

**NJC****Speciation and reactivity of heptavalent technetium in strong acids**

Journal:	<i>New Journal of Chemistry</i>
Manuscript ID	NJ-FOC-12-2017-004912.R1
Article Type:	Focus
Date Submitted by the Author:	18-Apr-2018
Complete List of Authors:	Poineau, Frederic; UNLV, Burton-Pye, Ben; Lehman College Sattelberger, Alfred; Argonne National Laboratory, Office of the Director Czerwinski, Kenneth; University of Nevada Las Vegas German, Konstantin; A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Fattahi, Massoud; SUBATECH Laboratory,

SCHOLARONE™
Manuscripts



Journal Name

ARTICLE

Received 00th January

20xx,

Accepted 00th January

20xx

DOI:

10.1039/x0xx00000x

www.rsc.org/

Speciation and reactivity of heptavalent technetium in strong acids

Frederic Poineau,^a Benjamin P. Burton-Pye,^{b, c} Alfred P. Sattelberger,^a Kenneth R. Czerwinski,^a Konstantin E. German^d and Massoud Fattahi^e

Abstract. Technetium is the workhorse of the radiopharmaceutical imaging agents; it is also an important byproduct of the nuclear industry. Studies of the chemistry of Tc in strong acids are relevant to nuclear applications, environmental remediation and fundamental chemistry. Nitric acid is used at the industrial level for spent fuel reprocessing while H₂SO₄ and HClO₄ are used at the laboratory scale for Tc separation from Mo or U. During reprocessing activities, radiolysis products from nitric acid (e.g., H₂O₂) and from organics extracting agents (e.g., alcohols) are formed and these might interact with Tc(VII). An understanding of Tc(VII) chemistry in the presence of H₂O₂ and/or organics in acidic solution is important to predict its behavior in separation processes. Concerning environmental remediation, sulfur has been proposed to immobilize Tc as Tc₂S₇. Technetium heptasulfide can be obtained from the reaction of Tc(VII) with H₂S gas in acidic solutions. A better understanding of Tc₂S₇ formation could give information to predict its formation and behavior in the environment. Under oxidizing conditions, the aqueous chemistry of Tc(VII) is dominated by TcO₄⁻. In high acid concentration, pertechnetic acid can be formed and control the reactivity of Tc. Speciation data on Tc(VII) in concentrated acids are still sparse, and the structure and reactivity of pertechnetic acid are unknown. Here, the speciation of Tc(VII) in sulfuric, nitric and perchloric acids and its reactivity with H₂O₂, methanol and H₂S is reviewed. Experimental results and density functional calculations show the formation of TcO₃(OH)(H₂O)₂ in concentrated H₂SO₄ and HClO₄. In 12 M–13 M H₂SO₄, Tc(V) species and Tc(IV) polymeric species were respectively detected in the presence of methanol and H₂S. Finally, peroxy pertechnetic acid was identified in nitric and sulfuric acid in the presence of H₂O₂.

1. Introduction

Technetium is the lightest radioelement; its two isotopes of interest are ⁹⁹Tc ($t_{1/2} = 2.1 \times 10^5$ y, $\beta_{\max} = 294$ keV) and ^{99m}Tc ($t_{1/2} = 6$ h, $\gamma = 140$ keV).¹ The versatile chemistry of Tc and the optimal nuclear properties of ^{99m}Tc, make this isotope the workhorse of radiopharmaceutical applications.² The isotope ⁹⁹Tc is an important fission product of the nuclear industry (yield ~ 6% from ²³⁵U); one metric ton of spent fuel contains ~850 g of ⁹⁹Tc in its elemental form.³ The isotope ⁹⁹Tc is also present in large quantity in radioactive wastes which are stored

in underground tanks at the Hanford site (estimated 1310 ± 220 kg of ⁹⁹Tc contained in tanks).⁴

Studying the speciation and reactivity of Tc in acidic media is relevant to nuclear application (i.e., aqueous separation and waste form development) and environmental remediation. On the fundamental side, it will allow for a better understanding of the redox properties of Group 7 transition metals.

For nuclear application, studies in acidic media will give us the ability to predict the behavior of Tc in separation processes where concentrated acids are used. In some reprocessing schemes, Tc would be separated from the spent fuel and disposed of in a durable waste form.⁵ In a typical reprocessing scenario, the spent fuel would be dissolved in concentrated nitric acid, Tc(0) would be oxidized to Tc(VII) and separated from the other elements by liquid-liquid extraction using an extracting agent, e.g., tributylphosphate (TBP, C₁₂H₂₇O₄P) in an organic solvent such as dodecane or kerosene.⁶ At the laboratory scale, the separation of Tc from irradiated Mo or U involves the dissolution of the target followed by distillation in H₂SO₄ or HClO₄.^{7, 8} Those experiments indicated that the Tc

^a Department of Chemistry and Biochemistry, University of Nevada Las Vegas, Las Vegas, NV, 89154, USA.

^b Department of Chemistry, Lehman College of the City University of New York, NY, 10468, USA.

^c Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, NY 10016, USA.

^d A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russian Federation.

^e Laboratory Subatech, Ecoles des Mines de Nantes, Nantes, France.

Electronic Supplementary Information (ESI) available: [Experimental Section, additional XAFS, NMR and DFT data]. See DOI: 10.1039/x0xx00000x

species formed in H_2SO_4 and/or HClO_4 was volatile. Under oxidizing conditions and in the pH range 1-14, the aqueous chemistry of Tc(VII) is dominated by the pertechnetate anion, TcO_4^- . In high acid concentration, TcO_4^- can be protonated and pertechnetic acid can be formed.⁹ Speciation data on Tc(VII) in concentrated acids are still sparse, and the structure of pertechnetic acid is unknown.

