Spectroscopic Characterization of Tc(I) Tricarbonyl Species Relevant to the Hanford Tank Waste − 17379

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ABSTRACT

Technetium-99 (Tc) generated from the fission of ^{235}U and ^{239}Pu in high yields is one of the most difficult contaminants to be addressed at the U.S. Department of Energy (DOE) Hanford Site. Among radioactive contaminants, Tc presents a unique challenge in that it has a long half-life ($T_{1/2} = 2.11{\times}10^5$ y), exhibits diverse chemical properties and typically highly mobile in the environment leading to several uncertainties regarding treatment and disposition options. The complex behavior of Tc under storage, treatment, and immobilization conditions significantly affects its management options. The overall objective of the Technetium Management program at Pacific Northwest National Laboratory is to provide the DOE Office of Environmental Management with practical solutions to Tc needs encountered in the processing of Hanford tank waste and vadose zone remediation; and technical activities are being performed in the areas of Tc characterization, treatment, and disposition. One specific task is focused on elucidation of the identity and properties of non-pertechnetate species in the liquid Hanford tank waste. Previous analysis of the tank waste samples provided strong evidence that non-pertechnetate species can be comprised of $Tc(CO)_3{}^+$ complexes containing Tc in oxidation state +1. This paper describes our current results on the development of spectroscopic library of Tc(I) tricarbonyl species for their characterization and identification in the Hanford tank wastes.

INTRODUCTION

Technetuim-99 (^{99}Tc), generated from the fission of ^{235}U and ^{239}Pu, is a major risk-driving component in the liquid fraction of nuclear waste tanks at the DOE Hanford Site in Washington state. Among radioactive constituents in the tank waste, ^{99}Tc presents a unique challenge. The long half-life ($\beta = 292$ keV; $T_{1/2} = 2.11{\times}10^5$ y), complex chemical behavior in tank waste, and high mobility in subsurface environments make Tc one of the most challenging radionuclides to dispose of and/or remediate. Previous attempts to remove Tc from the Hanford tank waste using an ion-exchange process specific to pertechnetate ($TcO_4{}^-$) only met with limited success and were particularly less successful for the tank wastes, including tanks SY-101 and SY-103, containing organic complexants such as nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), citrate, and gluconate.[1, 2] This suggests that a significant fraction of the soluble Tc can be present as non-pertechnetate low-valent Tc (oxidation state < +7) (non-$TcO_4{}^-$). The chemical identities of these non-$TcO_4{}^-$ species are poorly understood.

X-ray absorption analysis of the waste samples collected from the actual SY-101 and SY-103 tank waste supernatants suggested the presence of the non-pertechnetate species derived from Tc(I) carbonyl moiety.[3]   During last two years, our PNNL team has expanded this work and demonstrated that high ionic strength solutions typifying tank waste supernatants promote oxidative stability of the *fac*-$[Tc(CO)_3]^+$ species[*].[4, 5]   Recent work by our group has significantly expanded this hypothesis, demonstrating that Tc(I) carbonyl compounds can be generated from reduction of TcO_4^- in simulated Hanford tank waste in the presence CO at elevated temperature,[5] and on-going monitoring of these samples indicates long-term stability of Tc(I) carbonyl and Tc(VI) non-pertechnetate.[6] These results support the hypothesis that Tc(I)-containing $[Tc(CO)_3]^+$ species can be a prominent component of Hanford tank waste.

Designing strategies for effective Tc processing, including separation and immobilization, necessitates understanding the molecular structure of these non-pertechnetate species and their identification in the actual tank waste samples. To-date, only limited information exists regarding the nature and characterization of the Tc(I), Tc(IV), and Tc(VI) species.   One objective of this project is to identify the speciation of non-pertechnetate compounds in the Hanford waste. To do this, we are developing a spectral library of reference non-pertechnetate compounds that can be compared against actual waste samples. The main emphasis is spectroscopic characterization Tc(I) tricarbonyl $[Tc(CO)_3]^+$ compounds. In addition, we evaluate Tc in the intermediate oxidation states including Tc(IV) and Tc(VI).

