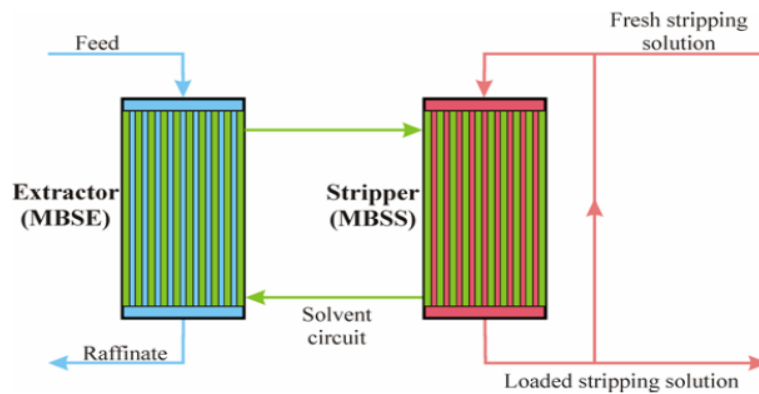


Figure 12 - Flow sheet of simultaneous MBSE and MBSS processes ^[77]

Traditionally, contactors with flat sheet and cylindrical walls were used in MBSX or MBSS, but due to new developments, hollow fibre contactors in cylindrical modules in several sizes are commercially available.^[83] There are two configurations of hollow fibre contactors, i.e. they can either be run with parallel flow of the phases or with cross flow of the phases. A hollow fibre contactor with a cross flow of the phases is shown in Figure 13.^[84]

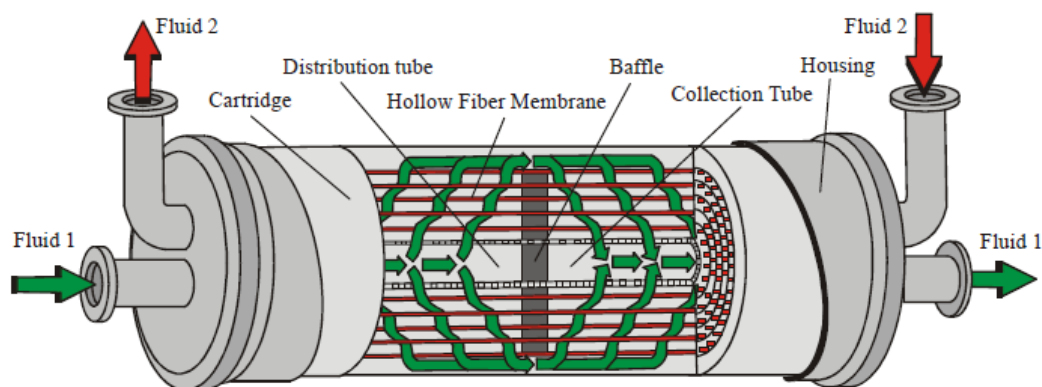


Figure 13 - Two phase hollow contactor with cross flow of phases (Liqui Cel Extra-Flow)^[84]

A modular hollow fibre contactor, containing planar elements with a flowing head of fibres and cross flow of one phase, can also be used as a two phase contactor.^[85] For a more detailed discussion, various reviews on two phase hollow fibre contactors have been published.^[78,81,86] The mass-transfer characteristics of two phase contactors have also been elaborated by Schlosser et al.^[77] Accordingly, it was shown that the mass transfer of solutes between two liquid phases in membrane contactors is regulated by the phase equilibrium and the mass transfer resistance involved.^[87]

2.7 Future of SX and Pertraction

The Southern African subcontinent has one of the highest concentrations of mineral wealth, and the value-added recovery of industrial minerals and metals is expected to increase in future, requiring the further development of separation, especially SX technology for the SA market.^[39]

A better understanding is needed for the continued use of multiphase systems for separation and recovery purposes for the successful use in industrial applications. Investigation need to be done into the working of mass-transfer, the reactions taking place, interfacial efficiencies and development of new contactor generations for the advancement in the field of SX technology. For achieving this goal, a better understanding of the physical chemistry of experimental data involved with the separation and recovery of metals is needed by utilising molecular modelling and quantum chemistry methods, hereby developing new types of extractants.^[88]

Other areas that need optimisation in SX:^[89]

- Speciation of the mass-transfer for the optimisation of chemical separations.
- Investigation into new recovering techniques with regards to the purity of the obtained products.
- Advancements into the recovering of organic phases that degrade.
- Reclamation of product waste and investigation into the analyses and formation of waste products.
- Researching the role of surfactants (chemical compounds that lower the interfacial tension between two liquids) in SX for the optimisation of separation and mass-transfer.

To date, less than 20% of plants have successfully changed from mixer settler units to pertraction units, but this can change in future. As current units are applied in industry, the technology will change to fit real solutions, to produce the expected mass-transfer kinetics for an economically viable industry. New types of monitoring equipment and techniques are needed for plant operation and obtaining data for modelling, which will be used by designers and manufacturers for scale-up.^[89]

An informed decision for the scale-up to plant size industry or to abandon the process is determined by:^[89]

- Quality and purity of the end-product (dependant of product specifications)
- Ease and economy of the recovery of the end-product
- The environmental impact of such an industry
- Health and safety impacts on the workers
- Sustainability of the materials used for construction and
- Process variables including the compositions of the streams, flow rates and operating conditions.

This is a promising technology, with pitfalls still to be investigated. As the understanding of this technology increases, so will its uses increase.

2.8 Conclusion

Since Ta and Nb are usually found together in nature and since Ta and Nb have similar properties, there have been more than 200 years of investigations on the separation of the two metals. In spite thereof, the separation to date remains tedious and expensive with numerous challenges. These metals have significant applications in the modern world, of which the most important are for structural purposes and nuclear power plant uses.

Ta and Nb are mined all over the world, with most of the minerals coming from Brazil and Australia. These minerals are mainly leached with high hydrofluoric and sulphuric acid concentrations and high temperatures. Separation of Ta and Nb traditionally occurs via a chlorination route using distillation for separation or a fluorination route where SX is employed for separation. Extraction of the metals with extractants including MIBK, TBP, amines and octanols have been and are currently under investigation. Further research has also focused on the recovery of the metal from the organic phase.

The latest SX technology is based on membrane-based solvent extraction or pertraction. Commercial pertraction units are available, with great advantages toward the ease of separation and the low cost of the process. It is therefore likely that more emphasis will be focussed on this technology in future.

Chapter 3

Materials & Methods

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3.1 Materials

The following materials were used in this study:

Extractants: Di-iso-octyl-phosphinic acid (PA) - Sigma Aldrich

Di-(2-ethylhexyl)-phosphoric acid (D2EHPA) - Sigma Aldrich

2-Thenoyl-trifluoro-acetone (TTA) - Sigma Aldrich

Tri-n-octyl-amine (Alamine 336) - Cognis

Tri-octyl-methyl ammonium chloride (Aliquat 336) - Sigma Aldrich

1-Octanol - Alfa Aesar, 2- and 3-Octanol - Sigma Aldrich

Solvent: Cyclohexane - Saarchem product from Merck

Acids: 32% Hydrochloric acid (HCl) - Saarchem product from Merck

55% Nitric acid (HNO₃) - Saarchem product from Merck

95% Sulphuric acid (H₂SO₄) - Saarchem product from Merck

70% Perchloric acid (HClO₄) - ACE Chemicals

Base salts: Sodium carbonate (Na₂CO₃) - Saarchem product from Merck

Sodium hydroxide (NaOH) - CJ Chem.

Thiourea – Rochelle Chemicals

Commercial Ta/Nb metal: 99.5% NbF₅ and TaF₅ salt - Alfa Aesar

1000 ppm NH₄TaF₆ in H₂O with trace amounts of F⁻ - Alfa Aesar

10000 ppm NH₄TaF₆ in H₂O with trace amounts of HF - Ultraspec

1000 ppm and 10000 ppm NH₄NbF₆ in H₂O with trace amounts of HF - Ultraspec

3.2 Methods

3.2.1 General Procedure

Ta/Nb solutions were prepared by dissolving Nb and Ta salts in deionised water (water with a resistivity of $>18 \text{ M}\Omega/\text{cm}$ was obtained from a Milli-Q system, Millipore). In addition, an acid at various concentrations was added to the aqueous phase. The organic phase was subsequently prepared by adding specific amounts of various extractants to the solvent cyclohexane with the addition of 3% of a modifier. A constant volume phase ratio of 1:1, consisting of 25 mL from both the aqueous and the organic phases were placed in a polypropylene bottle before being shaken in a Labcon shaker/heater at 25°C and 350 rpm for 60 min, to ensure equilibrium had been reached (Figure 14). After extraction, the biphasic solution was poured into a separation funnel and the liquid phases were left to settle at 25°C . After separating the phases, the aqueous phase was analysed by ICP-OES (Thermo Scientific iCap 6000 series – iTEVA software), with an analytical error of 10%. In Appendix A the quantitative determination of Ta and Nb by ICP-OES is presented.

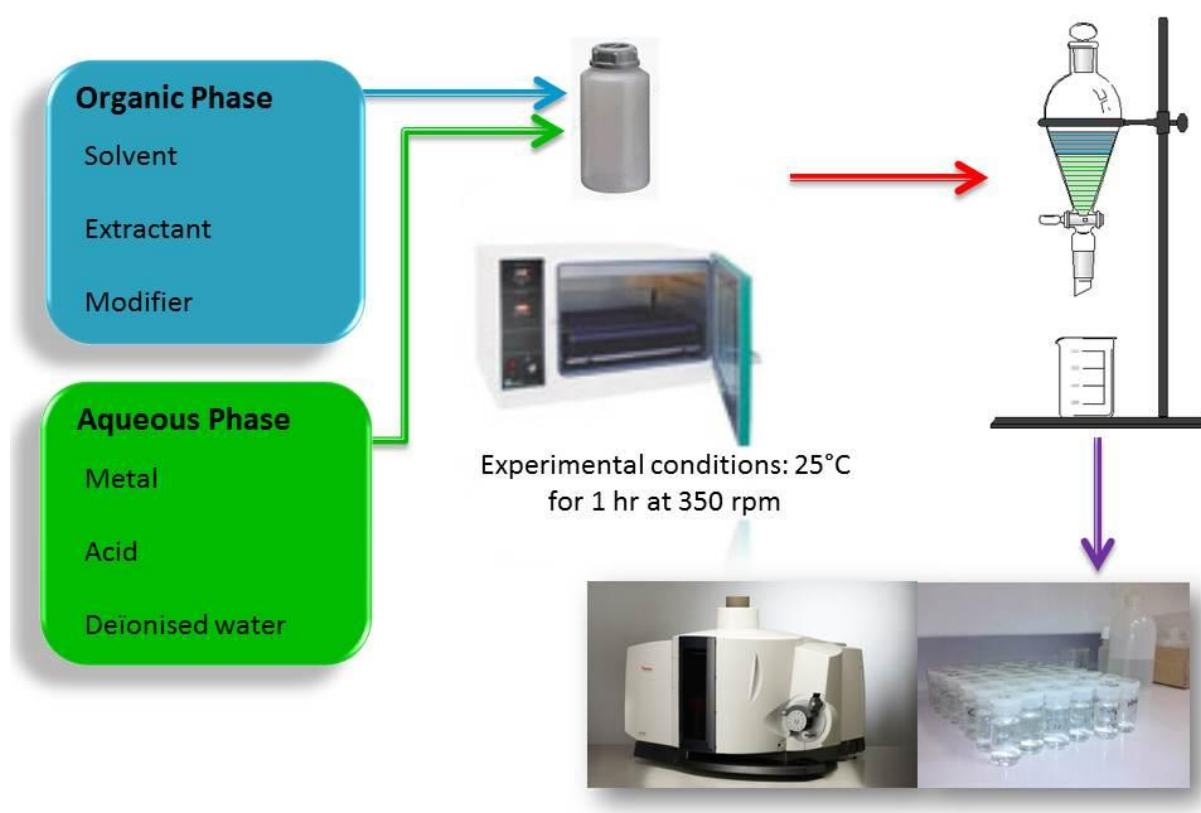


Figure 14 - Experimental setup used for solvent extraction

3.2.2 SX with Ta(Nb)F₅

3.2.2.1 Effect of Acid and Extractant

To determine the solvent extraction of Ta(Nb)F₅, a stock solution of 5 g/L of both TaF₅ and NbF₅ (Stock 1) was prepared. Four different acids, HCl (0 – 9 mol/dm³), HNO₃ (0 – 10 mol/dm³), H₂SO₄ (0 – 15 mol/dm³) and HClO₄ (0 – 10 mol/dm³) were prepared in 250 mL volumetric flasks and used to determine the best combination for extraction. 24 mL of Stock 1 was added to each acid concentration. Cyclohexane was used as the solvent and 3% v/v 1-octanol was added as the modifier for the organic phase. To determine with which type of extractant the Ta and Nb metal formed complexes, eight different extractants were used, including the cation exchangers PA and D2EHPA, the neutral solvating extractant TTA and the anion exchangers Alamine 336, Aliquat 336, 1-octanol, 2-octanol and 3-octanol. The extractant to metal ratio (E/M per molar ratio) for this study was 10:1. Extraction experiments were carried out as stated in the general experimental procedure described in Section 3.2.1.

3.2.2.2 Effect of E/M Ratio

From the results obtained in Section 3.2.2.1, the extractants PA and D2EHPA were used to determine the effect of the extractant to metal ratio on the extraction. Cyclohexane was used as solvent and 3% v/v 1-octanol was used as the modifier for the organic phase. The extractant to metal ratio was varied from 0.1:1 to 20:1. For these experiments, 3 of the above acids, at two concentrations each, were evaluated in the aqueous phase, including HCl (5 and 9 mol/dm³), HNO₃ (7 and 10 mol/dm³) and H₂SO₄ (4 and 10 mol/dm³). 24 mL of Stock 1 was added to each 250 mL of acid at a specific concentration. Extraction experiments were carried out as stated in the general experimental procedure described in Section 3.2.1.

Subsequently, from the above experiments, H₂SO₄ (4, 7, 10, 12 and 15 mol/dm³) was re-evaluated by again using the two extractants, PA and D2EHPA, including a wider range of acid concentration as well as repeating 4 and 10 mol/dm³ H₂SO₄ to obtain repeatability data. The extractant to metal ratio was again varied from 0.1:1 to 20:1. Cyclohexane was used as the solvent and 3% v/v 1-octanol was used as the modifier for the organic phase.

3.2.3 SX with $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$

After showing the suitability of the separation technique for Ta and Nb, the next step entailed the optimisation of the solvent extraction. In this section the Ta and Nb fluoride solution $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ was used.

According to the results obtained from the study with $\text{Ta}(\text{Nb})\text{F}_5$, a feasibility study was conducted to determine whether the extraction of $\text{Ta}(\text{Nb})\text{F}_5$ was similar to the extraction of $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$. For this purpose, 100 ppm of $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ (in H_2O solution) was added to an aqueous phase containing 4, 10 and 14 mol/dm^3 H_2SO_4 (prepared in 250 mL volumetric flasks). For the organic phase, batch extractions were done with both PA and D2EHPA with an E/M molar ratio of 10:1. Cyclohexane was used as the solvent and 3% v/v 1-octanol was used as the modifier for the organic phase. Extraction experiments were carried out as stated in the general experimental procedure described in Section 3.2.1.

3.2.3.1 Effect of H_2SO_4 Concentration in Aqueous Phase Solutions

After demonstrating the suitability of $(\text{NH}_4)\text{Ta}(\text{Nb})\text{F}_6$ for SX using the above described procedure, a more detailed study was undertaken to optimise the acid concentration, E/M ratio and contact time.

To determine the effect of acid concentration on extraction, an aqueous phase consisting of H_2SO_4 (0 to 8 mol/dm^3) with 100 ppm of $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ in H_2O solution was prepared in 250 mL volumetric flasks. For the organic phase, PA and D2EHPA were used as extractants in a E/M ratio of 10:1. Cyclohexane was used as the diluent and 3% v/v 1-octanol was used as the modifier.

3.2.3.2 Effect of Extractant Concentration

To determine the effect of the extractant to metal ratio, the two extractants used for the organic phase were again PA and D2EHPA. Cyclohexane was used as the solvent and 3% v/v 1-octanol was used as the modifier for the organic phase. The extractant to metal ratio was varied from 0.1:1 to 20:1. H_2SO_4 with a concentration of 4 mol/dm^3 (in a 250 mL volumetric flask) containing 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ in an H_2O solution was used. Extraction experiments were carried out as stated in the general experimental procedure described in Section 3.2.1.

3.2.3.3 Effect of Contact Time

To determine the rate of extraction, the aqueous phase consisted of 4 mol/dm³ H₂SO₄ containing 100 ppm NH₄Ta(Nb)F₆ in an H₂O solution. For the organic phase, the extractants PA and D2EHPA were used to determine the kinetic equilibrium of extraction of Ta and Nb. Cyclohexane was used as the solvent and 3% v/v 1-octanol was used as the modifier for the organic phase. The extractant to metal ratio was 10:1 to ensure maximum extraction.

Extraction experiments were carried out by preparing a constant volume phase ratio of 1:1 (25 mL from both the aqueous and the organic phases, shaken in polypropylene bottles in a Labcon shaker/heater at 25 °C and 350 rpm. Contact time was varied from 1 minute to 120 minutes. After extraction, the biphasic solution was poured into a separation funnel and the liquid phases were left to settle and separate at 25 °C. After separation, the aqueous phase was analysed by ICP-OES.

3.2.4 SX Recovery

For the recovery of the metals, 1L aqueous and organic solutions were prepared as follows: The aqueous phase consisted of 4 mol/dm³ H₂SO₄ with 100 ppm of NH₄Ta(Nb)F₆ in an H₂O solution. The organic phase consisted of PA as the extractant in an E/M ratio of 10:1 for maximum extraction, with cyclohexane as the solvent and 3% v/v 1-octanol as the modifier. Extraction experiments were carried out as stated in the general experimental procedure described in Section 3.2.1. From this extractive procedure, a loaded organic phase was obtained and used further.

Stripping experiments were done using the loaded organic phase. Stripping agents, including acids [H₂SO₄ (0 to 8 mol/dm³) and HCl (0.05 to 8 mol/dm³)], bases [Na₂CO₃ (0.05 to 5 mol/dm³) and NaOH (0.01 to 3 mol/dm³)] and other stripping agents including thiourea (0.01 to 1 mol/dm³) with 0.5 mol/dm³ HCl and water, were used in the aqueous phase in an attempt to recover the metal from the organic phase.

The general recovery experimental procedure was similar to the initial extraction experiments: Recovery experiments were done by taking a constant volume phase ratio of 1:1 (25 mL from both the aqueous stripping and loaded organic phases), placing it in a polypropylene bottle and shaking it in a Labcon shaker/heater at 25 °C and 350 rpm for 60 min. After extraction, the biphasic solution was poured into a separation funnel and the liquid phases were left to settle and separate at 25 °C. The aqueous phase was analysed by ICP-OES.