During reprocessing activities, due to the presence of radionuclides in solution, radiolysis products could form, interact with Tc(VII) and affect the process. Previous studies have shown that hydrogen peroxide was detected after the alpha irradiation of nitric acid while butanol was one of the radiolytic degradation products of TBP.^{10, 11} The understanding of the Tc(VII) chemistry in the presence of H_2O_2 and/or organics in acidic solution is important to predict its behavior in the nuclear fuel cycle. In the presence of hydrogen peroxide, peroxo-complexes could form and change the behavior of Tc(VII). Currently, Tc(VII) peroxo-complexes are unknown and only Tc(VI) nitrido peroxo complexes have been reported.¹² The redox chemistry of Tc(VII) in the presence of organics is poorly studied; for example, the nature of the reaction of Tc(VII) with primary alcohols is unknown, while it has been well studied for Mn(VII).¹³

Concerning environmental remediation, sulfur has been proposed to immobilize Tc in the environment in the form of Tc_2S_7 .¹⁴ Amorphous Tc_2S_7 can be obtained via the reaction of Tc(VII) with hydrogen sulfide gas in acidic solutions (HCl or H_2SO_4).⁸ In the presence of H_2S , the mechanisms of formation of Tc_2S_7 are unknown and the exact structure and composition of Tc_2S_7 are still unclear.¹⁵ The understanding of Tc_2S_7 formation could provide information to better understand the nature of this solid and predict its behavior in the environment. During the past seven years, we have investigated the speciation of Tc(VII) in sulfuric, nitric and perchloric acids and studied its reactivity with H_2O_2 , methanol and H_2S . Using a combined experimental/theoretical approach, we have characterized the structure of pertechnetic acid, identified new Tc(V) and Tc(IV) complexes coordinated to sulfate/bisulfate ligands and a series of Tc(VII) peroxo-complexes. The formation mechanism of those complexes, as well as their structures and speciation in solution is reviewed here.

2. Speciation of Tc(VII) in H_2SO_4 , HClO_4 and HNO_3

The speciation of Tc(VII) was studied after the dissolution of KTcO_4 or NH_4TcO_4 in H_2SO_4 , HNO_3 and HClO_4 at various concentrations (1-18 M for H_2SO_4 , 1-13.7 M HClO_4 , 1-15.8 M HNO_3).^{16, 17} After dissolution of the salt, a yellow color was observed for $\text{H}_2\text{SO}_4 > 8$ M and for $\text{HClO}_4 > 10$ M while for HNO_3 , all the solutions remained clear. The speciation of Tc was initially investigated by ^{99}Tc -NMR spectroscopy. The representation of the ^{99}Tc chemical shift vs. TcO_4^- in the various acids is presented in Figure 1. In HNO_3 , the ^{99}Tc -NMR chemical shift monotonically decreased as the acid concentration increased (0 ppm in 2 M HNO_3 to -12.8 ppm in 15.6 M). The shift and the narrow line-width (Figure S1, Table S1) of the spectrum were consistent with the presence of TcO_4^- . In 2 - 8 M HClO_4 and 2-6 M H_2SO_4 , the ^{99}Tc -NMR spectra

were identical to those in HNO_3 and consistent with the presence of TcO_4^- . A shift occurred for ~ 9 M HClO_4 , the spectra broadened and a plateau was observed above 11.6 M HClO_4 . In H_2SO_4 , the shift occurred about 8 M, the spectra broadened and a plateau was observed at ~ 12 M. The peak broadening could be due to formation of a lower symmetry species or faster ligand kinetic exchange. In order to determine if the broadening is due to exchange, low temperature NMR measurements would need to be performed. In 13.7 M HClO_4 , the linewidth of the ^{99}Tc spectra (20 ppm) is narrower than the one in 18 M H_2SO_4 (90 ppm) (Figure S1). This phenomenon is due to the high viscosity of sulfuric acid. The ^{99}Tc -NMR chemical shift of Tc(VII) species is a function of the coordination environment of the Tc atom and can vary between 0 and 430 ppm.¹⁸ The shift of the yellow species measured in 12 M H_2SO_4 (290 ppm) and in 13.7 M HClO_4 (230 ppm) were consistent with the presence of a species with a TcO_3^+ core.^{18c} To better understand the molecular structure of the yellow species, Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) measurements were performed on solutions of KTcO_4 in 12 M H_2SO_4 and 11.6 M HClO_4 . The model used to fit the EXAFS spectrum was based on the structure of $\text{Re}_2\text{O}_7(\text{H}_2\text{O})_2$.¹⁹ In H_2SO_4 , EXAFS results indicated the presence of 3 Tc=O groups at 1.70 Å, one Tc-O at 2.07 Å and one Tc-O at 2.23 Å. Similar results (Figure S2, Table S2) were obtained in 11.6 M HClO_4 . Overall, the EXAFS results were consistent with the stoichiometry $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$. The structure of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ was studied by Density Functional Theory (DFT) methods. The computed equilibrium geometry of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ closely matched the structural parameters found by EXAFS spectroscopy (Figure 2).

The speciation of Tc(VII) in HClO_4 and HNO_3 was further studied by UV-visible spectroscopy. In HClO_4 , the transformation from TcO_4^- to $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ (Figure 2) is characterized by an isobestic point at 325 nm and the spectra in 13.7 M HClO_4 exhibits three bands ($\lambda_{\text{max}} = 337, 279$ and 246 nm).

The spectra of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ in HClO_4 compare well with the one in 12 M H_2SO_4 which exhibits a band at 241 nm ($5511 \text{ M}^{-1} \cdot \text{cm}^{-1}$), a shoulder at 279 nm ($1800 \text{ M}^{-1} \cdot \text{cm}^{-1}$) and a band at 335 nm ($275 \text{ M}^{-1} \cdot \text{cm}^{-1}$). The spectra of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ differ from that of TcO_4^- which only exhibits bands at 244 and 288 nm. Theoretical studies (Figure S3 and Table S3) indicate that the band at 335 nm in $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ is due to a combination of LMCT (O \rightarrow Tc) one-electron transitions: HOMO-1 \rightarrow LUMO+2 and HOMO \rightarrow LUMO+1.¹⁶

3. Reactivity of Tc(VII) with H_2O_2

The reactivity of Tc(VII) with H_2O_2 was studied in HNO_3 ²⁰ and in H_2SO_4 ²¹. Solutions of KTcO_4 in HNO_3 (3 M-12 M)/ H_2O_2 (0.1 M and 4.25 M) were prepared. UV-visible measurements have shown that for $\text{HNO}_3 \geq 7$ M and $\text{H}_2\text{O}_2 = 4.25$ M, Tc(VII) reacted immediately and red solutions were obtained, while no reaction occurred for $\text{H}_2\text{O}_2 = 0.1$ M.