The spectroscopic techniques selected for the identification of the non-pertechnetate species include ^{99}Tc nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), infrared (IR) and x-ray absorption spectroscopy (XAS). Each individual spectroscopic technique being utilized has its own distinct advantages and will provide fingerprint like information about the individual components of tank waste. IR spectroscopy provides information regarding Tc-CO bonding in the spectral region largely free of interferences and is suitable for analysis of the electronic and geometric structure of Tc compounds containing the $[Tc(CO)_3]^+$ moiety. XAS spectroscopy allows differentiation among Tc species simultaneously present a variable oxidation states, albeit it is limited to the samples contacting sufficiently high concentrations of Tc. [99]Tc NMR spectroscopy is ideally suited for monitoring diamagnetic Tc(I) and Tc(VII) species. Small changes in ligand substitution result in large changes in chemical shift giving each compound a signature that is readily monitored.   EPR spectroscopy is a complimentary technique to ^{99}Tc NMR and provides structural information on paramagnetic Tc species, which are generally of an even numbered oxidation state, and inaccessible via NMR spectroscopy. EPR spectroscopic measurements have very little interference from diamagnetic impurities present in solution, and thus is an ideal technique for studying paramagnetic species in complex mixtures. This work demonstrates that Tc(VI) even at low concentrations generates unique EPR signal suitable for identification of Tc this

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[*] All Tc(I) carbonyl compounds described in this report have *facial* octahedral geometry, and in the following text the notation "*fac-*" is omitted for clarity.

oxidation state.

In conjunction with the aforementioned techniques, density functional theory (DFT) computations are being performed to benchmark calculated parameters against the empirical results. This allows us to simultaneously pursue two routes towards determination of tank waste composition; characterizing the spectral fingerprints of individual species likely present in tank waste for facile identification of tank waste composition, and developing the capability to computationally predict the chemical structure of spectral signatures not yet catalogued in our database. Once fully benchmarked the DFT computations will be used to predict species, which are likely present in Hanford tank waste but difficult to synthetically access in a laboratory environment.

RESULTS

To prepare Tc(I) compounds containing a $[Tc(CO)_3]^+$ center, TcO_4^- was initially reduced to Tc(V) in the form of the stable compound $[Bu_4N][TcOCl_4]$ followed by second step borane reduction using the modified procedure that was originally reported elsewhere.[7] The product, $[Et_4N]_2[Tc(CO)_3Cl_3]$, is readily dissolved in water, and the Cl^- ligands are exchanged with H_2O, OH^-, and/or organic ligands present in the aqueous solution so that $[Et_4N]_2[Tc(CO)_3Cl_3]$ serves as a convenient source of Tc(I)-tricarbonyl species. The structures of the $[Tc(CO)_3]^+$ species included in the spectral database are given in Figure 1.

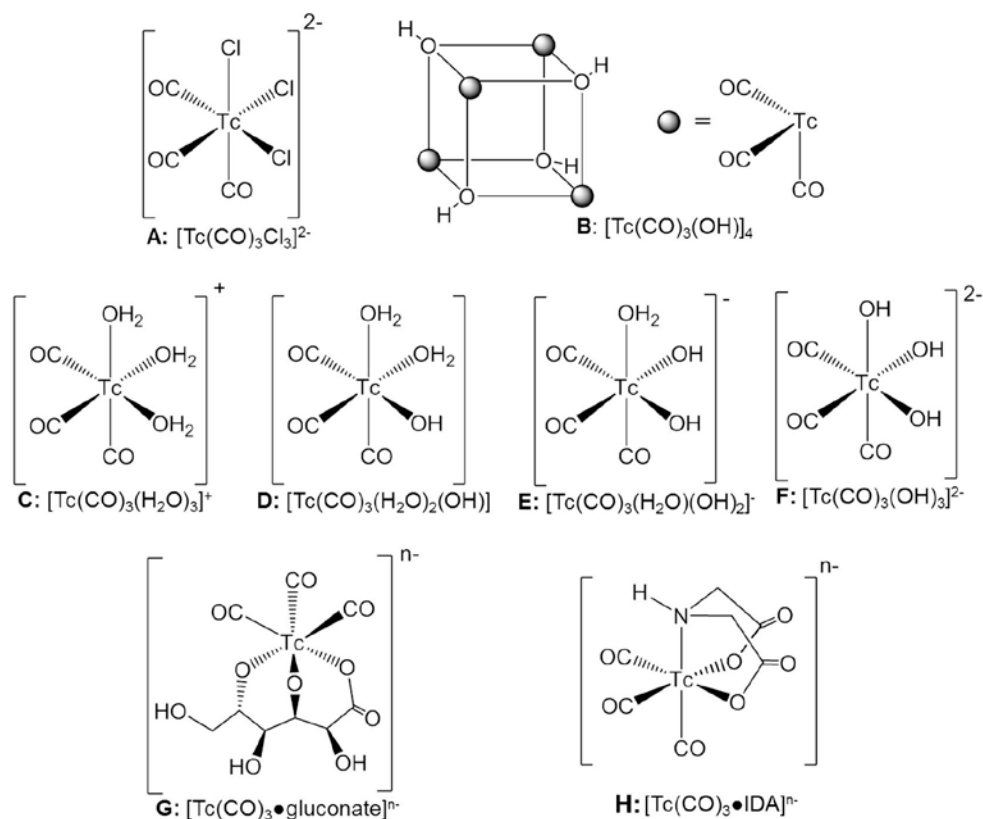**Figure 1**.   Molecular structures of $[Tc(CO)_3$ $[Tc(CO)_3]^+$ complexes included in the spectral database.

