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Possible methodology for niobium, tantalum and scandium separation in ferrocolumbite

W. Purcell^{1,2}, H. Potgieter², M. Nete¹ and H.Mnculwane¹

¹Department of Chemistry, University of the Free State, Bloemfontein, South Africa

²School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

Abstract

Ferrocolumbite is a well-known source of Ta, Nb and Sc. However, separation of these elements from such ores/process tailings, as well from each other is problematic, typically involves numerous separation steps and very corrosive and hazardous chemicals. An investigation was therefore launched to evaluate alternative separation options. As part of this endeavour it was necessary to investigate accurate quantification methods to be able to trace the elements during any proposed process.

Ferrocolumbite was successfully dissolved with $\text{NH}_4\text{F}\cdot\text{HF}$ (1:10 sample to flux ratio at 200 °C for 60 min), which yielded solutions containing 91% Ta, 96 % Nb and 99% Sc recoveries while satisfactory LODs (0.07768, 0.01045 and 0.001085 respectively) were also obtained. Inclusion of a magnetic separation step (only 31% Fe in magnetic portion) to simplify the down-stream beneficiation processes did not contribute to the successful removal of Fe/Ti. Methyl isobutyl ketone (MIBK) successfully extracted the Ta in the ore (94 %) into the organic layer and left Nb (88 %) and Sc (99 %) in the aqueous layer at $[\text{H}_2\text{SO}_4] < 8 \text{ M}$. At higher acid levels ($[\text{H}_2\text{SO}_4] > 10 \text{ M}$) the Sc present in the non-magnetic portion of the ore migrated in significant amounts and quantities (95 %) to the organic layer. Thus a possible process for the separation of the three elements from one another was created. Octan-1-ol yielded similar results to MIBK while methyl isoamyl ketone (MIAK) successfully removed Ta from the aqueous layer (87 %), but left the two other elements in the aqueous layer, even at 16 M $[\text{H}_2\text{SO}_4]$. A process flow sheet for the possible separation of Nb, Ta and Sc from ferrocolumbite and mine tailings is proposed.

1. Introduction

Columbite-tantalite (coltan) refers to a solid solution series, which is formed between two different minerals, namely columbite and tantalite with columbite the niobium-rich group member and tantalite the tantalum-rich member (Beurlen et al., 2008). The international Mineralogical Association (IMA) discredited the general reference to columbite as mineral and replaced it with the more specific designations of ferrocolumbite (Columbite-(Fe)), which is rich in Fe and manganocolumbite (Columbite-(Mn), which is rich in Mn (Burke, 2008). Ferrocolumbite is the most common columbite specimen, the manganocolumbite less common while the Mg rich columbite, magnesiocolumbite (columbite-(Mg)) is the least common. In general, despite being discredited, the name columbite is still used without further designations.

The columbite found in Brazil is normally mined for its rich niobium content (31 – 79 % Nb₂O₅) (Pohl, 2011) and not necessarily for its smaller amounts of tantalum. The chemical characterization of these minerals also indicate the presence of moderate quantities of iron and titanium, but also small quantities of scandium (0.135 %) and only one other “adopted” rare earth element, yttrium (0.17 %). The chemical characterization of the discarded mine tailings after the initial processing of the columbite ore at these mines or processing plants indicate the presence of large amounts of iron, moderate amounts of tantalum and niobium and smaller amounts of scandium (0.996 %) and yttrium (0.38 %).

The tantalite found in most African countries are normally tantalum rich and niobium poor and are often referred to as “blood or conflict minerals” due to the fact that finances obtained from the selling of these minerals are used to buy weapons and ammunition (Hayes and Burge, 2003). These armed and criminal elements then commit serious human rights violations, which include the mistreatment of the miners and other civilians, the use of child labor, committing widespread sexual violence as well as indiscriminate executions. International efforts such as the "Dodd-Frank Act" (Section 1502 of the US law) require that companies using gold, tin, tungsten and tantalum in the manufacturing of their products need to make efforts to determine if those materials came from the DRC or an adjacent country and to carry out a "due diligence" review of their supply chain (bag-and-tag) to control and legalize the tantalum market and to prevent the funding of armed or criminal groups in eastern DRC (Wolfe, 2015; Lee, 2011).

The main elements in the columbite-tantalite series, namely tantalum and niobium, are extremely important in modern day technology such as the use of Ta in cell phones, laptops and iPads while Nb is used as superconductors and in the manufacturing of super alloys in the construction industry (Eckert and Hermann, 1996; Ruiz et al, 2002) and as implants in medical industry (Matsuno et al, 2001). The presence of Sc as impurity in the Brazilian columbite is very interesting. Sc is not a scarce element in the earth's crust (42 most abundant element in earth's crust), but it has a low affinity for other minerals and is therefore seldom found in high grade, high volume deposits, which is commercially viable for production (Kemp and Wolf, 2006).

Even at elevated concentration in minerals its processing is difficult. It is commonly found in association with tungsten and tin in minerals such as wolframite, thortveitite, monazites and some granitic pegmatites (Krebs, 2006). Current estimates indicate the global market volume for Sc is between 10 and 15 tons per annum (U.S. Geological Survey, 2015). At these low levels of production, it is not surprising that the development of new products containing the metal is almost non-existent, although the metal has enormous potential to be used in high-tech applications due its unique properties. Added to aluminum, it produces a new alloy, which is heat-tolerant, corrosion-resistant, strong, and has excellent weldable properties, which is in high demand in the aircraft and automobile industry (Krebs, 2006). It is also used in the production of high-intensity lamps due to its unique optical properties and in the manufacturing of solid oxide fuel cells due to its exceptional heat resistance and electrical properties (U.S. Geological Survey, 2015).

Recently we completed a comprehensive and fundamental investigation on the dissolution and subsequent hydrometallurgical separation of Ta and Nb in different tantalite samples from different locations in Africa (Nete et al, 2012; Nete et al, 2013; Nete et al, 2014). Results from these studies indicated that methyl isoamyl ketone (MIAK) was very successful as solvent extractant to remove Ta from the rest of the elements in an 8 M H₂SO₄ solution with almost no Nb contamination. The Nb was successfully separated from the rest of the elemental impurities present in the mineral ores using a Dowex Marathon wba anion exchange resin.

A number of objectives were targeted in this study. The first was to accurately quantify the three elements of interest (Ta, Nb and Sc) in natural columbite as well as in mine tailings, secondly to determine whether the dissolution and separation process mentioned above is also viable for columbite beneficiation and thirdly to determine the efficiency of the extraction process at higher acidity levels. The study also included the tracing of the three elements during each of the hydrometallurgical process steps to determine a possible extraction and isolation process for Sc from these kinds of minerals and waste material.

2. Experimental

2.1 Equipment and materials

Adjustable-volume Gilson Pipetman (100 μ L – 1000 μ L) and Brand Transferettes (1 mL – 10 mL) micro-pipettes were used for the accurate measuring and transfers of solutions. The glassware (beakers and volumetric flasks) used for all the elemental analysis was of Schott Duran, grade (A) type. The magnetic susceptibility of the samples was determined with a Sherwood Scientific magnetic susceptibility balance (MSB) at 25 °C. A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer was used for the qualitative and quantitative analyses of the ferrocolumbite and mine tailing samples. The operating conditions reported in **Table 1** were maintained for all the analyses.

