Dissolution and Quantification of Tantalum-Containing Compounds: Comparison with Niobium

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ABSTRACT

Dissolution and quantification of different tantalum compounds was undertaken as part of the development of local processes for the beneficiation and separation of tantalum and niobium from different mineral ores. Dissolution of Ta metal powder, TAN-1 CRM, TaF_5, $TaCl_5$ and Ta_2O_5 was undertaken with different acid, alkaline fluxes as well as with microwave digestion while quantification was performed using ICP-OES analysis. The success of the different dissolution methods was evaluated on percentage recovery basis, the results discussed and finally compared with those obtained from the corresponding niobium compounds. Quantification results obtained from this study clearly indicated that the percentage recovery of tantalum depended on i) the type of tantalum source and ii) the dissolution process of the different tantalum compounds. Excellent recoveries were obtained with water soluble TaF_5 and $TaCl_5$ with 101(1) and 100(2) % respectively. Low tantalum recovery was obtained for Ta metal and Ta_2O_5 with microwave digestion in the presence of strong acids (4.1(8) and 9.7(8) %, respectively in the presence of H_2SO_4) and acidic fluxes (1.5(5) % with $K_2S_2O_7$). Improved recoveries were obtained using basic fluxes for both the metal and the oxide. Fluxing the metal with KOH resulted in a 85(3) % Ta recovery while a maximum of 68(4) % Ta recovery was obtained for Ta_2O_5. Tantalum recoveries of between 75(10) and 90(6) % were obtained for TAN-1 CRM (Ta present as Ta_2O_5) and 95(6) % for Ta_2O_5 with $Li_2B_4O_7$ as fluxing agent on the removal of the excess of boric acid prior to analysis. A stability study indicated constant recovery in a basic medium while a decrease of up to 10 % in tantalum recovery was obtained in an acidic environment. A comparison with the niobium results obtained in a previous study highlighted the different acid/base properties of the two oxides as well as a possible alternative dissolution/separation step for the two elements from the mineral ore.

KEY WORDS

Dissolution, microwave, fluxes, tantalum, recovery.

1. Introduction

Niobium and tantalum (part of Group V on the periodic table) usually occur together in nature and estimations indicate that Nb is about 50 times more abundant than Ta in the earth's crust. A number of literature sources also refer to the difficulty in the separation of Nb and Ta due to their physical (e.g. ionic radii) and chemical similarities (similar complexes).[1] More than 150 different niobium-containing minerals have been reported and are roughly divided into two groups, namely titano-niobates or tantalo-niobates.[2,3] Pyrochlore, which is predominantly mined in Brazil, is the most important titano-niobate mineral and contains up to 60 % Nb_2O_5.[4] Columbite and tantalite, with the general formula $(Fe,Mn)(Nb,Ta)_2O_6$, are mainly mined in Australia and Nigeria and are the most important minerals containing a combination of tantalum and niobium with 25–60 % Nb_2O_5 and 1–50 % Ta_2O_5.[5]

Common to titano-niobates and tantalo-niobates are their chemical inertness.[2] The two main elements are present in the minerals as pentoxides, M_2O_5, which are extremely resistant to acid and alkali attack at moderate temperatures and pressure. The first successful dissolution and separation of niobium and tantalum involved the use of anhydrous hydrofluoric acid.[6,7] The addition of KF after the dissolution of the two metal oxides

resulted in the selective crystallization of slightly insoluble K_2TaF_7 while the more soluble $K_2NbOF_6.H_2O$ remained in solution (10–12 times more soluble than the tantalum salt at ~1 % HF). This discovery subsequently led to the development of the vast fluoride and halide chemistry of the two metals which is known today.