Solution ^{99}Tc NMR spectroscopy of $[Tc(CO)_3]^+$ species

The obtained ^{99}Tc NMR spectroscopic database is summarized in Table 1, and the representative ^{99}Tc NMR spectra of the $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$ compounds in 5 M NaNO$_3$ solution at variable pH and in the Hanford waste simulant are shown in Figures 2 and 3, respectively.
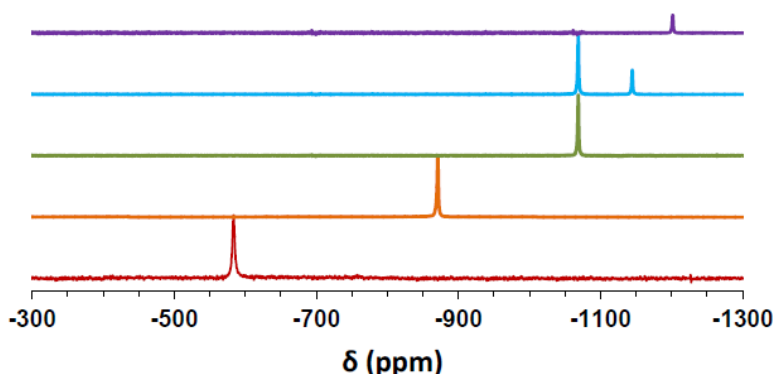
Figure 2. Solution ^{99}Tc NMR spectra of the $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$ species obtained from $[Tc(CO)_3Cl_3]^{2-}$ in 5 M $NaNO_3$ at variable pH.   Bottom, red trace: $[Tc(CO)_3(OH)]_4$ at pH = 6.5 – 11 (δ = -585 ppm).   Second from the bottom, orange trace: $[Tc(CO)_3(H_2O)_3]^+$ at pH = 0 – 6 (δ = -868 ppm).   Middle, green trace: $[Tc(CO)_3(H_2O)_2(OH)]$ at $[OH^-]$ = 0.1 – 3 M (δ = -1070 ppm).   Second from the top, light blue trace: $[Tc(CO)_3(H_2O)_2(OH)]$ and $[Tc(CO)_3(H_2O)(OH)_2]^-$ at $[OH^-]$ = 6 M (δ = -1070 and -1140 ppm).   Top, violet trace: $[Tc(CO)_3(OH)_3]^{2-}$ at $[OH^-]$ = 10 M (δ = -1215 ppm).
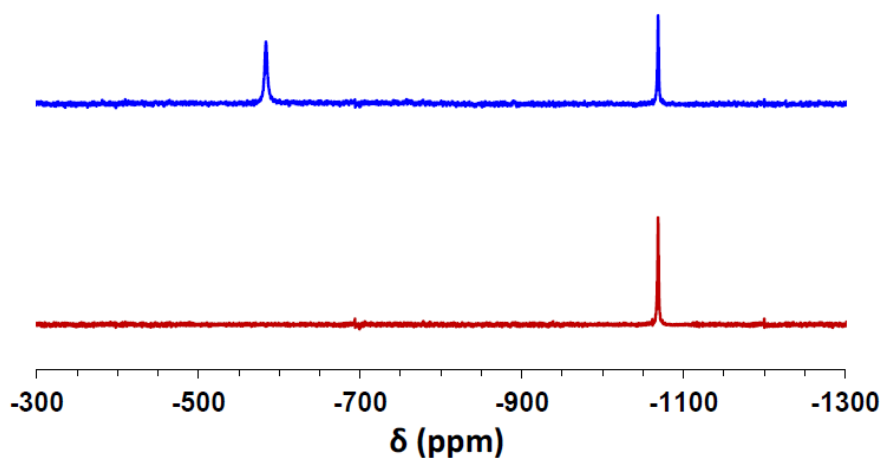

Figure 3.   Simulant solution ^{99}Tc NMR spectra of $[Tc(CO)_3(H_2O)_2(OH)]$ (δ = -1070 ppm) obtained by dissolution of $[Tc(CO)_3Cl_3]^{2-}$ (bottom, red trace) and $[Tc(CO)_3(OH)]_4$ (top, blue trace).