The red solutions were highly unstable and rapidly decomposed by release of oxygen. The UV-visible spectra of the solution in 7 M to 12 M HNO_3 exhibit a single band (Figure 3) centered at

500 nm which was attributed to a Tc(VII) peroxo-complex. The intensity of the band increased with the nitric acid concentration. The decrease of water activity when moving from 3 M to 12 M HNO₃ was probably responsible for the peroxidation of TcO₄⁻ in high acid concentration.²²

The high instability of the red Tc solutions precluded an analysis by EXAFS and ⁹⁹Tc NMR spectroscopy; the nature of the species was further investigated by theoretical methods.

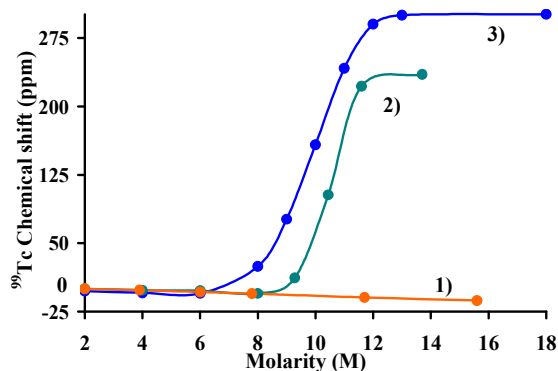


Figure 1. Representation of the ⁹⁹Tc-NMR chemical shift vs. TcO₄⁻ as a function of the acid concentration (M) of the solutions obtained after dissolution of KTCO₄ or NH₄TcO₄ in: HNO₃ (1, orange), in HClO₄ (2, green) and in H₂SO₄ (3, blue).

By analogy with Mo²³ and Re²⁴, Tc(VII) peroxo species (Tc(O₂)₄⁻, TcO(O₂)₃⁻, TcO₃(O₂)⁻, TcO(O₂)₂(H₂O)(OH) and TcO₂(O₂)(H₂O)₂(OH)) were initially proposed, their structure, stability and UV-visible spectra were studied by DFT and Time Dependent-DFT (TD-DFT). Among those species, calculations predicted the TcO(O₂)₂(H₂O)(OH) and TcO₃(O₂)⁻ complexes to have the highest chemical stability, while the calculated spectrum of TcO(O₂)₂(H₂O)(OH) compares well with the experimental one (Figure S4). It was proposed that TcO(O₂)₂(H₂O)(OH) was the peroxidation product of Tc(VII) in HNO₃. The computed equilibrium geometry of TcO(O₂)₂(H₂O)(OH) exhibits a distorted pentagonal bipyramidal geometry. In the complex, the peroxo and the hydroxyl ligands form an approximate pentagon with the oxo and water ligands in apical positions (Figure 3).

In H₂SO₄, the reaction of Tc(VII) with H₂O₂ led to the observation of two species: a blue species for H₂SO₄ ≥ 9 M and H₂O₂ = 0.17 M and a red species for H₂SO₄ = 6 M and H₂O₂ ≥ 2.12 M.

UV-visible measurements (Figure 4) have shown that the formation of the blue species was accompanied by the appearance of bands in the region 500-800 nm. The UV-visible spectra in 9 M H₂SO₄ exhibit bands at 275, 520 and 610 nm; the spectra in 13 M and 18 M H₂SO₄ exhibit two bands, respectively, at 520 and 610 nm and at 520 and 650 nm. These results were consistent with the one previously obtained from the reaction TcO₂ with H₂O₂ in H₂SO₄, where it was shown that blue complexes with bands centered at 500 nm and 650 nm

were observed for H₂SO₄ ≥ 12 M and H₂O₂ = 0.25 M.²⁵ The experimental UV-visible spectrum of the blue species was compared to the theoretical spectra (Figure S5) of the Tc(VII) peroxo species previously calculated (i.e., Tc(O₂)₄⁻, TcO(O₂)₃⁻, TcO₃(O₂)⁻, and TcO₂(O₂)(H₂O)₂(OH)).

The calculated spectra of Tc(O₂)₄⁻ and TcO₃(O₂)⁻ did not exhibit bands in the region 500-700 nm and are not consistent with the experimental spectra and this precludes their presence

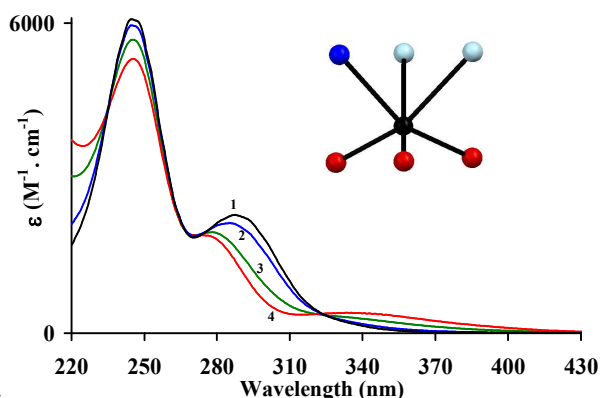


Figure 2. UV-visible spectra of the solutions obtained after dissolution of NH₄TcO₄ in: 1) 8 M, 2) 9.3 M, 3) 10.4 M and 4) 13.7 M HClO₄. Insert - optimized DFT structure of TcO₃(OH)(H₂O)₂. Distance (Å) found by DFT: Tc=O = 1.74, 1.74, 1.72, Tc-H₂O = 2.31 and Tc-OH = 2.02. Color of ligand and atoms: Tc in black, OH⁻ in dark blue, H₂O in light blue and O²⁻ in red.

in solution. The experimental spectrum was more consistent with those calculated for TcO₂(O₂)(H₂O)₂(OH) and/or TcO(O₂)₃⁻. This method has already been used on TcO₄⁻ and provided accurate results.²⁶

In 6 M H₂SO₄, the UV-visible spectra of the red species was identical to the one obtained from the reaction of TcO₄⁻ with H₂O₂ in HNO₃ and consistent with the presence of TcO(O₂)₂(H₂O)(OH).