3.2.5 Membrane-based Solvent Extraction

For the membrane-based solvent extraction (pertraction), the following conditions were used. One litre of 4 mol/dm³ H₂SO₄ with 100 ppm NH₄Ta(Nb)F₆ in an H₂O solution was added to an equal volume of PA solution to obtain an E/M ratio of 10:1 with cyclohexane as the solvent and 3% v/v 1-octanol as the modifier. A Liqui Cel Extra-Flow hollow fibre membrane tube was used with an aqueous inlet pressure of 68.947 kPa (10 Psi), aqueous outlet pressure of 55.158 kPa (8.0 Psi), organic inlet pressure of 34.474 kPa (5.0 Psi) and organic outlet pressure of 27.579 kPa (4.0 Psi), maintaining a flow rate of 128 L/h. Samples were taken at various intervals during the contacting period which ranged from 1 to 120 minutes. In Figure 15, a schematic representation of the pertraction setup is given.

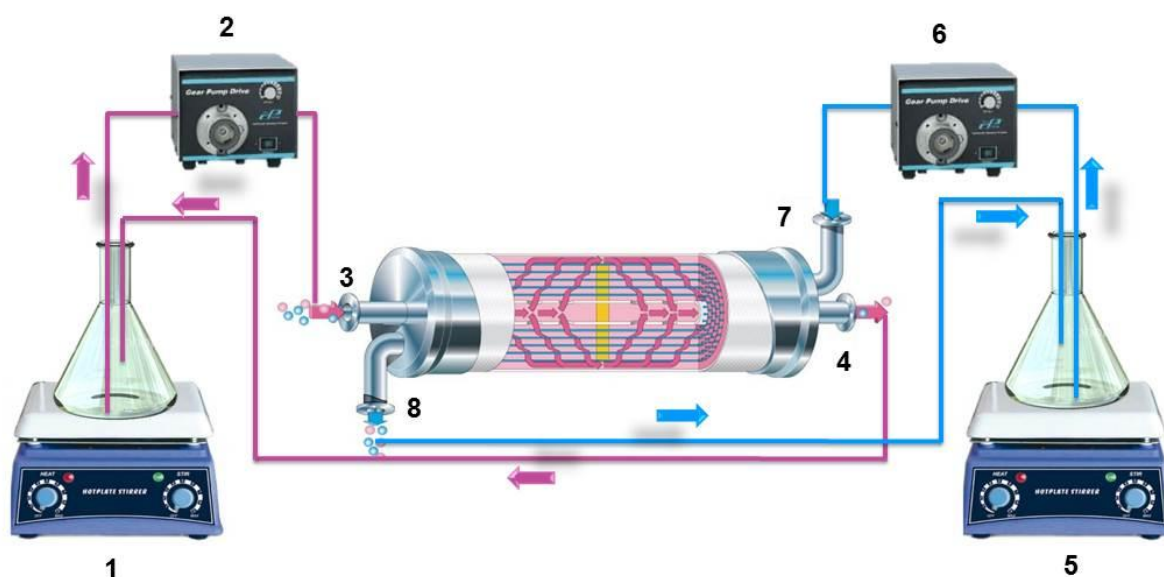


Figure 15 - Membrane-based solvent extraction experimental setup (1 – Conical flask with aqueous phase on stirrer, 2 – pump for aqueous phase, 3 – aqueous phase inlet, 4 – aqueous phase outlet, 5 – conical flask with organic phase on stirrer, 6 – pump for organic phase, 7 – organic phase inlet, 8 – organic phase outlet)

After pertraction, the recovery procedure was as follows: An equal volume of aqueous and organic phases are used in these experiments, where in one experiment deionised water (1L) was used, while in another experiment 4 mol/dm³ H₂SO₄ was used as the aqueous stripping phase to recover the extracted Ta and Nb from the loaded organic phase back into an aqueous phase.

For accuracy purposes, a control sample was taken before the pertraction experiment by shaking equal volumes of the aqueous phase (4 mol/dm³ H₂SO₄ with 100 ppm of NH₄Ta(Nb)F₆ in an H₂O solution) and organic phase (PA solution to obtain an E/M ratio of 10:1 with cyclohexane as solvent and 3% v/v 1-octanol as the modifier) in the shaking incubator at 25 °C and analysing the residual Ta/Nb in the organic phase using ICP-OES.

Chapter 4

Results & Discussion

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4.1 SX with Ta(Nb)F₅

Various Ta and Nb salts are commercially available, including Ta(Nb)F₅, Ta(Nb)Cl₅ and K₂Ta(Nb)F₇. Since aqueous solubility is required for solvent extraction, the aqueous solubility of these salts was determined and the pentafluorides dissolved with ease in deionised water. K₂Ta(Nb)F₇ was insoluble, while the pentachlorides formed a sol-gel solution. As a result, Ta(Nb)F₅ was used in this study, which was prepared as a 22.4 mmol/dm³ stock solution.

4.1.1 Effect of Acid and Extractant

To determine the effect of acids and extractants, four different acids, including HClO₄ (0 – 10 mol/dm³), HNO₃ (0 – 10 mol/dm³), HCl (0 – 9 mol/dm³) and H₂SO₄ (0 – 15 mol/dm³), were used as the aqueous phase, while eight different extractants were used in the organic phase, including the cation exchangers PA and D2EHPA, the neutral solvating extractant TTA, and the anion exchangers Alamine 336, Aliquat 336, 1-octanol, 2-octanol and 3-octanol (as discussed in Section 3.2). The following results are discussed with reference to the aqueous phases used.

Figures 16 and 17 show the respective results for the Ta and Nb extraction in a perchloric acid medium. According to Figure 16, the extractants PA and D2EHPA showed the highest extraction (94% and 91%, respectively) at 7 mol/dm³ HClO₄. When using Alamine 336 and Aliquat 336, precipitation occurred (most probably due to hydrolysis), resulting in a 100% extraction at 0 mol/dm³ HClO₄. Precipitation and thus hydrolysis of the metal also occurred with the addition of HClO₄, but decreased with increasing acid content. The highest extraction achieved with Alamine 336 was 55% and with Aliquat 336 53% which, similarly to PA and D2EHPA, occurred at an HClO₄ concentration of 7 mol/dm³. Similarly to Alamine 336 and Aliquat 336, precipitation also occurred when using TTA at low HClO₄ concentrations. According to ICP results, 50% extraction was attained at 0 mol/dm³ HClO₄, while the highest extraction of 64% was again achieved at 7 mol/dm³ HClO₄. TTA therefore performed similarly to the behaviour observed with Alamine 336 and Aliquat 336. 1-, 2- and 3-octanol showed an average of 59% extraction of Ta, again at 7 mol/dm³ HClO₄. The octanols' performance is therefore comparable to the results obtained by Alamine 336, Aliquat 336 and TTA when using HClO₄. The shape of the extraction curve is possibly due to speciation, which unfortunately fell beyond the scope of this study, but which will be investigated in the near future.

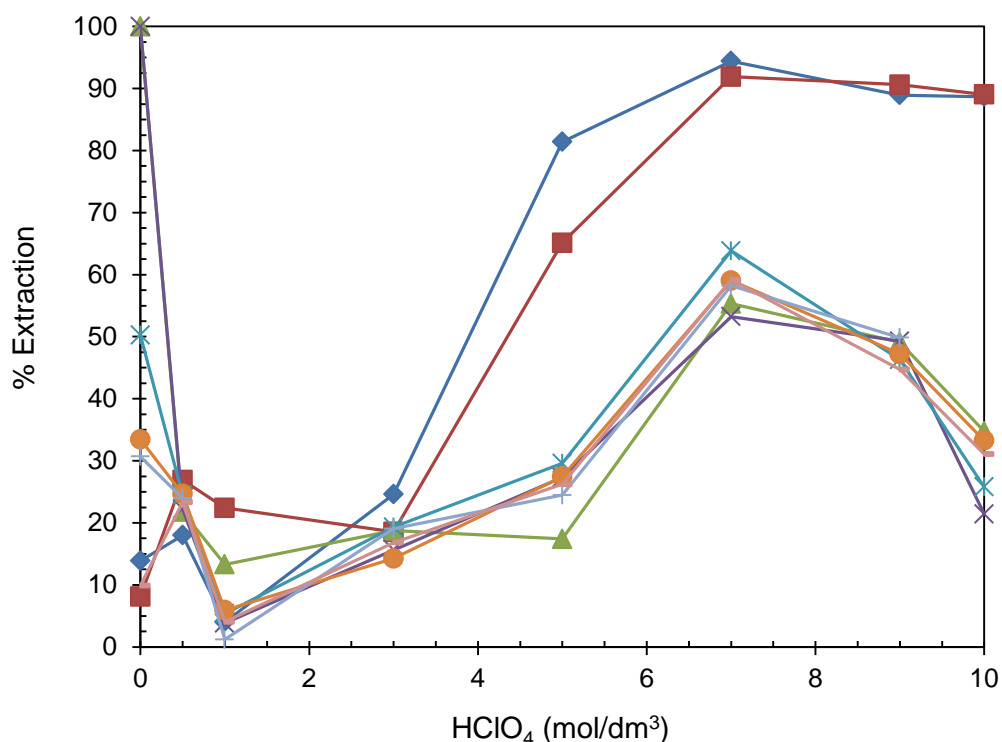


Figure 16 - Extraction of Ta (2.03×10^{-3} mol/dm³) using HClO₄ (0 – 10 mol/dm³) with eight different extractants at 25°C, E/M ratio of 10:1, phase ratio of 1:1 (♦ - PA, ■ - D2EHPA, ▲ - Alamine 336, × - Aliquat 336, * - TTA, ● - 1-octanol, + - 2-octanol, - 3-octanol).

Figure 17 represents the results obtained for the Nb extraction in a perchloric acid medium. The extractants PA and D2EHPA yielded 92% and 91% extraction, respectively, at 7 mol/dm³ HClO₄, confirming their superior ability to extract Ta and Nb in a perchloric medium. Precipitation (and hydrolysis) was also a problem for Nb with Alamine 336 and Aliquat 336, resulting in a 100% extraction with Alamine 336 and a 72% extraction with Aliquat 336 at 0 mol/dm³. The highest SX extraction achieved with Alamine 336 was 72%, while being 63% for Aliquat 336. Similarly, precipitation and hydrolysis of the metal was a problem with TTA, where 72% was the highest extraction achieved, which was again observed at 7 mol/dm³ HClO₄. 1-, 2- and 3-octanol showed an optimum extraction of 65% for Nb in 7 mol/dm³ HClO₄, which was again comparable to the results obtained with Alamine 336, Aliquat 336 and TTA.

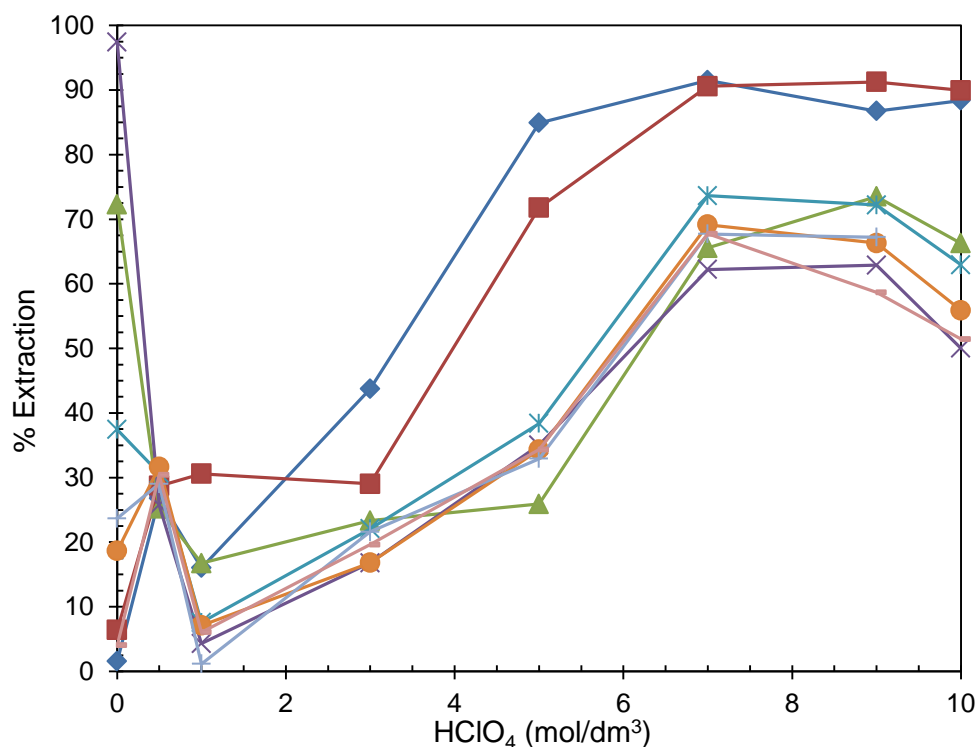


Figure 17 - Extraction of Nb (2.98×10^{-3} mol/dm³) using HClO₄ (0 – 10 mol/dm³) with eight different extractants at 25°C, E/M ratio of 10:1, phase ratio of 1:1 (♦ - PA, ■ - D2EHPA, ▲ - Alamine 336, × - Aliquat 336, * - TTA, ● - 1-octanol, + - 2-octanol, - 3-octanol).

When comparing Figure 16 with Figure 17, it is clear that PA and D2EHPA have the highest affinity for extracting Ta and Nb in a HClO₄ medium at concentrations of 7 mol/dm³ and above, while the other extractants all behaved similarly for both Ta and Nb. The highest extraction was achieved at 7 mol/dm³ HClO₄, except for the extraction of Nb using Alamine 336 and Aliquat 336, where the highest extraction was achieved at 9 mol/dm³. Precipitation and hydrolysis were significant problems when the samples were allowed to age for 4 days or more after extraction and before analyses.

Figure 18 shows the separation factors of Ta and Nb for the eight extractants investigated using HClO₄, where the separation factor (β) was calculated according to Equation 4 (Chapter 2). PA showed a separation factor of 1 at 0 mol/dm³ HClO₄, which decreased as the acid concentration increased, meaning that although the extraction increased as the HClO₄ concentration increased, the selectivity towards Ta decreased. Similar results were obtained for D2EHPA, where the highest separation factor (0.3) was achieved at 3 mol/dm³, decreasing further as the concentration increased. Alamine 336, Aliquat 336, TTA, 1-octanol and 3-octanol showed no significant correlation between the separation factor and the HClO₄ concentration, but the separation factor increased above 7 mol/dm³ HClO₄. According to Vin

and Khopkar^[90], when the pH is below 0, Nb extracts more readily while when the pH is above 1, Ta extracts more readily. Therefore, between 0 and 1 mol/dm³ HClO₄ a difference in extraction occurs because of the pH change in this region. At 0 mol/dm³ the pH is 7, at 0.5 mol/dm³ the pH is 0.3 and at 1 mol/dm³ the pH is 0. Because of the low selectivity towards the metal separation, in addition to the precipitation problems observed, this acidic medium was not investigated further.

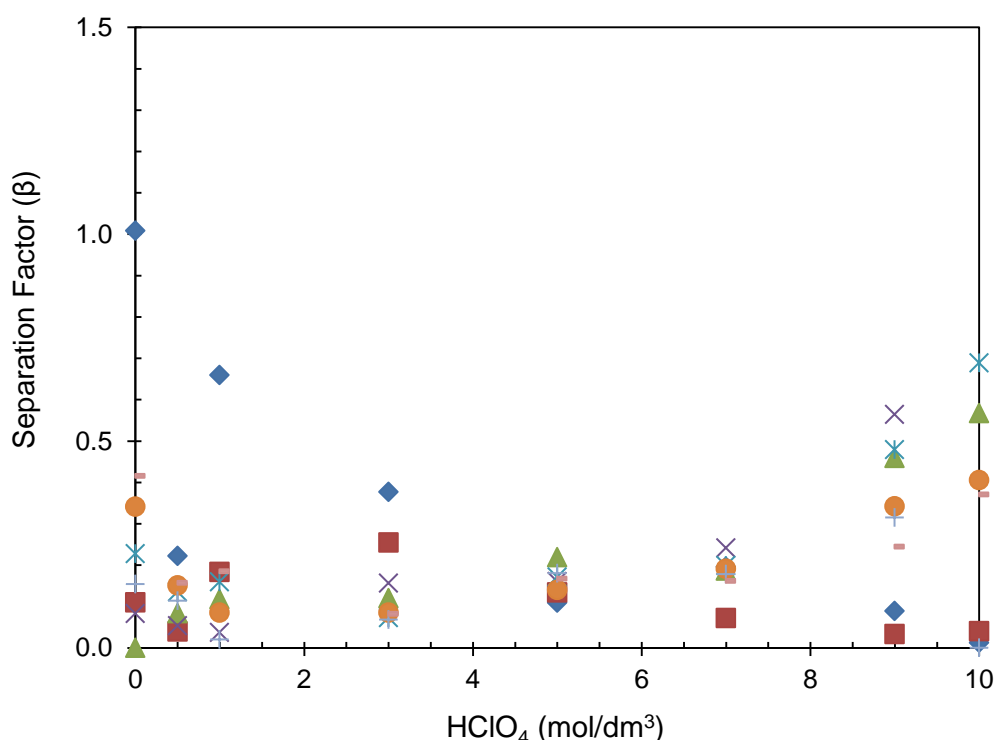


Figure 18 – Separation factor for the extraction of Ta (2.03 mol/dm³) and Nb (2.98 mol/dm³) using HClO₄ (0 – 10 mol/dm³) with eight extractants at 25°C, E/M ratio of 10:1, phase ratio of 1:1 after 1 hr at 350rpm (♦ - PA, ■ - D2EHPA, ▲ - Alamine 336, × - Aliquat 336, * - TTA, ● - 1-octanol, + - 2-octanol, - 3-octanol).

In Figure 19 the Ta and Nb extraction as well as the separation factors obtained in a nitric acid environment is presented. In Figure 19(i) the results for the Ta extraction are presented. Similarly to the results obtained for HClO₄, PA and D2EHPA showed an increased extraction as the HNO₃ concentration increased, yielding the highest extractions of 86% and 73%, respectively, at 10 mol/dm³ HNO₃. At 0 mol/dm³ HNO₃, 100% extraction of Ta with Alamine 336 and Aliquat 336 was achieved, but similarly to the extraction in HClO₄, precipitation of the metal caused this high extraction percentage to be measured with the ICP-OES. Both Alamine 336 and Aliquat 336 showed levels of extraction in the range of between 0 and 20%, while extraction seemed independent of the HNO₃ concentration. Again, in TTA, the metals

precipitated at 0 mol/dm³ HNO₃ and no extraction was achieved above 0 mol/dm³ HNO₃. Similarly, 1-, 2- and 3-octanol did not provide any extraction in HNO₃, except for the slight increase observed at an HNO₃ concentration of 4 mol/dm³.

