

# Spectroscopic and structural characterization of reduced technetium species in acetate media

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Received: 29 November 2010 / Published online: 17 February 2011  
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**Abstract** The reduction of ammonium pertechnetate by sodium borohydride in 0.1 M NaOH/glacial acetic acid has been studied. The reduction products (solids and solutions) have been characterized by UV–Visible spectroscopy, Scanning Electron Microscopy/Energy-dispersive X-ray emission spectroscopy (SEM/EDS), and X-ray absorption fine structure (XAFS) spectroscopy. UV–Visible spectra of the solution, after reduction, exhibit bands at 350 and 500 nm that have been attributed to the formation of polymeric Tc(IV) species. SEM/EDS on the solid (X-ray amorphous) indicates the absence of metallic Tc and the presence of oxygen. EXAFS measurements further indicate that the precipitate exhibits a  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]$  core structure. XANES is consistent with the formation of Tc(III) and/or Tc(IV). Results infer that reduction of aqueous Tc(VII) by borohydride in the presence of acetic acid does not produce metallic Tc, but a mixture of various oxidation states of Tc near Tc(III) and Tc(IV).

**Keywords** Technetium · Borohydride · Reduction · Acetate · EXAFS

## Introduction

Technetium, element 43, is the lightest artificial element. It is produced in large quantities from spent nuclear fuel where it constitutes approximately 6% of the fission

product via decay of  $^{99}\text{Mo}$  and by direct production from uranium. In the context of nuclear reprocessing, technetium is envisioned to be removed from spent fuel, converted to a waste form, or transmuted, in a separation process [1–3]. The separation of uranium from pertechnetate can be achieved using anion exchange resins. After separation, the technetium stream is collected, converted to Tc metal and immobilized into a potential metallic waste form for long-term storage [4–6]. In this process, the conversion of the Tc stream to the metal involves many steps: evaporation to dryness, precipitation of an insoluble pertechnetate salt and reduction of pertechnetate to the metal by hydrogen at elevated temperatures, or other methods [7–11]. Minimizing steps involved in the production of the metal from a concentrated stream of  $\text{TcO}_4^-$  would be more convenient. The ability to directly convert Tc(VII) to Tc metal is of great interest in the context of nuclear reprocessing.

There has been limited study regarding the structural interpretation of Tc compounds by XAFS, in which most has been limited to radiopharmaceuticals and specifically the auto-reduction of Tc(VII) in aqueous, alkaline solutions [12, 13] forming Tc(IV/V) alkoxide complexes. In this context, the aqueous reduction of pertechnetate by borohydride in the presence of acetic acid to form Tc metal has been considered [14, 15]. Reduction of pertechnetate with borohydride in the presence of acetic acid produces a dark compound was previously reported to be the metal [16]. The degree of oxidation was determined by cerium titration. No other characterization, structural or otherwise, was performed. In the present article, we reinvestigated the reduction of pertechnetate with borohydride, in acetic acid, and report on the characterization of recovered products of Tc by various spectroscopic techniques.

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## Experimental method

### Synthesis

The reduction of pertechnetate with sodium borohydride was performed according to the procedure published in the literature [14]. An ammonium pertechnetate solution ( $[Tc] = 0.022 \text{ M}$ ,  $0.224 \text{ mmol Tc}$ ) was purged for 10 min with Argon gas prior to the drop-wise addition of a sodium borohydride/sodium hydroxide solution ( $8.7 \text{ mmol NaBH}_4$  in  $3 \text{ mL } 0.1 \text{ M NaOH}$ ) with a needle through a septum. The solution remained translucent but slowly undertook a pink hue indicative of the formation of Tc(V) or Tc(VI) intermediates [17, 18]. After 3 min,  $10 \mu\text{L}$  concentrated acetic acid was added. Significant gas evolution accompanied by the formation of a brown colored solution and precipitation of a dark solid was observed. A total of  $80 \mu\text{L}$  concentrated acetic acid was added. After 20 min the production of gas was no longer apparent. The suspension was collected with a pipette and centrifuged. The supernatant was removed and the solid was rinsed with three times with  $6 \text{ mL DI H}_2\text{O}$ . The final black compound (Sample A, X-ray amorphous) was dried under vacuum in a desiccator over a period of 24 h ( $17.9 \text{ mg Tc}$ ,  $81\%$  yield). The supernatant was characterized by UV-Visible spectroscopy and the recovered solid by SEM/EDS and XAFS spectroscopy.