Table 1: Operating conditions ICP-OES

Parameter	Condition
RF power	1.2 kW
Coolant gas flow	14.0 L/min
Plasma gas flow	1.2 L/min
Carrier gas flow	0.7 L/min
Sample uptake method	Peristaltic pump
Spray chamber	Glass cyclonic
Type of nebuliser	Concentric

Ultra-pure water (0.02 to 0.00 $\mu\text{S}/\text{cm}$) obtained *via* reverse osmosis was used for all the analytical solution preparations. All chemicals, reagents and samples (with their known purity) were used without further purification. HCl (32 %), HNO₃ (65 %), H₂SO₄ (95 - 99 %), MIAK (\geq 98 %), H₂SO₄ (95 - 97 %), ammonium bifluoride (NH₄F·HF) and the ICP standards containing 1000 mg/L Nb, Ti, Sn, W, Si, Ta, Y and Sc as well as a multi-element standard (32 elements) containing 1000 mg/L each of Mn, Al, Fe and other more common elements were bought from Merck. Th and U standards (1000 mg/L) were bought from De Bruyn Spectroscopic and the ICP standard solution containing 100 mg/L Sc was bought from Spectrascan. The ICP standard solution containing 100 mg/L Zr was purchased from Sigma-Aldrich. 1-octanol (99.5 %) was purchased from Associated Chemical Enterprises while the methyl isobutyl ketone (MIBK) (99 %) was sourced from Saarchem. The two different mineral samples, namely the columbite sample and Ta/Nb residue/tailing sample, labelled as Sample A and Sample B respectively (see Figure 1), originating from Brazil, were supplied by the London and Scandinavian metallurgical Co. The analytical results reported in this paper represent the average of three replicate analyses while the standard deviations are reported in such a way that it reflect the uncertainty in the calculated results (last digit of a result).

**Figure 1:** Columbite sample (A) and residue (B)

2.2 Preparation of standard solutions

All glassware used in this study was soaked in 55 % HNO₃ for about 24 hours and then rinsed 2-3 times with ultra-pure water and dried prior to use. A set of calibration standards for ICP-OES analysis was prepared by dilution of the appropriate volumes of the primary ICP standards with water in 100.0 mL volumetric flasks to make 0.5, 1.0, 3.0, 5.0 and 10.0 mg/L concentrations. The acidity of the solutions was adjusted by addition of 10 mL 95 – 97 % H₂SO₄ before they were filled to the mark with ultra-pure water. Blank solution preparations were similar to the calibration solutions and were used for background corrections. All prepared standard solutions were homogenized and left to stand for 5 hours before use. Quantitative analyses were performed using the ICP-OES at the selected wavelengths. Wavelength selection was based on sensitivity of the analytical line and the lack of interference by other elements in solution. Ta, Nb and Sc were analysed at 228.916, 309.418 and 361.384 nm respectively. The limit of detection (LOD) was determined using an average of the triplicate measurements of the standard solutions' intensities and ten replicate measurements of the blank solution.

2.3 Optimizing the experimental conditions using Sample A

2.3.1 Dissolution of Sample A with NH₄F·HF fusion

Approximately 0.05 g of Sample A was weighed (accurately to 0.1 mg) in a platinum crucible and thoroughly mixed with approximately 0.5 g of NH₄F·HF flux (1:10 sample to flux ratio). The mixture was fused at 200 °C for 30 min in a high temperature oven and a white amorphous solid melt was obtained. The melt was dissolved in ultra-pure water and the solution was magnetically stirred for 5 min. Some of the solid sample remained in the solution. The residue was then filtered and the filtrate was quantitatively transferred into 100.0 mL volumetric flasks and filled to the mark with ultra-pure water. A 10.0 mL solution was pipetted into a 100.0 mL volumetric flask and 10 mL 95 – 97 % H₂SO₄ was added. The solution was left to cool down and filled to the mark with ultra-pure water for quantitative analysis using ICP-OES. The results are reported in **Table 2** as the equivalent oxides of the most stable oxidation state of the elements for comparison with previously reported values.

Table 2: Ammonium bifluoride fusion of Sample A at different times and different sample:NH₄F•HF ratios at 200 °C

Element	Expected %*	Experimental %			
		1:10 ratio and 30 min	1:10 ratio and 60 min	1:10 ratio and 90 min	1:20 ratio and 30 min
Nb ₂ O ₅	43.74	36.24	42.12	45.32	39.85
Fe ₂ O ₃	29.49	26.12	29.23	29.51	26.98
TiO ₂	10.63	9.63	10.45	10.36	10.31
Al ₂ O ₃	0.89	5.09	-	-	-
Mn ₃ O ₄	2.10	1.14	1.66	1.69	1.19
SnO ₂	1.42	3.94	4.29	4.86	4.19
U ₃ O ₈	<0.05	0.00	0.00	0.01	0.00
ThO ₂	<0.055	0.00	0.01	0.01	0.00
WO ₃	0.81	0.65	0.58	0.51	0.76
Ta ₂ O ₅	4.51	3.81	4.09	5.82	4.83
ZrO ₂	0.64	0.34	0.18	0.05	0.34
SiO ₂	1.63	64.31	-	-	-
Y ₂ O ₃	0.15	0.050	0.036	0.09	0.039
Sc ₂ O ₃	0.135	0.066	0.134	0.133	0.075

*Reported results from the London and Scandinavian Metallurgical Co Limited (LSM) Analytical Services

The incomplete sample dissolution and low recoveries obtained from the 1:10 sample to flux ratio compared to their expected content values in Table 1 prompted a further investigation to optimize the experimental conditions for the dissolution method of this mineral sample. The Al₂O₃ results were found to be highly inaccurate, possibly due the presence of residual fluoride from ammonium bifluoride. The SiO₂ results were highly inaccurate and this could have been due to the formation of ammonium and were not included in subsequent analyses (Timokhin and Komarova, 1986).

2.3.2 Influence of sample:flux ratio and the fusion time on Sample A

Three portions of Sample A (approximately 0.05 g) were weighed (accurately weighed to 0.1 mg) in three different platinum crucibles. In the 1st crucible, Sample A was mixed with NH₄F•HF flux in ratio of 1:20 sample:flux and fused for 30 min at 200 °C. The 2nd and the 3rd portions were mixed with NH₄F•HF flux in ratio of 1:10 sample:flux and fused at 200 °C for 60 min and for 90 min respectively. The obtained melts were allowed to cool to ambient temperature and then dissolved in water and visual inspection indicated that small portions of the sample had not dissolved in the mixtures. The undissolved solids were removed by filtration and the solutions were quantitatively transferred to 100.0 mL volumetric flasks and filled to the mark with ultra-

pure water. 10.0 mL aliquots of each solution were transferred to another 100.0 mL volumetric flask and 10 mL 95 – 97 % H₂SO₄ was added to each volumetric flask. The solutions were left to cool down and then filled to the mark with ultra-pure water for quantitative analysis using ICP-OES. The obtained results are given in **Table 2**. Comparing the analytical results obtained in the above sections with those of the expected results, a 60 min digestion period at 200 °C with a 1:10 sample:flux ratio was selected as optimum experimental conditions for the rest of the investigation (comparing the % content of the major elements such as Nb, Ta and Sc).