Not surprisingly the dissolution, separation and purification processes of the two metals from the minerals are dominated by halogen chemistry. Dissolution methods of the minerals involve the use of 70–80 % HF[2,3], sometimes in the presence of nitric or sulphuric acid, chlorination and alkaline fusion with sodium hydroxide or potassium carbonate in the presence of oxidizing agents. A recent article demonstrated the successful dissolution of different niobium compounds, including the oxide, using either lithium tetraborate (LTB) as flux or microwave digestion.[8] ICP results indicated a recovery of 98.8(7) % Nb_2O_5 with microwave digestion in the presence of H_2SO_4, while 103(2) % was recovered with the LTB flux process. Quantitative results also indicated the complete microwave dissolution of pure Nb foil with a recovery of 99.90(8) %. This study also clearly demonstrated the importance of the removal of excess boric acid as the volatile $B(OEt)_3$ ester from the reaction mixture prior to quantification for the accurate determination of niobium.

The success of these two methods then prompted the question

of whether they would also be as successful in the dissolution of the equivalent tantalum salts and if any possible differences could possibly lead to novel separation processes. This paper deals with a quantitative study in the dissolution of different tantalum compounds, using microwave digestion as well as different fluxing agents, and compares the results with those obtained for niobium. This study excludes the use of HF and any HF containing mixtures.

2. Experimental

2.1. Equipment

An Anton Paar Perkin-Elmer Multiwave 3000 microwave reaction system equipped with an 8SXF100 rotor and eight polytetrafluoroethylene (PTFE) reaction vessels was used for the acid dissolution of samples. Flux fusions were performed in Pt crucibles using a high temperature oven supplied by Labequip. Grade B volumetric flasks and glassware bought from Merck were used in this study. A Shimadzu ICPS-7510 ICP-OES sequential plasma spectrometer controlled by a computer was used for the wet analysis of the samples under investigation.

2.2. Reagents

Tantalum powder (99.99 %), Ta_2O_5 (99.0 %), $TaCl_5$ (99.8 %) and TaF_5 (98.00 %) were bought from Sigma Aldrich (high purity range) while the 1000.0 ppm Ta standard was purchased from Merck. A certified reference standard, TAN-1 (% Ta = 0.236(5) or % Ta_2O_5 = 0.288(6)) was bought from the Canadian Certified Reference Material Project (CCRMP) of the Canadian Centre for Mineral and Energy Technology. The H_2SO_4 (95–98 %), HNO_3 (65 %), HCl (32 %), H_3PO_4 (85 %) which were all 'Pro Analise' standard and methanol (99.5 %) were purchased from Merck. Lithium and sodium tetraborate (99.95 %) was bought from Johnson Matthey Materials Technology while $LiBO_2$ and KOH (85 %) were bought from Sigma Aldrich. Double-distilled water was used in all cases.

2.3. Experimental Procedures

2.3.1. *ICP-OES*

The operating parameters of the instrument (Table 1) were continuously monitored to ensure the maximum performance and reliability of the ICP-OES results. All the analyses were performed 20 to 30 min after the spectrometer was turned on to achieve a stable plasma as well as constant and reproducible sample introduction. Ta intensity measurements were taken at the first order wavelength of 226.230 nm. Linear calibration curves with R^2 ranging between 0.9988 and 0.9999, intercept between –0.0781 and –0.0263 and slopes between 0.2143 and 0.3064 were obtained for all the quantitative determinations. Other validation parameters[9,10] such as accuracy, precision, LOD/LOQ and stability were also investigated. Values that are reported are the average of at least three replicate analyses. All the prepared solutions (standards and samples) were left for 5

6 hours prior to analysis since there were indications of an increase in recovery from lower than 90 % to the stable final recovery values that are reported.

2.3.2. *Determination of Limits of Detection*

A blank solution and five 100.0 mL standard solutions containing 0.4, 1.0, 3.0, 5.0, and 10.0 ppm of Ta were prepared in the presence of 5 mL HNO_3. The intensities used for the calculation of the LOD are the average of three replicate measurements in the standard solution and ten replicate measurements in the blank solution for Ta. LOD was calculated from $LOD = k.s_b/m$ with $k = 3$, s_b = standard deviation of the blank readings and m = slope of the calibration curve. The LOD was determined as 0.00427 ppm and LOQ was 0.0427 ppm Ta (10 times higher).