### XAFS spectroscopy

Measurements were completed at the Advanced Photon Source (APS) at the BESSRC-CAT 12 BM station at Argonne National Laboratory. Technetium reference compounds and sample A ( $\text{NH}_4\text{TcO}_4$ ,  $\text{TcO}_2$ , Tc metal and sample A) were diluted ( $\sim 1\%$  Tc by mass) in boron nitride. XAFS spectra were recorded at the Tc-K edge ( $21,044 \text{ eV}$ ) in fluorescence mode at room temperature using a 13 elements germanium detector. A double crystal of Si [1 1 1] was used as a monochromator. The energy was calibrated using a molybdenum foil (Mo-K edge =  $20,000 \text{ eV}$ ). For each sample, four spectra were recorded in the  $k$  range  $[0-14] \text{ \AA}^{-1}$  and averaged. Background contribution was removed using Athena [19] software and data analysis was performed using Winxas [20]. For the fitting procedure, amplitude and phase shift function were calculated by Feff8.2 [21]. Input files were generated by Atoms [22] using crystallographic structures of the technetium dioxide [23]. Adjustments of the  $k^3$ -weighted EXAFS spectra were performed under the constraints  $S_0^2 = 0.9$ . A single value of energy shift ( $\Delta E_0$ ) was used for all scattering.

### Other techniques

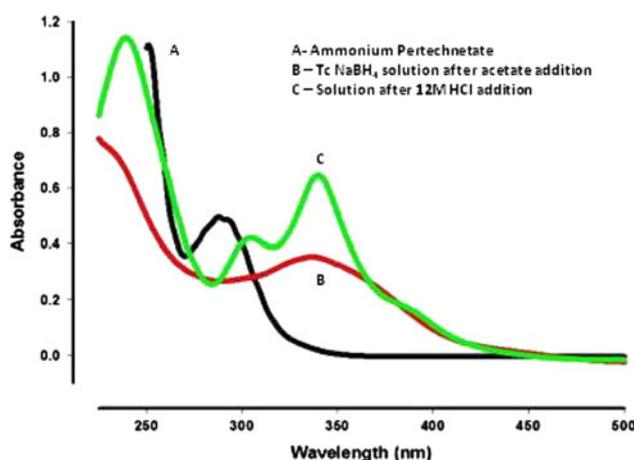
$^{99}\text{Tc}$  concentrations were evaluated by liquid scintillation (LS) counting using a Packard 2500 scintillation analyzer. The scintillation cocktail used was ULTIMA GOLD AB<sup>TM</sup> (Packard). The concentrations of solutions prior to and following reduction were determined using calibration curves performed in solution with a composition similar to the experimental parameters. All recorded UV-visible spectra were collected at room temperature in a  $1 \text{ cm}$  quartz cell on a Cary 6000i double beam spectrometer with background subtraction. SEM/EDS measurements were performed using a JEOL-5610 scanning electron microscope, equipped with secondary electron and backscattered electron detectors with EDS capability.

## Results and discussion

### UV-visible spectroscopy

#### Liquid

UV-Visible spectra were acquired (Fig. 1.) on the solution: (i) prior to reduction, (ii) after borohydride/acetic acid reduction and (iii) after dissolution of the recovered precipitate in  $12 \text{ M HCl}$ . UV-Visible measurements of the solution after borohydride reduction has also shown the disappearance of pertechnetate spectra (peak at  $289 \text{ nm}$ ) and appearance of bands at  $350$  and  $500 \text{ nm}$ . The band at  $500 \text{ nm}$  may be indicative of the formation of a polymeric Tc(IV) complex with acetate [24]. Addition of concentrated HCl to the supernatant solution showed a



**Fig. 1** UV-Vis spectra of initial solution, after the borohydride reduction of pertechnetate in the presence of acetic acid, and after addition of concentrated HCl

characteristic double peak absorbing strongly at 300 and 350 nm indicating the production of  $\text{TcCl}_6^{2-}$ .