Table 1. ^{99}Tc NMR spectroscopic database of the $[Tc(CO)_3]^+$ compounds.

Complex	Solvent	Experimental ^{99}Tc NMR chemical shift (ppm)	Half width of ^{99}Tc resonance (Hz)	Calculated ^{99}Tc NMR chemical shift (ppm)	Absolute deviation from experiment (ppm)
TcO_4^-	H_2O	-3 – +3	20	0	0
	5 M NaNO$_3$/NaOH	-3 – +3	20	0	0
	Simulant	-3 – +3	20	0	0
$[Tc(CO)_3(H_2O)_3]^+$	5 M NaNO$_3$/HNO$_3$ pH = 0 – 7	-868	100	-837	31
Tc(CO)$_3$(OH)]$_4$	H_2O	-583	480	-620	37
	5 M NaNO$_3$/NaOH pH = 7 – 11	-585	480	-620	35
	Simulant	-590	500	-	-
$[Tc(CO)_3(H_2O)_2(OH)]$	5 M NaNO$_3$/0.01 – 10 M NaOH	-1062	90	-1067	5
	Simulant	-1070	100	-	-
$[Tc(CO)_3(H_2O)(OH)_2]^-$	5 M NaNO$_3$/3 – 10 M NaOH	-1140	110	-1173	33
$[Tc(CO)_3(OH)_3]^{2-}$	5vM NaNO$_3$/>10 M NaOH	-1210	130	-1305	95
$[Tc(CO)_3\bullet(DTPA)]^-$	5 M NaNO$_3$/0.1 M NaOH	-915	600	Not calculated	N/A
	Simulant	-910	700		
$[Tc(CO)_3\bullet(NTA)]^-$	5 M NaNO$_3$/0.1 M NaOH	-918	550		
	Simulant	-915	650		
$[Tc(CO)_3\bullet(EDTA)]^-$	5 M NaNO$_3$/0.1 M NaOH	-916	550		
	Simulant	-920	650		
$[Tc(CO)_3\bullet(IDA)]^-$	5 M NaNO$_3$/0.1 M NaOH	-850 (broad) -998	1000 700	Calculations are currently underway	N/A
	Simulant	-820 -1000	1000 750		
$[Tc(CO)_3\bullet(gluconate)]^{n-}$	5 M NaNO$_3$/0.1 M NaOH	-1100 (broad) -1232 -1254	1000 650 550		
	Simulant	-1100 (broad) -1240 -1259	1000 700 600		

The NMR data for all compounds are nearly identical in all tested solution matrices, including water, 5 M $NaNO_3$, or simulant, demonstrating that anions (other than hydroxide) typifying tank supernatant matrix exhibit no interaction with the $[Tc(CO)_3]^+$ framework.   This finding is important for utilization of NMR spectroscopy for the identification of the $[Tc(CO)_3]^+$ species in Hanford tank waste.

The compositions of the $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$ species depend on the solution alkalinity and can be easily identified by their distinct chemical shifts and half-line widths.   The triaqua $[Tc(CO)_3(H_2O)_3]^+$ only exists in acidic solutions, and starts undergoing extensive deprotonation starting at near-neutral pHs.   Therefore, $[Tc(CO)_3(H_2O)_3]^+$ is unlikely to exist in the tank waste.   The mono-hydroxo species $[Tc(CO)_3(H_2O)_2(OH)]$ is observed to be persistent in alkaline solutions, though at high Tc concentrations it can undergo oligomerization to form the tetrameric species $[Tc(CO)_3(OH)]_4$ over time, which is stable in the intermediate pH range (pH= 6.5 to 11).   At high concentrations of OH⁻, the $[Tc(CO)_3(H_2O)(OH)_2]^-$ species is also observed, though $[Tc(CO)_3(H_2O)_2(OH)]$ is the predominant species.   At very high hydroxide concentrations, it is possible to see the $[Tc(CO)_3(OH)_3]^{2-}$ species.

Density functional theory computations are being used to model the $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$ spectra that are being experimentally generated during construction of the spectral library.   Despite the difficulties in modeling a highly challenging solvent system with strong intermolecular interactions such as hydrogen-bonding, the DFT computations are able to closely estimate chemical shifts present in ^{99}Tc NMR spectra, as can be seen in Table 1. For the systems with well-defined chemical structures in aqueous solvent similar to tank waste conditions, DFT computations are predicting chemical shifts to within 100 ppm in a Tc spectral window that is greater than 10,000 ppm wide.   Many of the species modeled, particularly the tricarbonyl aqua and tricarbonyl hydroxide species, are modeled even more accurately and fall within 40 ppm of the experimentally observed signals. Given the large range present in the ^{99}Tc NMR spectral window, DFT computations have proved a valuable tool for structural verification and identification of ^{99}Tc NMR assignments for new species.

