

**Properties of Tc(I) Tricarbonyl Derivatives Relevant to Hanford Tank Waste Supernatants
– 14352**

Tatiana Levitskaia *, Brian Rapko *, Syandev Chatterjee *, Mathew Edwards *, Sergei Sinkov
*, Reid Peterson *

* Pacific Northwest National Laboratory

ABSTRACT

In strongly alkaline environments typical for the Hanford tank waste, soluble Tc-99 exists as Tc(VII) in the form of pertechnetate (TcO_4^-) and non-pertechnetate species containing Tc in low oxidation states. It has recently been suggested that the dominant non-pertechnetate species are derived from Tc(I) tricarbonyl moiety $\text{Tc}(\text{CO})_3^+$. Chemical properties of $\text{Tc}(\text{CO})_3^+$ derivatives have been previously investigated in relationship to the radiopharmaceutical applications which utilize trace quantities of Tc-99m isotope under controlled pH of the buffered saline solution. In the tank waste supernatants, Tc-99 exists at high micro-molar concentrations in the highly alkaline media containing multitude of other constituents including several organic ligands, and chemical speciation and redox properties of $\text{Tc}(\text{CO})_3^+$ remain largely unknown. Our research program is aimed at gaining understanding of the speciation behavior of $\text{Tc}(\text{CO})_3^+$ complexes including such phenomena as hydrolysis, oligomerization, coordination of small organic ligands present in the tank supernatant, and solubility of the complex species. This paper describes our current results on $\text{Tc}(\text{CO})_3^+$ speciation behavior collected using various characterization techniques including Tc-99 NMR, UV-vis, and FTIR spectroscopies.

INTRODUCTION

Among radioactive constituents present in the Hanford tank waste technetium-99 (Tc) poses multitude of the distinctive problems associated with its radiotoxicity, unique and relatively poorly understood chemistry, and high mobility in the environment. Technetium is one of the most difficult contaminants to be addressed at the U.S. Department of Energy (DOE) Hanford Site because of its complex chemical behavior in tank waste and limited incorporation in mid- to high-temperature immobilization processes. Approximately 30,000 curies of Tc were produced at the Hanford Site. Of this, a small amount either has been released to cribs or has leaked from the single-shell tanks, while the balance remains in the Hanford tank wastes and must be dispositioned in approved waste forms.

The majority of the Tc at the Hanford Site is soluble Tc in the supernatant fraction of both single- and double-shell tanks. In strongly alkaline environments, Tc exists as pertechnetate (TcO_4^- ; Figure 1A) (oxidation state +7) and in the reduced forms (oxidation state < +7) collectively known as non-pertechnetate (non- TcO_4^-) species. Pertechnetate is a well-characterized anion that can be removed from LAW by an anion exchange and/or extraction method. However, previous attempts to remove Tc from the Hanford tank waste using the ion-exchange process specific to pertechnetate were only somewhat successful due to the presence of other, lower-valent forms of Tc in the waste supernatant. Identification of the structure, stability, and chemical properties of these non- TcO_4^- species will enable rational design of their separation methods.

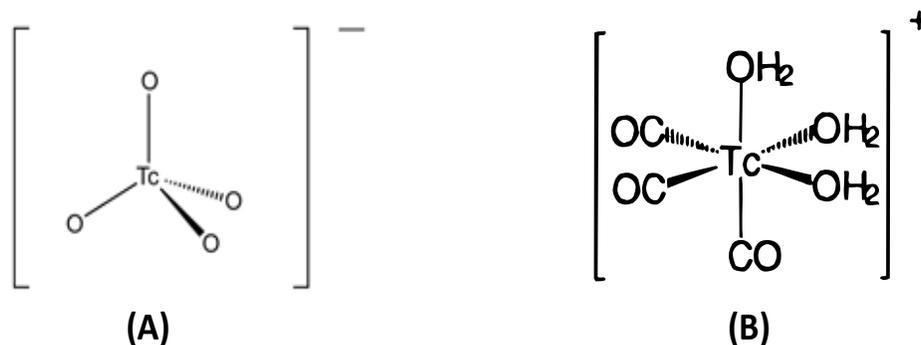


Figure 1. Structures of TcO_4^- (A) and $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ (B).