### Solid

The product (<1 mg) was dissolved into 10 mL 12 M HCl. After 24 h, UV-Visible spectra was recorded (Fig. 1). This spectra, after dissolution, was determined to be identical to that of  $\text{TcCl}_6^{2-}$ . Previous studies have reported, in the presence of 12 M HCl metallic Tc does not actively dissolve, nor actively corrode, while various Tc(IV) species have been shown to convert to hexachlorotechnetate [25, 26]. This evidence further provides confirmation that the reduced Tc precipitate is not the metal but a lower valent Tc complex that is susceptible to attack by HCl.

### SEM/EDS analysis

The recovered solid was collected and mounted on carbon tape to observe the Tc microstructure (Fig. 2). The solid sample did not show the presence of a crystalline phase and EDS confirmed the presence of both oxygen and Tc throughout the sample. In order to obtain further information on the structure of the solid product, XAFS analysis was performed.

### XAFS spectroscopy

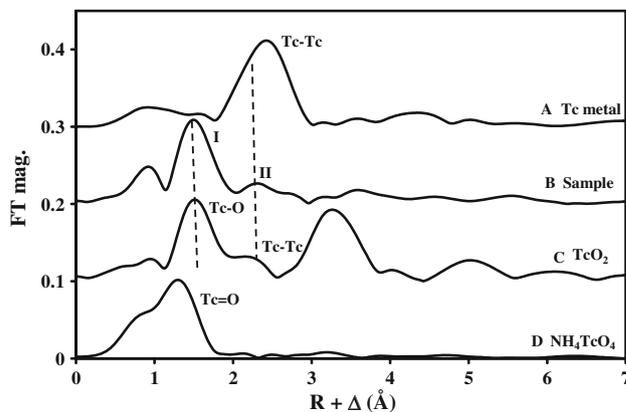
**EXAFS.** The EXAFS spectra of: Tc metal,  $\text{NH}_4\text{TcO}_4$ ,  $\text{TcO}_2$  and sample A were  $k^3$ -weighted and a Fourier transformation done in the  $k$ -range  $[3, 12.5] \text{ \AA}^{-1}$ . The Fourier transform of sample A (Fig. 3), different from Tc metal, exhibit one major peak (I) centered at  $R + \Delta R \sim 1.5 \text{ \AA}$ . Comparison with reference compounds indicate that peak I, is located at the same position that the Tc–O peak of  $\text{TcO}_2$  and could be attributed to Tc–O scattering. A lower intensity peak (II) is noticed at  $R + \Delta R \sim 2.3 \text{ \AA}$ . Comparison with Tc metal and  $\text{TcO}_2$  indicate that peak II may be due to a Tc–Tc contribution. The adjustments of the experimental EXAFS spectra were performed using the

Tc–O and Tc–Tc scattering wave functions determined for  $\text{TcO}_2$ . The procedure was performed in two steps: (a) adjustment between  $R + \Delta R = [1.15, 1.95] \text{ \AA}$  and  $R + \Delta R = [2.05, 2.65] \text{ \AA}$  (b) adjustment of the total spectra using the parameters previously determined in (a).

Adjustment between  $R + \Delta R = [1.15, 1.95] \text{ \AA}$   
and  $R + \Delta R = [2.05, 2.65] \text{ \AA}$

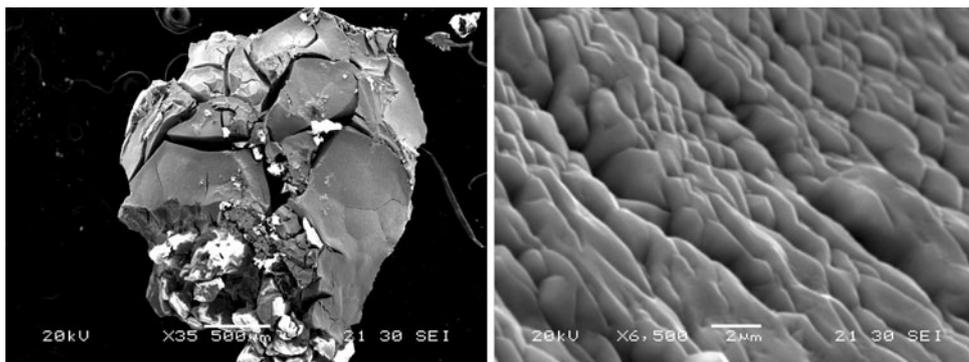
$R + \Delta R = [1.15, 1.95] \text{ \AA}$ . A window filter was done on the FT between  $R + \Delta R = [1.15, 1.95] \text{ \AA}$ . The Fourier transform was back transformed and the corresponding EXAFS spectra fitted in the  $k$ -range  $[3, 12.5] \text{ \AA}^{-1}$  using the  $\text{Tc}_0 \leftrightarrow \text{O}$  scattering. For the adjustment procedure, the  $\text{Tc}_0\text{--O}$  distance,  $\Delta_{\text{Tc-O}}^2$  and coordination number were allowed to vary. The fitted  $k^3$ -EXAFS spectra and the Fourier transform obtained are presented Fig. 4. The results of the adjustments indicate that the first coordination shell around the absorbing atom is constituted by 5.6 (1.1) O atoms at 1.99(2)  $\text{ \AA}$ .