Among small chelateors evaluated for the feasibility of the complex formation with $[Tc(CO)_3]^+$, only gluconate and IDA were found to form strong complexes, with IDA being the most coordinating, potentially due to coordination of the amino nitrogen in addition to carboxylic oxygens to the Tc center.   NTA, EDTA, and DTPA formed weak complexes and were not able to effectively compete with hydroxide ligands for Tc coordination sites; therefore, their existence in the tank wastes is deemed unlikely.

While previous work[3]   had demonstrated the presence of $[Tc(CO)_3 \bullet Gluconate]^{n-}$ in Hanford tank waste from EXAFS analysis, the exact coordination environment around the Tc center had not been determined yet.   Comprehensive analyses using ^{99}Tc NMR

conducted in this work revealed that complexation of gluconate results in three distinct $[Tc(CO)_3 \bullet Gluconate]^{n-}$ chemical environments. Based on molecular modelling calculations, the resonances at -1232 and -1254 ppm are tentatively attributed to species similar to **G** in Figure 1. The broad resonance at -1100 ppm is speculatively attributed to a polynuclear $[Tc(CO)_3 \bullet Gluconate]^{n-}$ species. Similarly, IDA also exhibits a remarkably high affinity towards $[Tc(CO)_3]^+$ in both 5 M $NaNO_3$/0.1 M NaOH and the simulant, showing an intense resonance at about -1000 ppm and a weaker and broader resonance at about -850 ppm. The resonance at -1000 ppm is assigned to a $[Tc(CO)_3 \bullet IDA]^{n-}$ species whose structure is tentatively assigned to the structure **H** (Figure 1) based on a similar structure proposed by Rattat and coworkers during the reaction of $[^{99m}Tc(CO)_3(H_2O)_3]^+$ with IDA.[8]

Overall based on the assembled ^{99}Tc NMR spectral database, it is concluded that pertechnetate and the various $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$ and $[Tc(CO)_3 \bullet Ligand]^{n-}$ complexes, which the presence of can be anticipated in tank waste, can be unambiguously identified by NMR spectroscopy provided they exist at concentration levels observable by this technique (high micromolar and above).

Solution IR spectroscopy of $[Tc(CO)_3]^+$ species

The IR fingerprint region (<1300 cm^{-1}) of the aqueous 5 M $NaNO_3$/0.1 M NaOH and simulant solutions contains interfering bands due to the oxy-anions, and therefore is unsuitable for the identification of the solutes. However, the carbonyl spectral region (1700-2500 cm^{-1}) is devoid of spectral interferences and can be useful for the determination of the $[Tc(CO)_3]^+$ species. The solutions containing weak complexing agents such as NTA, EDTA, and DTPA as well as $[Tc(CO)_3(H_2O)_2(OH)]$ species generated IR spectra nearly identical to that of a $[Tc(CO)_3(H_2O)_2(OH)]$ solution (not shown). The IR spectral overlay of the $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$, and $[Tc(CO)_3 \bullet Gluconate]^{n-}$ and $[Tc(CO)_3 \bullet IDA]^{n-}$ compounds in the carbonyl region shown in Figure 4, demonstrates structure-dependent characteristic CO vibrations. Gluconate and IDA complexes show multiple vibrations in the Tc-carbonyl region (1600-2300 cm^{-1}) which are attributed to carboxylate vibrations of the Tc-coordinated ligands in addition to the characteristic Tc-CO vibrations arising from the $[Tc(CO)_3]^+$ backbone.
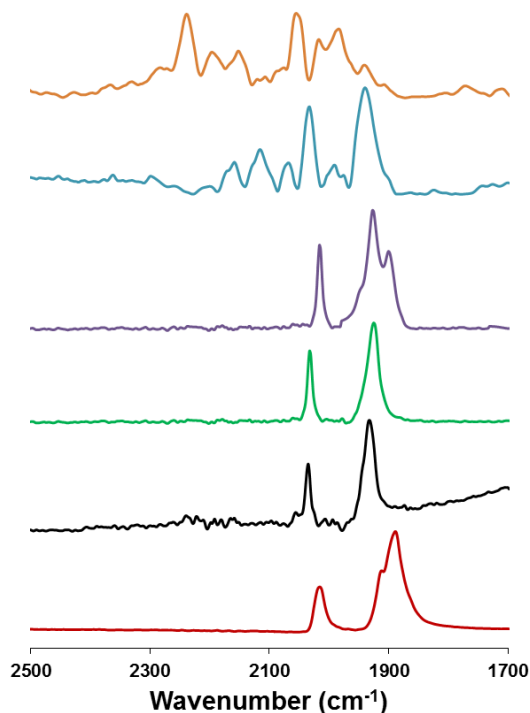
Figure 4.   Carbonyl IR spectral region of the $[Tc(CO)_3]^+$ species in solution. Bottom, red trace: $[Tc(CO)_3Cl_3]^{2-}$ in MeCN.   Second from bottom, black trace: $[Tc(CO)_3(H_2O)_3]^+$ in 5 M $NaNO_3$ at pH = 0 – 6.   Third from bottom, green trace: $[Tc(CO)_3(OH)]_4$ in 5 M $NaNO_3$ at pH = 7 – 11. Third from top, violet trace: $[Tc(CO)_3(H_2O)_2(OH)]$ in 5 M $NaNO_3$/0.1 M NaOH.   Second from top, blue trace: $[Tc(CO)_3 \bullet Gluconate]^{n-}$ in 5 M $NaNO_3$/0.1 M NaOH.   Top, orange trace: $[Tc(CO)_3 \bullet IDA]^{n-}$ in 5 M $NaNO_3$/0.1 M NaOH.

