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Recovery of tantalum from synthetic sulfuric leach solutions by solvent extraction with phosphonate functionalized ionic liquids

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Abstract

A series of phosphonate-functionalized task-specific ionic liquids (TSILs) have been synthesized and studied for selective extraction of tantalum from a sulfuric acid medium. The results described here show that high distribution coefficient values can be achieved for the selective separation of tantalum (Ta). Such a system can be used as an alternative to TBP for the separation and purification of tantalum by solvent extraction.

Keywords

Solvent extraction, Task-specific ionic liquids; Tantalum; Ta recovery

1. Introduction

The unique properties of tantalum (Ta) have contributed to its importance for use in the steel, electronics and other high-tech industries (Albrecht, 1989). Tantalum is mainly used in the production of capacitors and semiconductors for electronics devices. Technological needs make Ta an economically and strategically important substance to industrialized countries.

New supply sources may be strategically developed, such as diversification of geographic supply location or efforts to recycle this element from manufacturing scrap (Mackay and Simandl, 2014). Interestingly, an unexplored supply avenue is recycling Ta from electronic capacitors, particularly from end-of life products, such as Waste Electrical and Electronic Equipment (WEEE).

In mineral deposits, tantalum is almost always associated with niobium (Černý and Ercit, 1989). Tantalum and niobium are difficult to separate because of their similar physical and chemical properties (Agulyansky, 2004). The extraction and refining of tantalum, including its separation from niobium in the various tantalum-containing solutions, have been performed through hydrometallurgical processes. Thus, a variety of organic solvents, such as methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), cyclohexane and 2-octanol, are used for tantalum and niobium separation either from other impurities or from each other (Zhu and Cheng, 2011).

Globally, MIBK is the most popular and commonly used extractant due to its extraction efficiency. However, MIBK is fire- and explosion-hazardous, which are major disadvantages for such a process.

Similar to an extraction with MIBK, the TBP extraction method from a mixture of hydrofluoric and sulfuric acids (Zhou et al., 2005) (HF-H₂SO₄ system) produces higher quantities of Ta than

niobium (Nikolaev and Maiorov, 2007). The selective separation of niobium and tantalum from impurities (e.g., iron, manganese, silicon, titanium) was reported to be more efficient with TBP than with MIBK (Nishimura et al., 1964a; Nishimura et al., 1964b).

Room-temperature ionic liquids (ILs), can be used as alternative diluents or extractants of volatile organic compounds in these extraction processes due to their nonflammability and nonvolatility (Brennecke and Maginn, 2001; Huddleston et al., 1998; Visser et al., 2001). Since Dai *et al.* (Dai et al., 1999) revealed the potential of ILs for liquid-liquid extraction, many studies have developed various extractants or synergistic systems diluted in ILs or have used “task-specific ionic liquids” (TSILs) (Billard et al., 2011; Rout et al., 2013; Sukhbaatar et al., 2015; Sun et al., 2012a; Sun et al., 2012b; Turgis et al., 2016). TSILs can act as both the organic phase as well as the extracting agent, thus avoiding the difficulties encountered due to extractant/solvent miscibility.

Recently, we synthesized a novel family of ketone-functionalized task-specific ionic liquids for the selective extraction of tantalum from sulfuric acid medium (Turgis et al., 2018). This system can serve as an alternative to the MIBK extraction method. Indeed, the extraction behavior of Ta with TSIL which is a mimic of the methyl isobutyl ketone was suggested to be most effective and allowing to overcome the limitations associated with the physico-chemicals properties of MIBK. The recovery of Ta after extraction and the recyclability of TSILs have also been demonstrated.

In the present work, we studied a method for liquid-liquid extraction of Ta(V) that applies functionalized hydrophobic ionic liquids based on ammonium, piperidium, imidazolium, pyrrolidinium or pyridinium cations bearing a phosphonate moiety similar to the functional group of TBP. It was assumed that the functional group introduced to the ionic liquid as a phosphonate $R-P=O(OR)_2$ will act in the same manner as the phosphate group $P=O(OR)_3$ of TBP. In the literature, there are only a few examples of TSILs bearing phosphoryl groups, and in all cases, the studies are dedicated to the extraction of actinides (Li et al., 2015; Ouadi et al., 2007; Rout et al., 2010; Rout et al., 2012). Here, TSILs bearing phosphoryl groups are investigated for extracting and stripping tantalum from sulfuric acidic medium in regards to the separation from niobium and from impurities that can be found as competitive ions in acidic leach liquors of capacitors.

2. Experimental section

2.1 Materials and reagents

All chemicals and reagents used in this study were of analytical grade and purchased from Sigma-Aldrich or Alfa Aesar. They were each purified by distillation prior to use. Anhydrous solvents were purchased from Acros (AcroSeal®). ICP calibration and verification standards were purchased from SCP Sciences.

Density measurements were performed with a DSA 5000 thermoregulated digital densimeter (Anton Paar). The apparatus measures densities using an oscillating U-tube with an accuracy of 0.00001 g/cm^3 and temperature controlled to within 0.001°C . All measurements were conducted at $25.005 \pm 0.004^\circ\text{C}$. An RM 200 Lamy rheometer with a CP-400 cone plate system was used to measure viscosity. A plate-plate geometry (PP25, diameter 24.981) was chosen to measure shear viscosities under thermostatic control (25°C) from shear rates of 0.1 to 300 1/s. Shear rates were increased by 10 points per decade. The measurement duration per point was set to 6 s.

Pre- and postextraction acid concentration in the aqueous and TSIL phases was analyzed using a Metrohm 809 Titrando by titration with either 0.1 or 0.01 M NaOH (Fluka Analytical).

Solubility of the TSIL in the aqueous phase was determined by quantifying cation concentration in aqueous solution via Total Organic Content (TOC) measurements using a Shimadzu TOCVCSH analyzer based on a 680°C combustion catalytic oxidation/NDIR method.

The solubility of water in the TSILs was determined via Karl Fischer coulometric titration with Hydranal® Composite 2 using a Metrohm 831 KF Coulometer or a Metrohm 809 Titrando. The TSIL was in contact with the aqueous phase for 1 hour; then, the two-phase system was centrifuged, and the TSIL water content was measured.

NMR analyses were performed on a Bruker 400 ultrashield VS spectrometer. Displacements are reported in ppm using the solvent (CDCl₃: 7.26 ppm ¹H; 77.16 ppm ¹³C) as an internal reference. The purity of various compounds was determined via NMR analysis and can be assumed to be ≥95%.

Metal concentrations were measured before and after extraction by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) using a SPECTRO ARCOS spectrometer.

Powder X-ray diffraction patterns were recorded on a Bruker D8 advance diffractometer using CuKα radiation ($\lambda = 1.5418 \text{ \AA}$). The data were collected in Bragg-Brentano geometry over 2θ range of 10°–80° with a step size of 0.015°. The crystallite size (L) was estimated from the line broadening of the XRD peaks using the Scherrer formula:

$$L = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength of the X-rays, β is the full-width at half-maximum height (rad), and θ is the diffraction angle.