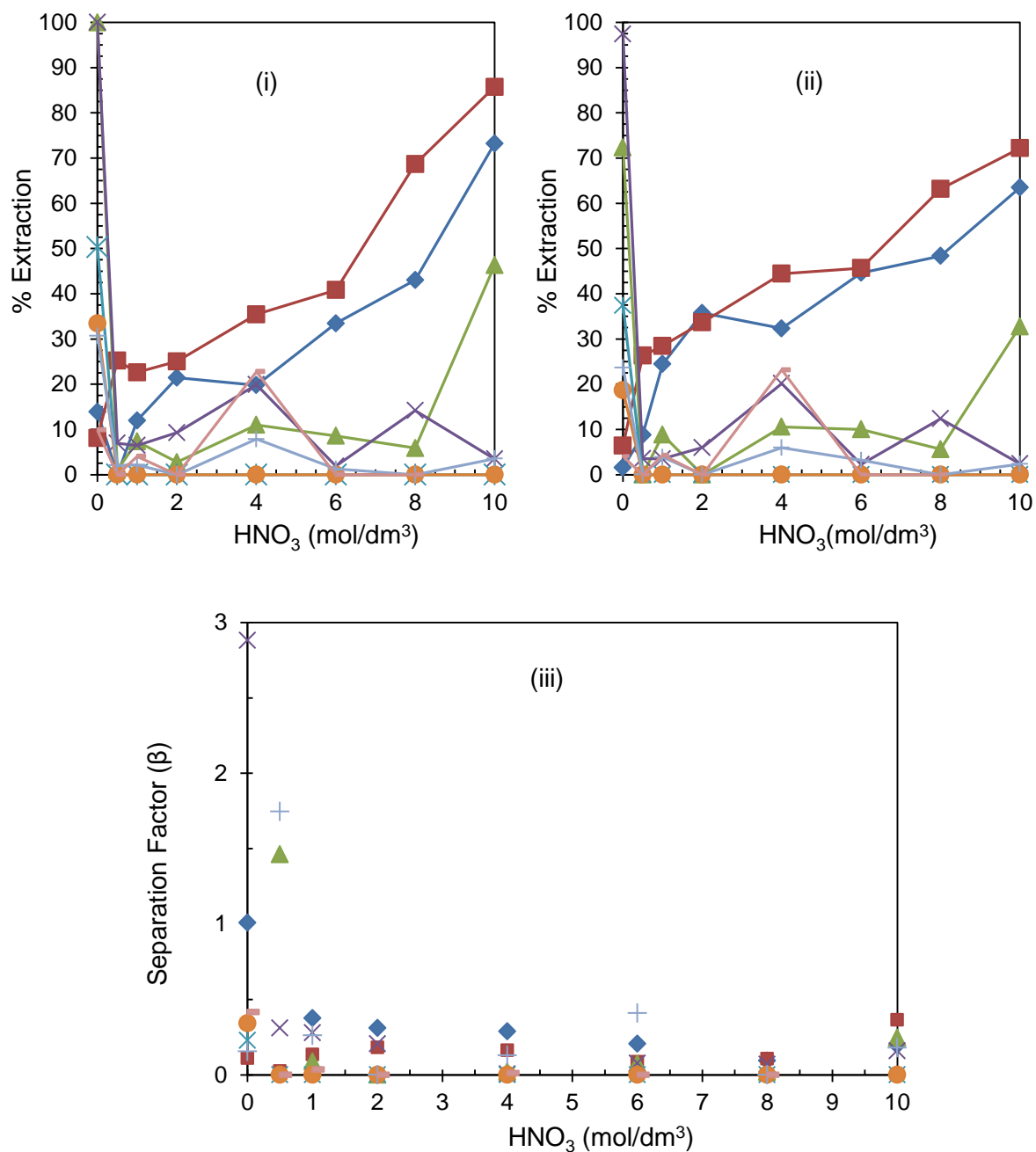


Figure 19 – Extraction of (i) Ta (2.03 x 10⁻³ mol/dm³) (ii) Nb (2.98 x 10⁻³ mol/dm³) and (iii) the separation factor for Ta and Nb using HNO₃ (0 – 10 mol/dm³) with eight different extractants at 25°C, E/M ratio of 10:1, phase ratio of 1:1 (◆ - PA, ■ - D2EHPA, ▲ - Alamine 336, × - Aliquat 336, * - TTA, ● - 1-octanol, + - 2-octanol, - - 3-octanol).

In Figure 19(ii), the results for the Nb extraction in a nitric acid medium are presented. PA and D2EHPA again yielded the highest extraction of 64% and 72%, respectively, at 10 mol/dm³ HNO₃. The extraction increased nearly linearly with increasing HNO₃ concentration over the entire HNO₃ concentration range. Alamine 336 and Aliquat 336 again showed 72% and 100% extraction, respectively, in 0 mol/dm³ HNO₃, due to precipitation rather than extraction-based removal of the metal from the aqueous phase. After the initial precipitation-based extraction, the extractant-based extraction ranged between 0 and 20% seemingly independent of the HNO₃ concentration. Apart from the initial precipitation, no extraction was achieved with TTA. Similarly, all three octanol extractants showed negligible extraction, irrespective of the HNO₃ concentration.

When comparing Figures 19(i) and (ii), PA and D2EHPA showed the best extraction results for both Ta and Nb at 8 – 10 mol/dm³ HNO₃. Precipitation was again a problem with the amine extractants, TTA and the alcohols. It is interesting to note that the slight extraction observed with TTA at 4 mol/dm³ for Ta was also observed when using Nb, suggesting that this increased extraction was not due to an experimental error, but probably due to an HNO₃ dependant complexation behaviour of TTA. Therefore, similarly to the behaviour in a HClO₄ medium, the suitability of these extractants in a nitric acid medium, for an industrial setup, would require further investigation.

Figure 19(iii) represents the separation factors of Ta and Nb for the eight extractants investigated. At higher concentrations than 0.5 mol/dm³ HNO₃, the separation factor was below 1. Thus no significant selectivity was observed. Aliquat 336 showed a separation value of 2.9, due to the precipitation at 0 mol/dm³. TTA, 1-, 2- and 3-octanol showed separation factors below 0.5. Overall, PA yielded the highest separation factor over the entire HNO₃ acid range, meaning that PA gave the best selectivity for the separation of Ta from Nb.

The results for the Ta extraction in a hydrochloric acid medium are presented in Figure 20(i). PA and D2EHPA showed a near linear extraction as the HCl concentration increased, with the highest extractions of 87% and 84%, respectively, at 9 mol/dm³ HCl, as was observed in HClO₄ and HNO₃. Due to the precipitation from the aqueous phase with Alamine 336 and Aliquat 336 in the organic phase, again a 100% extraction of Ta in 0 mol/dm³ HCl was observed. In accordance with the results obtained with HClO₄ and HNO₃, no precipitation was observed when acid was added to the system. Both Alamine 336 and Aliquat 336 yielded an extraction that was independent of the HCl concentration below 7 mol/dm³, while increasing at concentrations above 7 mol/dm³. Again TTA caused precipitation at 0 mol/dm³ HCl. TTA and the octanols yielded extractions that ranged between 0 and 20%, which seemed independent of the HCl concentration, as was observed with HNO₃.

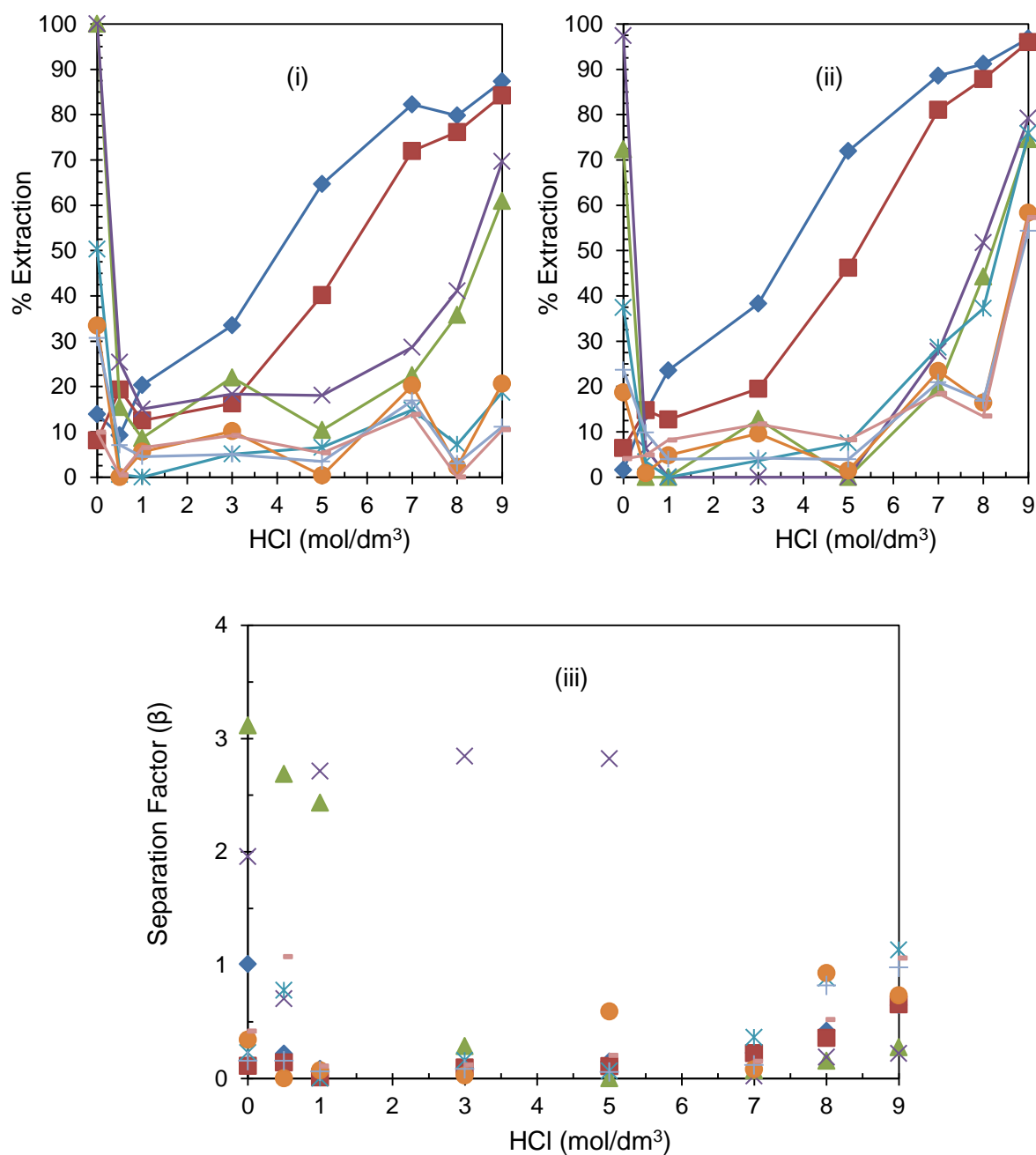


Figure 20 - Extraction of (i)Ta (2.03×10^{-3} mol/dm³) (ii) Nb (2.98×10^{-3} mol/dm³) and (iii) the separation factor for Ta and Nb using HCl (0 – 9 mol/dm³) with eight different extractants at 25°C, E/M ratio of 10:1, phase ratio of 1:1 (♦ - PA, ■ - D2EHPA, ▲ - Alamine 336, × - Aliquat 336, * - TTA, ● - 1-octanol, + - 2-octanol, - 3-octanol).

The results for the Nb extraction in a hydrochloric acid medium are displayed in Figure 20(ii). PA and D2EHPA again showed increased extraction as the HCl concentration increased, as was observed with HClO₄ and HNO₃. The highest extractions of 97% and 96% were obtained for PA and D2EHPA, respectively, at 9 mol/dm³ HCl. Alamine 336 and Aliquat 336 showed 72% and 97% extraction, respectively, in 0 mol/dm³ HCl, again due to precipitation of the

metal from the aqueous phase. Apart from the precipitation, TTA yielded the best extraction (76%) at 9 mol/dm³ HCl. The amine extractants, TTA and the octanols showed no extraction dependence on the HCl concentration up to 5 mol/dm³. Above 5 mol/dm³, the extraction with the amine extractants, TTA and the octanols increased to a highest extraction which ranged between 54 and 59% at 9 mol/dm³ HCl.

Comparing Figures 20(i) and (ii), PA and D2EHPA showed an extraction that increased linearly with increasing acid concentration, with the best extraction results for both Ta and Nb at 9 mol/dm³ HCl. Extraction of both Ta and Nb in Alamine 336 and Aliquat 336 was initially independent of acid concentration up to 5 mol/dm³ HCl, whereafter extraction increased. The extraction trend with TTA and the octanols was similar, i.e. initially the extraction was independent of the HCl concentration up to 5 mol/dm³ HCl, before increasing with a further increase in the acid concentration, similar to the extraction with Alamine 336 and Aliquat 336.

The separation factors for the extraction experiments of Ta and Nb in an HCl medium are presented in Figure 20(iii). The separation factors for all the extractants, except for Alamine 336 and Aliquat 336, were below 1. The separation factor of the amine extractants were between 2 and 3.

The results for the Ta extraction in a sulphuric acid medium are presented in Figure 21(i). PA and D2EHPA again showed an increase in extraction with an increase in acid concentration, as was observed with HClO₄, HNO₃ and HCl, but PA was more effective at concentrations below 8 mol/dm³ H₂SO₄ than observed with the other acidic mediums. PA showed the best extraction of 97% at 15 mol/dm³, while D2EHPA showed 81% extraction at 12 mol/dm³ H₂SO₄. As usual, precipitation was a problem with Alamine 336 and Aliquat 336 at 0 mol/dm³ H₂SO₄. Extraction with Alamine 336 and Aliquat 336 was similar to the extraction achieved with HClO₄, i.e. initially the extraction was independent of the H₂SO₄ concentration (<5 mol/dm³), whereafter extraction increased (± 60%) between 8 and 12 mol/dm³ H₂SO₄, before extraction decreased again. No extraction was achieved with TTA when acid was added, which differs from the data observed with HClO₄. The octanols showed no extraction in H₂SO₄, as had been observed with HNO₃.

The results for the Nb extraction in a sulphuric acid medium are displayed in Figure 21(ii). For PA and D2EHPA, extraction increased as the H₂SO₄ concentration increased, similarly to the extraction data for Ta. PA showed an 85% extraction of Nb in 15 mol/dm³, while D2EHPA showed a 59% extraction at 12 mol/dm³ H₂SO₄.

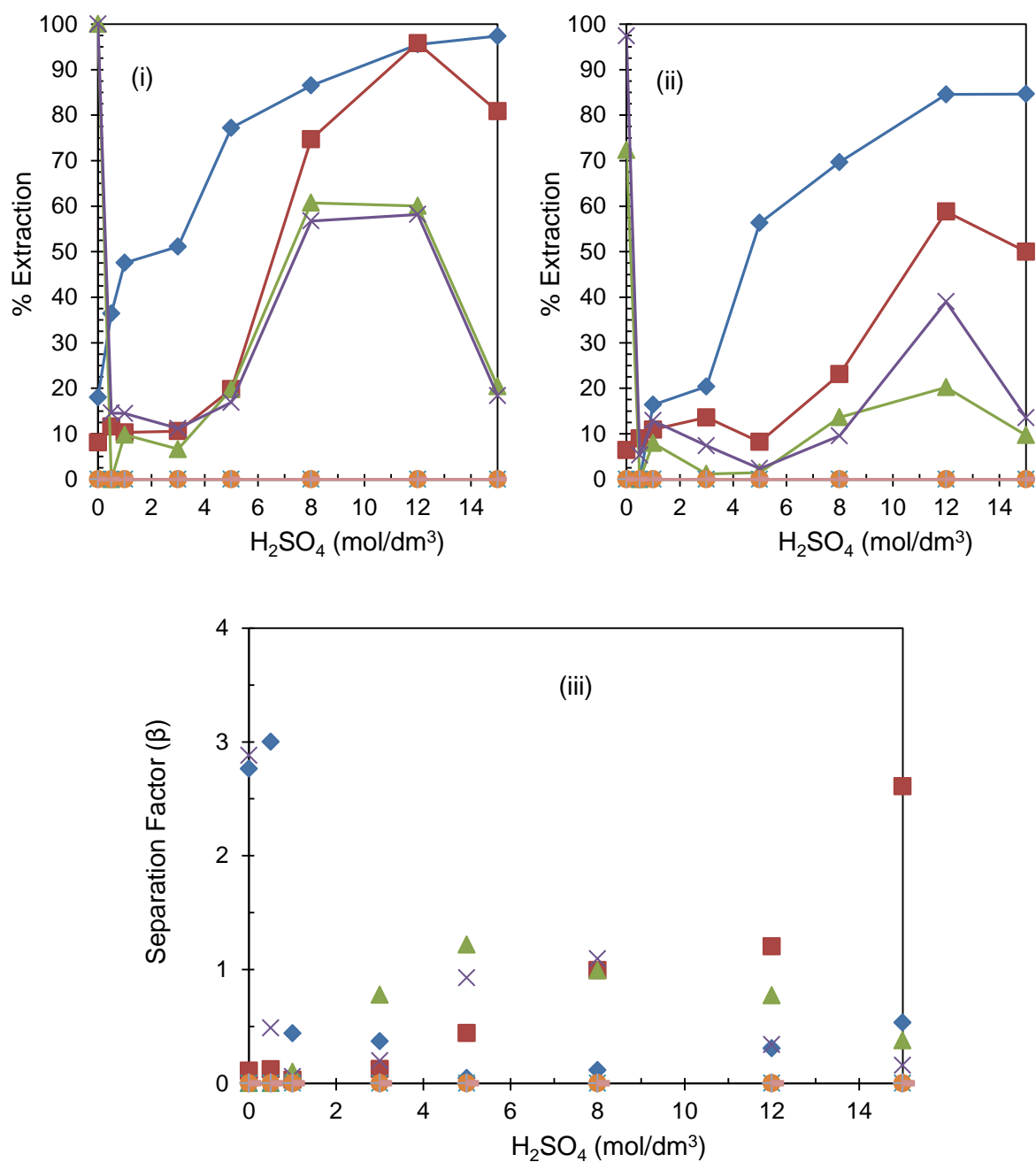


Figure 21 - Extraction of (i) Ta (2.03×10^{-3} mol/dm³), (ii) Nb (2.98×10^{-3} mol/dm³) and (iii) the separation factor for Ta and Nb using H_2SO_4 (0 – 15 mol/dm³) with eight different extractants at 25°C, E/M ratio of 10:1, phase ratio of 1:1 (♦ - PA, ■ - D2EHPA, ▲ - Alamine 336, × - Aliquat 336, * - TTA, ● - 1-octanol, + - 2-octanol, - 3-octanol).

Again precipitation was a problem with Alamine 336 and Aliquat 336 and thus 72% and 97% extraction, respectively, was achieved at 0 mol/dm³. The highest solvent extraction, however, achieved with Alamine 336 and Aliquat 336 was below 40% at 12 mol/dm³ H_2SO_4 , which was lower than for the extraction observed when using $HClO_4$. Again precipitation of the metal

was a problem with TTA and the octanols and no extraction was achieved, which was similar to the extraction of Ta in H_2SO_4 .

When comparing the extraction of Ta and Nb (Figures 21(i) and (ii)), it is clear that both Ta and Nb have a high affinity for extraction with PA and D2EHPA in an H_2SO_4 acidic medium at concentrations above 12 mol/dm^3 . However, Nb extraction was generally less over the entire acid range in PA, D2EHPA, Alamine 336 and Aliquat 336 when compared to Ta, although this tendency towards increased extraction with increasing acid concentration corresponds with the extraction observed for Ta.

The separation factors for the extraction experiments for both Ta and Nb in an HNO_3 medium are represented in Figure 21(iii). Except for PA and Aliquat 336 at low acid concentrations and D2EHPA at high concentrations, separation factors for all eight extractants were below 1.2. The high separation factor (2.9) of Aliquat at $0 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ was again due to precipitation of the metal. Thus, PA and D2EHPA showed adequate selectivity, with separation factors for PA of 2.8 and 3 at 0 and 0.5 mol/dm^3 , respectively, and a separation factor for D2EHPA of 2.6 at $15 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$, towards the extraction of Ta from Nb in an H_2SO_4 acidic medium.