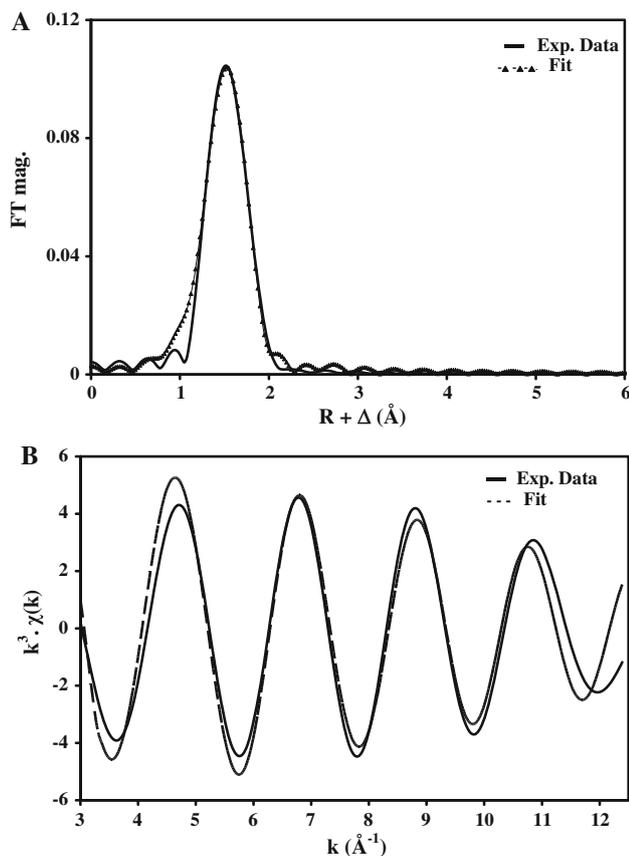
$R + \Delta R = [2.05, 2.65] \text{ \AA}$ . A window filter was done on the FT between  $R + \Delta R = [2.05, 2.65] \text{ \AA}$ . The Fourier transform was back transformed and the corresponding EXAFS spectra fitted in the  $k$ -range  $[4.5, 12.5] \text{ \AA}^{-1}$  using



**Fig. 3** Fourier transform between  $k = [3, 12.5] \text{ \AA}^{-1}$  of  $k^3$ -EXAFS spectra of Tc metal, sample A,  $\text{TcO}_2$  and  $\text{NH}_4\text{TcO}_4$

**Fig. 2** SEM (Large precipitate and surface morphology) micrograph of the reduction product obtained from the reaction between  $\text{NH}_4\text{TcO}_4$  and  $\text{NaBH}_4$  in the presence of acetic acid in water