2.3.3. *Preparation of Standard Solutions for Microwave-assisted Acid Digestion Analyses*

The calibration curve solutions were prepared by introducing 0.1, 0.2, 0.3, 0.5 and 1.0 mL of the 1000 ppm ICP-OES standard solutions into five 100.0 mL volumetric flasks using a micropipette. To these, 5.00 mL of whichever acid was used to digest the sample was added. The solutions were then diluted to the mark with distilled water to prepare 1.0, 2.0, 3.0, 5.0, and 10.0 ppm Ta concentrations. The blank solutions were prepared by diluting 5.00 mL of the acid being used to the 100.0 mL mark of the volumetric flask and were used for background correction.

2.3.4. *Microwave Digestion General Procedure and Parameters*

The polytetrafluoroethylene (PTFE) reaction vessels used for this digestion were cleaned by steaming the vessels with 8 mL of 55 % nitric acid in microwave-heated sealed vessels for 15 min followed by rinsing several times with double-distilled water and drying of the vessels before use. Tantalum samples (metal powder and Ta_2O_5) were accurately weighed (to 0.1 mg) and quantitatively transferred into each pre-cleaned vessel and 10.00 mL analytical grade acid (H_2SO_4, HNO_3, H_3PO_4, or *aqua regia*) was pipetted into each reaction vessel. The vessels were then placed into the ceramic jackets and transferred to a rotor of the microwave digestion system, sealed, tightened and finally taken to the microwave reaction system. The microwave parameters shown in Table 2 were kept constant for all the digestions of the tantalum samples. The results are reported in Table 3.

2.3.5. *Standard Addition Calibration Curve for Fusion Digestion Analysis*

The standard addition calibration method was used for the analyses of all the solutions that were obtained by flux fusion digestion methods to compensate for potential matrix effects. 10.00 mL aliquots of a sample solution were added to the five 100.0 mL volumetric flasks followed by 5.00 mL of the acid or base used to dissolve the melt. Different quantities of 1000 ppm standard solutions were then added to these to yield sample concentration of 0.0, 1.0, 3.0, 5.0 and 10.0 ppm standard solutions

Table 1 ICP-OES operating conditions.

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

Table 2 Microwave operating conditions used for the acid assisted digestion.

Power	800 W
Pressure	60 bar (maximum)
Max rotor pressure increase	0.5 bar/s
Ramp Time	15 min
Hold time	45 min
Temperature	240 °C (maximum)
Acid volume	10 mL

Table 3 Recovery of tantalum compounds using acid and microwave digestion

Compound	Acid	Recovery/%
TaF_5	HNO_3	101(1)*
$TaCl_5$	HNO_3	100(2)*
Ta_2O_5	HNO_3	4.2(6)
	H_2SO_4	9.7(8)
	H_3PO_4	6.9(8)
	Aqua regia	3.9(7)
Ta metal powder	HNO_3	5(1)
	H_2SO_4	29(2)
	HCl	8.7(6)
	Aqua regia	3.9(6)

* Acid dissolution at room temperature.

after dilution. The solutions were then diluted to the mark with distilled water in 100.0 mL volumetric flasks.

2.3.6. *Dissolution of TaF₅ and TaCl₅*

Samples of approximately 0.2 g of tantalum(V) fluoride were accurately weighed (to 0.1 mg) and quantitatively transferred to a 100.0 mL volumetric flask, 5.00 mL nitric acid was added and the flask was filled to the mark with distilled water.

Samples of approximately 0.2 g of tantalum(V) chloride were accurately weighed and quantitatively transferred to a 200 mL beaker. Initially 3 mL EtOH[11] was added to the beaker to dissolve the solid, followed by approximately 80 mL of distilled water. This solution was then heated to 70 °C for 30 min to remove the EtOH (to prevent carbon clogging of the ICP torch). The solution was then filtered to remove the opaque precipitate that formed at this stage, and the filtrate was quantitatively transferred to a 250.0 mL volumetric flask. 0.50 mL of this solution was subsequently transferred to a 100.0 mL volumetric flask, 5 mL of HNO_3 was added and the flask was filled to the mark with distilled water.