The obtained FTIR spectroscopic database is summarized in Table 2.   The IR-spectroscopic data demonstrate that the Tc-carbonyl region (1600-2300 cm^{-1}) is anticipated to be free from most interferences coming from various oxy-anions present in tank waste supernatants, and can be potentially utilized for the determination of the $[Tc(CO)_3(H_2O)_{3-n}(OH)_n]^{1-n}$ complexes.   Identification of the $[Tc(CO)_3 \bullet Ligand]^{n-}$ compounds can be difficult due to the overlapping signals from the carboxylic group coordinated to Tc.

DFT modelling has also been performed in order to predict the experimentally observed carbonyl stretching frequencies observed in FTIR spectroscopy.   The tabulated results can be viewed in Table 2.   Identical computational methods were

used for the IR frequencies as were used in the ^{99}Tc NMR computations. The resulting in carbonyl stretching frequencies require a uniform shift of only 0.8% to be realigned with experimentally observed spectra. Given that inorganic carbonyl ligands are one of the few vibrations to occur in this region, coupled with drastic changes observed in inorganic carbonyl IR spectral signatures with minor changes in metal center electron density, and geometrical changes make this a powerful predictive tool.

Table 2. FTIR spectroscopic database of the $[Tc(CO)_3]^+$ compounds.

Complex	CO vibrations (cm^{-1})	*DFT calculated CO vibrations (cm^{-1})
$[Tc(CO)_3Cl_3]^{2-}$	1889, 1915(sh), 2017	1885, 1885, 2052
$[Tc(CO)_3(H_2O)_3]^+$	1931, 1943(sh), 2036	1943, 1943, 2103
$[Tc(CO)_3(OH)]_4$	1925, 1939(sh), 2032	Calculations in progress
$[Tc(CO)_3(H_2O)_2(OH)]$	1898, 1923, 1945(sh), 2016	1899, 1901, 2056
$[Tc(CO)_3(Gluconate)]^{n-}$	2162, 2115, 2067, 1989, 1937, 1956(sh), 2034	Not calculated
$[Tc(CO)_3(IDA)]^-$	2243, 2193, 2152, 2051, 2012, 1981, 1939	Not calculated

[99]Tc Electron Paramagnetic Resonance (EPR) Spectroscopy

EPR spectra are analyzed primarily through examination of two experimental parameters known as the g-value, and the a-value. The g-value is a dimensionless measure of the strength of the magnetic field generated by the unpaired electron, which is being experimentally probed. Small changes in the chemical environment correspond to a shift in observed g-value relative to that of an unbound electron. This is analogous to chemical shift measured in NMR spectroscopy, and can be used as evidence of metal oxidation state and chemical composition.