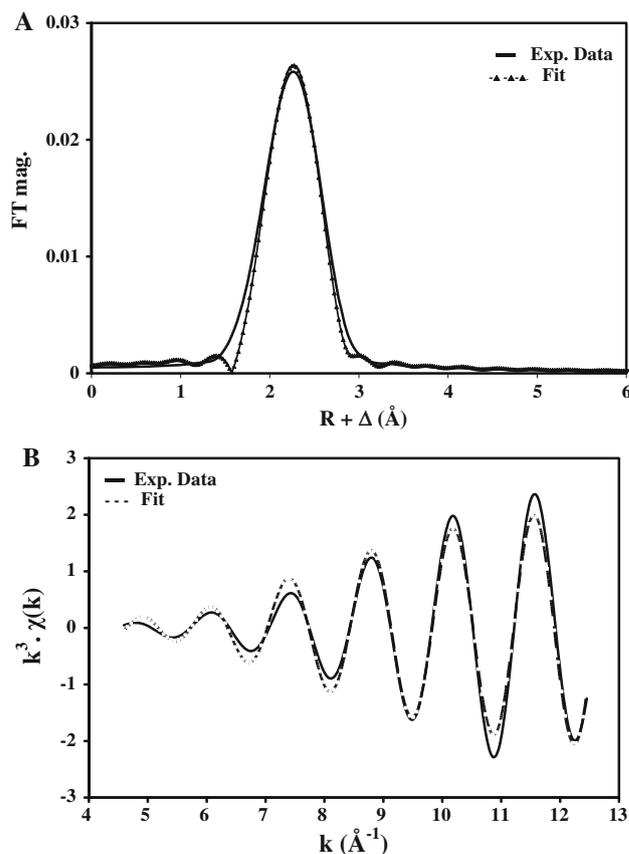
**Fig. 4** Adjustment of filtered Fourier transform (a) and back transformed  $k^3$ -EXAFS (b) spectra of sample A. Fourier Filtering between  $R + \Delta R = [1.15, 1.95]$  Å; adjustment between  $k = [3, 12.5]$  Å $^{-1}$

the  $\text{Tc}_0 \rightleftharpoons \text{Tc}_1$  scattering. For the adjustment procedure, the distances,  $\text{Tc}_0\text{-Tc}_1$ ,  $\Delta^2$  and coordination number were allowed to vary. The fitted  $k^3$ -EXAFS spectra and the Fourier transform obtained are presented Fig. 5. The results of the adjustments indicate that the second coordination shell around  $\text{Tc}_0$  is constituted by 0.6(1) Tc atoms at 2.57(2) Å.

#### Adjustment of the total EXAFS spectra

The total EXAFS spectrum was fitted in  $k$ -range [3, 12.5] Å $^{-1}$  using the  $\text{Tc}_0 \rightleftharpoons \text{O}$  and  $\text{Tc}_0 \rightleftharpoons \text{Tc}_1$  scattering. The adjustment was conducted according the following procedure:

- The coordination number of O and Tc1 around  $\text{Tc}_0$  were fixed to those determined in “Adjustment between  $R + \Delta R = [1.15, 1.95]$  Å and  $R + \Delta R = [2.05, 2.65]$  Å”
- The distances  $\text{Tc}_0\text{-O}$  and  $\text{Tc}_0\text{-Tc}_1$ , and the corresponding  $\Delta^2$  were allowed to vary.

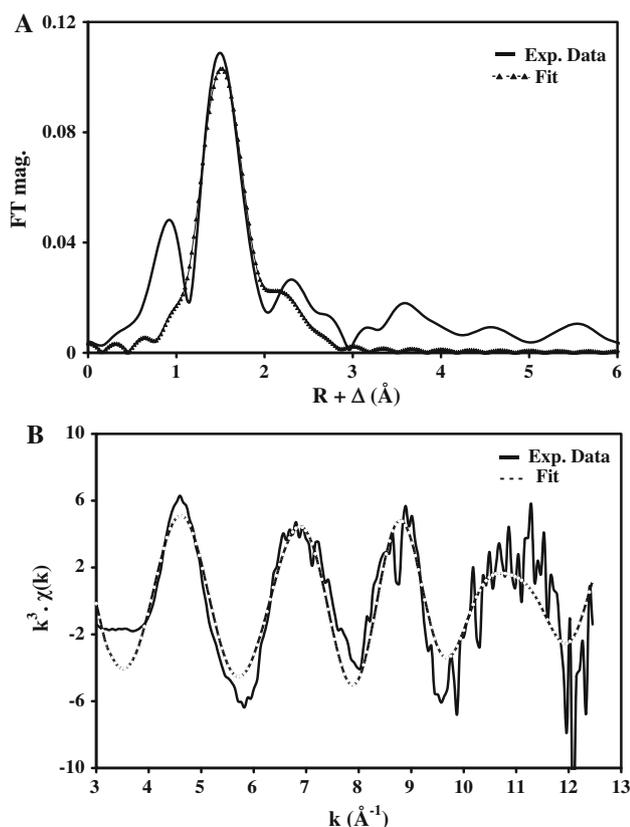


**Fig. 5** Adjustment of filtered Fourier transform (a) and back transformed  $k^3$ -EXAFS (b) spectra of sample A. Fourier Filtering between  $R + \Delta R = [2.05, 2.65]$  Å; adjustment between  $k = [4.5, 12.5]$  Å $^{-1}$