SEM analyses were obtained with a TESCAN VEGA3 scanning electron microscope coupled with an EDX Bruker QUANTAX microanalyzer.

2.2. Synthesis of TSILs

The general procedures for synthesis of TSILs and their characterization are reported in the supporting information.

2.3. Extraction experiments

Ta(V) stock solutions (1–10 g/L) were prepared at the desired acidity (H₂SO₄ 0–9 M) from 10000 mg/L ICP standard from SCP Science (aqueous solution of NH₄TaF₆ with 4% hydrofluoric acid). A synthetic solution mimicking the leaching of capacitors was prepared from Ta(V) and Nb, 10000 mg/L and 1000 mg/L ICP standards and starting from metallic salt of Fe, Mn, Ni and Ag. The desired concentrations were prepared by dilution using ultrapure water (Milli-Q, Millipore, 18 MΩ/cm) and the acidity was adjusted with sulfuric acid. The initial concentrations of each metal were measured by inductively coupled plasma/atomic emission spectroscopy (ICP/AES).

Extractions were performed by shaking defined volumes of TSIL and aqueous phases using a temperature-controlled shaker (Infor-ht® ecotron) at 25°C and 400 rpm for 1 hour. Various aqueous to TSIL phase ($V_{\text{aq}}/V_{\text{IL}}$) volumetric ratios have been used. The aqueous and TSIL phases remained well separated, forming biphasic systems with any variation of volume phases occurring after the extraction process.

After the extraction, separation of the phases was assisted by centrifugation (4000 rpm for 5 min), and the aqueous phase was analyzed by ICP/AES. The organic phase was subjected to stripping using ultrapure water (MilliQ, Millipore, 18 M Ω /cm).

Stripping experiments were performed at 25°C by contacting the loaded IL phase with water for 1 hour (aqueous to IL phase volumetric ratio V_{st}/V_{IL} of 1, 2 or 5). After separation by centrifugation (4000 rpm for 10 min), concentrations of each metal were measured in the aqueous phase by ICP/AES. All experiments were conducted in duplicate with a precision of $\pm 5\%$.

The efficiency of TSIL to selectively extract Ta towards iron was evaluated using the following parameters.

The distribution ratio (D) was determined using the following equation:

$$D = \frac{[Ta]_{IL}}{[Ta]_{aq}} = \frac{C_i - C_f}{C_f} \times \frac{V_{aq}}{V_{IL}}$$

where C_i and C_f are the concentrations of the metal ions in the aqueous phase before and after extraction, respectively. V_{aq} is the volume of the aqueous phase, and V_{IL} is the volume of the ionic liquid phase.

The extraction efficiency (%E) was determined using the following equation:

$$\%E = \frac{D}{D + \frac{V_{aq}}{V_{IL}}} \times 100\%$$

The stripping percentage (%S) was calculated as follows for $V_{st}=V_{IL}$

$$\%S = \frac{[Ta]_{st}}{[Ta]_{IL}} \times 100\%$$

where $[Ta]_{st}$ and $[Ta]_{IL}$ are the concentrations of the metal ions in the stripping aqueous phase after stripping and the concentrations of the metal ions in the loaded TSILs phase before stripping, respectively. The stripped TSIL phases were reused in further cycles of the extraction-stripping process. The separation factor ($SF_{Ta/M}$) is given by:

$$SF = \frac{D_{Ta}}{D_M}$$

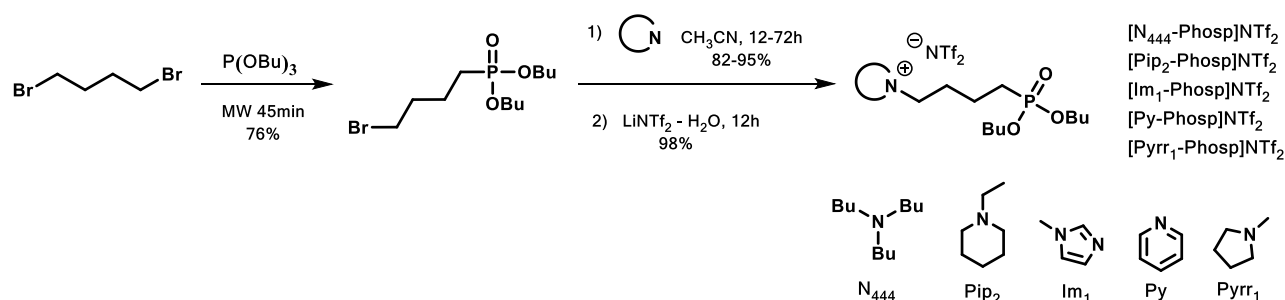
where D_{Ta} and D_M are the distribution ratios of the Ta and M competitive ions, respectively.

3. Results and discussion

3.1. Synthesis

The functionalized hydrophobic ionic liquids based on ammonium, piperidinium, imidazolium, pyridinium or pyrrolidinium cations bearing phosphonate moieties have been synthesized according to Scheme 1.

Dibromobutane and tributyl phosphite were heated for 45 min under microwave irradiation leading to dibutyl (4-bromobutyl)phosphonate. The synthesized dibutyl (4-bromobutyl)phosphonate was reacted with tributylamine (N_{444}) or a heterocyclic amine, such as ethylpiperidine (Pip_2), methylimidazolium (Im_1), pyridine (Py) or methylpyrrolidine ($Pyrr_1$), to form the corresponding quaternary salts. The metathesis with $LiNTf_2$ converted the bromide anions into bis(trifluoro-methanesulfonyl)amide, thus providing the desired hydrophobic ionic liquids. The NMR and HRMS characterizations of the products are provided in the experimental section. The density and viscosity values of the TSILs bearing a phosphonate functionality are reported in Table 1, along with their corresponding water content.



Scheme 1. Synthetic strategy for bis(trifluoromethylsulfonyl)imide (NTf₂)-based TSILs bearing a phosphonate functionality.

Table 1. Physical and chemical properties of the bis(trifluoromethylsulfonyl)imide (NTf₂)-based TSILs phosphonate tested in this study.

TSIL cation (MW g/mol)	Density 25°C (g/cm ³)	Viscosity 25°C (mPa.s)	Water content (ppm)
N₄₄₄ (434.4)	1.192853 (69)	1497(3)	5371(39)
Pip₂ (362.3)	1.283228 (38)	1069(1)	6080(58)
Im₁ (331.2)	1.315355 (35)	263(2)	7798(64)
Py (328.2)	1.323672 (26)	389(2)	2815(52)
Pyr₁ (334.2)	1.292857 (37)	303(1)	9951(31)

3.2. Extraction experiments

3.2.1. Preliminary extraction experiment

All synthesized TSILs are liquid at room temperature and present a sufficiently low viscosity to be directly employed as pure extracting phase/extracting agents in liquid-liquid extraction experiments. The distribution ratios of Ta remain almost constant after 15 min at 25°C, which is the amount of time presumed necessary for Ta to reach an equilibrium state with the TSIL. To illustrate this result, a kinetic study for Pip₂ is provided in Figure SI-1 (see supporting information). To ensure complete extraction and establish a comparison, all studies were conducted at a duration of 1 hour.