The reaction between Tc(VII) and H₂O₂ in sulfuric acid was studied by ⁹⁹Tc-NMR spectroscopy. In 6.5 M H₂SO₄/4.9 M H₂O₂, the ⁹⁹Tc-NMR spectra of the red solution (Figure S6 and Figure S7) exhibits a broad signal centered at + 5.5 ppm which was consistent with the presence of Tc(VII) species with a lower symmetry than TcO₄⁻. These results confirm that the peroxidation of TcO₄⁻ in 6.5 M H₂SO₄/4.9 M H₂O₂ solutions is accompanied by a change of symmetry of the molecule.

4. Reactivity of Tc(VII) with MeOH

The reactivity of Tc(VII) with MeOH was studied in H₂SO₄²⁷ and HNO₃. Solutions (1 mL) of NH₄TcO₄ in 6 M and 13 M H₂SO₄ were prepared and methanol (20 μL) was added to the solution. In 6 M H₂SO₄, no reaction was observed while in 13 M H₂SO₄, the solution turned green. Similar reaction in 6 M and 9 M HNO₃ did not yield the green species.

In H₂SO₄, the green solution (Figure 5) exhibited bands at 190 nm ($\epsilon_{\text{max}} = 8540 \text{ M}^{-1} \text{ cm}^{-1}$), 255 nm ($\epsilon_{\text{max}} = 5060 \text{ M}^{-1} \text{ cm}^{-1}$), and 695 nm ($\epsilon_{\text{max}} = 33 \text{ M}^{-1} \text{ cm}^{-1}$). Cerium titrations were

performed on the green species and the results indicated an average oxidation state of 4.93(10), consistent with the presence of Tc(V). The green species was analyzed by ^{99}Tc NMR. The absence of NMR signals in the region 0–800 ppm and the fact that reduced paramagnetic species do not exhibit a signal in this region indicates the absence of Tc(+7) in solution. The green species was studied by EXAFS spectroscopy. The model used to fit the EXAFS spectrum was based on the structure of $\text{K}_4[\text{MoO}_2(\text{SO}_4)_3]$.²⁸

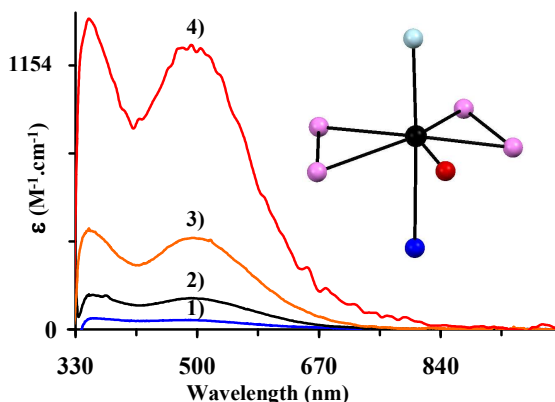


Figure 3. UV-visible spectra of the Tc(VII) solution in $\text{HNO}_3/\text{H}_2\text{O}_2$. $[\text{H}_2\text{O}_2] = 4.25 \text{ M}$, $[\text{Tc}] = 0.26 \text{ mM}$. Spectra in: 1) 7 M HNO_3 , 2) 8 M HNO_3 , 3) 9 M HNO_3 and 4) 12 M HNO_3 . Optimized DFT structure $\text{TcO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OH})$. Distance (Å) found by DFT: Tc–OH = 1.918, Tc– H_2O = 2.396, Tc–O = 1.684, Tc–Oa(Oa) = 1.961 Å, Tc–Ob(Oa) = 1.970 and Oa–Ob = 1.500. Color of ligand and atoms: Tc in black, OH[−] in dark blue, H_2O in light blue, O^{2−} in red and O[−] in violet.

The results of the adjustment indicate the environment of the absorbing atom to be constituted by 1.0(2) O atoms at 1.65 Å, 4.4(9) O atoms at 2.07 Å, 0.5(1) S atoms at 2.89 Å and 1.9(4) S atoms at 3.30 Å. The EXAFS results (Figure S8, Table S4) were consistent with the presence of octahedral complexes with the $[\text{Tc}=\text{O}]^{3+}$ core coordinated to sulfates in both bidentate and monodentate modes. Based on the EXAFS results, complexes with the stoichiometry $\text{TcO}(\text{HSO}_4)_2(\text{H}_2\text{O})_2(\text{OH})$ and/or $\text{TcO}(\text{HSO}_4)_3\text{OH}^-$ were proposed. It cannot be excluded that the green solution was a mixture of those complexes. Those complexes are the first Tc oxo-sulfate species characterized to date. Theoretical calculations confirmed the stability of the proposed complexes. The optimized structure of $\text{TcO}(\text{HSO}_4)_3\text{OH}^-$ is presented in Figure 5. In those complexes, the distances found by DFT were in good agreement with the EXAFS results.