2.3.7. *Fusion Dissolution of the Various Tantalum Samples using Different Flux Reagents*

Approximately 0.1 g of each tantalum sample was weighed accurately to 0.1 mg and thoroughly mixed with approximately 2.0 g of the different fluxes ($K_2S_2O_5$, 1:1 mixture of KH_2PO_4/Na_2HPO_4, KOH, Na_2CO_3, $LiBO_2$, $Na_2B_4O_7$, $Li_2B_4O_7$ for Ta_2O_5,

KOH and $Li_2B_4O_7$ for the CRM) in a platinum crucible. The mixture was placed in a high temperature oven, set between 350 and 1100 °C depending on which flux was used, for intervals ranging from 30 to 120 min (see Table 4). The melts were removed and immediately placed in a cold water bath to crack the glassy melt in order to accelerate the dissolution process. 10 mL of concentrated acid (HNO_3, H_3PO_4 and H_2SO_4 for the CRM, tartaric acid and H_2SO_4 for Ta_2O_5) was added to the cold melt. In the case of the borate fluxes 30 mL of methanol was immediately added to the solution and the solution heated to *ca.* 40 °C with constant stirring. The addition of methanol to the solution containing the high boron concentration facilitated the production of the highly volatile $B(OMe)_3$ ester. Both the boron ester (presence observed by green flame when ignited) and the excess methanol were finally removed by heating the solution at elevated temperatures for 90 min. The solutions were quantitatively transferred to 100.0 mL volumetric flasks and diluted to the mark with distilled water.

3. Results and Discussion

3.1. Microwave Digestion

The acid and acid-assisted microwave dissolution results are summarized in Table 3. The 100 % recovery for both the halide salts clearly indicates the complete dissolution and accurate quantification of the tantalum compounds using nitric acid or a methanol/nitric acid mixture. The small standard deviation also points to good precision in these analyses. The recovery results for Ta_2O_5 and Ta metal powder in the same table however indicate extremely poor dissolution of these two compounds under extremely harsh conditions, i.e. concentrated acids at high temperatures and pressure. The best dissolution of Ta_2O_5 was obtained using sulfuric acid with ~ 10 % recovery while only 8 % was recovered with phosphoric acid. The dissolution of the Ta metal was slightly better under acidic conditions at high temperature and pressure with a recovery of 29 % using sulfuric acid. However no dissolution was achieved with the other acids that were investigated. The relatively large standard deviations point to less satisfactory precision and low accuracy compared to the tantalum content of the original sample.

3.2. Flux Dissolution

The flux dissolution results in Table 4 are much more promising with regard to effective dissolution when compared to that

Table 4 Recovery of tantalum compounds using flux digestion.