As described in the literature, tantalum extraction efficiency is low at low acidity (Zhu and Cheng, 2011). Its extraction usually starts with a concentration of 3 M sulfuric acid. Therefore, preliminary experiments were conducted to investigate the effect of the IL cation on the extraction behavior of Ta(V) from 6 M H₂SO₄ when extracting with pure TSILs.

The metal ion distribution ratios (D_{Ta}), extraction efficiency (%E) and stripping efficiency (%S) for all TSILs have been determined using a 6 M H₂SO₄ solution containing 1 or 7 g/L tantalum, and the results are summarized in Table 2.

Table 2. Distribution coefficient (D), extraction percent (E) and stripping efficiency (S) of bis(trifluoromethylsulfonyl)imide (NTf₂)-based TSILs phosphonate from a 6 M H₂SO₄ solution containing 1 or 7 g/L of Tantalum and 0.15 or 1 M of HF, respectively, $V_{aq}/V_{IL} = 1$. Stripping: MilliQ water; $V_{st}/V_{IL} = 2$.

TSIL cation	[Ta] = 1 g/L		[Ta] = 7 g/L	
	D (%E)	S (%)	D (%E)	S (%)
N ₄₄₄	8 (88.9)	19	1088 (99.9)	16
Pip ₂	6.8 (87.1)	98	107.1 (99.1)	70
Im ₁	4.8 (82.8)	84	13.4 (93)	71
Py	4.9 (83.1)	79	14.2 (93.4)	85
Pyrr ₁	5.9 (85.5)	83	30.4 (96.8)	66
TBP	3.6 (78.3)	23	216 (99.5)	5 <

High distribution coefficients were obtained for all tested TSILs. The extraction efficiency was determined to be similar among ammonium, piperidium, pyrrolidinium, imidazolium and pyridinium cations. Indeed, Ta is almost quantitatively extracted by TSILs with a performance close to that of TBP. The stripping of Ta from loaded TSILs is an important parameter in selective recovery of Ta and recycling of TSILs, which will be then engaged for the next extraction-stripping cycles.

The behavior of the N₄₄₄-Phosp is close to that of TBP, which has a very strong affinity for Ta in the conditions studied, however, stripping with water is not efficient.

The use of deionized water as a stripping solution resulted in recovery of Ta with high yields, with the exception of the TSIL bearing an ammonium cation (N₄₄₄-Phosp) (Table 2).

3.2.2. Extraction-stripping cycles

Based on the extraction and stripping efficiencies, we selected [Pip₂Phosp]NTf₂ to investigate further for extraction and recovery of Ta. Consequently, a series of extraction-stripping experiments was performed using [Pip₂Phosp]NTf₂ to validate the recyclability of the TSIL phase.

The TSIL was combined with an equal volume of feed solution, 6 M H₂SO₄ containing 7 g/L of tantalum ($V_{aq}/V_{IL} = 1$); then, the loaded TSIL phase containing Ta was stripped with deionized water (st) at a V_{st}/V_{IL} ratio of 2. The stripped TSIL phase was subsequently reused for a new extraction-stripping cycle under similar experimental conditions. The results illustrated in Figure 1 highlight that the recycled TSIL phase shows the same extractive behaviors as the fresh TSIL for at least 5 cycles, with average Ta extraction efficiencies at approximately 98%.

3.2.3. Effect of Ta concentration

To determine the amount of Ta that can be extracted by [Pip₂Phosp]NTf₂, a series of experiments was conducted with various V_{aq}/V_{IL} ratios by increasing the amount of aqueous feed solution while maintaining other conditions (6 M H₂SO₄, 7 g/L Ta), as illustrated in Figure 2.

In fact, Figure 2 shows that the amount of Ta extracted begins to plateau when V_{aq}/V_{IL} is higher than 80. The loading capacity, which corresponds to the maximum concentration of Ta that the TSIL can contain, was estimated to be higher than 180 g/L.

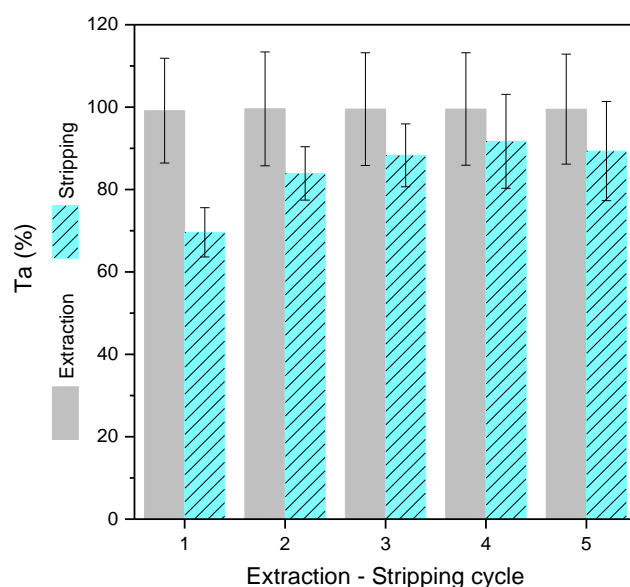


Fig. 1. Ta(V) extraction and stripping percentages for [Pip₂Phosp]NTf₂ obtained when the number of extraction-stripping cycles was increased. Organic phase: pure [Pip₂Phosp]NTf₂. Aqueous phase: [Ta] = 7 g/L, [H₂SO₄] = 6 M, [HF] = 1 M; V_{aq}/V_{IL} = 1. Stripping: MilliQ water; V_{st}/V_{IL} = 2.

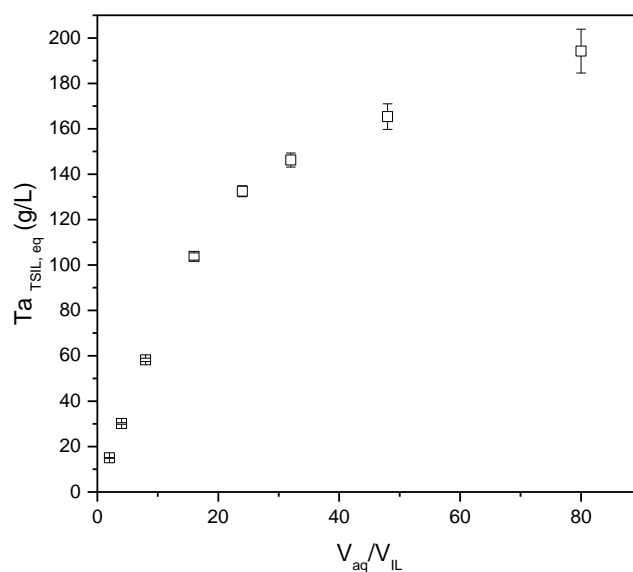


Fig. 2. Equilibrium tantalum concentration in [Pip₂Phosp]NTf₂ ($[Ta]_{TSIL,eq}$) as a function of the V_{aq}/V_{IL} ratio. Organic phase: pure [Pip₂Phosp]NTf₂. Aqueous phase: [Ta] = 7 g/L, [H₂SO₄] = 6 M, [HF] = 1 M.