2.3.3 Application of the optimal experimental conditions for the dissolution of Samples A and B

The NH₄F·HF fusion and dissolution procedures were repeated for Sample A and Sample B. Approximately 0.05 g (accurately weighed to 0.1 mg) of each mineral sample was thoroughly mixed with 0.5 g of NH₄F·HF in platinum crucibles and fused at 200 °C for 60 min. The obtained melts were cooled to room temperature and dissolved in water and visual inspection indicated that small amounts of the sample did not dissolve in the mixtures. After filtering, the filtrates were quantitatively transferred to 100.0 mL volumetric flasks and filled to the mark with ultra-pure water and allowed to stabilize for 4 hours. These were further diluted by pipetting 10.0 mL aliquot of each solution to 100.0 mL volumetric flasks, adding 10 mL 95 – 97 % H₂SO₄, and allowing the solutions to cool to room temperature before filling them to the mark with ultra-pure water. The ICP-OES analyses of the two samples are reported in **Table 3**.

The analytical results in **Table 3** indicated that Fe and Ti (most probably ilmenite) were the impurities with the highest concentration and it was decided to try and remove the two metals prior to dissolution to limit the amount and type of down-stream impurities. Magnetic separation was used to remove the magnetically susceptible properties prior to dissolution and solvent extraction separation.

Table 3: Quantitative results obtained after the fusion dissolution of Samples A and B with $\text{NH}_4\text{F}\cdot\text{HF}$ (1:10 sample:flux ratio) at 200 °C for 60 min

Element	Sample A		Sample B	
	Expected % *	Experimental % [#]	Expected %*	Experimental % [#]
Nb_2O_5	43.74	42.14	3.89	3.51
Fe_2O_3	29.49	28.86	39.93	34.02
TiO_2	10.63	0.34	1.58	0.93
Mn_3O_4	2.10	1.74	0.26	0.29
SnO_2	1.42	4.85	2.45	0.33
U_3O_8	<0.05	0.002	0.19	0.00
ThO_2	<0.055	0.00	0.18	0.00
WO_3	0.81	0.77	0.31	0.07
Ta_2O_5	4.51	4.61	0.35	0.53
ZrO_2	0.64	0.06	1.38	0.17
Y_2O_3	0.15	0.09	0.38	0.03
Sc_2O_3	0.135	0.14	0.795	0.51

*Reported results from the London and Scandinavian Metallurgical Co Limited (LSM) Analytical Services

Average of three replicates

2.4 Magnetic removal of Fe and Ti in Samples A and B

2.4.1 Magnetic susceptibility determinations

The magnetic susceptibility of Samples A and B were determined as follows: the MSB balance was reset to zero and the empty capillary tube was weighed and then placed into the balance to determine the R_0 value. After this, the capillary tube was refilled with sample to a height between 2.6 cm and 3.1 cm. The capillary tube with the sample was re-weighed and the R value was recorded. The mass susceptibility (χ_g) of the samples was calculated as 1.301×10^{-6} and $0.0713 \times 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$ for Samples A and B respectively.

2.4.2 Magnetic removal of Fe and Ti from Samples A and B

The magnetic particles in 1.0 g portions of Samples A and B were repeatedly removed (using a permanent magnet) until visual inspection indicated that all the magnetic material was collected. The collected magnetic and non-magnetic portions were accurately weighed (0.1 mg), quantitatively transferred to platinum crucibles and thoroughly mixed with $\text{NH}_4\text{F}\cdot\text{HF}$ in a 1:10 sample:flux ratio. The mixtures were fused at 200 °C for 60 min in the high temperature oven. The fusion melts were then cooled to ambient temperature and dissolved with ultra-pure water.

Visual inspection indicated that some of the samples did not dissolve in the mixtures. The mixtures were filtered and the filtrate solutions were quantitatively transferred to 100.0 mL PTFE volumetric flasks and filled to the mark with ultra-pure water. A 10 mL aliquot of each solution was transferred to another 100.0 mL volumetric flask and the acidity of the solution adjusted with of 95 – 97% H₂SO₄, cooled and then filled to the mark with ultra-pure water. The solutions were analysed using ICP-OES and the results are presented in **Table 4**. The impact of magnetic separation differences are better observed in the graphical presentations in Figures 2 and 3 for Sample A and B respectively. These results clearly indicated that the elements of interest were present in both the portions (magnetic and non-magnetic) and thus no additional benefit was obtained from such a separation. Despite this observation, it was also obvious that a larger concentration of the elements of interest occurred in the non-magnetic portion of samples A and B, and hence the subsequent solvent extraction concentrated on the non-magnetic fraction of the samples.

Table 4: ICP-OES results for the elemental quantification of the magnetic and non-magnetic portions of Samples A and B

Element	Sample A (%)*			Sample B (%)*		
	Expected	Magnetic	Non-magnetic	Expected	Magnetic	Non-magnetic
Nb ₂ O ₅	43.74	11.81	26.73	3.89	1.18	2.15
Fe ₂ O ₃	29.49	9.32	17.58	39.93	11.32	20.63
TiO ₂	10.63	3.57	6.14	1.58	0.40	0.42
Mn ₃ O ₄	2.10	0.51	0.99	0.26	0.20	0.10
SnO ₂	1.42	0.07	0.30	2.45	0.07	0.14
U ₃ O ₈	<0.05	0.00	0.00	0.19	0.00	0.00
ThO ₂	<0.055	0.00	0.00	0.18	0.00	0.00
WO ₃	0.81	0.25	0.52	0.31	0.02	0.02
Ta ₂ O ₅	4.51	1.35	2.99	0.35	0.22	0.23
ZrO ₂	0.64	0.02	0.03	1.38	0.01	0.13
Y ₂ O ₃	0.15	0.02	0.03	0.38	0.02	0.01
Sc ₂ O ₃	0.135	0.06	0.09	0.795	0.23	0.24