From the eight extractants (PA, D2EHPA, Alamine 336, Aliquat 336, TTA, 1-, 2- and 3-octanol) tested, PA and D2EHPA showed the best extraction results for both Ta and Nb, irrespective of the acid used. This suggests that both Ta and Nb tend to preferentially form complexes with the cation exchangers PA and D2EHPA, but less so with the neutral (TTA), the anion exchangers (Alamine 336 and Aliquat 336) and the octanols.

4.1.2 Effect of E/M Ratio

Having evaluated the effect of different acids and their concentrations on the extraction as a function of the type of extractant, the following section will focus on the effect of the E/M ratio on the extraction of Ta and Nb. Based on the superior extraction achieved in the previous section, both PA and D2EHPA were selected for this study. The extractant to metal molar ratio was varied from 0.1:1 to 20:1 and cyclohexane was used as the diluent with 3% v/v 1-octanol used as the modifier for the organic phase. Due to precipitation problems occurring with HClO_4 , these experiments were done using only the following three acids; i.e. HNO_3 (7 and 10 mol/dm^3), HCl (5 and 9 mol/dm^3) and H_2SO_4 (4 and 10 mol/dm^3).

The extraction results for both Ta and Nb for the 7 and 10 mol/dm^3 nitric acid medium with PA are presented in Figure 22(i). The highest extraction for both Ta and Nb was achieved

with 10 mol/dm³ HNO₃, irrespective of the E/M ratio used. In 7 mol/dm³ HNO₃, the best extraction (99% with respect to Ta) was achieved with PA at a 20:1 mole ratio (51 mmol/dm³). To determine the repeatability of these experiments, extraction (56% with respect to Ta) at 7 mol/dm³ HNO₃ in a 10:1 mole ratio PA (26 mmol/dm³), was compared to the 38% extraction at 7 mol/dm³ HNO₃ in Figure 19(i). Although this indicates a clear discrepancy, possibly due to human error, this variation decreased significantly when comparing the 10 mol/dm³ HNO₃ results. In 10 mol/dm³ HNO₃, the best extraction (98% with respect to Ta) was achieved at a mole ratio of above 15:1 (39 mmol/dm³ PA), whereas the extraction (88% with respect to Ta) at 10 mol/dm³ HNO₃ in a 10:1 mole ratio PA compares favourably with the 73% extraction obtained at 10 mol/dm³ HNO₃ as presented in Figure 19(i), resulting in an error of just above 10%. Irrespective of the acid concentration or the extractant used, the extraction increased with an increasing E/M ratio, which is understandable as more extractant should equal more metal extracted.

The separation factors of Ta and Nb in HNO₃ are represented in Figure 22(ii). According to these separation results, the selectivity ranged between 0 and 1.2, with the best selectivity attained at lower E/M ratios, which would imply that the increased competition of Ta and Nb for extractant at lower E/M ratios favours the selectivity for Ta.

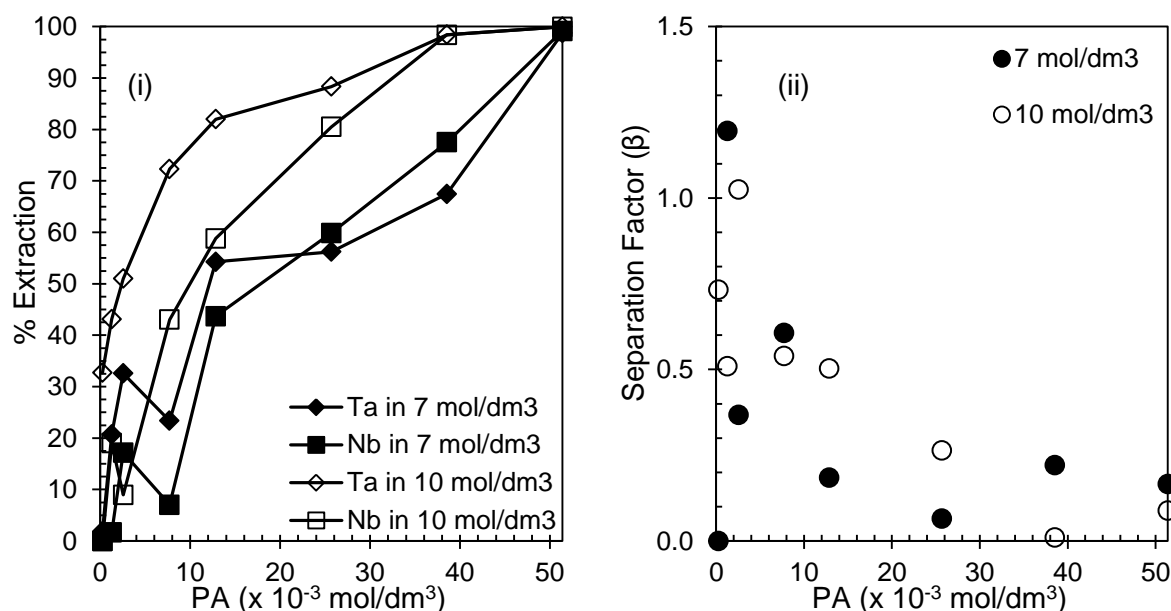


Figure 22 – (i) Extraction of Ta and (ii) the separation factor of Ta and Nb in 7 and 10 mol/dm³ HNO₃ with PA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

The extraction results for the 7 and 10 mol/dm³ nitric acid medium with D2EHPA are presented in Figure 23(i). The best extraction data was yet again achieved in 10 mol/dm³ HNO₃. In 7 mol/dm³ HNO₃, the best extraction (99% with respect to Ta) was achieved at and above a 15:1 mole ratio (39 mmol/dm³ D2EHPA) with no separation of Ta and Nb. When comparing these results to the data presented in Figure 19(i) and (ii), the difference at 7 mol/dm³ was just above 10% for both Ta and Nb, showing adequate repeatability for D2EHPA. In 10 mol/dm³ HNO₃ the best extraction was achieved above a 10:1 mole ratio (25 mmol/dm³ D2EHPA) again with no significant selectivity between Ta and Nb. The separation factors for the extraction of Ta and Nb in 7 and 10 mol/dm³ HNO₃ with D2EHPA are presented in Figure 23(ii). The separation factors ranged between 0 and 0.6, meaning that although adequate extraction was achieved, there was no significant selectivity towards a metal for extraction. It is further noteworthy that, unlike for PA, the selectivity did not significantly increase at lower E/M ratios.

No literature was found on the extraction of Ta and Nb in a nitric acid medium, but Biswas et al^[91] found an increase in the extraction of uranium(IV) with increasing HNO₃ concentration. According to our results, both PA and D2EHPA yielded high extractions at an E/M mole ratio above 10:1 in HNO₃. The selectivity for D2EHPA ranged between 0 and 0.6 and was again the highest at relatively low extractant concentrations (0 to 20 mmol/dm³).

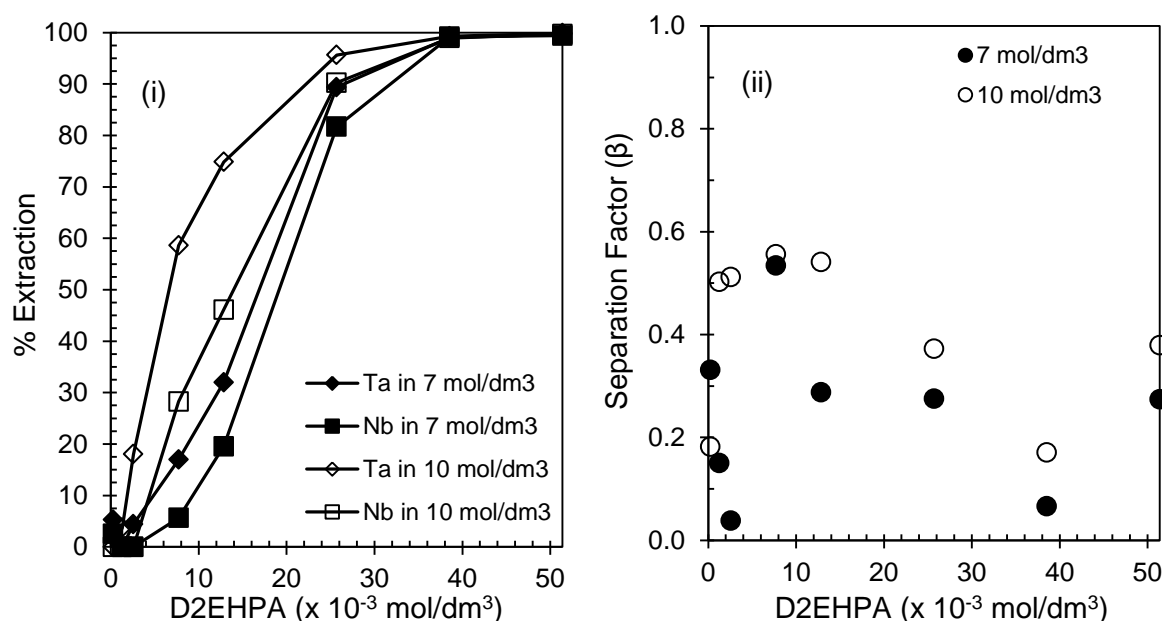


Figure 23 – (i) Extraction of Ta and (ii) the separation factor of Ta and Nb in 7 and 10 mol/dm³ HNO₃ with D2EHPA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

Figure 24(i) represents the extraction results for the 5 and 9 mol/dm³ hydrochloric acid medium with PA. The highest extraction achieved with PA was similar to what has been observed for HNO₃ at the higher acid concentrations. In 5 mol/dm³ HCl the best extraction (80% with respect to Ta) was achieved at a mole ratio of 10:1 (26 mmol/dm³ PA) with a separation factor of 0.6 (Figure 24(ii)) for Ta and Nb. The extraction (80% with respect to Ta) at 5 mol/dm³ HCl in a 10:1 mole ratio PA, according to Figure 20(i), was significantly higher than the 65% extraction obtained at 5 mol/dm³ HCl, suggesting inadequate repeatability. In 9 mol/dm³ HCl the best extraction (95%) was achieved at a mole ratio >10:1 (26 mmol/dm³ PA) with the separation factor 0.6. When comparing these results to Figure 20(i), the error margin was, however, below 10%. When comparing these results to the extraction in HNO₃, it seems that higher extractions were possible in HCl, especially at lower E/M ratios.

The separation factors of Ta and Nb in 5 and 9 mol/dm³ HCl with PA are presented in Figure 24(ii). The separation factors for PA in HCl ranged between 0 and 0.8, showing that the improved extraction obtained when using HCl came at the cost of the selectivity and was independent of the E/M ratio.

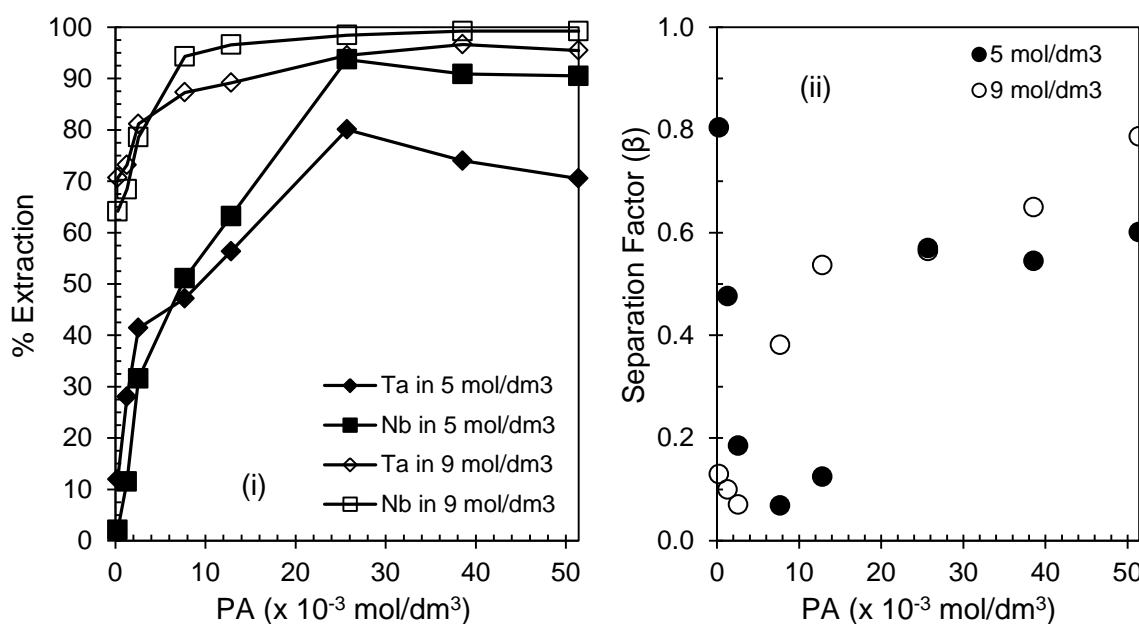


Figure 24 – (i) Extraction of Ta and (ii) the separation factor of Ta and Nb in 5 and 9 mol/dm³ HCl with PA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

Figure 25 presents the results for the 5 and 9 mol/dm³ hydrochloric acid medium with D2EHPA. According to Figure 20(i), the lower HCl concentration (5 mol/dm³) showed higher

extraction than the 9 mol/dm³ HCl for the first time when using D2EHPA, which was reversed for PA (Figure 24). Vin and Khopkar^[90] found that Ta was preferentially extracted from 0.1 to 2 mol/dm³ HCl while Nb was preferentially extracted from 1-10 mol/dm³ HCl when using D2EHPA, thus confirming the acid concentration dependence of the Ta and Nb extraction, specifically in an HCl environment. The best extraction in 5 mol/dm³ was achieved above a 5:1 mole ratio (13 mmol/dm³ D2EHPA) with no significant separation of Ta and Nb.

In 9 mol/dm³ HCl the best extraction (80%, with respect to Ta) was achieved at a 10:1 mole ratio (26 mmol/dm³ D2EHPA) with a separation factor of 0.6 (Figure 25(ii)) for Ta and Nb. Comparing these results to the extraction data obtained at 10 mol/dm³ HCl in Figure 20, these results are reproducible with a margin of error of less than 5%. While the use of D2EHPA resulted in a high extraction at an E/M mole ratio above 5:1 in 5 mol/dm³ HCl, it came at the cost of selectivity. Figure 25(ii) presents the separation factors obtained in 5 and 9 mol/dm³ HCl with D2EHPA. The separation factors ranged between 0 and 0.6, confirming that although 100% extraction was achieved, low preferential selectivity towards Ta or Nb was observed.

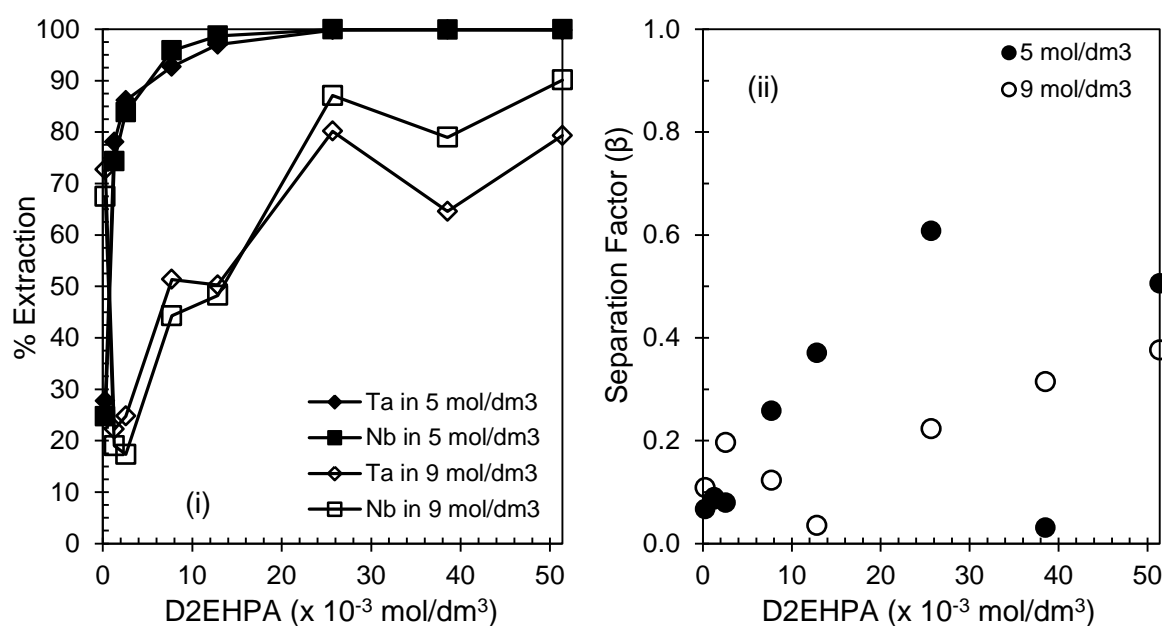


Figure 25 – (i) Extraction of Ta and (ii) the separation factor of Ta and Nb in 5 and 9 mol/dm³ HCl with D2EHPA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

The results for the last of these three E/M ratio as a function of acid (HNO₃, HCl and H₂SO₄) studies, when varying 4 and 10 mol/dm³ H₂SO₄ using PA and D2EHPA, are presented in

Figure 26 and Figure 27, respectively. According to Figure 26(i), the best extraction (65% with respect to Ta) in 4 mol/dm³ H₂SO₄ was achieved at a higher than 3:1 mole ratio (8 mmol/dm³ PA) with a separation factor of 0.4 (Figure 26(ii)). Above 10 x 10⁻³ mol/dm³ PA the extraction levelled off before increasing again above 25 x 10⁻³ mol/dm³. The extraction (57% with respect to Ta) at 4 mol/dm³ H₂SO₄ in 10:1 mole ratio PA (26 mmol/dm³), was compared with the 64% extraction (with respect to Ta) at 4 mol/dm³ H₂SO₄ presented in Figure 21(i), showing an error of below 10%.

In 10 mol/dm³ H₂SO₄ the best extraction (97%) with respect to Ta was achieved above a 3:1 mole ratio (8 mmol/dm³ PA) with a separation factor of above 1.8. When comparing extraction results (100% with respect to Ta) at 10 mol/dm³ H₂SO₄ in a 10:1 mole ratio PA (26 mmol/dm³), to the 92% extraction (with respect to Ta) at 10 mol/dm³ H₂SO₄ in Figure 21(i), is clear that the error margin was significantly below 10% for these experiments. It is again clear that in the presence of H₂SO₄, the PA preferentially complexed the Ta, as was observed in HNO₃ but not in HCl.

The separation factor data of the extraction of Ta and Nb in 4 and 10 mol/dm³ H₂SO₄ with PA are represented in Figure 26(ii). The separation factors in 10 mol/dm³ are in the range of 1.2 to 2.3, which is higher compared to the separation factors (in a range of 0 to 0.7) in 4 mol/dm³ H₂SO₄.