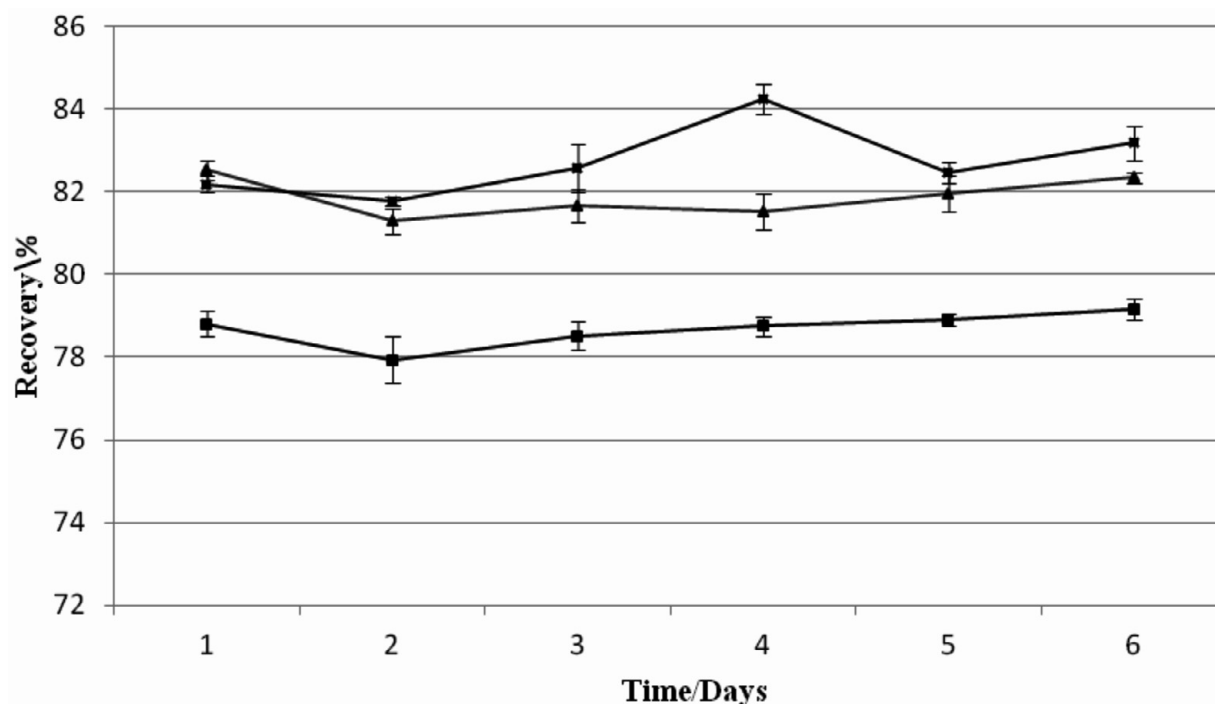| Compound	Flux				Acid	Recovery/%
	Type	Ratio	Temp/°C	Time/min		
Ta_2O_5	$K_2S_2O_7$	1:15	1000	45	Tartaric acid	<1
	$K_2S_2O_7$	1:18	1000	60	H_2SO_4	1.5(5)
	KH_2PO_4/Na_2HPO_4	1:18	350	30	None	1.8(4)
	$Li_2B_4O_7$	1:14	1100	90	H_3PO_4	76(5)
	$Li_2B_4O_7^a$	1:14	1100	90	H_3PO_4	95(6)
	$LiBO_2$	1:10	1100	85	H_3PO_4	65(4)
	$Li_2B_4O_7$	1:12	1100	85	HNO_3	24(3)
	Na_2CO_3	1:11	900	90	None	53(8)
	$Na_2B_4O_7$	1:16	1000	90	H_3PO_4	68(3)
	KOH	1:24	600	120	None	68(4)
TAN-1	$Li_2B_4O_7$	1:14	1100	90	HNO_3	75(10)
		1:14	1100	90	H_2SO_4	87(10)
		1:14	1100	90	H_3PO_4	90(6)
	KOH	1:10	600	120	HNO_3	17(7)
Ta metal powder	KOH	1:100	65	300		85(3)

Figure 1 Tantalum metal recovery with time using KOH as flux reagent.

of the microwave digestion. Recoveries in excess of 70 % were obtained using borate fluxes in combination with either sulfuric or phosphoric acid. The removal of the excess boric acid after the dissolution of the flux melt increased the yield from 76 to 95 %, in accordance with the observation made by Nete.[8] Nitric acid appeared to be the least effective in the dissolution of the melt with a recovery of 24 %. Extremely low Ta recoveries of 1.5 % and less were obtained with pyrosulphate as fluxing agent.

The dissolution of the CRM, using the different fluxes was also not quantitative but appeared to be much more promising with recoveries in excess of 87 % obtained with the borate fluxes. These results are in accordance with the results obtained for Ta_2O_5 since the tantalum is, in fact, present as the oxide in the CRM. Nitric acid was again ineffective in the extraction of tantalum from the melt. A qualitative study by ICP-OES indicated the presence of large amounts of Al and Si, minor amounts of W, Fe, Sn, Nb, Ti and Cu and trace amounts of Ni, Au, Mn, Ag, Zn, V, Co, Cr and Cd in TAN-1. Literature[11] indicated spectral interference by Al and Fe at 226.230 nm and Cr, Fe, Mn and V at 268.511 nm for Ta analysis. However the comparative recoveries of 95 % for pure Ta_2O_5 compared to the 90 % for TAN-1 indicate solubility constraints rather than spectral interference from these impurities. The results in Table 4 also indicate that the powdered tantalum metal also partially dissolved in KOH at elevated temperatures and atmospheric pressure with a recovery of 83 %.