In order to generate a sample of Tc(VI), solution of TcO_4^- in a 5 M $NaNO_3$/2 M NaOH matrix was subjected to a working electrode potential of -800 mV vs. a Ag/AgCl reference electrode. The solution in the vicinity of the working electrode surface was collected and analyzed to EPR spectroscopy experiments at 125 K. The Tc(VI) EPR spectrum in 5 M $NaNO_3$/2 M NaOH is show in Figure 5, black trace. Examination of

the spectrum shows evidence of an axial spin system (two of three axes in the atomic reference frame are degenerate) with an overlap of 10 resonances for $g_\parallel$ and 10 resonances for g perpendicular.   The sharp spectral response in combination with observed hyperfine splitting and approximate g-value is consistent with an electron spin ½ system in which spin density primarily resides on a ^{99}Tc nucleus in near cubic symmetry.   Due to the electrochemical potential at which the samples were generated[9] coupled with UV-vis spectroelectrochemical determination of electron transfer stoichiometry through Nernstian analysis, we feel confident that this EPR spectrum is due to a Tc(VI) species.
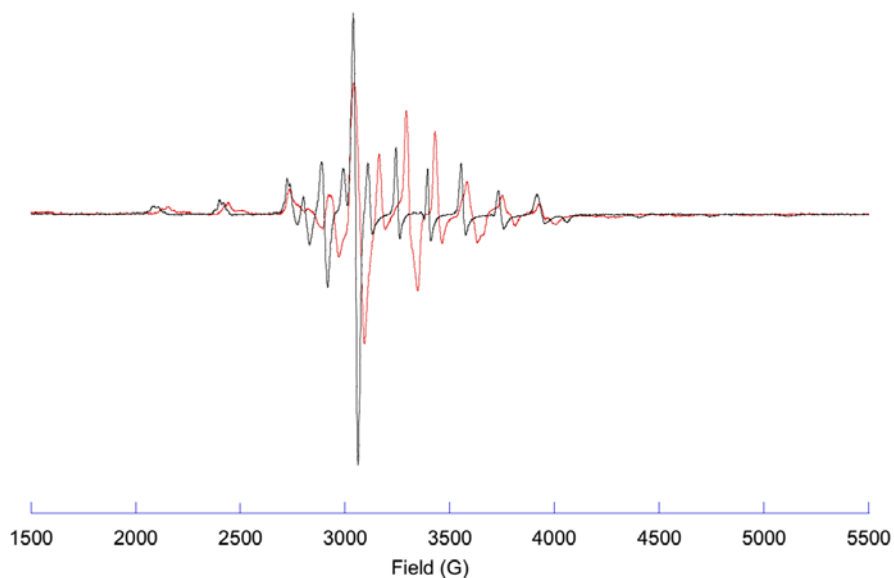

Figure 5.   Overlay of EPR spectra corresponding of electrochemically generated Tc(VI) species (black trace) and chemically synthesized Tc(VI) species in presence of gluconate (red trace).

To compare EPR spectra of the TcO_4^{2-} species and coordinated Tc(VI), a product obtained from the chemical reduction of TcO_4^- in the simulant solution in presence of CO at elevated temperature and pressure as described in our previous report [Levitskaia et al. 2014] was subjected to analysis by EPR spectroscopy (Figure 5, red trace). This spectrum shows many similarities to that of TcO_4^{2-} species, albeit considerable line broadening is present, which is attributable to the more complex chemical composition of the reaction mixture present. The frequency shift between these two spectra is due to the different chemical environment of Tc(VI) in the Tc(VI)•gluconate complex.   The chemically generated Tc(VI)•gluconate species has been found to be remarkably stable, with a single solution store at room temperature being capable of generating a spectral response in excess of a year after generation.

Tc(IV) species were generated electrochemically by holding the solution at -1,000 mV vs. a Ag/AgCl reference electrode, wherein the product was electrodeposited on the surface of the working electrode.   The working electrode was then subjected to EPR spectroscopy experiments.   Spectra due to Tc(IV) species are anticipated to have a more complex appearance and considerable line broadening over Tc(VI) species due to the increased total electron spin of the system to greater than ½.   As can be seen in Figure 6, line broadening due to the quartet ground state has caused line broadening to such a degree that specific hyperfine interactions are difficult to discern.
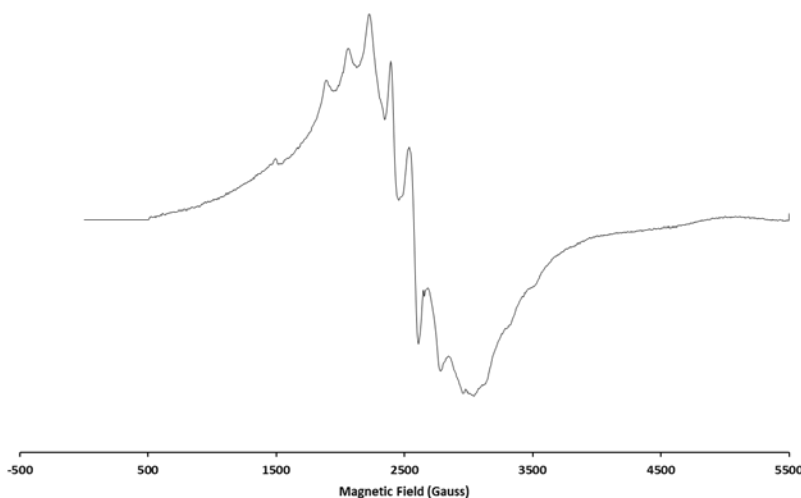