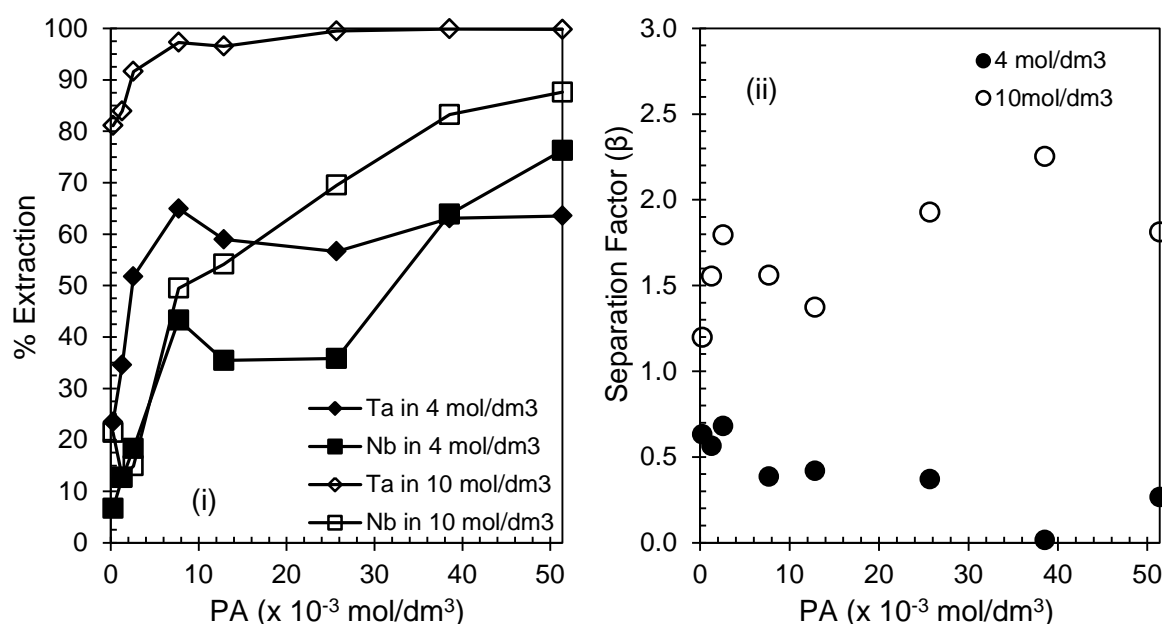


Figure 26 – (i) Extraction of Ta and (ii) the separation factor of Ta and Nb in 4 and 10 mol/dm³ H₂SO₄ with PA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

Using Eq. 3 where compound A denotes the more extracted metal species, only positive separation factor values are shown. Thus the selectivity towards Ta in PA is higher in 10 mol/dm³ than in 4 mol/dm³. When comparing the extraction data using PA for the three acids tested, H₂SO₄ yielded the highest separation factor.

According to Figure 27(i), the highest extraction with D2EHPA was also achieved with 10 mol/dm³ H₂SO₄, while the highest extraction (88% with respect to Ta) in 4 mol/dm³ H₂SO₄ was achieved at a 15:1 mole ratio (8 mmol/dm³ D2EHPA) with a separation factor of 0.1 (Figure 27(ii)). Principe and Demopoulos^[92] showed that, with higher concentrations of H₂SO₄, more Fe extracted with D2EHPA. Comparing the extraction results in Figure 27 to the extraction (64% with respect to Ta) at a mole ratio of 10:1 (26 mmol/dm³ PA) in 4 mol/dm³ H₂SO₄ as presented in Figure 21(i), an error below 20% was observed. In 10 mol/dm³ H₂SO₄ the highest extraction (97%, with respect to Ta) was achieved at a 20:1 mole ratio (51.4 mmol/dm³ D2EHPA) with a separation factor of 1.2 (Figure 27(ii)). The error was 5% when comparing this data to the extraction (92% with respect to Ta) obtained using 10 mol/dm³ HCl in Figure 21(i).

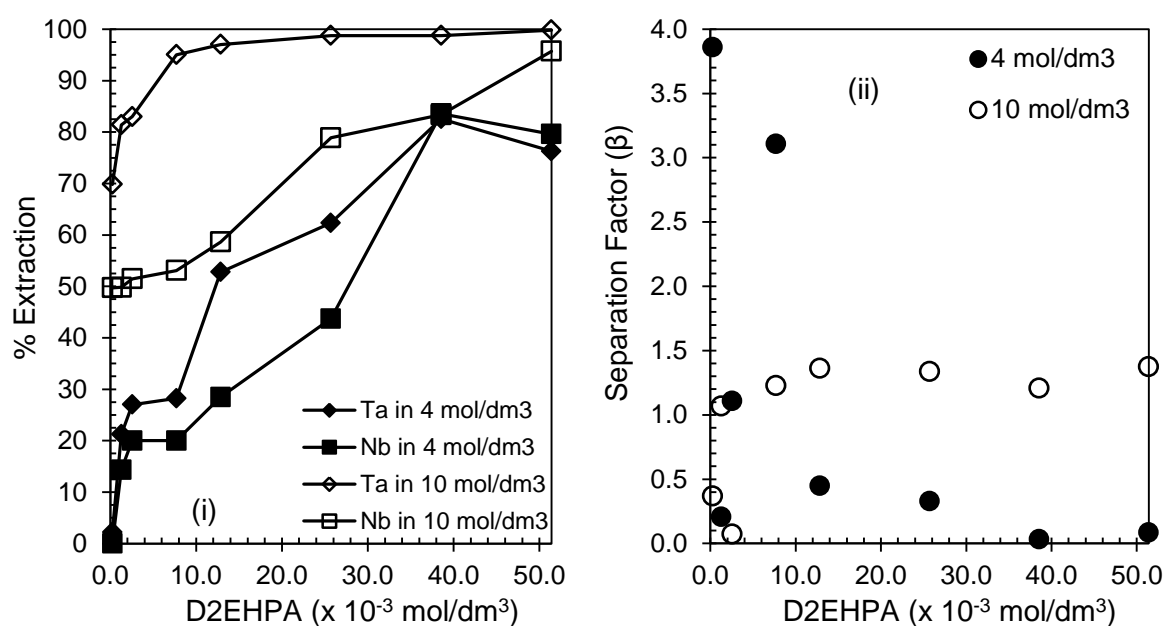


Figure 27 – (i) Extraction of Ta and (ii) the separation factor of Ta and Nb in 4 and 10 mol/dm³ H₂SO₄ with D2EHPA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

The separation factors of the extraction of Ta and Nb in 4 and 10 mol/dm³ H₂SO₄ with D2EHPA are represented in Figure 27(ii). Initially, 7 mol/dm³ H₂SO₄ gave higher separation

factors than $10 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$, but above a 5:1 E/M ratio, the selectivity towards Ta decreased significantly to a point where it was below the selectivity observed when using a 10 mol/dm^3 aqueous phase. Accordingly, D2EHPA would be suitable at $7 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ at low E/M ratios or when using $10 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$, irrespective of the E/M ratio used. Both PA and D2EHPA are suitable extractants for Ta and Nb at E/M mole ratios above 3:1 in H_2SO_4 , with PA obtaining slightly higher extraction and selectivity, especially at lower E/M ratios.

From the above experiments, it is clear that of the three acids tested, H_2SO_4 contributed to high extractions and superior selectivities. To further clarify the possible role of the H_2SO_4 concentration, a final set of experiments was conducted where a wider range of H_2SO_4 concentrations (4, 7, 10, 12 and 15 mol/dm^3) were evaluated, thereby determining the repeatability as well as broadening the acid concentration range, again using both PA and D2EHPA. The extractant to metal ratio was again varied from 0.1:1 to 20:1. Cyclohexane was used as diluent and 3% v/v 1-octanol was used as the modifier for the organic phase. Only the results obtained for Ta will be presented, as Ta is the primary metal to be separated from the Nb.

Figure 28(i) shows the extraction results for various H_2SO_4 concentrations using PA as the extractant. From literature^[92] it is expected that extraction increases as the concentration of H_2SO_4 increases, but according to Figure 28(i) it can be seen that 7 and $10 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ gave the best extraction of Ta, followed by $12 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$, $4 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ and $15 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$. A similar behaviour was observed for Nb (data not shown due to identical tendencies observed for Nb). This implies that a peak extraction is obtained in the mid-concentration region, which probably is related to speciation. However, further studies are required to validate this hypothesis.

The separation factors of Ta in the above mentioned H_2SO_4 media are presented in Figure 28(ii). Although the experiment with 7 and $10 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ showed the highest extraction, it did not show the highest separation factor. For 7 mol/dm^3 , the separation factor ranged between 1.8 and 4.7, while it ranged between 1.2 and 2.3 for 10 mol/dm^3 . The highest selectivity, however, was obtained when using $12 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$, again showing the inverse relation between percentage extraction and selectivity.

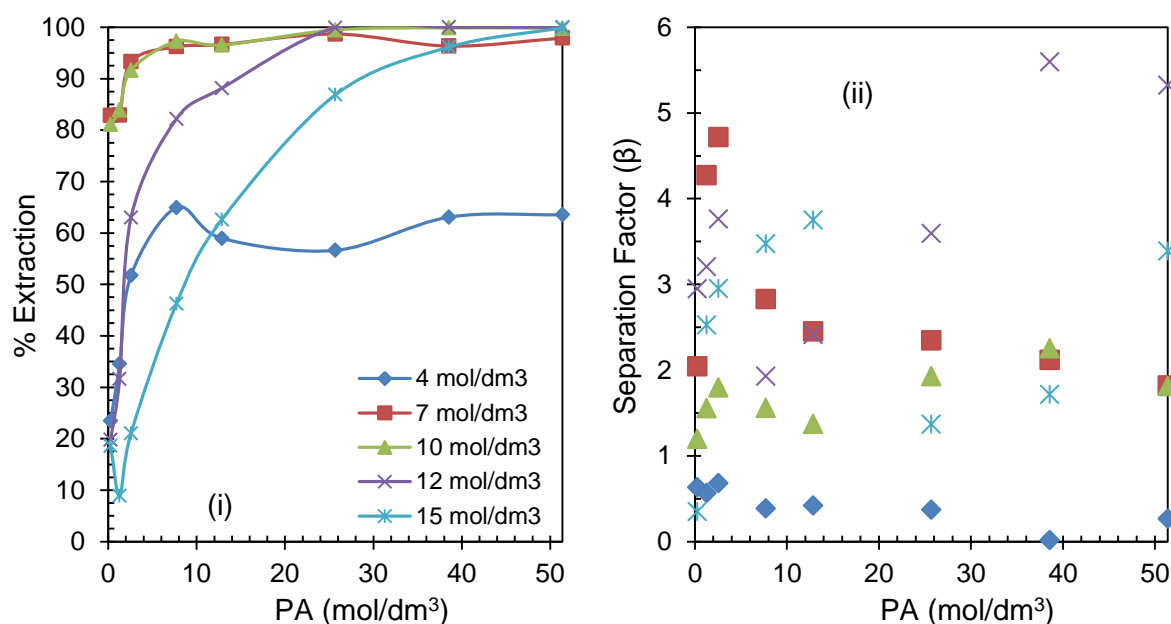


Figure 28 – (i) Extraction in respect of Ta and (ii) the separation factor of Ta with regards to Nb in 4, 7, 10, 12 and 15 mol/dm³ H₂SO₄ with PA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

When repeating the experiment using D2EHPA (Figure 29(i)) a similar extraction trend was observed, i.e. an initial increase in extraction with increasing acid concentration reaching an optimum at 7 and 10 mol/dm³, before declining again above 10 mol/dm³ H₂SO₄, especially at low E/M ratios. The separation factors of this experiment are represented in Figure 29(ii). A similar trend to that observed in Figure 28(ii) became apparent, but with lower separation values. For 7 mol/dm³, the separation factor ranged between 1.8 and 3.7 and for 10 mol/dm³, it ranged between 0.1 and 1.4. Again 12 mol/dm³ H₂SO₄ yielded the highest selectivity.

Comparing Figures 28(i) and 29(i) shows that similar results were obtained. An exception was the 4 mol/dm³ data line, which showed the lowest extraction with D2EHPA compared to PA. Both 7 and 10 mol/dm³ showed the best extraction in PA and D2EHPA, followed by the 12 and 15 mol/dm³ extractions and in both cases the highest selection was obtained at 7 and 12 mol/dm³ H₂SO₄. The margin of error in these experiments was below 5%.

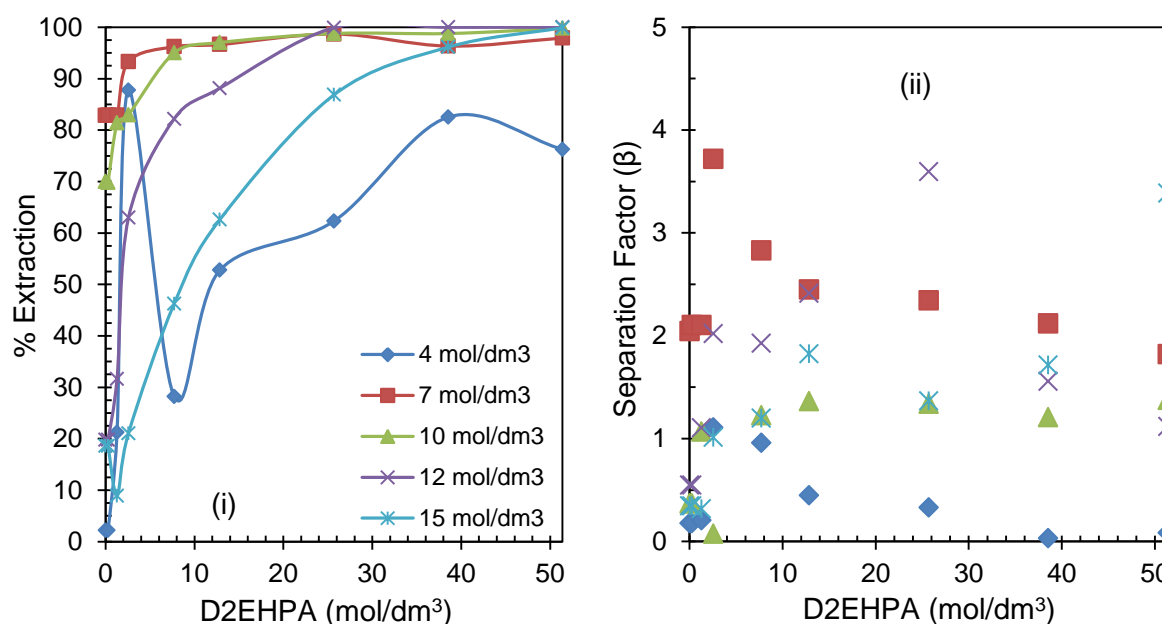


Figure 29 – (i) Extraction in respect of Ta and (ii) the separation factor of Ta with regards to Nb in 4, 7, 10, 12 and 15 mol/dm³ H₂SO₄ with D2EHPA (0.1:1 to 20:1 E/M mole ratio) at 25°C for 1 hr at 350 rpm.

In this section (Section 4.1), it was shown that for Ta(Nb)F₅, the highest extraction was attained at high acid concentrations when using PA and D2EHPA as extractants, while H₂SO₄ was the most suitable in terms of both extraction and selectivity.

4.2 SX with NH₄Ta(Nb)F₆

In this second optimisation series, the extraction of Ta and Nb fluoride solutions (NH₄Ta(Nb)F₆) was investigated. The results obtained in Section 4.1 were used as a guide for the best combination of variables for the selective extraction of Ta and Nb. Accordingly, a screening was conducted using aqueous phases containing 5, 10 and 14 mol/dm³ H₂SO₄ with 100 ppm NH₄Ta(Nb)F₆ added to the acid. For the organic phase, batch extractions were done with both PA and D2EHPA with an E/M ratio of 10:1. Cyclohexane was used as the diluent and 3% v/v 1-octanol was used as the modifier for the organic phase.

Figure 30 shows the sample results with 100 ppm NH₄Ta(Nb)F₆ solution with a 10:1 mole ratio of PA (25.7 mmol/dm³) in 5, 10 and 14 mol/dm³ H₂SO₄. In 5 mol/dm³ H₂SO₄, 100% extraction of Ta was achieved with 25% Nb extraction, with a separation factor of 5.4. When increasing the H₂SO₄ concentration to 10 mol/dm³, 100% extraction of Ta was again achieved. However, the Nb extraction increased to 57%, yielding a separation factor of 4.8.

By increasing the acid concentration to 14 mol/dm³ H₂SO₄, only 52% extraction of Ta was achieved with 9.2% Nb extraction, yielding a separation factor of 1. It is interesting to note that the extraction of both Ta and Nb decreased at 14 mol/dm³ H₂SO₄. It is clear that the best results in terms of extraction and selectivity were attained with 5 mol/dm³ H₂SO₄ when using PA and NH₄Ta(Nb)F₆.

The sample results with 100 ppm NH₄Ta(Nb)F₆ solution with 10:1 mole ratio of D2EHPA (25.7 mmol/dm³) in 5, 10 and 14 mol/dm³ H₂SO₄ are shown in Figure 31. A similar tendency to what has been observed for PA was observed; i.e. in 5 mol/dm³ H₂SO₄, 100% extraction of Ta was achieved with 20% Nb extracted, with a separation factor of 5.6. In 10 mol/dm³ H₂SO₄, 100% extraction of Ta was again achieved with an increase of the Nb (53%), with a separation factor of 4.9. In 14 mol/dm³ H₂SO₄, only 71% extraction of Ta was observed with 28% Nb extraction, with a separation factor of 0.8.

Thus for the extraction of Ta from NH₄Ta(Nb)F₆, both 5 and 10 mol/dm³ H₂SO₄ gave good results, but with respect to the selectivity towards Ta, 5 mol/dm³ H₂SO₄ gave the best results. Thus, both PA and D2EHPA showed high extraction and separation results when using 5 mol/dm³ H₂SO₄.

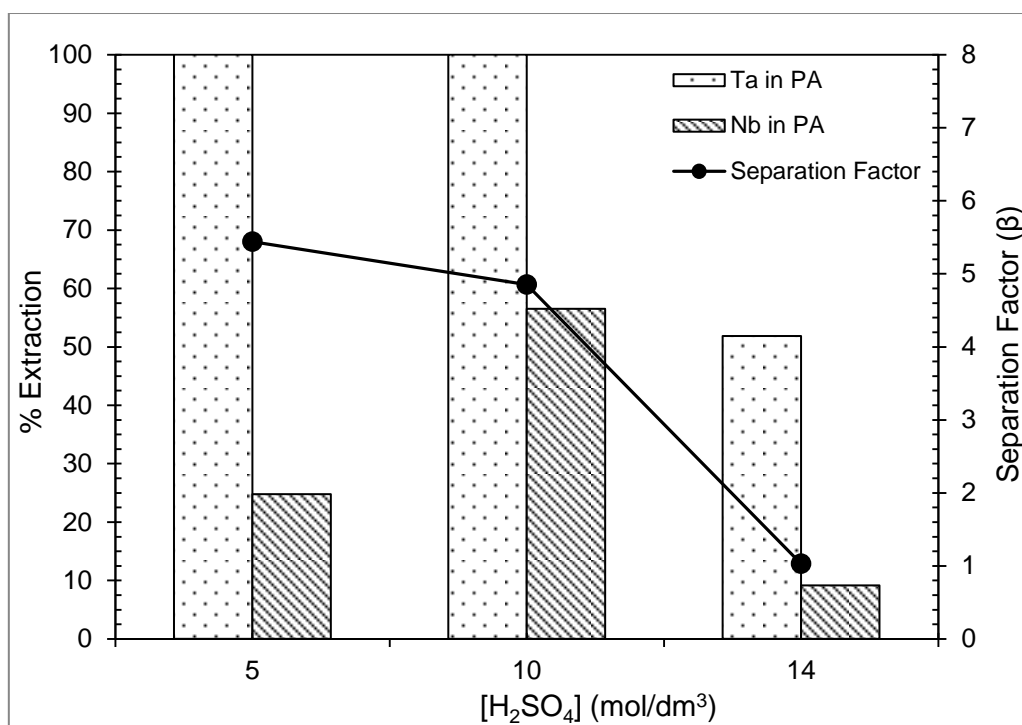


Figure 30 – Sample experiments with 100 ppm NH₄Ta(Nb)F₆ solution with a 10:1 mole ratio of PA (25.7 mmol/dm³) in 5, 10 and 14 mol/dm³ H₂SO₄ at 25°C for 1 hr at 350 rpm.