The fitted Fourier transform and  $k^3$ -EXAFS spectra are shown in Fig. 6. The structural parameters are presented in Table 1.

The first coordination shell around the absorbing atom is constituted by 5.6(1.1) O atoms at 1.98(2) Å and the second coordination shell is constituted by 0.6(1) Tc atoms at 2.57(2) Å.

Those results indicate that the reduction product of pertechnetate is not Tc metal. The number of O atoms indicates that Tc is octahedrally coordinated and the  $\text{Tc-O}$  distances are in the same range as  $\text{TcO}_2$  (1.981(1) Å). The  $\text{Tc-Tc}$  distance found is not in accordance with the one in Tc metal (i.e., 2.743 Å), [26] but more with those found in compounds that exhibit the  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]$  core structure [19, 27, 28]. The number of Tc atoms (i.e., 0.6(1)) and the presence of acetate, detected by IR, indicates that the product may contain dimeric species bonded by an acetate ligand. This results is in accordance with previous XAFS studies which indicate that reduction of pertechnetate with borohydride in aqueous media in the presence of diphosphonate lead to polymeric species exhibiting the  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]$  core structure [29].



**Fig. 6** Fitted experimental  $k^3$ -EXAFS spectra (a) and Fourier transform of  $k^3$ -EXAFS spectra (b) of sample A. Adjustment between  $k = [3, 12.5] \text{ \AA}^{-1}$

**Table 1** Structural parameter obtained by adjustment of the  $k^3$ -EXAFS spectra of sample A

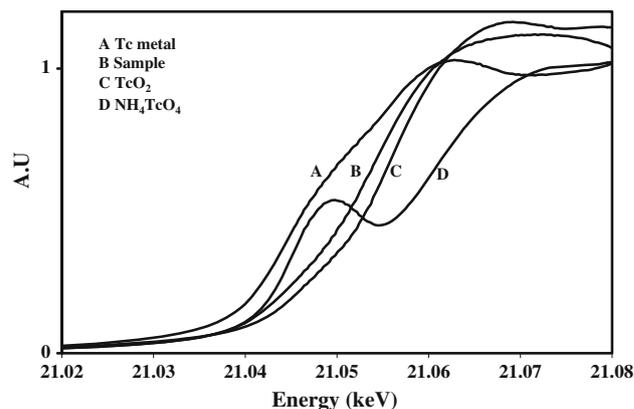
Sample A	Structural parameter		
	C.N.	R (Å)	a (Å <sup>2</sup> )
Tco-O	5.6	1.98	0.0031
Tco-Tc <sub>1</sub>	0.6	2.57	0.0035

Adjustment between  $k = [3, 12.5] \text{ \AA}^{-1}$ .  $E_0 = 4.99 \text{ eV}$

Techetium acetate species have already been reported but never structurally characterized [30]. It was mentioned that those species contain Tc at various oxidation states from (III, IV) and exhibit the  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]^{n+}$  ( $n = 4, 3$ ) core structure. In order to determine oxidation state of Tc in sample A, XANES study was performed.

### XANES

The XANES spectra of Tc metal,  $\text{TcO}_2$ , sample A and  $\text{NH}_4\text{TcO}_4$  (Fig. 7) were recorded, background subtracted and normalized. XANES spectroscopy is commonly used for characterization of the local geometry and oxidation state of absorbing atoms. Previous studies showed that Tc



**Fig. 7** Normalized Tc-K edge spectra of: (a) Tc metal, (b) Sample, (c)  $\text{TcO}_2$  and (d)  $\text{NH}_4\text{TcO}_4$

species with tetrahedral geometry (i.e.,  $\text{TcO}_4^-$ ) exhibit a pre-edge feature in their XANES spectra [31]. For the sample A, no pre-edge is observed which indicates that the sample does not contain any pertechnetate.