Reductive conditions generated by the water/nitrate radiolysis products, hydrogen, carbon monoxide, and/or presence of organic complexants promote formation of non- TcO_4^- species. Insoluble Tc in the form of hydrated technetium dioxide $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ (TcO_2 , oxidation state +4) is found in the solid sludge phases of the tank wastes. In presence of small organic complexants, it can solubilize in the liquid fraction of the waste forming such complexes as $\text{Tc}(\text{Gluconate})_2^{2-}$. However, reported Tc K-edge XANES spectra of the soluble species found in Tanks SY-101 and SY-103 could not be assigned to any known Tc(+4) complex, leading to their tentative identification as Tc(+1) in the form of the complex cationic species $[\text{Tc}(\text{CO})_3]^+$, shown in Figure 1B as the aqua solvate [1]. The chemical properties of these species have not been systematically investigated.

Currently there exists little information regarding chemical properties of the non- TcO_4^- species derived from the $\text{Tc}(\text{CO})_3^+$ coordination center, specifically under the conditions typical for the alkaline liquid fraction of the tank waste. The objective of this work is to investigate aspects of the nature and chemistry of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ cation with emphasis on its reactivity in the alkaline solutions. This report describes our to-date results, including synthesis of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ complex, its speciation behavior, and time stability in aerated solutions.

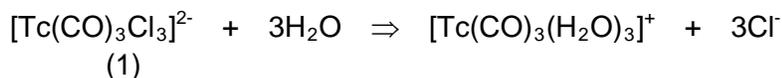
RESULTS

Synthesis of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$

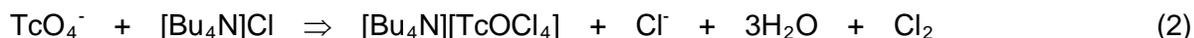
A key part of the conducted work involved the optimization of the synthetic procedure for obtaining analytical quantities of the *fac*- $\text{Tc}(\text{CO})_3^+$ as its triaqua complex. Our prior results [2] indicated that the Tc(+1) tricarbonyl species can be obtained by reducing aqueous TcO_4^- with sodium borohydride in the presence of CO under alkaline conditions and elevated temperature (50–80°C) in accord with the synthetic method reported elsewhere [3, 4]. One drawback of this method is that the reaction usually happens in the presence of a ligand, tartrate, which stabilizes the intermediate Tc(+5) compound, and it is difficult to separate this added ligand from the final product. Without stabilization of the intermediate Tc(+5) compound, the major reduction product is Tc(+4) in the form of $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ which precipitates from the aqueous reaction mixture.

To overcome the complications associated with the aqueous synthesis of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$, the

effort was directed toward the syntheses using an organic medium as the diluent. A convenient pathway is to initially obtain a stable $[\text{Tc}(\text{CO})_3\text{Cl}_3]^{2-}$ complex, which can be readily converted to the target $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ product by the simple exchange reaction 1.



One such approach involves a preparation of $[\text{Tc}(\text{CO})_3\text{Cl}_3]^{2-}$ precursor reported by Alberto et al. (1995) via two-step reduction of Tc(+7) to Tc(+1). In the first step, TcO_4^- is reduced to Tc(+5) in the form of stable compound $[\text{Bu}_4\text{N}][\text{TcOCl}_4]$ by the reaction 2 in 12 M HCl, which can be easily isolated [5]. This provides a more stable Tc(+5) source than the typically unstable Tc(+5) compounds formed *in situ*.



The second reduction step from Tc(+5) to Tc(+1) using diglyme solvent and borane tetrahydrofuran complex $\text{BH}_3\text{-THF}$ reductant in presence of CO at the elevated temperature is described by reaction 3:



Note that the boiling point of diglyme is 162°C , and so the reaction mixture can be safely heated to a higher temperature, with typically $110\text{-}120^\circ\text{C}$ required to achieve high product yield. This method resulted in the successful preparation of the $[\text{Et}_4\text{N}]_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ complex salt containing no TcO_4^- or $[\text{TcOCl}_4]^-$ starting materials. Infrared spectrum of the solid product showed the symmetric (1935 and 2030 cm^{-1}) and asymmetric (1765 and 1714 cm^{-1}) C=O stretching modes characteristic for the $\text{Tc}(\text{CO})_3^+$ moiety [6].

Solid $[\text{Et}_4\text{N}]_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ was then dissolved in water and converted to $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ product by the exchange reaction 1. The ^{99}Tc NMR spectrum of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ solution showed large band at -868 ppm, corresponding to $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ and a small band at -902 ppm, which corresponds to $[\text{Tc}(\text{CO})_4(\text{H}_2\text{O})_2]^+$ [7].