* Average of two analyses

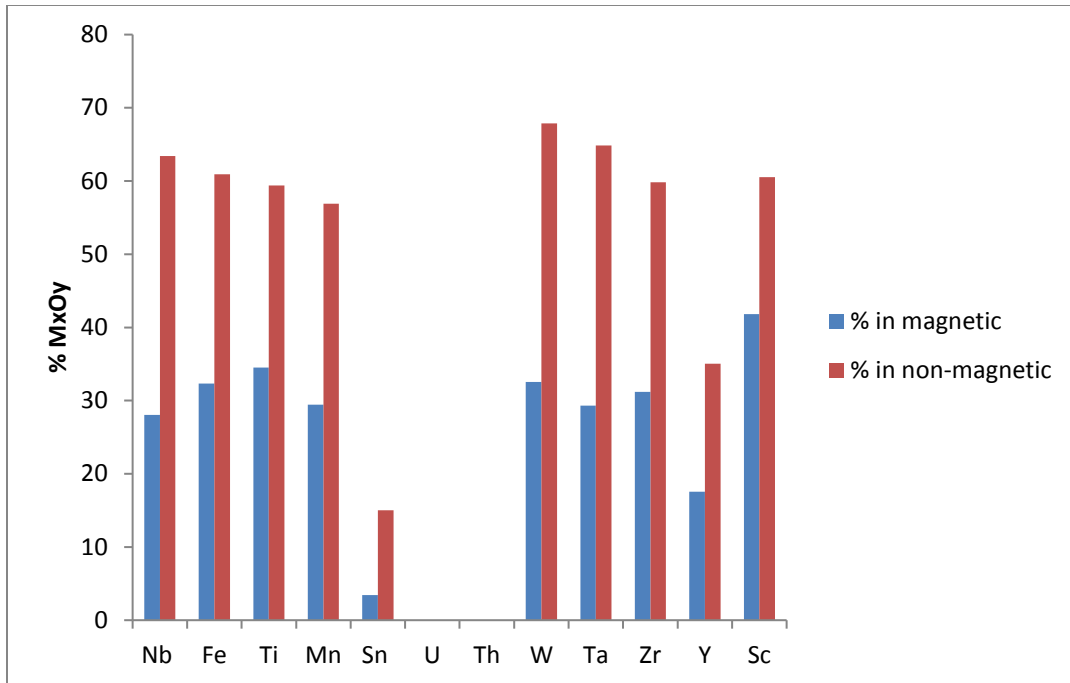


Figure 2: The % analytes present in Sample A after magnetic separation

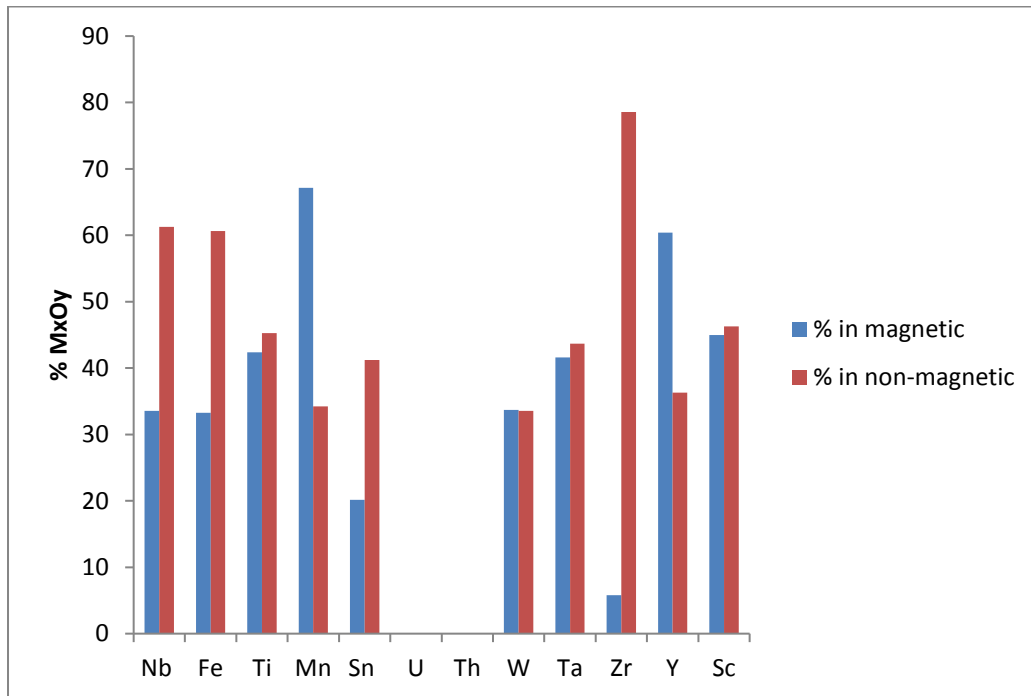


Figure 3: The % analytes present in Sample B after magnetic separation

2.5 Solvent extraction of tantalum from Sample A

The next step in the process involved the removal of Ta as one of the major elements in the samples, from the rest of the sample solution using solvent extraction. 5.0 mL of the bulk solution of Sample A obtained from the initial sample dissolution process (magnetic and non-magnetic portions) was transferred to a separating funnel and 5.0 mL of the desired H₂SO₄ concentration (2.0 M to 8.0 M) was added to the solution as indicated in the study by Nete et al (2014). The solution was thoroughly mixed for 5 min and the Ta was then extracted with two successive portions of 10.0 mL of MIBK. Each time the solution was allowed to stand for 5 min to allow for the complete separation of the two immiscible liquid phases. The aqueous solution (the bottom layer) was then collected in a 100 mL beaker. This aqueous solution was stirred on a hot plate set at 60 °C for 10 min to evaporate any dissolved organic solvent and transferred to 100.0 mL volumetric flasks. The two organic portions were combined and back extracted with two portions of 20 mL water. The solution was allowed to stand for 5 min for the complete separation of the liquid phases. The water layer was then collected in a 100.0 mL beaker. The water solutions were then combined and heated to evaporate any dissolved organic solvent and quantitatively transferred to a 100.0 mL volumetric flask. The acidity of the solutions was adjusted with H₂SO₄ to match the 1.848 M H₂SO₄ of the blank and of the standard solutions. The solutions were again allowed to cool to room temperature and the volumetric flasks were then filled to mark with ultra-pure water and subsequently analyzed using ICP-OES. The results obtained in this study are presented in **Table 5** and the average percentages obtained are graphically presented in **Figures 4** and **5**.

Table 5: Solvent extraction (2x) of Ta in Sample A using MIBK after NH₄F•HF fusion

Element	Expected (%)	[H ₂ SO ₄] (M)					
		Aqueous			Organic		
		2.0	4.0	8.0	2.0	4.0	8.0
Nb₂O₅	43.74	40.38	41.62	38.29	2.38	2.82	2.23
Fe ₂ O ₃	29.49	27.11	27.73	27.41	1.43	1.63	1.25
TiO ₂	10.63	10.93	11.06	10.65	0.43	0.52	0.38
Mn ₂ O ₄	2.10	1.90	1.90	1.91	0.17	0.18	0.16
SnO ₂	1.42	0.52	0.49	0.49	0.13	0.06	0.13
U ₃ O ₈	<0.05	0.00	0.00	0.00	0.00	0.00	0.00
ThO ₂	<0.055	0.00	0.00	0.00	0.01	0.00	0.00
WO ₃	0.81	1.13	1.10	1.01	0.16	0.09	0.08
Ta₂O₅	4.51	0.89	0.91	0.88	4.51	4.08	4.25
ZrO ₂	0.64	0.08	0.08	0.08	0.03	0.03	0.03
Y ₂ O ₃	0.15	0.08	0.08	0.08	0.05	0.05	0.05
Sc₂O₃	0.135	0.15	0.15	0.15	0.00	0.00	0.00

Bold = Elements of interest

The results in **Table 5** indicated that some of Nb was also extracted with Ta to organic phase. In the next part of the study the influence of increased [H₂SO₄] on the extraction of Nb and Sc from the non-magnetic portion of Sample A into the organic phase was determined.