Previous studies showed that the Tc K-edge position can be correlated to the oxidation state of the absorbing atom [32, 33]. For sample A, the position of its absorption edge (Table 2), 1.4 eV lower than  $\text{Tc}^{\text{IV}}\text{O}_2$  and 3.6 eV higher than  $(n\text{-Bu}_4\text{N})_2\text{Tc}_2^{\text{III}}\text{Cl}_8$ , indicate that its average oxidation is comprised between III and IV and consistent with the presence of the  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]^{3+}$  core structure. The XAFS experiment confirms the borohydride reduction product of pertechnetate in acetate media is not Tc metal but polymeric carboxylate technetium species containing trivalent technetium.

### Conclusion

The conversion of pertechnetate into metal and its incorporation into a waste form represents a challenge for the nuclear industry. Previous studies reported the use of borohydride as a method to reduce pertechnetate to the metal. In the context of a separation process, we have reinvestigated this method and characterised the reduction Tc and the product formed.

UV-Visible spectroscopy has shown that the borohydride reduction product of  $\text{TcO}_4^-$  in acetic acid solution exhibits spectra that can be attributed to a Tc(IV) polymeric species. XAFS measurements indicate that the precipitated product is not Tc metal but a compound exhibiting the  $[\text{Tc}(\mu\text{-O})_2\text{Tc}]^{3+}$  core structure. The reduction of Tc(VII) proceeds through an intermediate oxidation state producing a pink colored species in the initial stages of this reaction, that has been observed in other work, believed to be a Tc(V) or Tc(VI) [17, 18]. The precipitation of the technetium oxide inhibits further reduction to the

**Table 2** Shift of Tc K edge absorption relative to  $\text{NH}_4\text{TcO}_4$ 

Compound	Oxidation degree	K edge shift (eV)	Ref.
$\text{NH}_4\text{TcO}_4$	+7	0	
$\text{TcO}_2$	+4	-6.3	[This work]
$\text{TcO}_2 \cdot x\text{H}_2\text{O}$		-6.95	[12]
		-6.75	[9]
Sample A		-7.4	[This work]
$(n\text{-Bu}_4\text{N})_2\text{Tc}_2\text{Cl}_8$	+3	-11	[32]
Tc metal	0	-18	[This work]
		-19.85	

metal. Our results indicate that this method will be not suitable for reprocessing technetium directly to the metal. Nevertheless, recent studies on rhenium provided evidence that  $\text{ReO}_4^-$  could be partially reduced to the metal in methanol [15]. Current studies on Tc in non aqueous media are under progress and results will be reported in due course.