In spite of the ineffectiveness of all the dissolution methods to yield complete dissolution and 100 % recovery a very interesting tendency appeared from the results. The most successful recoveries for Ta_2O_5 were obtained from basic fluxes, i.e. the borates, carbonate and even hydroxide, but almost no recovery from the acid flux pyrosulphate.[11] The basic fluxes and solutions also appear to be partially effective in the dissolution of the metal and the CRM. These results clearly point to significant acidic properties for the Ta_2O_5. This also successfully explains the inability of the strong acids, even at elevated temperatures and pressure in the microwave, to dissolve the oxide and metal powder. The increase in dissolution can also be ascribed to the change from

aqueous medium to molten salt medium[11,12] which appears to be more effective in the breaking of the strong metal oxygen bonds to release the metal ions from the solid.

3.3. Effect of Other Parameters on Recovery

A number of other studies were also conducted in an effort to improve the accuracy (recovery) of the tantalum in the different methods. An increase in Ta_2O_5 to flux ratio from 1:15 to 1:18 for pyrosulphate (Table 4) showed no substantial increase in dissolution. The same was observed for KOH and LTB (1:10 to 1:20) as fluxes with an increase of fusion time from 90 min to 150 min. A change from external calibration to standard addition calibration for the flux digestion, as well as a change in the wavelength where analyses were performed (from 226.230 to 268.511 nm) showed little or no change in the recovery of the tantalum compound. Recovery was also studied over time in an effort to determine the stability of the prepared solutions. Initial analysis pointed to poor calibration curves immediately after preparation of the standard solutions which prompted sample analysis to be performed after approximately 8 hours of standing. The results in Fig. 1 clearly indicate relatively stable solutions of three different samples for up to 8 days in a slightly alkaline (less acidic) environment while those in Fig. 2 indicate a sharp decrease in stability of Ta_2O_5 after approximately three days in a more acidic medium. These results suggest a greater presence of less soluble tantalum compounds in a highly acidic environment compared to an alkaline or less acidic environment.

3.4. Comparison with Niobium Compounds

A summary of the analytical results for tantalum and niobium (Table 5) produce very interesting results. Good recoveries of both the metal halides were obtained (100 and 94 % for Ta and Nb, respectively) while flux dissolution with LTB also yielded comparable results (95 and 103 % for Ta and Nb, respectively). The difference in their chemical behaviour is demonstrated by the duration of the fluxing. It took only 30 min for Nb_2O_5 to yield complete dissolution (clear melt) while the Ta_2O_5 took 90 min. The most important difference in the dissolution of the oxides
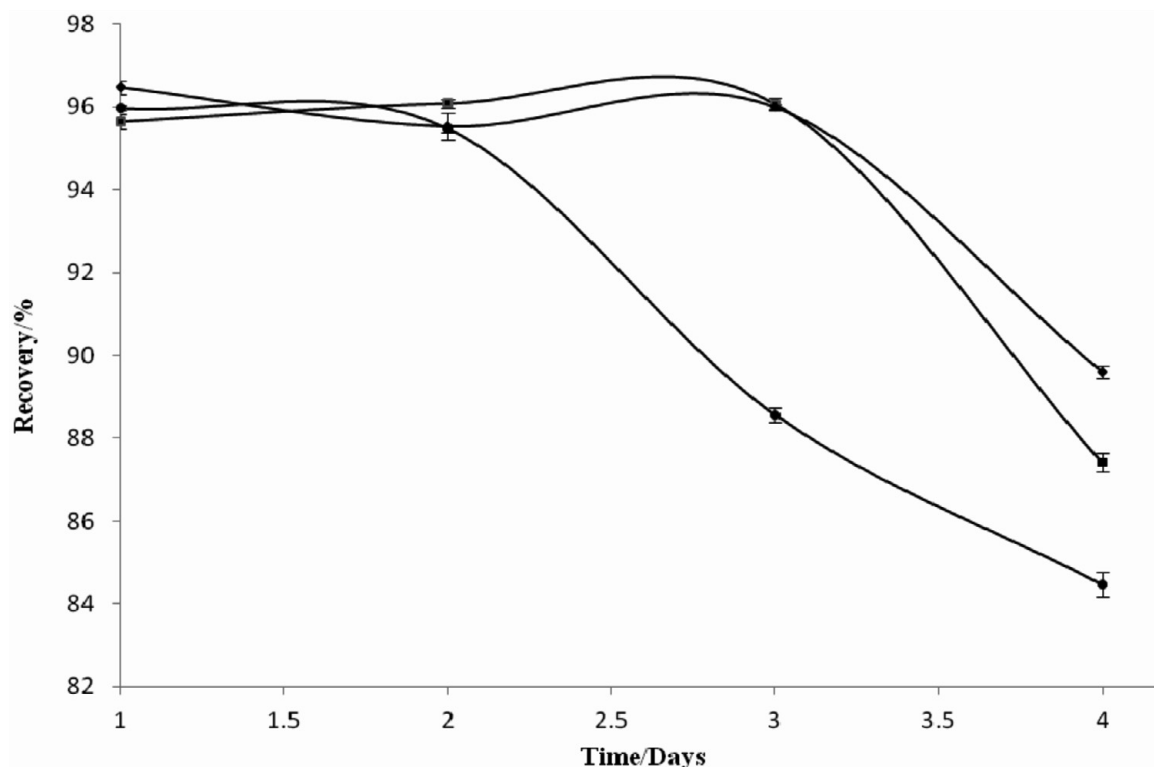
Figure 2 Tantalum pentoxide recovery with time using lithium tetraborate as flux reagent.