2.5.1 Solvent extraction of non-magnetic portion of Sample A with MIBK

Aliquots (5.0 mL) of the non-magnetic portion of Sample A obtained from **Section 2.4.2** were transferred to a separating funnel and 5 mL of desired concentration (4.0 – 16 M) H₂SO₄ solution was added to the solution. The solution was thoroughly mixed for 5 min and Ta and Nb were then extracted with two successive portions of 10.0 mL MIBK. The aqueous solution was collected in a 100 mL beaker and heated to remove any dissolved organic solvent then transferred to 100.0 mL volumetric flask. The organic phase was back extracted with two portions of 20 mL water and the water solutions were collected and combined in a 100 mL beaker and heated to remove any dissolved organic solvent. The aqueous portions were then quantitatively transferred to a 100.0 mL volumetric flask. The acidity of the solution was adjusted with H₂SO₄ to match the blank and the standard solution matrices. The solutions were then filled to the mark with ultra-pure water and subsequently analysed using ICP-OES. The results presented in **Figure 4** shows the relationship between the acid concentration and the % elemental extraction, especially Ta, Nb and Sc.

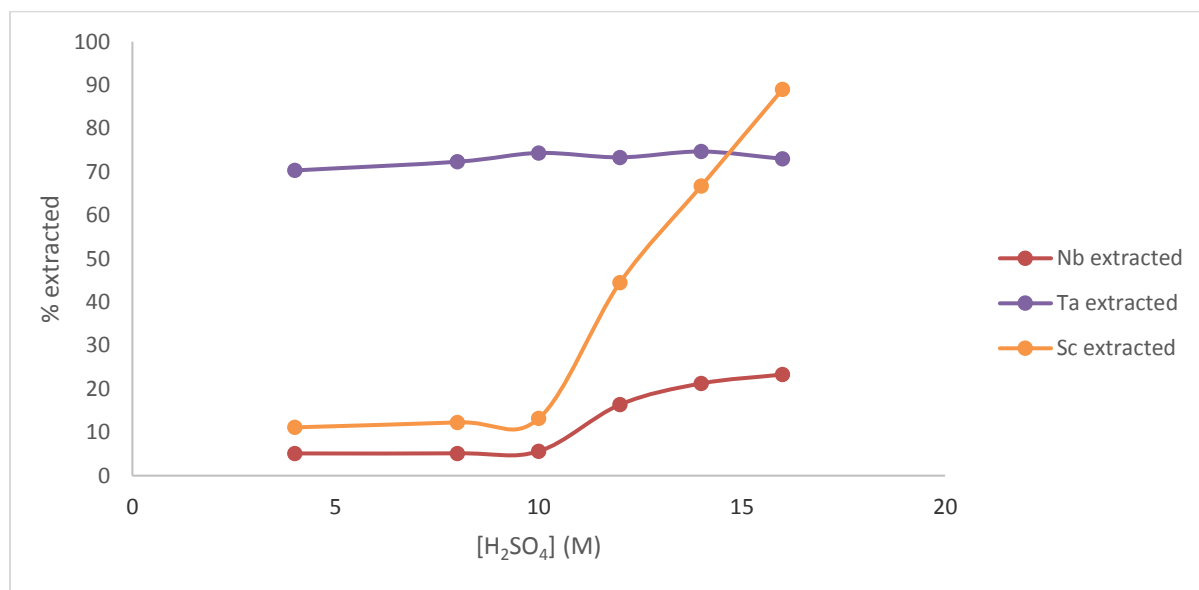


Figure 4: % Nb, Ta and Sc extracted with MIBK at different [H₂SO₄]

From the results in **Figure 4** it can be seen that the MIBK solvent could be used for both collective and selective extraction of Ta and Nb. However, the results indicated that as the acid concentration increased, Sc was also being extracted into the organic layer, which results in a substantial transfer of Sc from the aqueous layer. Once the initial separation of tantalum as well as the combination of niobium and scandium has been achieved through acid concentration variation below 10 M, a further separation of scandium and niobium can be accomplished with a further increase of [H₂SO₄] to 16 M H₂SO₄. Even though this was one method to separate scandium from the rest of the elements, it was decided to extend the investigation to include other potential organic extractants.

Despite its success as extractant, MIBK had a number of disadvantages that included a low flash point (14 °C) and relatively high solubility (1.91%) in aqueous solutions, which necessitated its evaporating before ICP-OES analyses. Octan-1-ol and methyl isoamyl ketone (MIAK) each have a solubility of 1.0×10^{-6} and 0.50 % in water and respective flash points of 81 and 43 °C (Nete, 2013) and were also included as organic extractants in this study.

2.5.2 Solvent extraction of tantalum and niobium in the non-magnetic portion of Sample A with octan-1-ol and MIAK

A 5.0 mL aliquot of the Sample A solution obtained in **Section 2.4.2** was mixed with 5 mL of desired concentration (4.0 – 16 M) H₂SO₄ solution in a separating funnel. Extraction of Ta and Nb was performed with two successive portions of 10.0 mL of each solvent and back extraction (from the organic phase) was done with two portions of 20 mL distilled water. All the aqueous solutions were heated to about 60 °C for 10 min in glass beakers to ensure that all the organic solvents were removed and then transferred to 100.0 mL volumetric flasks. The acidity of the solutions was adjusted to 1.8 M H₂SO₄ to match the blank and standard solutions. The solutions were allowed to cool to room temperature and then filled to the mark with ultra-pure water. The results in **Table 6** dealing with octan-1-ol follow the same trend as observed in **Figure 4** with MIBK as extractant. In contrast the results in **Table 7** indicated no detectable Sc extraction into the organic layer at all.

Table 6: Elemental analysis of the aqueous portion of the non-magnetic portion of Sample A with octan-1-ol at [H₂SO₄] between 4 and 16 M