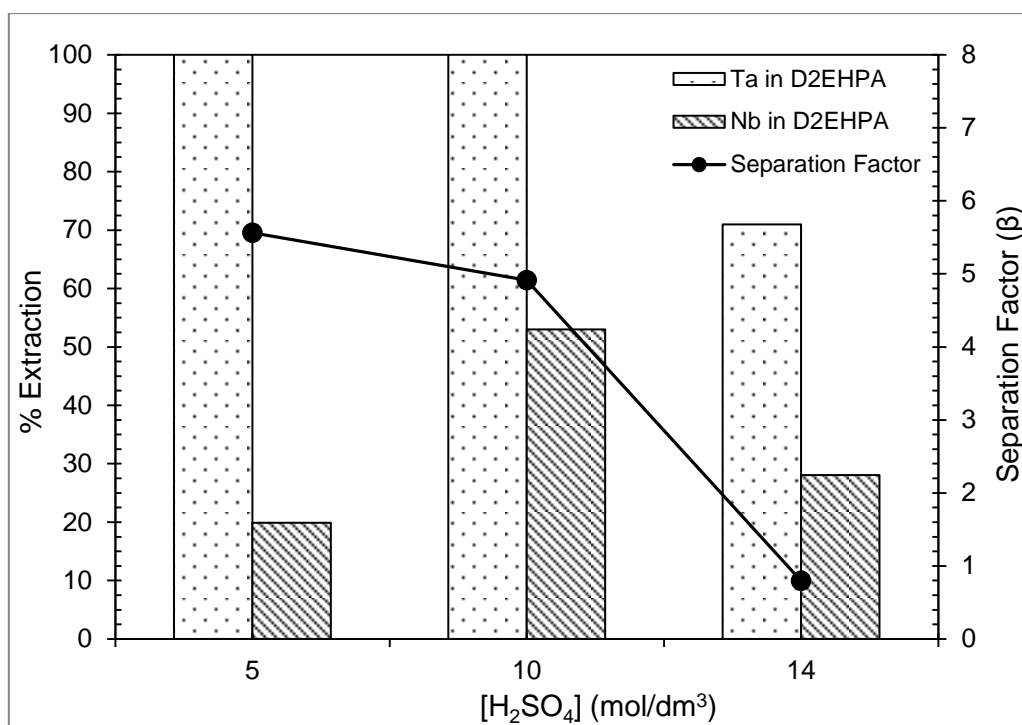


Figure 31 - Sample experiments with 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ solution with a 10:1 mole ratio of D2EHPA (25.7 mmol/dm³) in 5, 10 and 14 mol/dm³ H_2SO_4 at 25°C for 1 hr at 350 rpm.

4.2.1 Effect of H_2SO_4 Concentration

In view of the significant effect the acid concentration had both on selectivity and extraction, it was decided to conduct a more extensive study over the acid concentration range of 0 to 10 mol/dm³ H_2SO_4 , the area where the best extraction and selectivity had been observed in the acid concentration screening study. For this purpose the aqueous phase consisted of H_2SO_4 (0 to 10 mol/dm³) with 100 ppm of $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ in a H_2O solution. For the organic phase, PA and D2EHPA were used as extractants in an E/M ratio of 10:1. Cyclohexane was used as the diluent and 3% v/v 1-octanol was used as the modifier for the organic phase.

Figure 32(i) shows the extraction results and (ii) the separation factors of Ta and Nb with 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ solution with a 10:1 mole ratio of both PA and D2EHPA (25.7 mmol/dm³) as a function of H_2SO_4 . It is clear that the extraction trend is similar to the trend observed when using $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$, i.e. the amount of Ta extracted increased with increasing H_2SO_4 concentration reaching 100% extracted at 3 and 5 mol/dm³ H_2SO_4 for PA and D2EHPA, respectively. However, the extraction for Nb remained significantly lower for $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ both for PA and D2EHPA, with a slight increase in the Nb extraction above 5 mol/dm³.

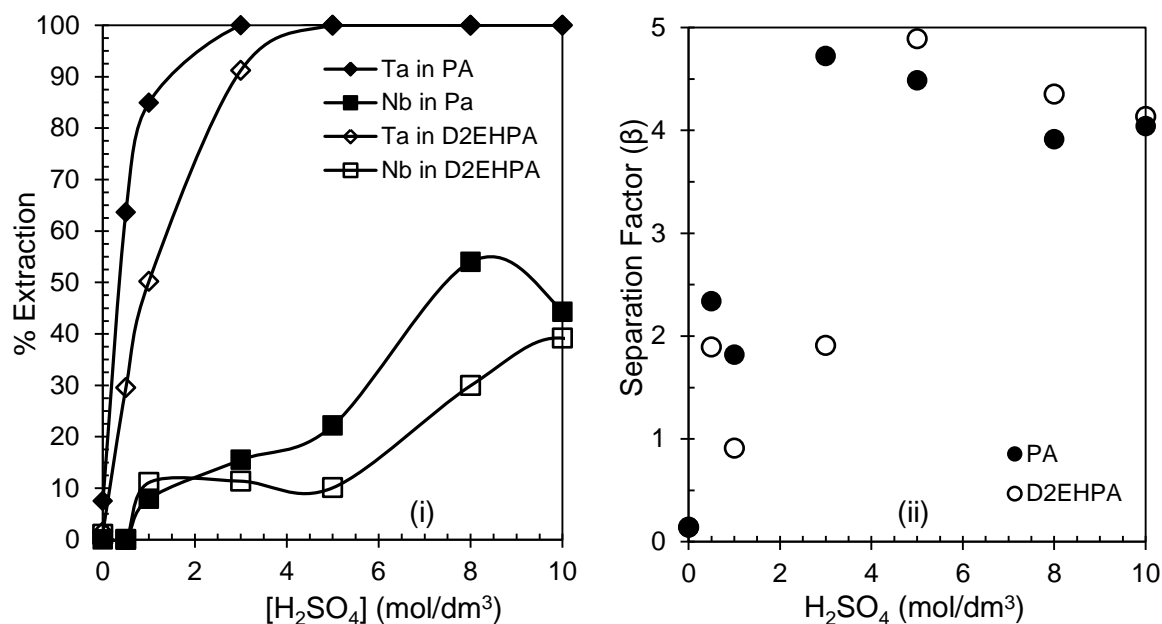


Figure 32 – Effect of $[H_2SO_4]$ (0 to 10 mol/dm³) experiments on (i) extraction of Ta and Nb and (ii) the separation factor of Ta and Nb with 100 ppm $NH_4Ta(Nb)F_6$ solution with a 10:1 mole ratio of PA and D2EHPA at 25°C for 1 hr at 350 rpm.

In terms of the selectivity (Figure 32(ii)) it is clear that when using PA, the selectivity increased, reaching a peak at 3 mol/dm³ H_2SO_4 (separation factor of 4.7) before declining slightly to 3.9 at 8 mol/dm³ H_2SO_4 . A similar trend was observed with D2EHPA. However, the highest separation (4.9) was observed at 5 mol/dm³ H_2SO_4 , before decreasing slightly at higher concentrations (4.1 at 10 mol/dm³ H_2SO_4).

These results confirm that, for the extraction of Ta from $NH_4Ta(Nb)F_6$, H_2SO_4 concentrations between 3 and 5 mol/dm³ with both PA and D2EHPA showed the best results, while 3 mol/dm³ H_2SO_4 with PA showed the best results in terms of selectivity. The results compare well with the results presented in Figure 30.

4.2.2 Effect of E/M Ratio

PA and D2EHPA were used to determine the effect of extractant to metal ratio. As was done previously, the extractant to metal ratio was varied from 0.1:1 to 20:1. Cyclohexane was used as the diluent and 3% v/v 1-octanol was used as a modifier for the organic phase. According to the results in Section 4.2.1, the H_2SO_4 concentration should be between 3 and 5 mol/dm³, thus 4 mol/dm³ H_2SO_4 was used with 100 ppm of $NH_4Ta(Nb)F_6$ in an H_2O solution as the aqueous phase.

Figures 33(i) and (ii) respectively show the results for the extractant to metal ratio of both PA and D2EHPA with 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$, and the separation factors.

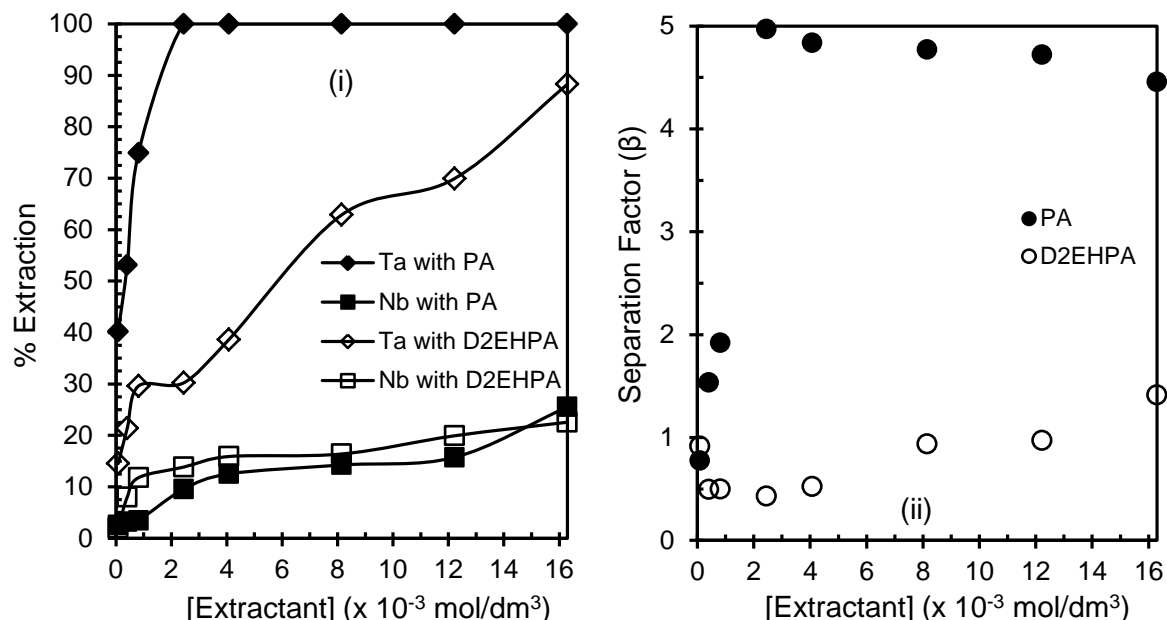


Figure 33 - Effect of PA and D2EHPA extractant to metal mole ratio of 0.1:1 to 20:1 (0 to 16.2 mmol/dm³) experiments on (i) extraction and (ii) the separation factor of Ta and Nb with 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ at 25°C for 1 hr at 350 rpm.

With PA, an E/M ratio of 3:1 gave 100% extraction of Ta and only 10% Nb, with a separation factor of 5. With D2EHPA, a maximum extraction of only 88% Ta was achieved with an E/M ratio of 20:1, while the highest separation factor attained was 1.4. To verify the D2EHPA results, the experiment was repeated and the same results were obtained with a margin of error of 5.6%. According to Figure 33, PA was the better extractant both for the extraction and separation of Ta and Nb.

4.2.3 Effect of Contact Time

To determine the optimal contact time for extraction, an aqueous phase consisting of 4 mol/dm³ H_2SO_4 with 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ in an H_2O solution was chosen. For the organic phase, both extractants PA and D2EHPA were used again to determine the effect of contact time on the extraction of Ta and Nb. Cyclohexane was used as the diluent and 3% v/v 1-octanol was used as a modifier for the organic phase. Since it was determined in Section

4.2.2 that an extractant to metal ratio of 3:1 and 20:1 was ideal for PA and D2EHPA, respectively, the extractant to metal ratio was chosen as 10:1 as an average for both extractants. The contact time was varied from 1 minute to 120 minutes.

In Figure 34(i) and (ii), the influence of contact time on extraction and the separation factors for Ta and Nb are presented, respectively.

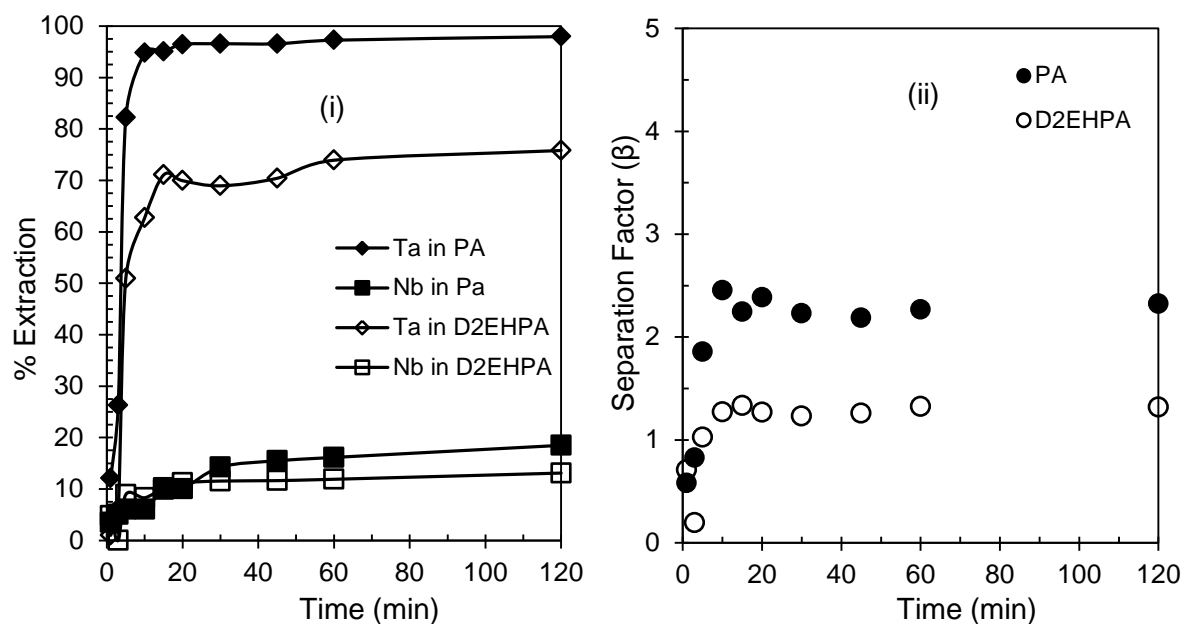


Figure 34 - Effect of contact time (0 – 120 min) on (i) extraction and (ii) the separation of Ta and Nb in 4 mol/dm³ H₂SO₄ with 100 ppm NH₄Ta(Nb)F₆ and extractant to metal mole ratio of 10:1 (8.1 mmol/dm³) PA and D2EHPA at 25°C for at 350 rpm.

It is noteworthy that the optimum extraction was achieved with PA after only 10 minutes with a 97% extraction of Ta and a 6% extraction of Nb, yielding a separation factor of 2.5. The optimum extraction with D2EHPA was achieved after 15 minutes with 76% extraction of Ta and 12% extraction of Nb, yielding a separation factor of 1.3.

Yet again, PA performed better in terms of the time needed for optimum extraction. Comparing the results at 60 min with an E/M ratio of 10:1 in Figure 46, a clear correlation can be seen with a margin of error of less than 5%.

This study has clearly shown that the 60 minutes used previously was adequate for reaching equilibrium prior to extraction.

4.3 SX Recovery

After the extraction of Ta and Nb into an aqueous phase, the next step entails the recovery or back extraction of the metal salts into an aqueous phase. While the purpose of the research endeavour was the selective extraction of Ta from a Ta(Nb) salt, which has clearly been illustrated in Section 4.2, it was deemed interesting to briefly evaluate the possible recovery using the previously obtained metal in the organic phase composition.

According to literature, little is known about common stripping agents for the recovery of Ta and Nb. Therefore, for comparative purposes, stripping agents that had successfully been used for the recovery of various other metals were evaluated for the recovery of Ta and Nb from the organic phase. Other stripping agents according to literature included the acids H_2SO_4 and HCl , the bases Na_2CO_3 and NaOH , as well as thiourea with HCl and distilled water.

Devi et al^[65] showed that concentrations of H_2SO_4 above 0.02 mol/dm^3 were needed for the recovery of manganese, while Mohapatra^[66], Htwe and Lwin^[67] and Zhu and Cheng^[68] used $1 \text{ M H}_2\text{SO}_4$ to recover Al from a D2EHPA organic phase. For this study, an aqueous phase consisting of 0 to $5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ was therefore evaluated. It is, however, clear from Figure 35 that less than 5% extraction of Ta was achieved while up to 20% of the Nb in the sample was recovered. From these results it is apparent that H_2SO_4 is not suitable as a stripping agent.

Shen and Xue^[69] used $0.1 \text{ mol/dm}^3 \text{ HCl}$ for the recovery of gold and $6 \text{ mol/dm}^3 \text{ HCl}$ for the recovery of palladium. Thus, 0.05 to $8 \text{ mol/dm}^3 \text{ HCl}$ acid concentrations were tested as an aqueous phase. However, the recovery was unsuccessful with HCl as no Ta was stripped into the aqueous phase.

In other studies, Kulkarni et al^[70] proposed using $0.5 \text{ mol/dm}^3 \text{ Na}_2\text{CO}_3$ for the recovery of U(IV), while Seyfi and Abdi^[71] suggested using a $2 \text{ mol/dm}^3 \text{ Na}_2\text{CO}_3$ solution for Ti(IV) recovery. Again 0.05 to $5 \text{ mol/dm}^3 \text{ Na}_2\text{CO}_3$ base concentrations were prepared and evaluated as aqueous phases. Since Na_2CO_3 crystallised above 2 mol/dm^3 , the experiments above 2 mol/dm^3 were not carried out. Concentrations of 0.05 to $2 \text{ mol/dm}^3 \text{ Na}_2\text{CO}_3$ were evaluated, but no extraction was achieved for Ta.

Venkateswaran and Palanivelu^[72] used $1 \text{ mol/dm}^3 \text{ NaOH}$ for the recovery of chromium(IV). Hence, 0.01 to $3 \text{ mol/dm}^3 \text{ NaOH}$ solutions were tested as aqueous phases. The lower concentrations (0.01 to $0.1 \text{ mol/dm}^3 \text{ NaOH}$) crystallised and the samples could not be analysed. The higher concentrations showed no stripping of Ta.