After the reaction of Tc(VII) with MeOH, spectroscopic measurement indicated the presence of formic acid (see SI). It was concluded that in 13 M H_2SO_4 , $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ was reduced to $\text{TcO}(\text{HSO}_4)_3\text{OH}^-$ and MeOH was oxidized to formic acid. The behavior of Tc(VII) was also studied under alpha-irradiation in 13 M or 18 M H_2SO_4 .²⁹ Alpha-irradiations ($E = 68 \text{ MeV}$, 132.9 kGy) were performed on Tc(VII) solution at the Arronax cyclotron (Nantes, France). After irradiation, green solutions with UV-visible and EXAFS spectra similar to the one of $\text{TcO}(\text{HSO}_4)_3(\text{H}_2\text{O})_2$ and/or $\text{TcO}(\text{HSO}_4)_3(\text{H}_2\text{O})(\text{OH})^-$

were obtained. Further, UV-visible experiments have shown that SO_2 was detected in solution after the irradiation of concentrated sulfuric acid. It was proposed that Tc(VII) was reduced by the SO_2 gas formed during the radiolysis of H_2SO_4 .

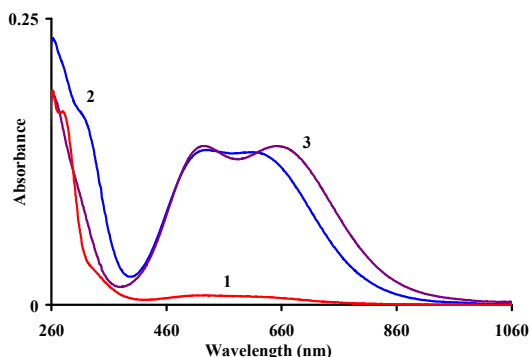


Figure 4. UV-visible spectra of Tc(VII) in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution. $[\text{Tc}] = 0.17 \text{ mM}$, $[\text{H}_2\text{O}_2] = 0.17 \text{ M}$. Spectra in: 9 M H_2SO_4 (1, red), 13 M H_2SO_4 (2, blue) and 18 M H_2SO_4 (3, purple)

5. Reactivity of Tc(VII) with H_2S

The reactivity of Tc(VII) with H_2S was studied in 12 M H_2SO_4 .³⁰ The KTcO_4 salt was dissolved in 12 M H_2SO_4 and the solution was purged with H_2S gas. During the reaction, the yellow solution rapidly turned brown and a black precipitate (Tc_2S_7) was observed. At the end of the reaction, the suspension was centrifuged, and a black precipitate and a brown supernate were obtained and analyzed. EXAFS analysis of the black precipitate indicated that the local structure around the Tc atom was similar to the one previously found for Tc_2S_7 .¹⁵

The supernate was analyzed by UV-visible and EXAFS spectroscopy. The UV-visible spectrum of the supernate (Figure 6) exhibited bands at 255 nm, 320 nm and a shoulder at 505 nm. Interestingly, the dissolution of black precipitate (Tc_2S_7) in 12 M H_2SO_4 led to a similar spectrum which suggests that the oxidation state of Tc in the supernate and in the precipitate might be identical.

The XANES spectrum of the supernate exhibits a shift of -7.5 eV vs TcO_4^- which is consistent with the presence of Tc(IV).^{15b} The EXAFS results indicate the environment of the Tc atom to consist of 1.3(3) O atoms at 1.81 Å, 3.8(8) O atoms at 2.03 Å, 0.7(1) S_{bid} atoms at 2.84 Å, 1.1(2) S_{mono} atoms at 3.16 Å and 0.7(3) Tc atoms at 3.62 Å. The EXAFS results (Figure S9, Table S5) are consistent with the presence of a polymeric species with the $[\text{Tc}-\text{O}-\text{Tc}]^{6+}$ core coordinated to: bisulfate ligands in monodentate and bidentate modes, water and/or hydroxide ligands. Based on the EXAFS results, the complex $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$ was proposed.

The DFT studies confirm the stability of $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$ and the geometrical parameters were in good agreement with the experimental ones (Figure 6). In order to gain a better understanding of the mechanism of formation of $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$, the reaction between TcO_4^- in 12 M H_2SO_4 and $\text{H}_2\text{S}(\text{aq})$ was followed by UV-visible spectroscopy.

Solutions of 12 M $\text{H}_2\text{SO}_4/\text{H}_2\text{S}$ were added to the Tc(VII) solution and color changes from yellow to green and then brown were observed.

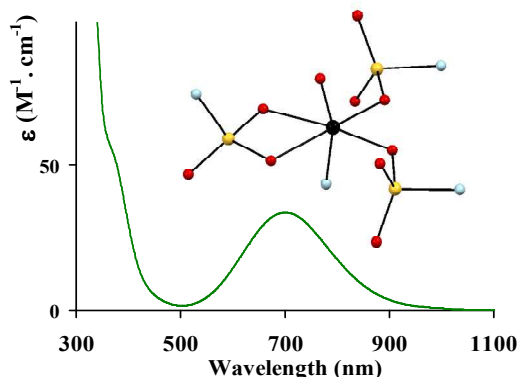


Figure 5. UV-visible spectrum in the region 300–1100 nm of the solution obtained after the reaction of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ with MeOH in 13 M H_2SO_4 . Insert - optimized DFT structure of $\text{TcO}(\text{HSO}_4)_3\text{OH}$. Distance (Å) found by DFT: $\text{Tc}=\text{O} = 1.69$, $\text{Tc}-\text{OH} = 1.89$, $\text{Tc}-\text{O}(\text{S}_{\text{bid}}) = 2.25$, $\text{Tc}-\text{O}(\text{S}_{\text{mono}}) = 1.99$, $\text{Tc}\cdots\text{S}_{\text{mono}} = 3.35$, $\text{Tc}\cdots\text{S}_{\text{bid}} = 2.92$. Color of atoms: Tc in black, O^{2-} in red, S in yellow, OH in light blue.