3.2.4. Ta extraction from multimetal-ion solutions

To investigate the selectivity of [Pip₂Phosp]NTf₂ for Ta upon extraction, an aqueous multimetal solution was prepared by adding competitive metals (Nb, Fe, Ni, Ag and Mn). Due to the significant effect of acid concentration on both selectivity and extraction performances, a more extensive study was conducted over a range of acid concentrations from 0.1 to 9 M H₂SO₄ containing a similar amount of Ta and competitive cations. The concentration of each metal ion in sulfuric acid solution was 2.5 g L⁻¹. The extraction behavior for each metal ion as a function of sulfuric acid concentration is plotted in Figure 3a. High selectivity for extraction of Ta can be achieved using the [Pip₂Phosp]NTf₂. Ta is mainly extracted from the aqueous phase over a wide acid concentration range with a distribution coefficient higher than 50, while the [Pip₂Phosp]NTf₂ has very low distribution coefficients for the other metal ions.

The TSIL [Pip₂Phosp]NTf₂ allows for the selective extraction of tantalum in regard to the set of competitive ions studied. Indeed, the separation factor values are always greater than 100 regardless of acidity, except for niobium, for which the selectivity of Ta / Nb decreases in sulfuric acid concentrations higher than 6 M but remains greater than 10 even at 9 M sulfuric acid (Figure 3b).

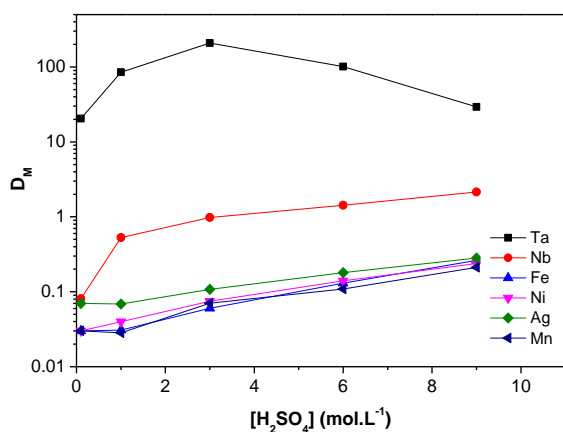


Fig. 3a. Variation in the distribution coefficient of Ta, Nb, Fe, Ni, Ag and Mn as a function of sulfuric acid concentration. Organic phase: pure [Pip₂Phosp] [NTf₂]. Aqueous phase: [metals] = 2.5 g/L, [H₂SO₄] = 0–9 M, HF=0.35 M, V_{aq}/V_{IL} = 1.

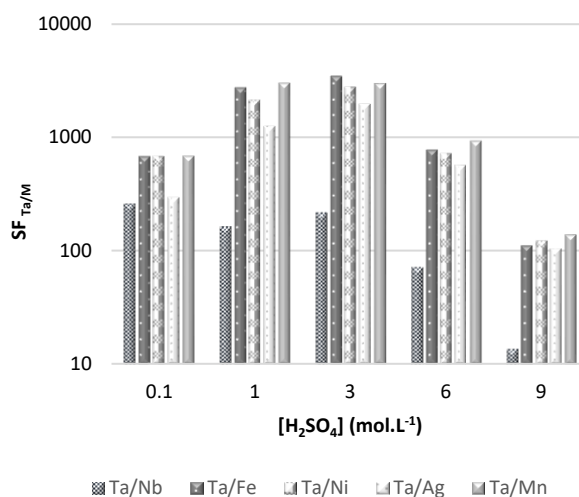


Fig. 3b. Separation factor (SF_{Ta/M}) as a function of sulfuric acid concentration. Organic phase: pure [Pip₂Phosp] [NTf₂]. Aqueous phase: [metals] = 2.5 g/L, [H₂SO₄] = 0–9 M, HF=0.35 M, V_{aq}/V_{IL} = 1.

3.2.5. Ta recovery

Stripping tantalum from the IL phase into an aqueous medium is an important step in recovering this metal. We showed that water can be effective at stripping Ta from [Pip₂Phosp]NTf₂. The stripping efficiency (%S) can be increased by changing the ratio of the stripping aqueous phase to the loaded IL phase (V_{St}/V_{IL} ratio).

The stripping efficiency from the loaded [Pip₂Phosp]NTf₂ obtained after combining the IL phase with a 6 M H₂SO₄ solution containing 7 g/L of tantalum has been evaluated at 70% for a V_{St}/V_{IL} ratio = 1 and higher than 95% for a V_{St}/V_{IL} ratio = 5.

Finally, the percent recovery of Ta from the aqueous stripping medium was determined by precipitation using an ammonium hydroxide (NH₄OH) solution. The tantalum strip solution was treated by adding 30 % ammonium hydroxide (NH₄OH). The molar ratio NH₄OH/Ta was varied between 1 and 10, and at least 4 molar equivalents of ammonia were needed to entirely precipitate the tantalum (see

supporting information Figure SI-2). After filtration, precipitates were washed with distilled water and dried at 100°C. After calcination at 900°C for 4 hours, pure tantalum pentoxide was obtained as suggested by XRD and SEM-EDS analysis (Figure 4 and supporting information Table SI-1 for microanalysis result). At this stage, the yield for Ta recovery was estimated to be > 95 %. Considering the full process, the overall yield for Ta recovery, from the initial extraction to the final calcination to form the oxide, was approximately 90%.

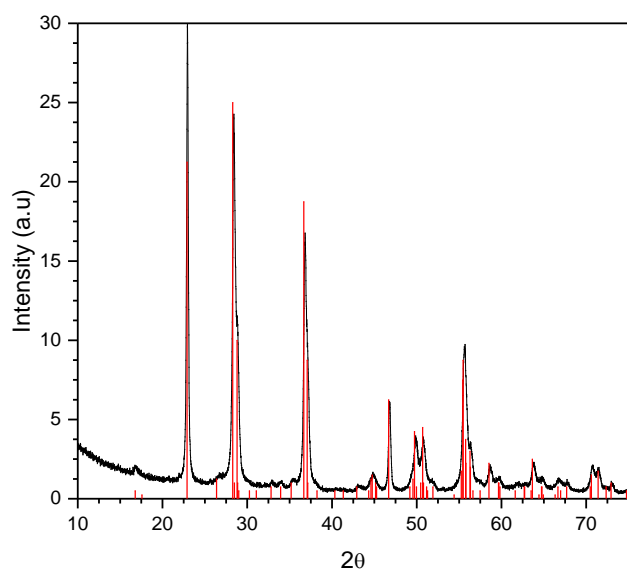


Fig. 4a. X-ray diffraction pattern of powder obtained after precipitation of the tantalum strip solution and annealing at 900°C for 4 hours. Ta₂O₅ orthorhombic phase (JCPDS: 25-922).