Element	Expected %*	[H ₂ SO ₄]/M											
		4.0		8.0		10.0		12.0		14.0		16.0	
		Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org
Nb ₂ O ₅	26.73	19.15	4.66	17.83	4.79	16.53	6.34	14.62	8.60	14.28	11.33	10.94	14.10
Fe ₂ O ₃	17.58	17.85	0.43	16.53	0.00	16.86	0.86	15.58	0.60	15.27	0.57	15.31	0.56
TiO ₂	6.14	5.26	0.54	5.11	0.86	5.29	0.38	4.79	1.02	4.93	0.99	4.99	0.67
Mn ₃ O ₄	0.99	1.05	0.13	1.24	0.12	1.10	0.20	1.25	0.35	1.29	0.36	1.28	0.20
SnO ₂	0.30	0.44	0.09	0.51	0.06	0.38	0.10	0.33	0.04	0.25	0.05	0.30	0.05
U ₃ O ₈	0.00	0.31	0.03	0.30	0.05	0.29	0.03	0.09	0.01	0.23	0.00	0.20	0.01
ThO ₂	0.00	0.01	0.01	0.05	0.09	0.06	0.09	0.00	0.06	0.00	0.09	0.00	0.06
WO ₃	0.52	0.39	0.02	0.56	0.05	0.60	0.02	0.45	0.12	0.47	0.18	0.52	0.09
Ta₂O₅	2.99	0.86	2.12	0.85	2.08	0.89	2.09	0.45	2.28	0.59	2.23	0.61	2.22
ZrO ₂	0.03	0.10	0.00	0.12	0.00	0.09	0.00	0.06	0.03	0.07	0.00	0.09	0.05
Y ₂ O ₃	0.03	0.04	0.02	0.06	0.02	0.04	0.03	0.04	0.03	0.04	0.05	0.03	0.05
Sc₂O₃	0.09	0.10	0.02	0.10	0.01	0.11	0.03	0.11	0.05	0.09	0.07	0.06	0.09

* Elemental content present in non-magnetic portion of Sample A (Table 4)

Bold = Elements of interest

Table 7: Elemental analysis of the aqueous and organic portions of the non-magnetic portion of Sample A with MIAK at [H₂SO₄] between 4 and 16 M

Element	Expected %*	[H ₂ SO ₄]/M									
		4.0		8.0		12.0		14.0		16.0	
		Aq	Org	Aq	Org	Aq	Org	Aq	Org	Aq	Org
Nb ₂ O ₅	26.73	21.42	0.88	20.12	0.91	20.56	0.57	25.26	0.28	20.36	0.74
Fe ₂ O ₃	17.58	14.70	1.45	16.00	2.83	16.23	2.44	24.00	3.34	17.80	5.55
TiO ₂	6.14	6.07	0.88	6.51	0.88	5.53	0.77	6.73	0.71	6.29	0.81
Mn ₃ O ₄	0.99	1.41	0.44	1.50	0.47	1.54	0.41	1.78	0.41	1.63	0.41
SnO ₂	0.30	0.31	0.12	0.40	0.17	0.33	0.14	0.61	0.55	0.38	0.27
U ₃ O ₈	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ThO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WO ₃	0.52	0.34	0.08	0.25	0.19	0.44	0.26	0.89	0.42	0.25	0.05
Ta ₂ O ₅	2.99	1.11	3.12	0.83	3.32	0.83	2.77	0.68	3.25	0.19	2.56
ZrO ₂	0.03	0.11	0.02	0.11	0.02	0.12	0.02	0.15	0.02	0.12	0.01
Y ₂ O ₃	0.03	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.00	0.00
Sc ₂ O ₃	0.09	0.08	0.00	0.08	0.00	0.07	0.00	0.09	0.00	0.07	0.00

* Elemental content present in non-magnetic portion of Sample A (Table 4)

Bold = Elements of interest

Octan-1-ol behaved like MIBK solvent, and an increase in Nb extraction is observed when an increase in acidity. However, the increase in acidity also increased the Sc extraction and subsequent transfer from the aqueous layer. On the other hand, MIAK did not extract Nb or Sc even at high acid concentration levels. Results in **Table 5** indicated that at least 2.23 % Nb₂O₅ was extracted at 8 M H₂SO₄ with MIBK. Since Sample B contained smaller amounts of Nb and Ta, MIBK was chosen for the removal of these two elements in Sample B.

2.5.3 Solvent extraction of the elements in the non-magnetic portion of Sample B with MIBK

A 5.0 mL aliquot of the bulk solution of Sample B non-magnetic portion obtained from **Section 2.4.2** was transferred to a separating funnel and 5 mL of 8.0 M H₂SO₄ solution was added to this solution. The solution was thoroughly mixed for 5 min and the Ta and Nb was then extracted with two successive portions of 10.0 mL MIBK. The aqueous portion was collected in a 100 mL beaker, heated to remove any dissolved organic solvent and then transferred to 100.0 mL volumetric flask. The organic phase was back extracted with two portions of 20 mL water, the water portions were combined, heated to about 60 °C for 10 min in a glass beaker to ensure that

all the organic solvents were removed and then quantitatively transferred to a 100.0 mL volumetric flask. The acidity of the solution was adjusted with H₂SO₄ to match the blank and the standard solutions matrices. The solutions were then filled to the mark with ultra-pure water and analysed using ICP-OES. The results are presented in **Table 8**. These results support those obtained in **Sections 2.5.1** and **2.5.2** with both Nb and Ta being extracted into the organic layer and Sc remaining in the aqueous layer at 8 M [H₂SO₄].

Table 8: Elemental analysis of the aqueous and organic portions of the non-magnetic portion of Sample B with MIBK at [H₂SO₄] = 8 M

Element	Expected %*	[H ₂ SO ₄] = 8 M	
		Aqueous	Organic
Nb₂O₅	2.15	0.03	2.10
Fe ₂ O ₃	20.63	18.16	2.95
TiO ₂	0.42	1.00	0.72
Mn ₃ O ₄	0.10	0.58	0.48
SnO ₂	0.14	0.07	0.001
U ₃ O ₈	0.00	0.00	0
ThO ₂	0.00	0.00	0
WO ₃	0.02	0.02	0.03
Ta₂O₅	0.23	0.03	0.21
ZrO ₂	0.13	0.02	0.01
Y ₂ O ₃	0.01	0.00	0.00
Sc₂O₃	0.24	0.23	0.00

* Elemental content present in non-magnetic portion of Sample B (Table 4)

Bold = Elements of interest

3. Discussion of results

3.1 LOD, LOQ and elemental analysis of Samples A and B

The limits of detection and the quantification were determined with the ICP-OES to determine the smallest concentrations of Ta, Nb and Sc that could be reliably detected and quantified in the different samples. The LOD for Sc was determined to be 0.001085 at 361.384 nm in H₂SO₄ while the LOD's for Ta was calculated as 0.07768 at 228.916 nm, and Nb as 0.01045 at 309.418 nm analytical lines, which indicated that the equipment and method was capable of detecting all three elements in the trace and ultra-trace concentration range. The LOQ's were calculated as 10x the LODs' values.

One of the major objectives of this study was to identify a dissolution method, which afforded the total dissolution of the ferrocolumbite mineral sample (Sample A) as well as the mine tailings (Sample B). The initial dissolution study performed on Sample A using NH₄F·HF as flux produced an easily soluble melt (water) fusion, but visual inspection indicated incomplete dissolution with the initial conditions used (1:10 sample:flux ratio at 200 °C for 30 min). The analytical results obtained (**Table 2**) were compared to concentrations reported by the London and Scandinavian Metallurgical Co Limited (LSM) Analytical Services to evaluate the extent of dissolution. About 83 % of the Nb₂O₅, 89 % of the Fe₂O₃ and 91 % of the TiO₂ (dominating elements in the sample) were recovered. Only about 49 % of the Sc₂O₃ was recovered.