Speciation of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ as a function of pH

Initial scoping experiments were conducted by changing the matrix of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ solution from the acidic to highly alkaline, and characterizing the resulting solutions by ^{99}Tc -NMR spectroscopy. The obtained results are summarized in Table 1.

It was observed that $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ exists in acidic solutions and undergoes hydrolysis at a pH of about $6 - 7$. The first hydrolysis product, $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$, is prominent in the alkaline solutions in the wide range of the hydroxide concentration. At near neutral pH, it is in the equilibrium with the parent $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ complex and polynuclear tetrameric species $[\text{Tc}(\text{CO})_3(\text{OH})]_4$. The latter disappears as pH increases. At about 1.8M NaOH, formation of the second hydrolysis product, $[\text{Tc}(\text{CO})_3(\text{OH})_2(\text{H}_2\text{O})]^-$, was observed. This solution also contained an additional resonance appearing at -1482 ppm in the NMR spectrum. The resonance at -1482 has not been previously reported in the literature. However, based on its unusually narrow profile with half-width of approximately $25 - 40$ Hz, it is concluded that it corresponds to the species of high symmetry, most likely $[\text{Tc}(\text{CO})_3(\text{OH})_3]^{2-}$.

Table 1. ^{99}Tc NMR Characterization of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ solution.

Solution pH and/or matrix	^{99}Tc resonance		Assignment ^{a)}
	Chemical shift ppm	Half-width Hz	
pH = 3, 5	-865 – -868	60 – 70	$[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$
pH = 7	-865 – -868	70	$[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$
	-586	80	$[\text{Tc}(\text{CO})_3(\text{OH})]_4$
	-1056 – -1062	100	$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$
pH = 12, 14	-1056 – -1062	100	$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$
1M NaOH	-1056 – -1062	100	$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$
1.8M NaOH	-1065	100	$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$
	-1146	100	$[\text{Tc}(\text{CO})_3(\text{OH})_2(\text{H}_2\text{O})]$
	-1482	40	-
			$[\text{Tc}(\text{CO})_3(\text{OH})_3]^{2-}$?

^{a)} Assignments are based on the references 7, 8, and 9.

In order to systematically identify the first buffer zone of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$, the pH of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ solution was adjusted to ~1.5 by the addition of HCl and incrementally increased using NaOH. For each solution, the pH was measured and the ^{99}Tc -NMR spectrum was acquired. Since the different Tc(I) tricarbonyl species exhibit characteristically distinct chemical shifts, ^{99}Tc -NMR can be used as a convenient mode of Tc(+1)-tricarbonyl speciation analysis. The observed results are displayed in Figure 2 and are summarized below.

- pH range 1.15 – 6.6: Tc(+1) exists as $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$
- At pH of 4 and above, a small amount of pertechnetate appeared in the solution. Its concentration gradually increased, presumably due to oxidative decomposition of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ and/or its hydrolysis product.
- pH range 6.8 – 7.4: the polynuclear tetrameric species $[\text{Tc}(\text{CO})_3(\text{OH})]_4$, evidenced by the chemical shift at approximately -586 ppm, appeared in the NMR spectra. The concentration of $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ increases with increasing pH, as evident from the integral values. Interestingly, the tetrameric species were observed at this lower pH prior to the appearance of the first hydrolysis product $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ itself, which suggests the greater stability of the tetrameric species.
- pH range 7.4 – 7.8: the generation of $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$, evidenced by the observed chemical shift at about -1056 ppm is observed. In this pH region, the concentrations of $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ and $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ increase with pH while the concentration of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ decreases. Indeed, by pH 7.8 the concentration of $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ exceeds that of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$.

- pH 8.0: sudden increase of $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ and decrease of $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ concentration such that their concentrations become comparable is observed, suggesting conversion of the tetramer to $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$.
- pH = 12 – 14: in addition to pertechnetate, only $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ species were found in the spectrum, supporting the conclusion on the predominant existence of the tetramer species lies only in a limited, slightly alkaline, pH range.