UV-visible measurements show that the green solution exhibits a low intensity band centered at 700 nm which was consistent with the presence of Tc(V) oxo-sulfate complexes (i.e., $\text{TcO}(\text{HSO}_4)_3(\text{OH})^-$). The formation mechanism of $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$ from TcO_4^- in 12 M H_2SO_4 were proposed as follows:

- Protonation of TcO_4^- to $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ ¹⁶
- H_2S reduction of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ to $\text{TcO}(\text{HSO}_4)_3(\text{OH})^-$ ²⁷
- H_2S reduction of $\text{TcO}(\text{HSO}_4)_3(\text{OH})^-$ to $\text{TcO}(\text{HSO}_4)_3(\text{OH})$
- Condensation³¹ of $\text{TcO}(\text{HSO}_4)_3(\text{OH})$ to $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$

6. Conclusions

In summary, the speciation of Tc(VII) in HNO_3 , HClO_4 and H_2SO_4 depends on the concentration and strength of the acid. Pertechnetic acid forms above 8 M HClO_4 and 7 M H_2SO_4 while in concentrated HNO_3 , TcO_4^- is still the predominant species. In H_2SO_4 and HClO_4 , pertechnetic acid is an octahedral complex with the formula $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$. The volatility of Tc in H_2SO_4 and HClO_4 is probably due to the neutral charge of $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$. The models described here for Tc(VII) in strong acids also explains some peculiarities observed in the liquid-liquid extraction and the electrochemical behavior of Tc.³²

In HNO_3 (≥ 7 M), TcO_4^- reacts immediately with H_2O_2 (> 4.25 M), and red solutions are obtained. UV-visible and theoretical studies are consistent with the formation of $\text{TcO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OH})$. In spent fuel reprocessing, the H_2O_2 concentration in nitric acid is expected to be well below 4.25 M¹⁰ which implies that $\text{TcO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OH})$ should not be observed. In H_2SO_4 , $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ reacts with methanol, H_2O_2 and H_2S . In 13 M H_2SO_4 , $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ is reduced to Tc(V) and methanol is oxidized to formic acid; Tc(V) complexes with stoichiometry $\text{TcO}(\text{HSO}_4)_2(\text{H}_2\text{O})_2(\text{OH})$ and/or

$\text{TcO}(\text{HSO}_4)_3(\text{OH})^-$ are proposed. In 12 M H_2SO_4 , $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ is stepwise reduced by H_2S to Tc(V) and Tc(IV). The Tc(IV) complex exhibits a $[\text{Tc}-\text{O}-\text{Tc}]^{6+}$ core coordinated to bisulfate ligands, and the stoichiometry $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$ is proposed.

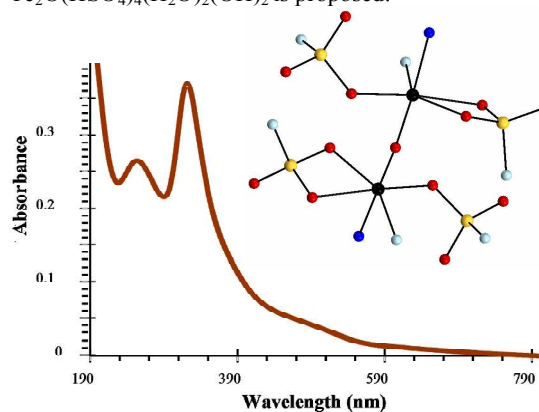


Figure 6. UV-visible spectrum of the solution (dilution 1:1000 in 12 M H_2SO_4) obtained after reaction of Tc(VII) with H_2S in 12 M H_2SO_4 . Insert - optimized DFT structure of $\text{Tc}_2\text{O}(\text{HSO}_4)_4(\text{H}_2\text{O})_2(\text{OH})_2$. Distance (Å) found by DFT: $\text{Tc}-\text{O}(\text{Tc}) = 1.82$, $\text{Tc}-\text{OH} = 1.89$, $\text{Tc}-\text{H}_2\text{O} = 2.20$, $\text{Tc}\cdots\text{S}_{\text{mono}} = 3.27$, $\text{Tc}\cdots\text{S}_{\text{bid}} = 2.83$, $\text{Tc}\cdots\text{Tc} = 3.63$. $\text{Tc}-\text{O}_{\text{mono}} = 2.04$, $\text{Tc}-\text{O}_{\text{bid}} = 2.22$. Color of atoms: Tc in black, O^{2-} in red, S in yellow, OH in light blue, H_2O in blue.

This complex is also obtained after dissolution of Tc_2S_7 in H_2SO_4 ; those results indicate that if H_2S would be used for Tc immobilization, the mobility of Tc in the environment might be controlled by Tc(IV) species. The reaction between $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$ and H_2O_2 leads to several Tc(VII) peroxo complexes: in 6 M H_2SO_4 , a red solution (i.e., $\text{TcO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OH})$) is observed while in 12 M and 18 M H_2SO_4 , blue solutions are obtained and $\text{TcO}_2(\text{O}_2)(\text{H}_2\text{O})_2(\text{OH})$ and/or $\text{TcO}(\text{O}_2)_3$ are proposed.

Heptavalent Tc is a very reactive species and further work is needed to get a better understanding of the breadth of its redox chemistry. Future work could focus on the nature and reactivity of Tc in concentrated aqueous HTcO_4 , $\text{H}_2\text{SO}_4/\text{HCl}$, HCl , H_3PO_4 and triflic acid. The concentration of aqueous pertechnetic acid led to the formation of a red species which structure is unknown; it has been proposed that the red species could be TcO_3 , Tc_2O_5 or a polymeric species with the stoichiometry $[\text{Tc}^{\text{VI}}_4\text{Tc}^{\text{VII}}_{16}\text{O}_{68}]\cdot 16\text{H}_2\text{O}$.^{33, 34, 35} Previous ⁹⁹Tc-NMR studies on the red species were consistent with the presence of Tc(VII) atoms in tetrahedral and octahedral environment but further works are needed to solve the mystery of the red species.³⁶ High valents Tc oxochlorides (TcO_3Cl , TcOCl_5^- , TOCl_4 , TcOCl_3) are still not well studied; the reaction of Tc(VII) in strong acids could be a simple route to produce and study those species. In concentrated H_2SO_4 , it was shown that Tc(VII) reacts with HCl to form a blue solution, the formula TcOCl_5^- was proposed but no structural data were reported.³⁷ In cold, concentrated aqueous HCl , the reduction of TcO_4^- leads to TcOCl_4^- , but the mechanism of this reaction is still unknown. It was proposed that $\text{TcO}_3\text{Cl}_3^{2-}$ is initially formed and is further reduced to TcOCl_4^- .³⁸ TcO_3Cl was also reported from the reaction of Tc(VII) in $\text{H}_2\text{SO}_4/\text{HCl}$ followed by extraction in CCl_4 but its structure is unknown. Technetium oxochlorides can