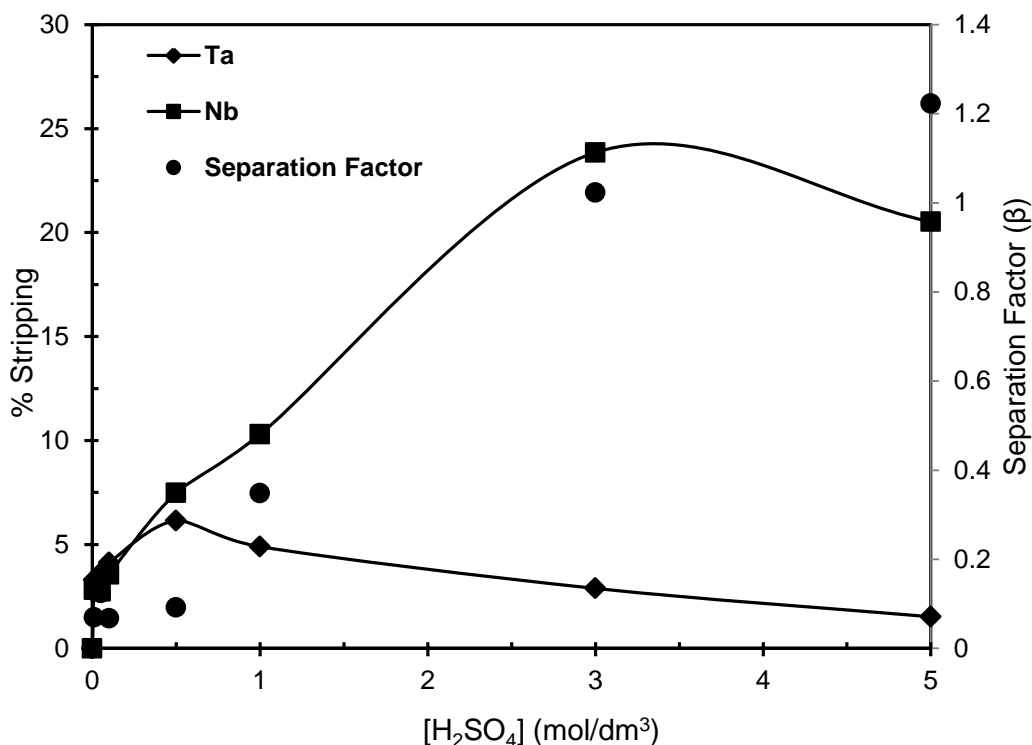


Figure 35 – Stripping experiment with 0 to 5 mol/dm³ H₂SO₄, at 25°C for 1hr at 350 rpm.

El-Hazek et al^[54] used only distilled water for the recovery of Ta and Nb and thus deionised water was evaluated in this experiment as the aqueous phase. The recovery was unsuccessful with H₂O as no Ta was stripped into the aqueous phase.

Li et al^[73] suggested using 1 mol/dm³ acid thiourea and Sun and Lee^[74] used 0.1 mol/dm³ to 1 mol/dm³ thiourea with 0.5 mol/dm³ HCl for the recovery of Au. Accordingly, 0.01M to 1M thiourea with 0.5M HCl acid concentrations were tested as aqueous phases. 0.7 to 1 mol/dm³ thiourea crystallised and those samples could not be analysed, while 0.01 to 0.7 mol/dm³ thiourea with 0.5 mol/dm³ HCl did not show any recovery of Ta.

In summary, H₂SO₄, Na₂CO₃, HCl, thiourea with HCl, NaOH and water were all tested as stripping agents to recover Ta from a loaded organic phase. Only with H₂SO₄ less than 5% of the metal could be recovered. With Na₂CO₃, HCl, thiourea with HCl, NaOH and water no recovery of Ta was achieved. It is clear that further studies will be required to find alternative solutions for the back extraction of the Ta and Nb from an organic stripping solution.

4.4 Membrane-based Solvent Extraction

As a possible pointer for further research, a brief experiment was finally conducted to evaluate the obtained batch extraction results when implemented in a membrane-based solvent extraction (MBSX) process. In Section 4.2, the effect of H_2SO_4 concentration, extractant concentration and contact time were presented for $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$. From these results the MBSX experiments was designed using a 4 mol/dm^3 H_2SO_4 with 100 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ solution-aqueous phase and PA as the extractant in a mole ratio of 10:1 in cyclohexane as the diluent and 3% v/v 1-octanol as the modifier.

A control sample was taken by combining equal volumes of the organic and aqueous phases, which were placed in a polypropylene bottle and shaken for 60 min at 350 rpm in the Labcon heater/shaker at 25°C.

In Figure 36 the MBSX results obtained from this run are presented. Only the first 30 minutes of samples were analysed, showing that the values were significantly lower than had been observed for the batch extractions where the data shown at 60 minutes was the control sample. From this graph it is clear that a maximum of 35% Ta and 19% Nb was extracted after 30 minutes, with a separation factor that remained below 1. Similar results were obtained when this experiment was repeated. Further studies would therefore be required to optimise the MBSX process.

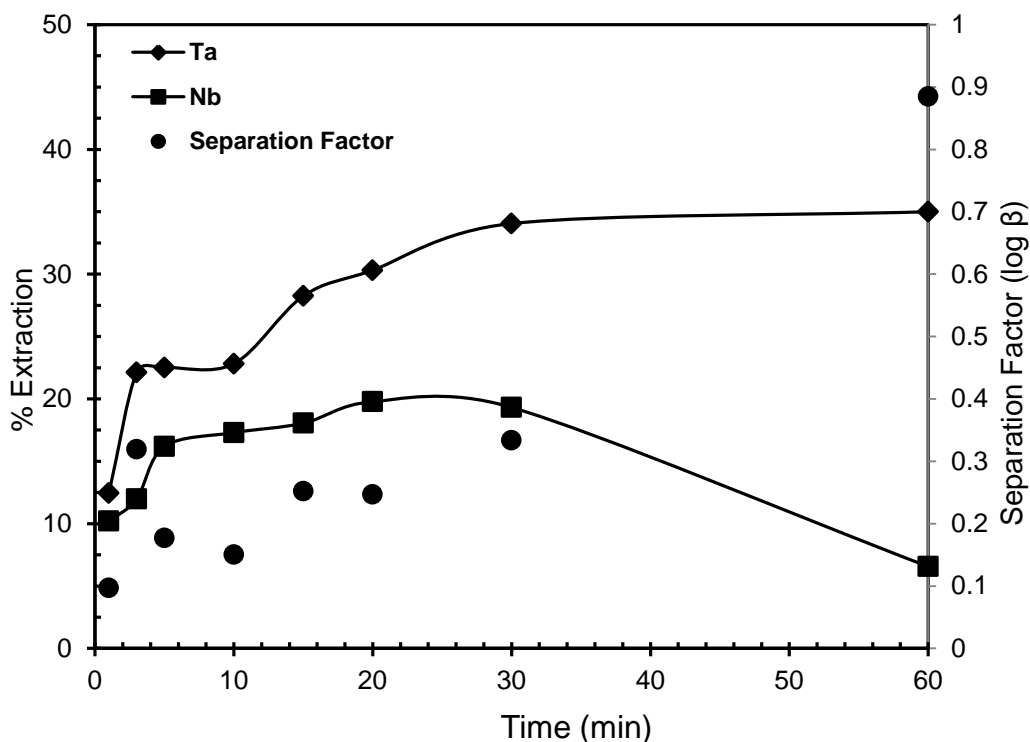


Figure 36 – MBSX with 4 mol/dm³ H₂SO₄ and 100 ppm NH₄Ta(Nb)F₆ in a 10:1 mole ratio of PA at 25°C at 350rpm for 1hr.

4.5 Conclusion

From the eight extractants (PA, D2EHPA, Alamine 336, Aliquat 336, TTA, 1-, 2- and 3-octanol) tested in four acids, including HClO₄, HNO₃, HCl and H₂SO₄, PA and D2EHPA showed the best extraction results for both Ta and Nb in Ta(Nb)F₅, irrespective of the acid used. This suggests that both Ta and Nb tend to preferentially form complexes with the cation exchangers PA and D2EHPA and less so with the neutral (TTA), anion exchangers (Alamine 336 and Aliquat 336) and the octanols. When comparing the separation factors of the four acids tested, H₂SO₄ showed the best results. It can therefore be concluded that, for the separation of Ta and Nb in Ta(Nb)F₅, PA and D2EHPA in the organic phase and H₂SO₄ in the aqueous phase were the best combination both in terms of extraction and selectivity.

In the second optimisation series, a NH₄Ta(Nb)F₆ solution was tested with H₂SO₄ in the organic phase and PA and D2EHPA in the organic phase. The range of 2 to 5 mol/dm³ H₂SO₄ showed the best results both in terms of the extraction and separation of Ta and Nb. An E/M ratio of 3:1 for PA and contact time of 10 minutes, compared to a 20:1 E/M ratio for D2EHPA and contact time of 15 minutes, showed to be the best combination for extraction

and the separation of Ta and Nb. In summary it seems that PA performed slightly better than D2EHPA.

The screening of the possible recovery of the metals from the organic phase proved to be more difficult than had been anticipated and further studies are required to find a suitable approach. It seems that Ta and Nb form stable complexes with PA and D2EHPA and the best recovery results obtained was from H_2SO_4 , where less than 5% Ta was recovered. The MBSX evaluation of the extraction of $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ also proved to be more complicated than the results obtained from the batch extractions would have suggested. Similar to the findings made for the recovery, it is clear that further studies are required for the optimisation of the MBSX process.

Chapter 5

Evaluation & Recommendations

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5.1 Introduction

Traditionally Ta and Nb are separated requiring harsh conditions with high concentrations of HF and H₂SO₄, using potentially dangerous extractants including MIBK, TBP and cyclohexanone. In this study the main objective was to separate Ta and Nb with solvent extraction using less harsh conditions and safer extractants. To determine the best combination in which the metal forms complexes with extractants, eight different extractants were used, namely the cation exchangers di-iso-octyl-phosphinic acid (PA) and di-(2-ethylhexyl)-phosphoric acid (D2EHPA), the neutral solvating extractant 2-thenoyl-trifluoroacetone (TTA), and the anion exchangers Alamine 336, Aliquat 336, 1-octanol, 2-octanol and 3-octanol with 3% v/v 1-octanol added as modifier to cyclohexane which was used as the diluent for the organic phase. Four different acids namely, HCl, HNO₃, H₂SO₄ and HClO₄, were used to determine the best combination for extraction and the extractant to metal ratio was varied between 0.1:1 and 20:1. Two different Ta and Nb sources were investigated, namely Ta(Nb)F₅ and NH₄Ta(Nb)F₆. The success and shortcomings of this study will be discussed on the basis of the aims presented in Chapter 1 (Section 1.3).

- In the first stage, Ta(Nb)F₅ salts were used in the aqueous phase to find the optimum conditions in terms of acid and extractant concentrations for extraction. All eight extractants were investigated. From the results, the best conditions for the extraction and separation of Ta and Nb in the fluoride salt was achieved when using the extractants PA and D2EHPA with an E/M ratio above 3:1 (7.7 mmol/dm³). According to these results it is clear that extraction occurred preferentially in a cation exchange mechanism. When samples were left for analysis after SX, precipitation occurred from the aqueous phase in samples containing Alamine 336, Aliquat 336 and TTA. It is therefore advisable that samples should be analysed within 3 days after extraction.
- Four different acids, HClO₄, HNO₃, HCl and H₂SO₄ were investigated to determine the most suitable acid-extractant combination for extraction. From the results, the best conditions for the extraction of Ta and Nb in the fluoride salt was achieved from H₂SO₄ above 10 mol/dm³ as the aqueous phase. For the optimum separation of Ta and Nb, H₂SO₄ concentrations between 0 and 3 mol/dm³ with PA and between 12 and 15 mol/dm³ with D2EHPA showed the best results.
- In the second stage, the extraction conditions of Stage 1 were evaluated using NH₄Ta(Nb)F₆, which is the compound currently used by Necsa. This section entailed

a study on the effect of acid concentration; effect of extractant to metal ratio and the effect that contact time had on extraction. The optimised conditions from the results of Stage 1 were tested on a stable $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ solution in H_2O containing trace amounts of HF. The best extraction occurred at concentrations above 3 mol/dm^3 H_2SO_4 with an E/M ratio above 3:1 (2.4 mmol/dm^3) for the extractant PA and 5 mol/dm^3 H_2SO_4 with an E/M ratio of 20:1 (16.3 mmol/dm^3) for the extractant D2EHPA. The optimum contact time for PA was reached after only 10 minutes, while 20 minutes were required for D2EHPA. Again there was an ageing effect of the aqueous phase and in this case it is not recommended to leave the solutions containing the metal to stand for more than one day.

- In Stage 3, the recovery of the metal from the organic phase as well as the application of the above findings in a membrane-based solvent extraction process (MBSX) was briefly investigated. Less than 5 % recovery from an H_2SO_4 aqueous phase and no recovery of the metal from the loaded organic phase with the other stripping agents could be achieved. It is clear that a stable compound is formed when Ta and Nb are extracted using PA and D2EHPA, necessitating further studies to improve the extraction. The optimum conditions from the bench-scale extraction of Ta and Nb were subsequently tested in a MBSX setup. However, possibly due to speciation, very low extraction was achieved.

5.2 Evaluation

5.2.1 Acids

Four different acids, including HClO_4 , HNO_3 , HCl and H_2SO_4 were investigated for the extraction and separation of Ta and Nb. In Table 3, K_a and $\text{p}K_a$ values of the most common acids are listed.^[93,94,95]

The dissociation constant, K_a , describes the tendency of a compound to dissociate into its ions. From the four acids used in this study, it is clear from Table 3 that HClO_4 had the highest K_{a1} value, and thus the lowest $\text{p}K_{a1}$ values, followed by HCl , H_2SO_4 and HNO_3 , meaning that HClO_4 dissociates more readily into its ions than the other acids. When comparing this trend to the extraction data presented in Chapter 4.1.1, it seems that with increasing acid concentration, the extraction decreased slightly with increasing $\text{p}K_a$ values both for Ta and Nb. For example, HNO_3 , with the highest $\text{p}K_a$ value, showed no significant

extraction when using Alamine 336, Aliquat 336, TTA or any of the octanols. Another example is the Nb extraction using D2EHPA where the Nb extraction decreased with increasing pK_a values. All these acids have a K_a value above 1 and are thus classified as strong acids.^[96] The exception to this trend seems to be H_2SO_4 , which yielded the highest selectivity due to a high Ta and low Nb extraction, especially at low H_2SO_4 concentrations. This different behaviour could, however, be related to the fact that H_2SO_4 was the only acid that has two K_a values for the dissociation of both hydrogen atoms.

Table 3 - K_a and pK_a values of different acids^[93,94,95]

Acid Name	Formula	Conjugated Base	K_{a1} (pK_{a1})	K_{a2} (pK_{a2})	K_{a3} (pK_{a3})
Hydroiodic acid	HI	I^-	$\approx 10^{10}$ (≈ -10)	-	-
Perchloric acid	$HClO_4$	ClO_4^-	$\approx 4 \times 10^8$ (- 8.6)	-	-
Hydrobromic acid	HBr	Br^-	$\approx 10^8$ (≈ -8)	-	-
Hydrochloric acid	HCl	Cl^-	$\approx 10^6$ (≈ -6)	-	-
Sulphuric acid	H_2SO_4	SO_4^{2-}	$\approx 10^4$ (≈ -4)	1.2×10^{-2} (1.9)	-
Nitric acid	HNO_3	NO_3^-	$\approx 10^2$ (≈ -2)	-	-
Hydronium ion	H_3O^+	H_2O	55.5 (-1.74)	-	-
Chromic acid	H_2CrO_4	$HCrO_4^-$	0.16 (0.8)	-	-
Hypo-phosphorous acid	H_3PO_2	PO_2^{3-}	0.1 (1)	-	-
Phosphorous acid	H_3PO_3	PO_3^{3-}	1.5×10^{-2} (1.82)	-	-
Phosphoric acid	H_3PO_4	PO_4^{3-}	7.5×10^{-3} (2.1)	6.2×10^{-8} (7.2)	4.8×10^{-13} (12.3)
Hydrofluoric acid	HF	F^-	6.3×10^{-4} (3.2)	-	-
Sulphurous acid	H_2SO_3	SO_3^{2-}	1.5×10^{-5} (41.8)	1.0×10^{-7} (7)	-

In Figure 37, various acids and their conjugated bases are presented according to their pH levels.^[97] It can be observed that the pH levels of the four acids investigated in this study ranged between 0 and -8. It could have been assumed that the higher the K_a value, the lower

the pH value and thus the same acid order achieved (Table 3) the same order of pH values. However, the pH order of HCl and H₂SO₄ is reversed, again confirming that H₂SO₄ behaves slightly different than the monoprotic acids.

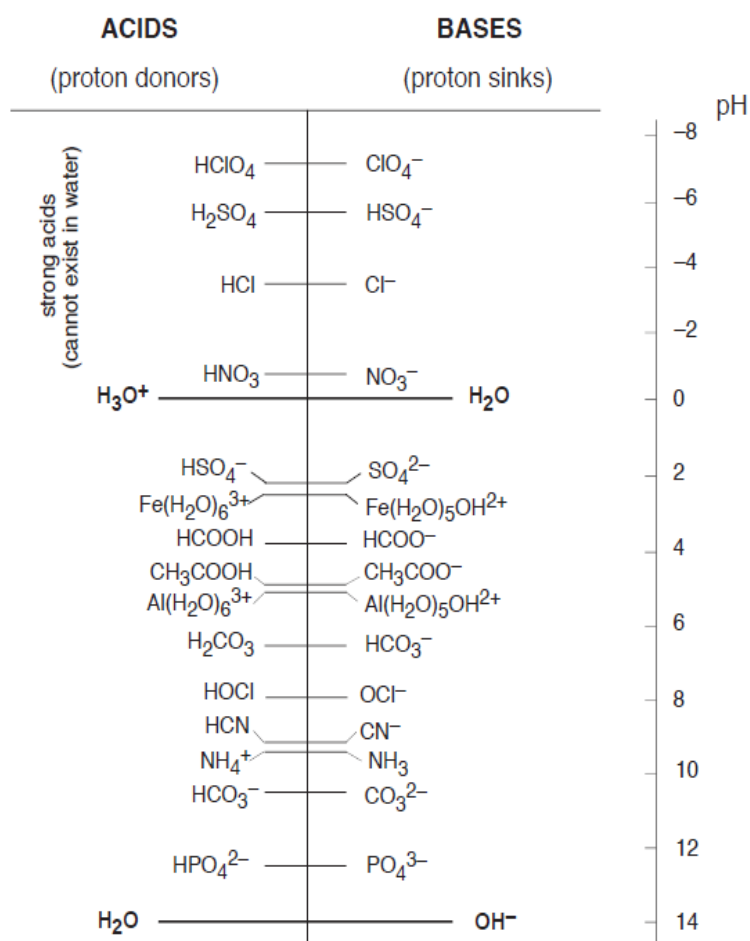
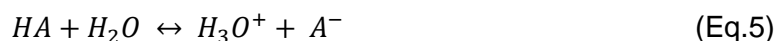


Figure 37 – pH levels of various acids and conjugated bases

Equation 5 represents a dissociation mechanism for acid (HA) in water, producing the hydronium ion (H₃O⁺) and a conjugated base (A⁻). According to the Henderson-Hasselbalch equation^[98], the pH of an acid HA is equal to the pKa value of HA plus the log value of the dissociated acid (A⁻) concentration divided by the initial acid concentration, as shown in Equation 6.



$$pH = pKa + \log \frac{[A^-]}{[HA]} \quad (\text{Eq.6})$$

Using this equation for the two step dissociation of H_2SO_4 , Figure 38 was obtained, which represents the formation of the conjugated species formed as a function of pH. At a pH of -6, only the H_2SO_4 species exist. As the pH increases, the concentration of HSO_4^- increases, with its highest concentration between pH -4 and -1.5, after which the concentration of SO_4^{2-} increases.