It was decided to investigate various experimental parameters such as sample to flux ratio and the fusion time to optimize the digestion method to effect complete dissolution and total elemental recovery. Both the increase in sample to flux ratio and duration of flux procedure improved elemental recovery, but the 1:10 sample to flux ratio and flux period of 60 min proved to an excellent experimental condition as illustrated by elemental recoveries of 96.30 % Nb₂O₅, 99.12 % Fe₂O₃ and 99.26 % Sc₂O₃.

The dissolution of both the samples was then repeated using the optimum condition and the results are reported in **Table 3**. Recoveries of 96(3) % Nb₂O₅, 97.9(9) % Fe₂O₃, 97.3(2) % TiO₂, 103.70(1) % Sc₂O₃ and 102.2(2) % Ta₂O₅ were obtained for Sample A, while 90.23(6) % Nb₂O₅, 85(2) % Fe₂O₃ and 64.15(2) % Sc₂O₃ were recovered for Sample B. The good recoveries obtained for the main elements in Samples A and B were regarded as sufficient to continue with the rest of the solvent extraction study. The chemical analyses (**Table 3**) of two samples indicated that about 90 % of the Nb₂O₅, Ta₂O₅, TiO₂ and Mn₃O₄ were removed from the original columbite ore. The remaining elements present in the tailings were Fe₂O₃ (39.03 %) as major impurity, Al₂O₃ (4.91 %), Nb₂O₅ (3.89 %) and smaller amounts of ZrO₂ (1.38%), Ta₂O₅ (0.35 %), TiO₂ (1.58 %) and notably Sc₂O₃ (0.795 %). These results suggested that the original extraction or beneficiation process did not remove any Sc from the mineral and that the Sc content was concentrated from 0.135 to 0.795 %.

3.2 Magnetic removal of major impurities from samples

The chemical analysis of both Samples A and B clearly identified Fe (Fe_2O_3) as the major contaminant. The magnetic removal of iron from both samples should have reduced the amount of down-stream impurities and simplify any beneficiation process. The first step was to separate the magnetic and non-magnetic portions of both the samples and dissolve them with $\text{NH}_4\text{F}\cdot\text{HF}$ as flux to evaluate of the extent of Fe removal (as well as the other elements of interest) from both samples during the magnetic separation step.

From the elemental composition of the samples (A and B) in **Table 3**, it was expected that Sample B would be magnetically more active with large amounts of Fe present in the sample compared to Sample A. Initially the magnetism in the samples was quantitatively determined as mass magnetic susceptibility (χ_g). The results indicated that Sample A contained much more magnetic particles ($1.301 \times 10^{-6} \text{ cm}^3\text{g}^{-1}$) than Sample B ($0.0713 \times 10^{-6} \text{ cm}^3\text{g}^{-1}$). These results were surprising since the Fe content increased from 28.86 % in Sample A to about 40 % in Sample B and yet its magnetic susceptibility decreased by a factor 100. In practice it implied that the chemical treatment of the original columbite mineral also changed the type of Fe compound in the final tailings, which rendered it less ferromagnetic (possible change in oxidation state). This was underlined by the quantitative results in **Table 4**, which indicated that poor separation or removal of Fe took place during the magnetic field exposure for both samples with a 50/50 separation between the magnetic and non-magnetic portion. The magnetic susceptibility in this columbite sample and its mine tailings samples was much lower than the values obtained for tantalite samples investigated by Nete (2012). The two tantalite samples had magnetic susceptibility values of 2.8 and $29.3 \times 10^{-6} \text{ cm}^3\text{g}^{-1}$ compared to the $1.3 \times 10^{-6} \text{ cm}^3\text{g}^{-1}$ of the original columbite ore sample. In that study the magnetic separation of the Fe from the rest of the elements was successfully applied to the tantalite samples with the high susceptibility values, while poor separation was also obtained for the tantalite sample with low susceptibility values. The experimental results (**Table 4**) for the magnetic separation in this study not only indicated the unsuccessful removal of the majority of Fe from the samples, but also indicated a substantial loss of Sc (40.00 % of Sc_2O_3 in Sample A was lost and 45.01 % Sc_2O_3).

3.3 Solvent extraction of elements with MIBK as extractant

Due to the incomplete magnetic removal of Fe and Ti from both samples, the subsequent solvent extraction separation was performed on the non-magnetic fraction of the samples. In this step, the efficiency of using MIBK as solvent for extracting the different elements was evaluated and the chemical behavior of ferrocolumbite with tantalite as natural mineral source was compared. The first step was to investigate the solvent extraction process using the complete Sample A.

3.3.1 Solvent extraction of elements in a Sample A with MIBK as extractant

The efficiency of MIBK as solvent extractant was evaluated on Sample A ($\text{NH}_4\text{F}\cdot\text{HF}$ dissolved) at different H_2SO_4 concentrations, ranging from 2.0 M to 8.0 M. The results indicated that the double extraction process (**Table 5**) removed 92.84 % Ta and 4.88 % Nb and 4.99 % Fe from the aqueous layer into the organic layer. The results also indicated that the majority of Sc (~100 %) remained in the aqueous solution at this acid concentration, which implied a possible beneficiation of Sc. Poor extraction of the other elements also confirmed the possible isolation of Ta compound from the columbite matrix. At acid concentrations between 8 and 10 M (see **Figure 4**) the extraction mechanism started to change, especially for Sc, which transferred from the aqueous to the organic layer with substantial amounts of Sc extracted at $[\text{H}_2\text{SO}_4]$ around 16 M.

The extent of extraction of each of the elements in the columbite sample by MIBK solvent at 8 M H_2SO_4 is reflected by the calculated extraction ratios (D) and is presented in **Table 9**. Important to note is that extraction ratio (D) calculated for Ta greatly exceeded that of all other elements in solution.

Table 9: Distribution ratios for elements present in columbite sample after x2 extraction process with MIBK solvent at 8.0 M H_2SO_4

Metal	Extraction ratio (D)
Nb	0.058
Fe	0.046
Ti	0.036
Mn	0.084
Sn	0.272
U	–
Th	–
W	0.075
Ta	4.808
Zr	0.395
Y	0.605
Sc	0.000

3.3.2 Solvent extraction of the non-magnetic portion of Sample A with different organic extractions

From **Section 2.5.3** it was clear that Ta could be selectively removed and isolated from the columbite sample by solvent extraction technique using MIBK at $\text{H}_2\text{SO}_4 \sim 8$ M. The results

obtained from octan-1-ol and MIAK indicated that octan-1-ol behaved like MIBK, at low $[H_2SO_4]$ and only Ta was extracted into the organic phase. At high $[H_2SO_4]$ Nb was also extracted with Ta into the organic layer. About 52.75 % Nb (**Table 6**) was extracted with octan-1-ol at $[H_2SO_4]$ of 16 M while 53.33 % of Sc was also extracted. On the other hand, MIAK only extracted Ta selectively even at high acid concentrations. An average of 100.4 % Ta was extracted with MIAK and only 2.77 % Nb was extracted at 16 M H_2SO_4 (**Table 7**). There was no notable amount of Sc that was extracted into the MIAK organic solvent.