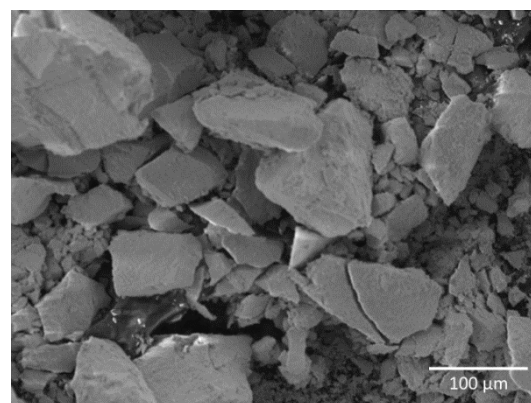


Fig. 4b. SEM image of as-synthesized Ta₂O₅.

Figure 4a shows the diffraction patterns for powders annealed at 900°C for 4 hours. Ta₂O₅ orthorhombic phase (JCPDS:25–922) was obtained with crystallites approximately 17 nm in size, estimated by the Scherrer formula. Figure 4b shows the SEM micrograph of a synthesized Ta₂O₅ in which the particles are aggregated in the form of grains with sizes of approximately 30 μm.

3.2.6. Extraction mechanism analysis

It appears that the extraction mechanism of an IL is very different compared to that of a conventional organic solvent (Billard et al., 2013; Turgis et al., 2016). Depending on the nature of the ligand, IL and aqueous phase, different mechanisms may be encountered, such as ion-exchange, neutral coextraction or neutral solvation (Janssen et al., 2015). Compared to the number of studies investigating the application of ILs in separations, task-specific ionic liquids (TSILs), which play dual roles of both hydrophobic solvents and extractants, have been the focus of relatively few studies (Bonnaffé-Moity et al., 2012; Ouadi et al., 2007; Paramanik et al., 2016; Sengupta et al., 2017; Visser et al., 2001). Additionally, in most prior cases, the TSIL is diluted in an organic solvent or another IL, and the extraction mechanisms involved are poorly described. To better understand the mechanism of extraction in the [Pip₂Phosp]NTf₂ media, the aqueous and TSIL phases have been analyzed after extraction by NMR, COT, KF, and potentiometry.

To estimate the extraction mechanism, ^{31}P NMR experiments have been performed at different $V_{\text{aq}}/V_{\text{IL}}$ ratios after combining the IL phase with the tantalum-containing acidic aqueous phase (Figure 5). By gradually increasing the $V_{\text{aq}}/V_{\text{IL}}$ ratio not only is a signal at 31.7 ppm corresponding to the free ligand observed, a signal at 32.2 ppm also appears and becomes more prominent as the $V_{\text{aq}}/V_{\text{IL}}$ ratio and the amount of Ta increase. Furthermore, we do not observe this signal when the TSIL was combined with a 6 M H_2SO_4 solution without tantalum.

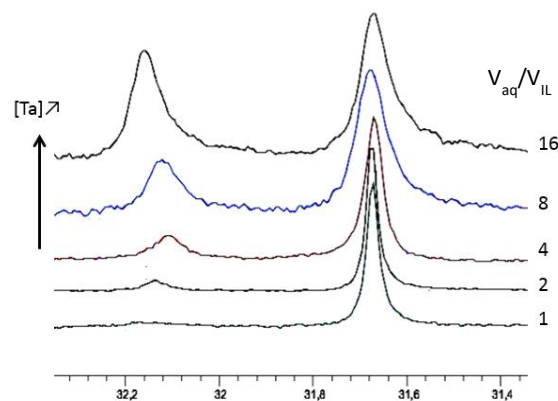


Fig. 5. ^{31}P NMR of the $[\text{Pip}_2\text{Phosp}]\text{NTf}_2$ phase after combining the IL phase with various amounts of acidic aqueous phase. Organic phase: pure $[\text{Pip}_2\text{Phosp}]\text{NTf}_2$. Aqueous phase: $[\text{Ta}] = 7 \text{ g/L}$, $[\text{H}_2\text{SO}_4] = 6 \text{ M}$, $[\text{HF}] = 1 \text{ M}$; $V_{\text{aq}}/V_{\text{IL}} = 1$ to 16.

These results indicate that no degradation of Ta occurs and that this secondary peak is related to the presence of Ta. This suggests that an ion pair complex is formed between Ta and the IL in the ionic liquid medium.

The solubility of the ionic liquid in various aqueous solutions was first studied by NMR analysis of the aqueous phase, tracking the ^{19}F nucleus for the NTf_2 anion and ^1H and ^{13}C for the IL cation. NMR analysis of the aqueous phase indicates the presence of both an anion and cation.

Various amounts of TSIL transferred into the aqueous phase when the initial feed changed from water to acidic solution in the presence or absence of Tantalum, suggesting that this value is not exclusively correlated to solubilization of the TSIL in the aqueous phase. This result supports an intrinsic solubilization and loss due to ion exchange. The amount of TSIL transferred into the aqueous phase was estimated by TOC analysis with approximately 15 g/L of organic content in the pure water compared to 210 g/L when the initial aqueous phase is acidified and contains Ta. This amount corresponds to 16.4 % of the initial TSIL quantity (Figure 6). The recycled IL organic phase exhibits extractive behaviors similar to those of a fresh $[\text{Pip}_2\text{Phosp}]\text{NTf}_2$ solution, with extraction efficiencies higher than 95% (Figure 1). This indicates that if an ion-exchange mechanism is involved, it has no negative effect on the extraction efficiency. This can be correlated to the high loading capacity of the TSIL.

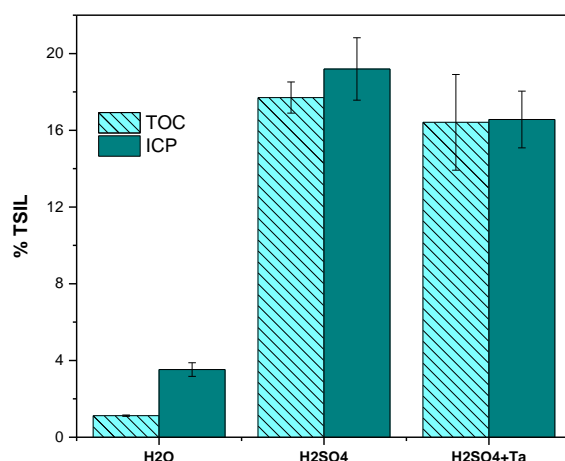


Fig. 6. TSIL percentage loss (% TSIL) of [Pip₂Phosp]NTf₂ ([Ta]_{TSIL,eq}) after contact with MilliQ water, 6 M H₂SO₄ or 6 M H₂SO₄ solution containing 7 g/L of tantalum and 1 M HF determined by total organic carbon analysis (TOC) or by Ionized Coupled Plasma analysis based on the Phosphorus element (ICP (Phosphorous)). $V_{aq}/V_{IL} = 1$.

Surprisingly, it has been observed that solubilization decreases progressively during the extraction cycles. As illustrated in Figure SI-3 (see supporting information), after the first cycle, the amount of TSIL loss in the aqueous phase is less than 2%.