have importance in the nuclear industry where chloride molten salts are used (molten salts reactors, pyroprocessing). Those oxychlorides could form when oxygen enter molten salts containing fission products. Study the chemistry of those oxychlorides could be key to understand the performance of the salt in molten salts reactors. In triflic acid, $TcO_3(OH)(H_2O)_2$ has been identified³⁹ but its reactivity with H_2O_2 and organics has not been studied. In H_3PO_4 , studies are non existent. Finally, future work could focus on the reactivity of $TcO_3(OH)(H_2O)_2$ in sulfuric acid with other organics (e.g., alkanes, alkenes, aldehydes, ketones, ...).

Conflicts of interest

“There are no conflicts to declare”.

Acknowledgements

This material is based upon work supported by the Department of Energy National Nuclear Security Administration through the Nuclear Science and Security Consortium under Award Number(s) DE-NA0003180 and/or DE-NA0000979. 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. The Arronax facility is greatly acknowledged for providing beam time and technical support for the alpha irradiation experiments.

Notes and references

- 1 E. V. Johnstone, M. A. Yates, F. Poineau, A. P. Sattelberger and K. R. Czerwinski, *J. Chem. Educ.*, 2017, **94**, 320.
- 2 (a) R. Alberto. In *Comprehensive Coordination Chemistry II*, McCleverty, J. A. Mayer, T. J. eds. Elsevier, Amsterdam, 2003, vol. 5, chap. 2. (b) R. Alberto, H. Braband and H. W. P. N'Dongo, *Curr. Radiopharm.*, **2009**, **2**, 254.
- 3 K. Schwochau, *Technetium: Chemistry and Radiopharmaceutical Applications* Wiley-VCH: Weinheim, Germany, 2000
- 4 J. G. Darab and P. A. Smith, *Chem. Mater.*, 1996, **8**, 1004.
- 5 F. Poineau, E. Mausolf, G. D. Jarvinen, A. P. Sattelberger and K. R. Czerwinski, *Inorg. Chem.*, 2012, **52**, 3573.
- 6 S. Matsumoto, G. Uchiyama, M. Ozawa, Y. Kobayashi and K. Shirato, *Radiochemistry*, 2003, **45**, 219.
- 7 (a) R. J. Meyer, R. D. Oldham and R. P. Larsen, *Anal. Chem.*, 1964, **36**, 1975. (b) G. E. Boyd, Q. V. Larsonan and E. E. Motta, *J. Am. Chem. Soc.*, 1960, **82**, 809.
- 8 G. E. Boyd, *J. Chem. Educ.*, 1959, **36**, 1.
- 9 C. L. Rulfs, R. A. Pacer and R. F. Hirsch, *J. Inorg. Nucl. Chem.*, 1967, **29**, 681.
- 10 G. Garaix, L. Venault, A. Costagliola, J. Maurin, M. Guigue, R. Omnee, G. Blain, J. Vandendorre, M. Fattahi, N. Vigier and P. Moisy, *Radiat. Phys. Chem.*, 2015, **106**, 394.
- 11 (a) M. V. Krishnamurthy and A. T. Sipahimalani, *J. Radioanal. Nucl. Ch.*, 1995, **199**, 197. (b) L. L. Burger and E. D. McClanahan, *Ind. Eng. Chem.*, 1958, **50**, 153.
- 12 (a) J. Baldas, S. F. Colmanet and G. A. Williams, *J. Chem. Soc. Dalton Trans.*, 1991, 1631. (b) J. Baldas, S. F. Colmanet, *Inorg. Chim. Acta*, 1990, **176**, 1.
- 13 (a) A. Fatiadi, *Synthesis*, 1987, **2**, 85. (b) R. M. Barter and J. S. Littler, *J. Chem. Soc.*, 1967, 205. (c) P. K. Sen, P. R. Samaddar and K. Das, *Transit. Metal Chem.*, 2005, **30**, 261.
- 14 (a) S. Kunze, V. Neck, K. Gompper and T. Fanghanel, *Radiochim. Acta*, 1996, **74**, 159. (b) K. E. German, Ya. Obruchnikova, A. V. Safonov, V. E. Tregubova, A. V. Afanas'ev, A. V. Kopytin, O. S. Kryzhovets, F. Poineau, E. V. Abkhalimov and A. A. Shiryayev, *Russ. J. Inorg. Chem.*, 2016, **61**, 1445.