**Acknowledgments** Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

## References

- Schroeder NC, Attrep M, Marrero T (2001) Technetium and iodine separations in the UREX process; LA-UR-01-6607. Los Alamos National Laboratory, Los Alamos, NM, pp 6–19
- Uchiyama G, Asakura T, Hotoju S, Mineo H, Kamei K, Watanabe M, Fujine S (2000) J Radioanal Nucl Chem 42:488–492
- Koltunov VS, Marchenko VI, Nikiforov AS, Smelov VS, Shmidt VS, Gomonova TV, Polunin AK, Kondra'ev BA (1986) Atomnaya Énergiya (trans.) 60:35–41
- Pereira C, Vandegrift GF, Regalbuto MC, Aase SB, Bakel AJ, Bowers D, Byrnes JP, Clark MA, Emery JW, Falkenberg JR, Gelis AV, Hafenrichter L, Leonard R, Quigley KJ, Tsai Y, Vander Pol MH, Laidler JJ (2005) Lab-scale demonstration of the UREX+2 process using spent fuel. In: 2005 Waste Management Symposium Proceedings, Tucson, AZ
- Poineau F, Du Mazaubrun J, Ford D, Fortner J, Kropf J, Silva GWC, Smith N, Long K, Jarvinen G, Czerwinski K (2008) Uranium/technetium separation for the UREX process—synthesis and characterization of solid reprocessing forms. Radiochim Acta 96:527
- Hartmann T, Poineau F, Czerwinski KR (2008) Synthesis and properties of metallic technetium and technetium-zirconium alloys as transmutation target and radioactive waste storage form in the UREX+1 process, Atalante
- Cobble JW, Nelson CM, Parker GW, Smith WT, Boyd GE (1952) J Am Chem Soc 74:1852
- Fried S (1948) J Am Chem Soc 70:442
- Muller O, White WB, Roy R (1964) J Inorg Nucl Chem 26:2075
- Peretrukhin VF, Rovnyi SI, Ershov VV, German KE, Kozar AA (2002) Russ J Inorg Chem 47:637
- Spitsyn VI, Kuzina AF, Tsarenko AF, Oblova AA, Balakhovskii OA, Kodochigov PN, Glazunov MP, Kaimin IV (1970) Radiochimia 12:617
- Terry J, Grzenia B, Papagiannopoulou D, Kyger J, Jurisson S, Robertson JD (2005) J Radioanal Nucl Chem 263(2):531–537
- Berning DE, Schroeder NC, Chamberlin RM (2005) J Radioanal Nucl Chem 263(3):613–618
- Pacer RA (1973) J Inorg Nucl Chem 35:1375
- Mendez E, Cerda MF, Castro Luna AM, Zinola CF, Kremer C, Martins ME (2003) J Colloid Interf Sci 263:119–132
- Pacer RA (1976) J Inorg Nucl Chem 38:817–818
- Rulfs CL, Pacer RA, Hirsch RF (1967) J Inorg Nucl Chem 29:681
- Majumdar SK, Pacer RA, Rulfs CL (1969) J Inorg Nucl Chem 31:33
- Newville M, Livins P, Yacoby Y, Stern EA, Rehr JJ (1993) Phys Rev B 47:14126
- Ressler T (1998) WinXAS: a program for x-ray absorption spectroscopy data analysis under MS-Windows. J Synchrotron Rad 5:118
- Rehr JJ, Albers RC (2000) Rev Mod Phys 72:621
- Ravel B (2001) ATOMS: crystallography for the X-ray absorption spectroscopist. J Synchrotron Rad 8:314
- Rodriguez EE, Poineau F, Llobet A, Sattelberger AP, Bhattacharjee J, Waghmare UV, Hartmann T, Cheetham AK (2007) J Am Chem Soc 129(33):10244–10248
- Kennedy CM, Pinkerton TC (1988) Technetium carboxylate complexes-I. A review of technetium, rhenium, and molybdenum carboxylate chemistry. Int J Radiat Appl Instrum A 39(11):1159–1165
- Ben Said K, Fattahi M, Musikas CI, Revel R, Abbe JCh (2000) Radiochimica Acta 88(9–11):567
- Lam DJ, Darby JB, Downey JW, Norton LJ (1961) Nature 192:744
- Lukens WW Jr, Bucher JJ, Edelstein NM, Shuh DK (2002) Products of pertechnetate radiolysis in highly alkaline solution: structure of  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ . Environ Sci Technol 36(5):1124–1129
- Vichot L, Ouvrard G, Montavon G, Fattahi M, Musikas C, Grambow B (2002) Radiochimica Acta 90(9–11):575–579
- Martin JL Jr, Yuan J, Lunte CE, Elder RC, Heineman WR, Deutsch E (1989) Inorg Chem 28:2899–2901
- Kennedy CM, Pinkerton TC (1988) Technetium carboxylate complexes-II. Structural and chemical studies. Appl Radiat Isot 39(11):1167–1177
- Allen PG, Siemering GS, Shuh DK, Bucher JJ, Edelstein NM, Langton CA, Clark SB, Reich T, Denecke MA (1997) Technetium speciation in cement waste forms determined by X-ray absorption fine structure spectroscopy. Radiochim Acta 76(1–2):77–86
- Almahamid I, Bryan JC, Bucher JJ, Burrell AK, Edelstein NM, Hudson EA, Kaltsoyannis N, Lukens WW, Nitsche H et al (1995) Electronic and structural investigations of technetium compounds by X-ray absorption spectroscopy. Inorg Chem 34(1):193–198
- Poineau F, Sattelberger AP, Conradson SD, Czerwinski KR (2008) Inorg Chem 47(6):1991–1999