Water and acid transferred into the TSIL phase during extraction (see below) can possibly explain this behavior. Once loaded with water and acid, the solubilization of TSIL is much less pronounced. Additionally, the TSIL may contain some sulfate as the counteranion which can play a role in this phenomenon. However, it is difficult to definitively conclude the presence of sulfate since it was not possible to discriminate sulfur from sulfate from that of the NTf₂ anion.

The [Pip₂Phosp]NTf₂ used for liquid-liquid extraction is not miscible with water but is hygroscopic, therefore, the solubility of water in TSIL can be quite high. The water concentration in the TSIL phase before and after extraction was measured by Karl Fisher coulometric titration. The solubility of water in the TSIL was found to be approximately 6%, while the amount transferred increases to almost half as high in the presence of acid and tantalum in the feed solution (Table 3).

Table 3. Water content in pure [Pip₂Phosp]NTf₂ and after 3 contact with 6 M H₂SO₄ solution containing 7 g/L of tantalum and 1 M HF, 6 M H₂SO₄ or MilliQ water. $V_{aq}/V_{IL} = 1$.

	% H ₂ O
TSIL	0.523 ± 0.016
TSIL/Ta (7 g/L); H ₂ SO ₄ 6 M; HF 1 M	2.963 ± 0.064
TSIL/H ₂ SO ₄ 6 M	2.975 ± 0.037
TSIL/H ₂ O	5.5 ± 0.134

After contact of the acidic aqueous phase (6 M H₂SO₄ or Ta 7 g/L – 6 M H₂SO₄ – 1 M HF) with the TSIL phase, a portion of the acid is extracted into the TSIL phase. Proton transfer from the aqueous phase to the IL phase represents about 8% of the initial acid concentration (see supporting information Table

SI-2). In the case of the feed solution containing tantalum, proton transfer is slightly higher than the aforementioned result, which can be related to the higher initial acidity of the solution. Again, the presence of protons in the IL phase did not affect the extraction efficiency, as evidenced by the reusability studies.

The role of the extracted acid in regard to the amount of water extracted during the extraction step should be further studied. Investigations such as SAXS, EXAFS or computational procedures could help to identify the role of water and acid in this process (Gaillard et al., 2012; Maiti et al., 2012; Sukhbaatar et al., 2015).

Based on the behaviors observed when investigating the mechanism of TSIL exchange, it appears that the combination of ion pair complex formation and ion-exchange mechanisms could be the driving force of the extraction. No concrete evidence allows the discrimination between these two mechanisms. The possibility of a mixed partitioning mode has been described in the literature (Dietz et al., 2003; Wehbie et al., 2017).

4. Conclusions

A novel family of phosphonate-functionalized task-specific ionic liquids (TSILs) were synthesized to study their ability to extract Ta from a sulfuric acid solution. Among the various TSILs that were synthesized, the potential of bis(trifluoromethylsulfonyl)imide N-(4-(dibutoxyphosphoryl) butyl)-N-ethylpiperidinium, [Pip₂Phosp]NTf₂, has been highlighted in regard to its tantalum recovery properties from sulfuric acid medium. The results clearly show that [Pip₂Phosp]NTf₂ is highly selective for the extraction of Ta, as demonstrated by a high separation factor against the competitive cations studied (Nb, Fe, Ni, Ag and Mn). The recovery of Ta can be performed by first using water to strip, followed by a precipitation step with ammonia in order to obtain Ta in its oxide form. A series of extraction-stripping cycles showed that the IL phase can be recycled without performance loss compared to fresh TSIL solutions.

These various findings suggest that Ta can be extracted via a combination of the ion pair complex formation and ion-exchange mechanisms. Considering the different observations, it is difficult to eliminate the possibility of either mechanism. Further analyses are under investigation to improve the mechanistic aspect of the extraction.

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Appendix A. Supplementary data

Supplementary data to this article can be found online.

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Electronic Supplementary Information for

Recovery of tantalum from synthetic sulfuric leach solutions by solvent extraction with phosphonate functionalized ionic liquids

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Synthetic Procedures & Characterizations

Synthesis of dibutyl (4-bromobutyl)phosphonate

Dibromobutane (47.87 g ; 26.47 mL ; 0.221 mol) and tributylphosphite (18.5 g ; 20 mL ; 0.073 mol) were introduced in a microwave reactor. The mixture was stirred and heated at 140°C for 45 min (400 W during 5 min. then 300 W). After cooling, the dibromobutane was removed under vacuum and the obtained crude product was purified through silica gel column chromatography (flash chromatography using a Reveleris X2) using cyclohexane/ethyl acetate 0-10% as the eluent, to afford a slightly yellow oil (18.43 g ; 0.056 mol ; 76%)

^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.93 (t, $J = 7.5$ Hz, 6 H, $\text{CH}_2\text{-CH}_3$); 1.40 (m, 4 H, $\text{CH}_2\text{-CH}_3$); 1.64 (m, 4 H, $-\text{CH}_2-$); 1.75 (m, 4 H, $-\text{CH}_2-$); 1.95 (m, 4 H, $-\text{CH}_2-$); 3.41 (t, $J = 6.5$ Hz, 2 H, $\text{CH}_2\text{-Br}$); 4.02 (m, 4 H, $(\text{O}-\text{CH}_2-)$).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 13.5 ($\text{O}-(\text{CH}_2)_3\text{-CH}_3$); 18.6 ($\text{O}-(\text{CH}_2)_2\text{-CH}_2\text{-CH}_3$); 21.1 (CH_2); 23.8 - 25.2 (d, $J = 140.0$ Hz, $\text{CH}_2\text{-P}$); 32.5 ; 32.6 ; 32.9 ; 33.1 ($-\text{CH}_2-$); 65.5 (d, $J = 7.0$ Hz, $\text{O}-\text{CH}_2-$).

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): 31.35

General procedure for the TSILs

To a mixture of 45 mmol (15 g) of bromobutylphosphonate in 20 mL of acetonitrile was added dropwise the desired amine (68 mmol) under argon at room temperature, over 30 min under vigorous stirring. The reaction mixture was then stirred at room temperature or 80°C for 12-72 h as function of the amine engaged in the reaction. Volatile compound were removed under vacuum and the residue dissolved in MilliQ water and washed several time with diethylether. The aqueous phase was then heated at 75°C in the presence of charcoal for 30min. After filtration over Celite, the solution was engaged for halide ion metathesis by NTf_2^- anion salts. To the solution of bromide salt (45 mmol) was added a solution of bis(trifluoromethane)sulfonimide lithium salt (13 g, 46 mmol) in 15 mL of MilliQ water. The mixture was stirred for at least 12 h at room temperature, and the biphasic mixture was then separated. The organic phase was washed with water until the silver nitrate test was negative; the organic phase was heated at 75°C in the presence of charcoal overnight. After filtration and concentration under vacuum, the ionic liquid was then dried under vacuum at 80 °C for 24 h.