- 15 (a) W. W. Lukens, J. J. Bucher, D. K. Shuh and N. M. Edelstein, *Environ. Sci. Technol.*, 2005, **39**, 8064. (b) Y. Liu, J. Terry and S. Jurisson, *Radiochim. Acta*, 2007, **95**, 717.
- 16 F. Poineau, P. F. Weck, K. German, A. Maruk, G. Kirakosyan, W. Lukens, D. B. Rego, A. P. Sattelberger and K. R. Czerwinski, *Dalton Trans.*, 2010, **39**, 8616.
- 17 F. Poineau, B. P. Burton-Pye, A. Maruk, G. Kirakosyan, I. Denden, D. B. Rego, E. V. Johnstone, A. P. Sattelberger, M. Fattahi, L. C. Francesconi, K. E. German and K. R. Czerwinski, *Inorg. Chim. Acta*, 2013, **398**, 147.
- 18 (a) V. A. Mikhalev, *Radiochemistry*, 2005, **47**, 319. (b) H. Braband, Y. Tooyama, T. Fox and R. Alberto, *Chem. Eur. J.*, 2009, **15**, 633. (c) K. J. Franklin, C. J. L. Lock, B. G. Sayer and G. J. Schrobilgen, *J. Am. Chem. Soc.*, 1982, **104**, 5303. (d) J. A. Thomas and A. Davison, *Inorg. Chim. Acta*, 1989, **161**, 39. (e) H. Braband and U. Abram, *Inorg. Chem.*, 2006, **45**, 6589.
- 19 H. Beyer, O. Glemser and B. Krebs, *Angew. Chem. Ind. Ed.*, 1968, **7**, 295.
- 20 F. Poineau, P. F. Weck, B. P. Burton-Pye, E. Kim, L. C. Francesconi, A. P. Sattelberger, K. E. German and K. R. Czerwinski, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4595.
- 21 F. Poineau, K. E. German, B. P. Burton-Pye, P. F. Weck, E. Kim, O. S. Kryzhovets, A. Safonov, V. Ilin, L. C. Francesconi, A. P. Sattelberger and K. R. Czerwinski, *J. Radioanal. Nucl. Ch.*, 2015, **303**, 1163.
- 22 W. Davis, P. S. Lawson, H. J. deBruin and J. Mroczek, *J. Phys. Chem.*, 1965, **69**, 1904.
- 23 (a) V. Nardello, J. Marko, G. Vermeersch and J. M. Aubry, *Inorg. Chem.*, 1995, **34**, 4950. (b) M. Arab, D. Bougeard, J. M. Aubry, J. Marko, J. F. Paul and E. Payen, *J. Raman Spectrosc.*, 2002, **33**, 390. (c) J. D. Lydon, L. M. Schwane and R. C. Thompson, *Inorg. Chem.*, 1987, **26**, 2606.
- 24 (a) W. A. Herrmann, J. D. G. Correia, F. E. Kuhn, G. R. J. Artus and C. C. Romao, *Chem. Eur. J.*, 1996, **2**, 168. (b) W. A. Herrmann and F. E. Kuhn, *Acc. Chem. Res.*, 1997, **30**, 169.
- 25 D. N. Tumanova, K. E. German, V. F. Peretrakhin and A. Y. Tsvadze, *Dokl. Phys. Chem.*, 2008, **420**, 114.
- 26 M. Ferrier, P. Weck, B. Burton-Pye, F. Poineau, E. Kim, A. Stebbins, L. Ma, A. Sattelberger and K. Czerwinski, *Dalton Trans.*, 2012, **41**, 6291.
- 27 F. Poineau, P. F. Weck, B. P. Burton-Pye, I. Denden, E. Kim, W. Kerlin, K. E. German, M. Fattahi, L. C. Francesconi, A. P. Sattelberger and K. R. Czerwinski, *Dalton Trans.*, 2013, **42**, 4348.
- 28 S. J. Cline Schaffer and R. W. Berg, *Acta Cryst.*, 2008, **E64**, i20.
- 29 I. Denden, F. Poineau, M. L. Schlegel, J. Roques, P. L. Solari, G. Blain, K. R. Czerwinski, R. Eschli, J. Barbet and M. Fattahi, *J. Phys. Chem. A*, 2014, **118**, 1568.
- 30 M. Ferrier, J. Roques, F. Poineau, A. P. Sattelberger, J. Unger and K. R. Czerwinski, *Eur. J. Inorg. Chem.*, 2014, **2014**, 2046.
- 31 F. Poineau, M. Fattahi, G. Montavon and B. Grambow, *Radiochim. Acta*, 2006, **94**, 291.
- 32 (a) M. Chotkowski and D. Polomski, *J. Radioanal. Nucl. Ch.*, 2017, **314**, 87. (b) M. Chotkowski and A. Czerwiński, *Electrochim. Acta*, 2012, **76**, 165.
- 33 (a) S. V. Krytchkov, M. S. Grigoriev and K. E. German, In *Technetium and Rhenium in Chemistry and Nuclear Medicine*. V.3. Ed. by M. Nicolini, G. Bandoli, U. Mazzi. New York: Raven Press, 1990. p. 253-264. (b) S. V. Krytchkov, A. F. Kuzina and K. E. German, In *Technetium and Rhenium in Chemistry and Nuclear Medicine*. V.3. Ed. by M. Nicolini, G. Bandoli, U. Mazzi. New York: Raven Press, 1990. p.275-292.
- 34 J. A. Rard, M. H. Rand, G. Anderegg and H. Waneer “chemical thermodynamics of technetium,” Ed. by A. Sandino and E. Ostholts. Noth Holland/Elsevier, Amsterdam, 1999 p. 112.
- 35 K. E. German, M. S. Grigoriev and A. M. Fedosseev, Abstracts of the 8th All-Russian conference on radiochemistry, 28 Sept - 2 Oct. 2015. Zheleznogorsk, 2015 p.50.
- 36 K. E. German, A. Y. Maruk, F. Poineau, P. Weck, G. A. Kirakosyan, V. P. Tarasov, K. Czerwinski and A. Sattelberger. 7th International symposium on technetium and rhenium. Book of proceedings. Jul. 4 - 8, 2011, Moscow, Russia (Eds. K. E. German, B. F. Myasoedov, G. E. Kodina, A. Y. Maruk, I. D. Troshkina), Publishing House Granitsa: Moscow, 2011, p. 99 - 100.
- 37 R. Kirmse, J. Stach and U. Abram, *Inorg. Chem.*, 1985, **24**, 2196.
- 38 A. Davison and A. G. Jones, *Int. J. Appl. Radiat. Isot.*, 1982, **33**, 875.
- 39 I. Denden, J. Roques, F. Poineau, P. L. Solari, M. L. Schlegel, G. Blain and M. Fattahi, *Radiochim. Acta*, 2017, **105**, 135.