using microwave assisted dissolution is the large (quantitative) recovery of the niobium compared to the tantalum. The results indicated a 90 % difference in recovery (99 *vs.* 9 %) for the two oxides using H_2SO_4 as solvent, suggesting more basic character for the niobium oxide or in other words, more reactivity towards acids. A possible explanation for this difference in acidity is the existence of more covalent tantalum–oxygen bond properties[1,2] for Ta_2O_5 compared to the more ionic nature of the equivalent niobium compound. An increase in covalent metal oxygen bond character results in less oxygen electron density available for hydrogen bonding and therefore decreases the possible interaction with acids.

Separation of the two metals normally commences with the complete dissolution of the samples which is then followed by separation. However, the difference in the chemistry of the two

metal oxides suggests separation during the dissolution step using microwave digestion in the presence of H_2SO_4 which may either decrease the number of steps in the separation process or improve separation.

4. Conclusion

Complete dissolution and quantification of the different tantalum compounds was only achieved with the halide compounds. Poor tantalum recovery was obtained for both tantalum metal and Ta_2O_5 using microwave digestion in spite of the harsh experimental conditions that prevailed during the dissolution step. Results obtained from this study also clearly indicated that a wide variety of basic fluxes are much more successful in the dissolution and subsequent recovery of tantalum from different sources compared to acidic fluxes. $Li_2B_4O_7$ appeared to be the most promising fluxing agent for both the highly inert Ta_2O_5 (TAN-1 CRM) and Ta metal samples on the condition that the excess of boron was removed prior to the tantalum quantification. It is also evident from the stability study that the quantification of the tantalum is sensitive to the pH of the solution after approximately three days. The differences in the chemistry of tantalum and niobium, as highlighted in a comparison of analytical results for these two elements, may be utilized in the separation and purification of the two metals from the different mineral ores.

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Table 5 Summary of quantification results for different tantalum and niobium compounds.

Compound	Dissolution method	Solvent	Compounds recovery/%	
			Ta	Nb[8]
M_2O_5	Microwave	HCl	[b]	2.3
		H_2SO_4	9.7	99.2
		HNO_3	4.2	0.1
		H_3PO_4	6.8	84
		Aqua regia	3.9	0.09
	LTB fusion	HNO_3	24	36.6
		H_2SO_4	[b]	103
		H_3PO_4	95	[b]
MF_5	Water		101	93.7
	Microwave	H_2SO_4	[b]	100.7
Metal	Microwave	H_2SO_4	4.18	99.9

[a] Boric acid removed from reaction mixture.
[b] Not conducted.

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