Bis(trifluoromethylsulfonyl)imide N-(4-(dibutoxyphosphoryl) butyl)-N-tributylammonium N₄₄₄

Tributylamine and dibutyl (4-bromobutyl)phosphonate were heated at 80°C for 72h. After the metathesis with LiNTf_2 , **N₄₄₄** was obtained as yellow ionic liquid (global yield 80.8%)

^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.87-0.97 (m, 15 H, $-\text{CH}_3$); 1.33-1.39 (m, 10H, $\text{CH}_2\text{-CH}_3$); 1.56-1.62 (m, 12 H, $-\text{CH}_2-$); 1.76 (m, 4 H, $-\text{CH}_2-$); 3.09-3.13 (m, 8H, $\text{N}-\text{CH}_2-$); 3.97 (m, 2 H, $(\text{O}-\text{CH}_2-)$).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 13.3; 13.5 ($-\text{CH}_3$); 18.6 ($-\text{CH}_2\text{-CH}_3$); 19.4; 22.1; 23.7; 25.5; 32.4; 32.5 ($-\text{CH}_2-$); 53.0; 58.8 ($\text{N}-\text{CH}_2$); 65.5 (d, $J = 7.0$ Hz, $\text{O}-\text{CH}_2-$); 115.0 - 118.2 - 121.4 - 124.5 (q, $J = 321$ Hz, CF_3).

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): 30.3

^{19}F NMR (376 MHz, CDCl_3) δ (ppm): -78.90

HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{53}\text{NO}_3\text{P}$ $[\text{M}]^+$ 434.3763, found 434.3760.

Bis(trifluoromethylsulfonyl)imide N-(4-(dibutoxyphosphoryl) butyl)-N-ethylpiperidinium Pip₂

Ethylpiperidine and dibutyl (4-bromobutyl)phosphonate were heated at 80°C for 72h. After the metathesis with LiNTf₂ **Pip₂** was obtained as slightly yellow ionic liquid (global yield 87.5%)

¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.94 (t, J = 7.5 Hz, 6 H, CH₂-CH₃); 1.32 (t, J = 7.5 Hz, 3H, N-CH₂-CH₃); 1.36-1.43 (m, 4H, CH₂-CH₃); 1.60-1.89 (m, 16 H, -CH₂-); 3.24 (m, 2 H, N-CH₂-); 3.31-3.40 (m, 4 H, N-CH₂-); 4.00 (m 4 H, (O-CH₂-).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 6.9 (-CH₃); 13.5 (O-(CH₂)₃-CH₃); 18.6 (O-(CH₂)₂-CH₂-CH₃); 19.5 (CH₂-CH₂-N); 20.0 ; 20.9 ; 21.6 ; 21.7 (CH₂-CH₂-N); 23.4 - 24.8 (d, J = 140.0 Hz, CH₂-P) ; 32.4 ; 32.5 (d, J = 6.5 Hz, O-CH₂-CH₂-) ; 54.0 ; 57.9 ; 59.2 (CH₂-N) ; 65.5 (d, J = 7.0 Hz, O-CH₂-) ; 115.0 - 118.2 - 121.4 - 124.6 (q, J = 321 Hz, CF₃).

³¹P NMR (162 MHz, CDCl₃) δ (ppm): 30.44

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -78.99

HRMS (ESI+) calcd for C₁₉H₄₁NO₃P [M]⁺ 362.2824, found 362.2824.

Bis(trifluoromethylsulfonyl)imide N-(4-(dibutoxyphosphoryl) butyl)-N-methylimidazolium Im₁

Methylimidazolium and dibutyl (4-bromobutyl)phosphonate were heated at room temperature for 24h. After the metathesis with LiNTf₂, **Im₁** was obtained as colourless ionic liquid (global yield 91.5%)

¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.92 (t, J = 7.5 Hz, 6 H, CH₂-CH₃); 1.37 (m, 4H, CH₂-CH₃); 1.59-1.84 (m, 8 H, -CH₂-); 2.00 (m, 2 H, -CH₂-); 3.92-4.00 (m, 7 H, N-CH₃ & (O-CH₂-); 4.19 (m, 2 H, N-CH₂-); 7.33-7.39 (d, 2 H, -CH-); 8.79 (s, 1 H, -CH-).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 13.5 (O-(CH₂)₃-CH₃); 18.6 (O-(CH₂)₂-CH₂-CH₃); 19.2 (CH₂-CH₂-N); 23.5 ; 24.9; 30.3; 30.5; 32.4; 32.5 (-CH₂-); 36.3 (N-CH₃); 49.4 (N-CH₂); 65.5 (d, J = 7.0 Hz, O-CH₂-) ; 115.0 - 118.2 - 121.4 - 124.5 (q, J = 321 Hz, CF₃) ; 122.4; 123.7 ; 136.2 (CH).

³¹P NMR (162 MHz, CDCl₃) δ (ppm): 30.65

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -79.09

HRMS (ESI+) calcd for C₁₆H₃₂N₂O₃P [M]⁺ 331.2150, found 331.2148.

Bis(trifluoromethylsulfonyl)imide N-(4-(dibutoxyphosphoryl) butyl)-pyridinium Py

Pyridine and dibutyl (4-bromobutyl)phosphonate were heated at room temperature for 12h. After the metathesis with LiNTf₂, **Py** was obtained as colourless ionic liquid (global yield 92.1%)

¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.90 (t, J = 7.5 Hz, 6 H, CH₂-CH₃); 1.36 (m, 4H, CH₂-CH₃); 1.59-1.84 (m, 10 H, -CH₂-); 2.17 (m, 2 H, -CH₂-); 3.98 (m, 4 H, (O-CH₂-); 4.63 (m, 2 H, N-CH₂-); 8.04 (t, 2 H, -CH-); 8.49 (t, 1 H, -CH-); 8.90 (d, 2 H, N-CH-).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 13.5 (O-(CH₂)₃-CH₃); 18.6 (O-(CH₂)₂-CH₂-CH₃); 19.0 (CH₂-CH₂-N); 23.3 ; 24.7; 31.7; 31.8; 32.4; 32.5 (-CH₂-); 61.5 (N-CH₂); 65.5 (d, J = 7.0 Hz, O-CH₂-) ; 115.0 - 118.2 - 121.4 - 124.5 (q, J = 321 Hz, CF₃) ; 128.6 ; 144.5 ;145.6 (C_{arom}).

³¹P NMR (162 MHz, CDCl₃) δ (ppm): 30.35

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -78.99

HRMS (ESI+) calcd for C₁₇H₃₁NO₃P [M]⁺ 328.2041, found 328.2038.