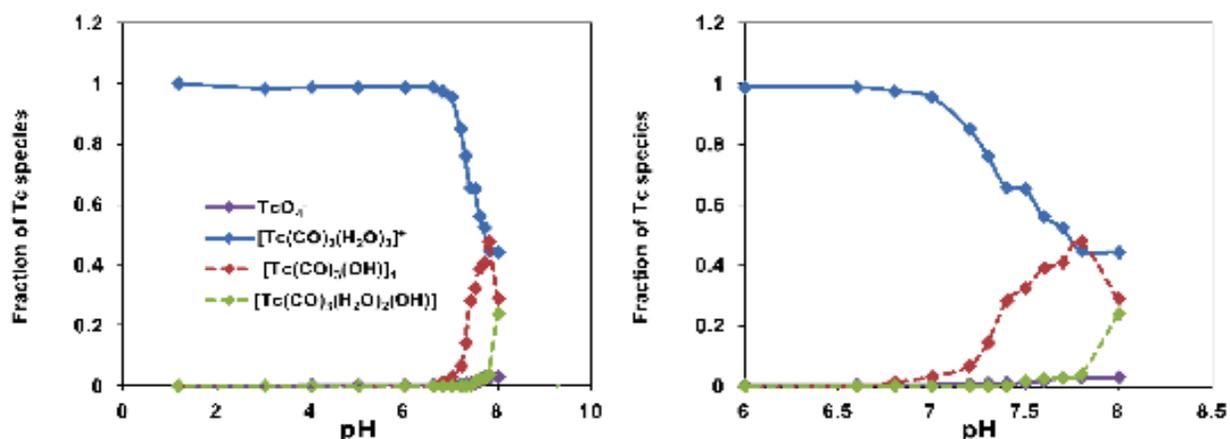


Figure 2. Speciation of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ as a function of pH observed by ^{99}Tc -NMR.

Based on the data reported in Figure 2, a pH speciation diagram containing fractions of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ and combined $\{[\text{Tc}(\text{CO})_3(\text{OH})]_4 + [\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]\}$ hydrolysis species was constructed (Figure 3). The first $\text{p}K_a$ value of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ species was estimated to be 7.75 based on the pH value at which concentrations of the parent $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ species and hydrolysis products were equal.

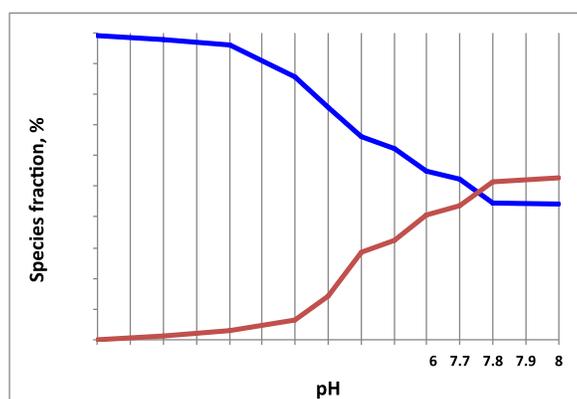


Figure 3. $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ speciation diagram obtained in the pH titration experiment. Blue trace: percent fraction of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ species. Red trace: percent fraction of the combined $\{[\text{Tc}(\text{CO})_3(\text{OH})]_4 + [\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]\}$ species. Fractions of the $[\text{Tc}(\text{CO})_4(\text{H}_2\text{O})_2]^+$ and TcO_4^- species are omitted for clarity.

Preparation and characterization of $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex

$[\text{Tc}(\text{CO})_3\text{Gluconate}]^-$ complex was prepared by the addition of the acidic $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ solution to the (0.2-0.5)M Potassium Gluconate/(1.5-2)M NaOH mixture in a 1:1 volume ratio. This method generated mixture of $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ and $[\text{Tc}(\text{CO})_3(\text{gluconate})]^-$ species in the resulting solution due to the competitive hydrolysis and complexation with gluconate reactions. Tc-99 NMR spectrum of the $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex demonstrated two bands at -1230 and -1247 ppm with the corresponding half-width of 270 and 300 Hz. It was observed that $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ converted to the $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex in about 6 hr with simultaneous oxidative formation of TcO_4^- (Figure 4).