Figure 6.   EPR spectrum of solid Tc(IV) species generated electrochemically from TcO_4^-.

XAS of Tc species

X-ray absorption spectroscopy measures the photon energy required to excite an inner core electron to an unoccupied orbital of a specific element. This in turn gives a means to measure the oxidation state of the atom being probed, and through mathematical modeling can also give information on the atoms bonded to the probed element This technique has the advantage that a specific element can be examined within a complex mixture of elements, but has the disadvantage that the signal of all species of that element are averaged in the resulting spectra.

Figure 7 is the XANES spectrum that is the result of reacting $Tc(CO)_3(H_2O)_2(OH)$ with IDA in 1 M NaOH. The resulting solution was evaporated to dryness and the resulting solid analyzed. Fitting of the spectra, using parameters obtained from standard spectra previously recorded, shows that the sample is combination of Tc(VII), Tc(IV), and Tc(I). The fit however is not perfect, and this is attributed to the fact that $Tc(CO)_3(H_2O)_3$ is being used as the Tc(I) standard rather than an isolated $[Tc(CO)_3 \cdot IDA]^{n-}$ complex. This shows that future application of the technique will

allow for not only elucidation of the Tc oxidation state, but will also give credence to proposed structures of Tc(I) compounds.
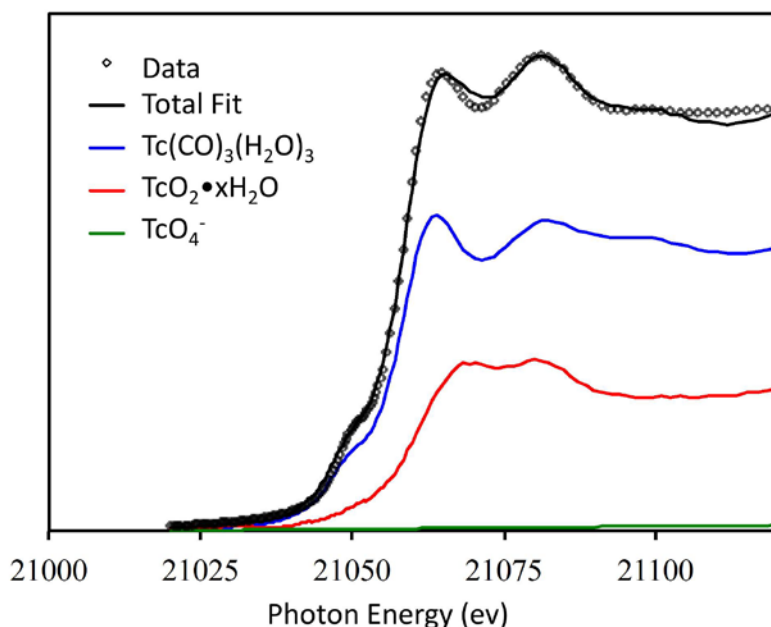

Figure 7. Tc K-edge XANES spectrum and fit of the pressurized reaction of $Tc(CO)_3(H_2O)_2(OH)$ with IDA.

Conclusions

Various $[Tc(CO)_3]^+$ species that are potentially contained in Hanford tank waste have been synthesized and characterized by IR spectroscopy, ^{99}Tc NMR spectroscopy, EPR spectroscopy, and X-ray absorption spectroscopy.   In conjunction with the aforementioned techniques, DFT computations are being benchmarked against the empirical results.   This allows us to simultaneously pursue two routes towards determination of tank waste composition: characterizing the spectral fingerprints of individual species likely present in tank waste for facile identification of tank waste composition, and developing the capability to computationally predict the chemical structure of spectral signatures not yet catalogued in our database. DFT calculations have been validated against our experimental ^{99}Tc NMR and IR spectra, and show exceptional agreement between theory and experiment with many NMR chemical shifts being reproduced within 40 ppm in a 10,000 ppm window.

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ACKNOWLEDGEMENTS