Bis(trifluoromethylsulfonyl)imide N-(4-(dibutoxyphosphoryl) butyl)-N-methylpyrrolidinium Pyrr₁

Methylpyrrolidine and dibutyl (4-bromobutyl)phosphonate were heated at 80°C for 48h. After the metathesis with LiNTf₂, **Pyrr₁** was obtained as colourless ionic liquid (global yield 86.3%)

¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.91 (t, J = 7.5 Hz, 6 H, CH₂-CH₃); 1.36 (m, 4H, CH₂-CH₃); 1.60-1.88 (m, 10 H, -CH₂-); 2.21 (m, 2 H, -CH₂-); 3.00 (s, 3 H, N-CH₃); 3.30 (m, 2 H, N-CH₂-); 3.49 (m, 4 H, N-CH₂-); 3.96 (m 4 H, O-CH₂-).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 13.5 (O-(CH₂)₃-CH₃); 18.6 (O-(CH₂)₂-CH₂-CH₃); 19.3 (CH₂-CH₂-N); 21.5 ; 23.4 ; 24.0; 24.1; 24.8 (-CH₂-); 32.4 ; 32.5 (d, J = 6.5 Hz, O-CH₂-CH₂-) ; 48.4 (N-CH₃) ; 63.8 ; 64.5 (CH₂-N) ; 65.5 (d, J = 7.0 Hz, O-CH₂-) ; 115.0 - 118.2 - 121.4 - 124.6 (q, J = 321 Hz, CF₃).

³¹P NMR (162 MHz, CDCl₃) δ (ppm): 30.30

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -79.00

HRMS (ESI+) calcd for C₁₇H₃₇NO₃P [M]⁺ 334.2511, found 334.2509.

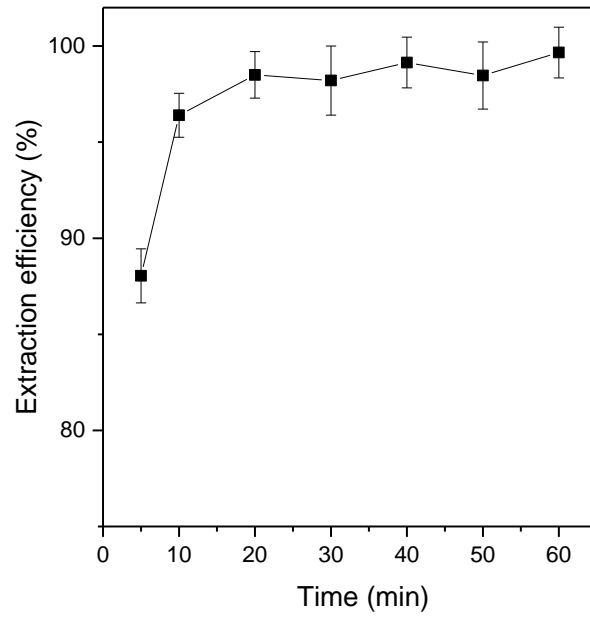


Figure SI-1. Extraction efficiency of Ta as a function of time
 Extraction conditions: Organic phase: pure [Pip₂Phosp]NTf₂ ; Aqueous phase: [Ta] = 7g/L, [H₂SO₄] = 6M, V_{aq}/V_{IL}=1.

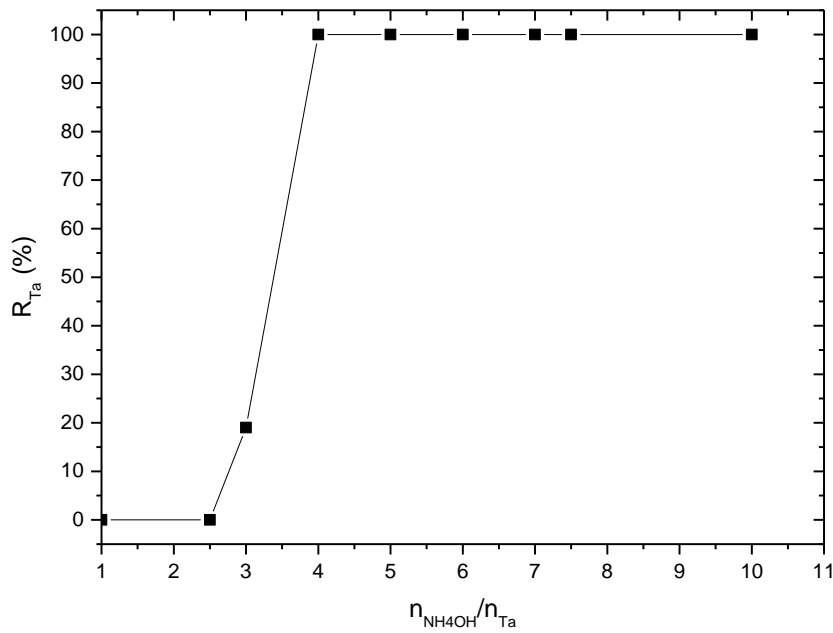


Figure SI-2. Recovery of Ta as a function of the molar ratio NH₄OH/Ta.

Table SI-1: X-EDS analysis of powders obtained after precipitation of the tantalum strip solution and annealed at 900°C for 4 hours.

Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. Error [%](1 sigma)	rel. error [%](1 sigma)
Oxygen	8	K-Serie	6977	17.69	19.52	73.28	2.64	14.93
Tantalum	73	L-Serie	36420	72.97	80.48	26.72	2.05	2.81
			Sum	90.66	100.00	100.00		

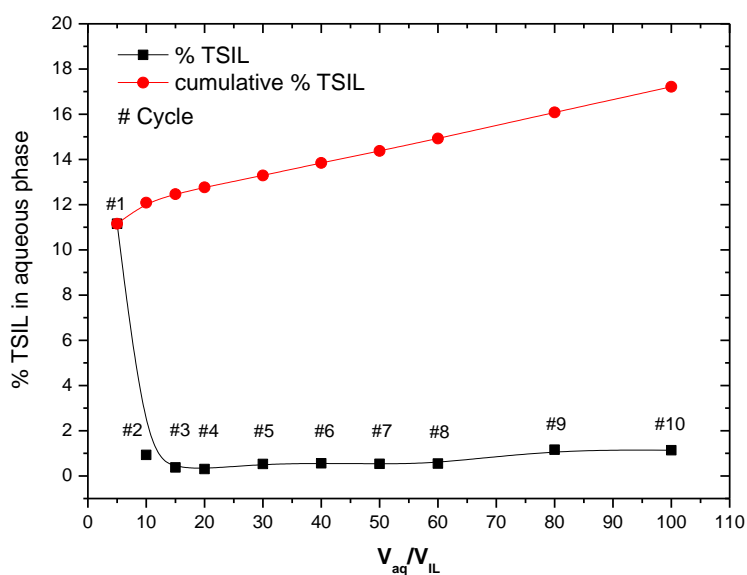


Figure SI-3. Loss of [Pip₂Phosp]NTf₂ as a function of extraction cycle (Aqueous phase: [Ta] = 7g/L, [H₂SO₄] = 6M, V_{aq}/V_{IL}=5 for cycle #1-4 and V_{aq}/V_{IL}=10 for cycle #5-10)

Table SI-2: Proton concentration in [Pip₂Phosp]NTf₂ after contacting with 6 M H₂SO₄ solution containing 7 g/L of tantalum and 1 M HF, 6 M H₂SO₄ determined by pH titration. V_{aq}/V_{IL} = 1.

	H ⁺ (M)
TSIL / Ta (7g/L); H ₂ SO ₄ 6M; HF 1M	1.051 ± 0.069
TSIL / H ₂ SO ₄ 6M	0.919 ± 0.065