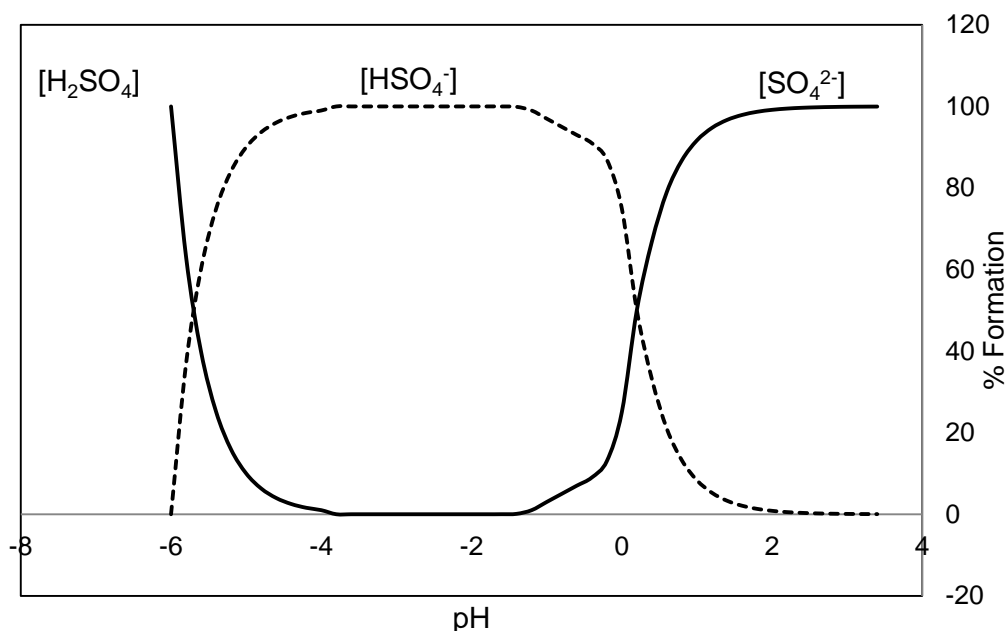


Figure 38 – The formation of the conjugated species of H_2SO_4 as a function of pH

In this study, the H_2SO_4 acid concentration ranged between 0 and 15 mol/dm³, indicating a pH range between 7 and -0.7. In this study, according to Figure 38, it seems that the SO_4^{2-} species predominated with a minimal influence of the HSO_4^- species. It is known that the sulphate species SO_4^{2-} can act as a ligand either by way of one (monodentate) or by two oxygen atoms (bidentate), forming a water soluble complex with most metals.^[99] It is therefore possible that this additional sulphate metal complex formation of Ta and Nb may be the reason why extraction and separation of these metals were most successful when using H_2SO_4 , compared to the use of HClO_4 , HCl and HNO_3 . However, further studies are required to verify the contribution of this acid complexation to the overall extraction and selectivity achieved.

5.2.2 Extractants

As mentioned previously, eight different extractants were investigated in this study including PA, D2EHPA, Alamine 336, Aliquat 336, TTA, 1-octanol, 2-octanol and 3-octanol. In Figure 39, the molecular structure of the eight extractants is depicted.

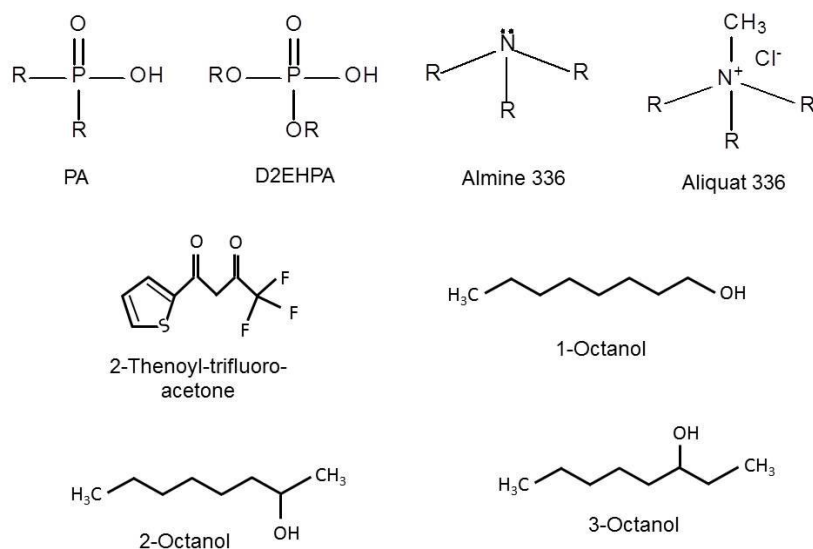


Figure 39 - Molecular structure of the eight extractants investigated

From Figure 39 it can be observed that PA and D2EHPA are the only two extractants containing both phosphorous as well as numerous oxygen atoms. Both of these oxoacids have acidic properties. However, at the high acidic content used in this study, it is assumed that they both remained protonated during extraction. As was discussed in Section 2.2.1, both Ta and Nb favour extraction in acidic conditions and therefore may additionally favour the preferred extraction by PA and D2EHPA. John et al,^[100] when studying the extraction of U(VI), found that the D2EHPA extraction of U(VI) was pH dependant and found the optimum pH for extraction to be above 0, which confirms the results found in Section 4.2.2. It is also apparent that both PA and D2EHPA have significant resonance stabilisation, which would result in an abundance of free electrons as well as subsequent increased molecular stability. More important, however, could be the fact that both PA and D2EHPA have a P atom at their core, compared for example to TTA that has an S atom as part of the thiophene ring. Since P has a larger diameter than C or N, it implies that the oxygen groups are positioned further away from the P core, facilitating the inclusion of a metal, thereby improving the extraction of Ta and Nb compared to the other extractants evaluated.

Xing-bin et al^[101] found that the extraction with D2EHPA in a H_2SO_4 acidic medium increased with the increase in extractant concentration. This increase of extraction was pH dependant and proceeded according to the cation exchange mechanism, which was confirmed by the finding in Section 4.2.2, i.e. that the extraction increased with an increase both in the PA and D2EHPA concentration. In conclusion, it is clear that the speciation of the extraction of Ta and Nb and its influencing factors, including the pH effect, H_2SO_4 concentration effect and extractant concentration effect need further investigation.

5.3 Recommendations

- In the batch extraction experiments, polypropylene bottles were used to shake the two phases in a shaking incubator for 1 hr at 25°C. Each bottle was removed from the incubator and the contents poured into a separating funnel. These batch extraction experiments are labour intensive and a significant amount of waste chemicals are produced. An investigation into other SX apparatuses or devices could be undertaken to reduce the amount of time and chemicals used.
- Although H_2SO_4 , from the investigation of four acids, seemed to be the best acid for the extraction and separation of Ta and Nb, investigation into other oxidising acids, including HI and HBr, as well as other bi- or triprotic acids, for example H_3PO_4 , would be beneficial to obtain a more complete picture of the speciation preferences of Ta and Nb.
- The cationic extractants PA and D2EHPA showed the best extraction and separation data for Ta and Nb. Other cationic extractants, including LIX® commercial reagents and trioctyl amine (TOA), could be investigated to obtain more data regarding the speciation while possibly yielding a better extractant for the optimum extraction and separation of Ta and Nb.
- Positive results have been obtained from this study, where Nb and Ta have been successfully extracted and separated with H_2SO_4 and PA, with PA showing a high selectivity towards Ta. Future studies could focus on using other forms of Ta and Nb

salts of which the speciation is known. Again, attention should be on the speciation of Ta and Nb in these various media. Molecular modelling may be a suitable tool to help unravel the speciation challenge.

- The Ta/Nb metal ratio in this study was kept constant at 1 to 1. However, Ta/ Nb minerals contain a variety of different ratios of Ta and Nb, as was shown in Table 1 (Section 2.1). Ratios to mimic the minerals found in nature could be investigated.
- It is clear that the recovery of Ta from the organic phase has not been optimised. Again speciation of Ta and Nb in various media probably influence the recovery. Molecular modelling may help in uncovering the speciation problem. Further stripping agents could also be investigated for the recovery of Ta and Nb from the organic phase.
- For the MBSX process, the next step should entail the optimisation of the MBSX conditions for the up-scaling to an industrial-scale pilot plant. An economic and environmental impact study would be needed to determine the economic viability of such a plant.

Chapter 6

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Appendix

Quantitative Determination of Ta and Nb

For the analyses of Ta and Nb, a Thermo-Scientific iCap 6000 Series ICP-OES, with the iTEVA software application was used. A Thermo-Scientific ICP-OES is presented in Figure A1.

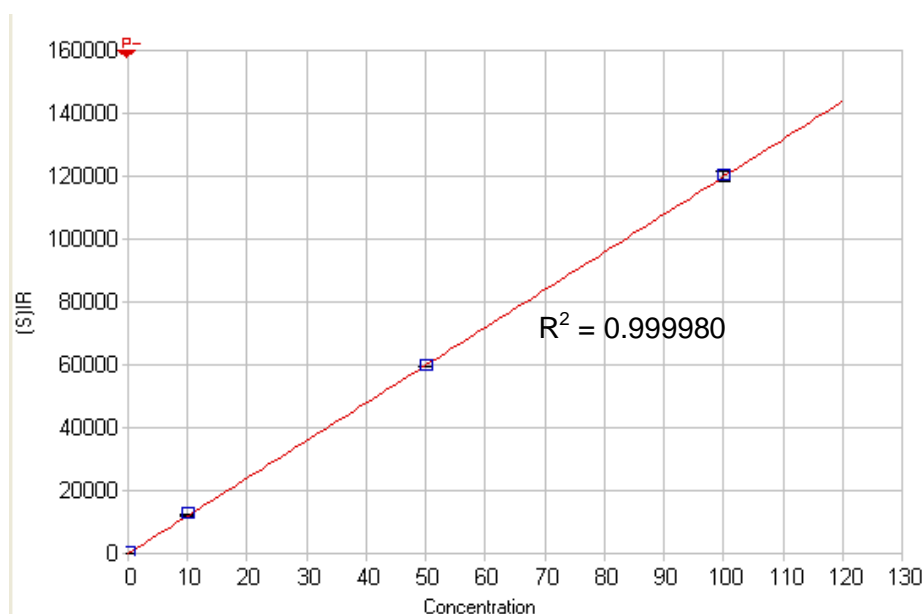


Figure A1 - Thermo-Scientific ICP-OES

Ultrapure ICP internal standards containing Ta and Nb were purchased from Alfa Aesar and de Bruyn Spectroscopic Solutions, respectively. The matrix of these standards consisted of 1000 ppm $\text{NH}_4\text{Ta}(\text{Nb})\text{F}_6$ in H_2O with trace amounts of HF, with less than 1.2 ppm impurities. Volumetric flasks were made up with different concentrations (10, 50, 100, 500 ppm) of both the Ta and Nb standard and used for the calibration of the ICP. According to the iTEVA software, the ICP was calibrated at two emission wavelengths for both Ta (226.2 and 268.5 nm) and Nb (309.4 and 319.4 nm) where the least amount of interference was observed. The calibration curve for each emission line for Ta is represented in Figures A2 and A3 (with Tables A1 and A2 representing the calibration data for Ta) and for Nb in Figures A4 and A5 (with Tables A3 and A4 representing the calibration data for Nb).

Table A1 - Calibration data for Ta at 226.2 nm emission line

Sample Name	Concentration (ppm)		% Difference
	Stated	Found	
Blank	0.000	0.000	0.000
Cal. 1	10.000	10.223	2.230
Cal. 2	50.000	49.736	-0.529
Cal. 3	100.000	100.040	0.041

**Figure A2 - Calibration curve for Ta at 226.2 nm emission line**

The correlation for the calibration curve for Ta at the 226.2 nm emission line (Figure A2) was $R^2 = 0.999980$. The average % difference (Table A1) in the standard solutions was 0.436%. The correlation for Ta at the 268.5 nm emission line (Figure A3) was $R^2 = 0.999944$, thus being lower than the calibration at 226.2 nm, with an average % difference (Table A2) of 0.339% and thus being lower than for the 226.2 nm emission line.

Table 2 - Calibration data for Ta at 268.5 nm emission line

Sample Name	Concentration (ppm)		% Difference
	Stated	Found	
Blank	0	0.000	0.000
Cal. 4	10	10.231	2.310
Cal. 5	50	49.281	-1.440
Cal. 6	100	100.490	0.487

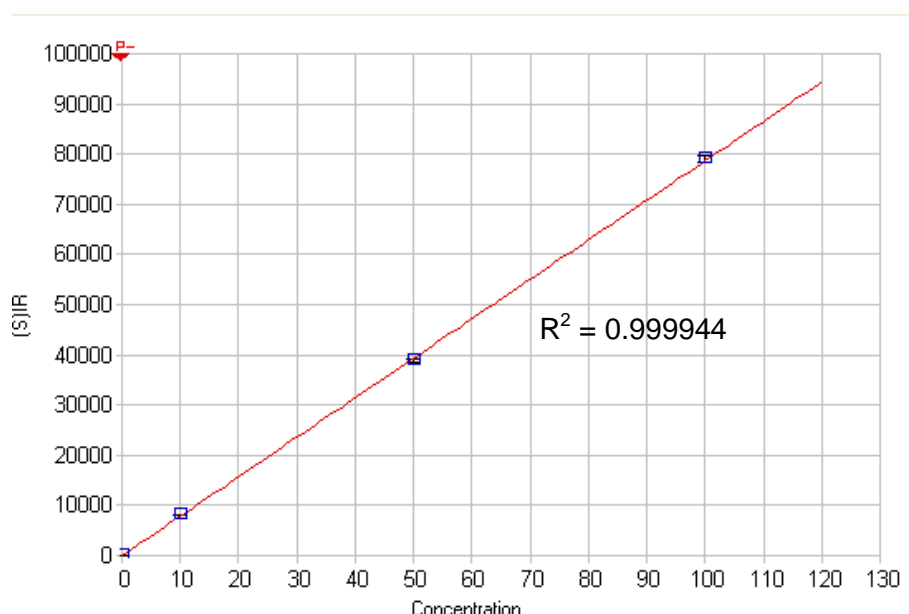


Figure A3 - Calibration curve for Ta at 268.5 nm emission line

The calibration curve for Nb at the 309.4 nm emission line (Figure A4) showed a correlation of $R^2 = 0.999978$. The average % difference (Table A3) in the standard solutions was 0.385%. The correlation for Nb at the 319.4 nm emission line (Figure A5) was $R^2 = 0.999962$, thus being lower than the calibration at 309.4 nm, with an average % difference (Table A4) of 0.702% and thus being higher than for the 309.4 nm emission line.

Table 3 - Calibration data of Nb at 309.4 nm emission line

Sample Name	Concentration (ppm)		% Difference
	Stated	Found	
Blank	0	0.000	0.000
Cal. 7	10	10.171	1.710
Cal. 8	50	49.58	-0.420
Cal. 9	100	100.250	0.250

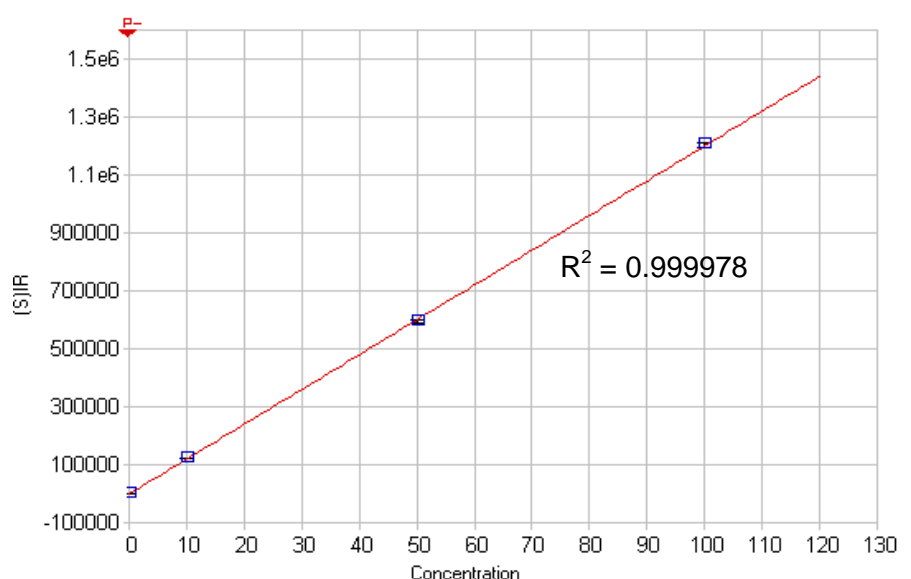


Figure A4 – Calibration curve of Nb at 309.4 nm emission line

Table 4 - Calibration data of Nb at 319.4 nm emission line

Sample Name	Concentration (ppm)		% Difference
	Stated	Found	
Blank	0	0.000	0.000
Cal. 10	10	10.312	3.120
Cal. 11	50	50.13	0.130
Cal. 12	100	99.558	-0.442

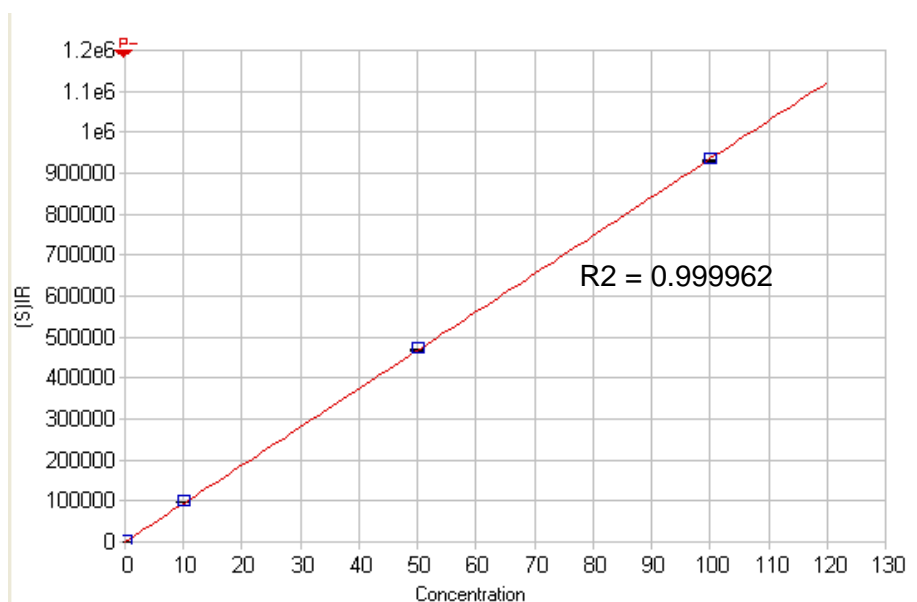


Figure A5 - Calibration curve of Nb at 319.4 nm emission line

From these results obtained for the calibration curves of Ta and Nb, it was concluded that the 226.2 nm and 309.4 nm emission lines for Ta and Nb, respectively, were most accurate. These emission lines were used for all analyses done for Ta and Nb.