3.3.3 Solvent extraction of Ta and Nb in non-magnetic portion of Sample B with MIBK

The results in **Table 8** clearly indicated that Ta and Nb was successfully extracted with MIBK from a $NH_4F \cdot HF$ solution present in Sample B (non-magnetic) with 8 M $[H_2SO_4]$. An average of 97.67 % Nb and 91.30 % Ta were extracted while 95.86 % Sc was recovered from the aqueous solution. It is clear from the metal quantification of the mine or process tailings (**Table 3**) that it contained substantial amounts of the target elements, which could be separated and beneficiated with this extraction process. Although both Ta and Nb were present in the MIBK at 8 M $[H_2SO_4]$, research results in this and in a previous study indicated the clean separation of the two elements using MIAK as extractant (Nete et al., 2014), which can be used for processing tailings.

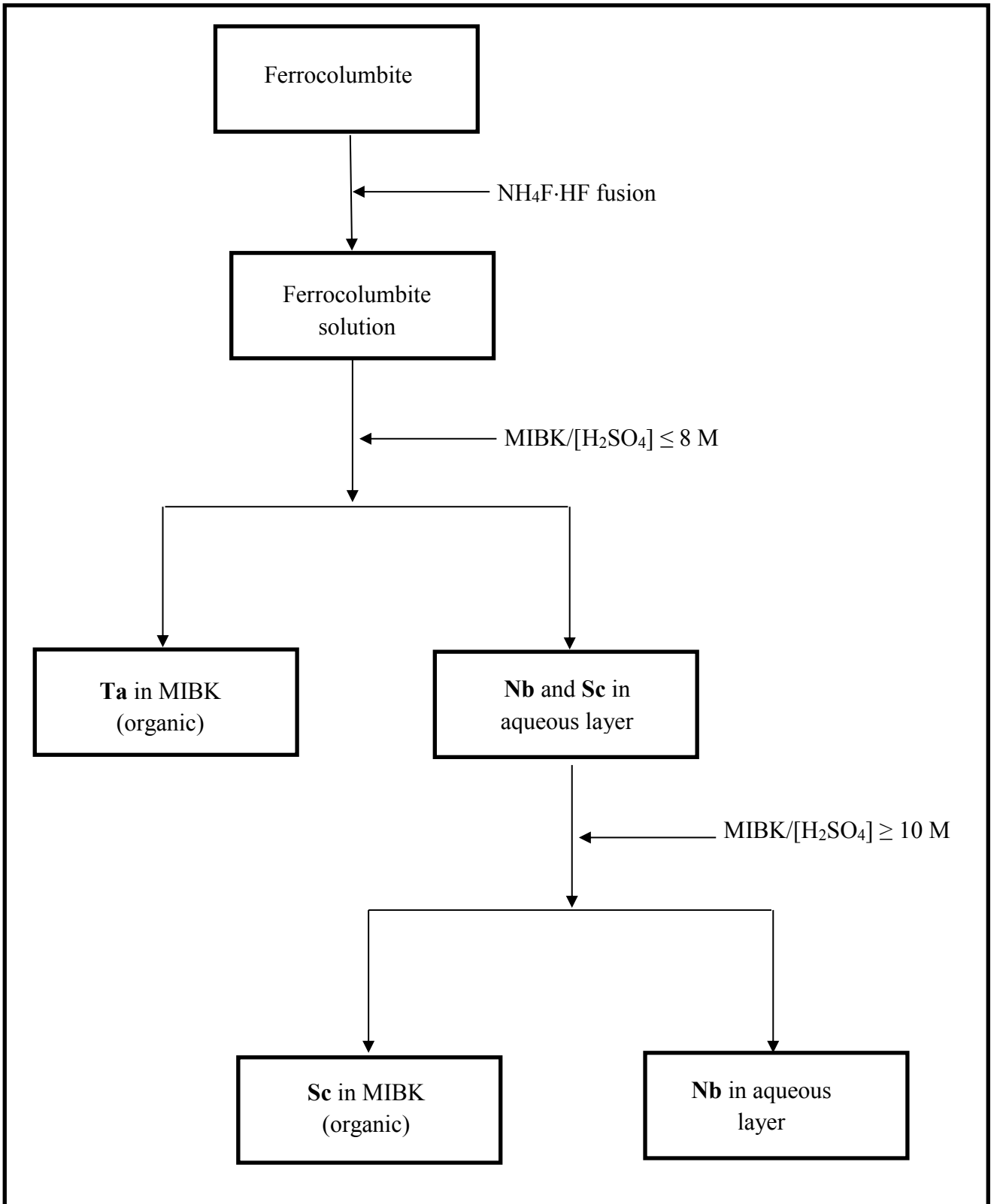
3.3.4 Summary of results

The degree to which the process was successful in separating the elements of interest is summarised in **Table 10**. The extraction results (co-extraction of Ta and Nb in high acidity aqueous solutions) and the clean separation of the two elements with MIAK at high acidity support the results reported in two previous studies (Nete et al., 2014). Based on some of the results in **Table 10**, a possible process flow diagram for the separation of the three target elements is proposed in **Figure 5**.

Table 10: Evaluation of various steps involved in the separation processes investigated (Sample A) in this study

Process	Description	Elemental Recovery (%)		
		Ta	Nb	Sc
Dissolution of the mineral samples by $NH_4F \cdot HF$	Complete dissolution of ore/tailings	99	96	99
Magnetic separation (removal of Fe and/or Ti)	Magnetic	30	27	44
	Non-magnetic	66	61	66
Solvent extraction with MIBK (8 M $[H_2SO_4]$)	Organic phase	94	5	0
	Aqueous phase	19	88	100
Solvent extraction with MIBK (16 M $[H_2SO_4]$)	Organic phase	73	23	89
	Aqueous phase	24	57	20

Figure 5: Process flow diagram for the separation of Ta, Nb and Sc in ferrocolumbite



4. Conclusion

The following conclusions can be drawn from this investigation:

- Ferrocolumbite was successfully dissolved with $\text{NH}_4\text{F}\cdot\text{HF}$ yielding a solution in which all three elements of interest were accurately quantified with satisfactory LOD/LOQ's
- Magnetic separation did not contribute to the successful removal of Fe/Ti to simplify the down-stream beneficiation processes
- MIBK successfully extracted Ta into the organic layer and left Nb and Sc in the aqueous layer at $[\text{H}_2\text{SO}_4] < 8 \text{ M}$. At higher acid levels, Sc ($[\text{H}_2\text{SO}_4] > 10 \text{ M}$) migrated in significant amounts/quantities to the organic layer. This creates a possible process for the separation of the three elements from one another
- Octan-1-ol yielded similar results to MIBK while MIAK successfully removed Ta from the aqueous layer, but left the two other elements in the aqueous layer, even at 16 M $[\text{H}_2\text{SO}_4]$
- Extraction process can successfully be applied to Ta, Nb and Sc recovery in mine/process tailings
- A process flow sheet for the possible separation of Nb, Ta and Sc from ferrocolumbite is proposed

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