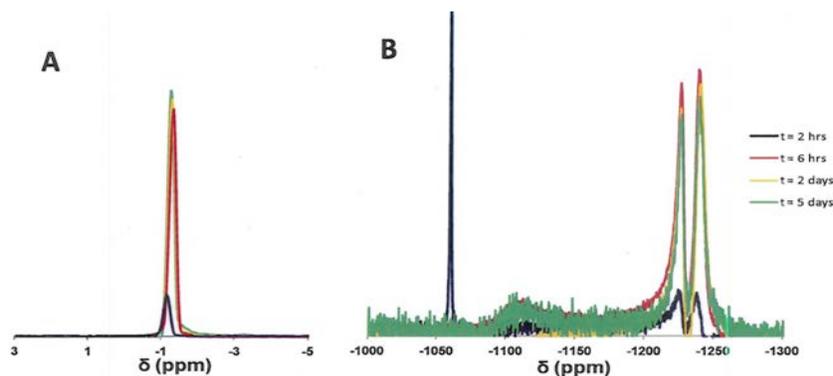


Figure 4. Monitoring the $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex by ^{99}Tc NMR: (A) increase of the TcO_4^- intensity with time (chemical shift ≈ -1.2 ppm); (B) initial conversion of $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ (chemical shift = -1056 ppm) to the $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex (chemical shift = -1230 and -1247 ppm).

IR and UV characterization of the $[\text{Tc}(\text{CO})_3]^+$ species

The solid $[\text{Et}_4\text{N}]_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ precursor to the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ aqueous product was characterized by IR spectroscopy (Figure 5, left pane). Characteristic TcCO bands at 1930 and 2030 cm^{-1} , attributed to the symmetric carbonyl stretch, and at 1721 and 1763 cm^{-1} , assigned to the asymmetric carbonyl stretch [6]. When $[\text{Et}_4\text{N}]_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ solid was dissolved in hot water, the IR spectrum of the resulting $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ aqueous solution showed the symmetric (1931 and 2035 cm^{-1}) and asymmetric (1750) C=O stretching modes almost identical to ones observed for the $[\text{Et}_4\text{N}]_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ solid precursor. The other asymmetric modes overlapped with O-H vibrational modes. The IR spectrum of the gluconate complex (Figure 5, right pane) exhibited both the symmetric carbonyl stretch vibrations at 1926 and 2030 cm^{-1} and the asymmetric carbonyl stretch vibrations at 1714 and 1765 cm^{-1} . Again, these bands are nearly identical to the corresponding carbonyl bands found in other $[\text{Tc}(\text{CO})_3]^+$ species. Based on these results it was concluded that while IR spectroscopy can be used for the confirmation of the presence of the $[\text{Tc}(\text{CO})_3]^+$ species, it is sensitive to the nature of the secondary ligand present in the complex.

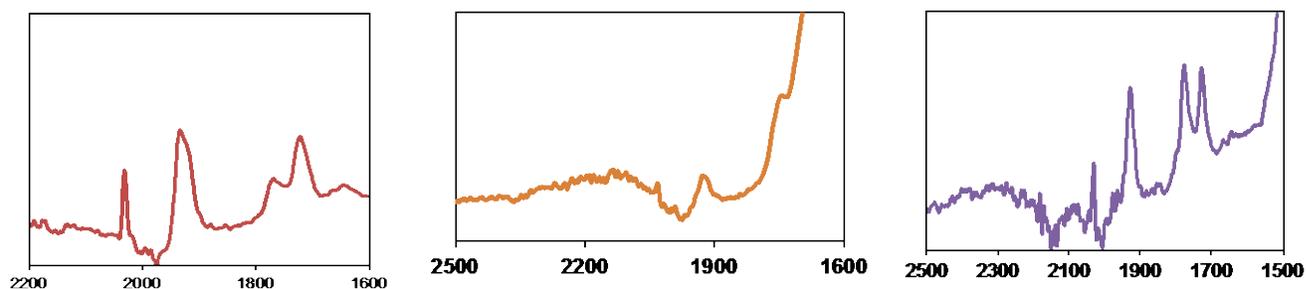


Figure 5. IR spectra of the aqueous solutions of the $[\text{Et}_4\text{N}]_2[\text{Tc}(\text{CO})_3\text{Cl}_3]$ solid (left pane), and $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ (middle pane), and $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ (right pane) complexes in the carbonyl region.

The most prominent $[\text{Tc}(\text{CO})_3]^+$ species, including $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ in the acidic 0.2 M HCl solution, $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ in the mildly alkaline solution, $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ at pH of 14, and $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex in 0.25 M potassium gluconate/0.7 M NaOH were characterized by UV spectroscopy (Figure 6). The $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ species exhibited a broad band at about 230 – 300 nm in agreement with an earlier report by Gorshkov et al., 2000 [7]. The UV profiles of the mono-hydroxo species were found to be similar, with the 280 nm band corresponding to $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ shifted to 290 nm for the tetramer compound. The $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex exhibits two strong bands at 246 and 277 nm.

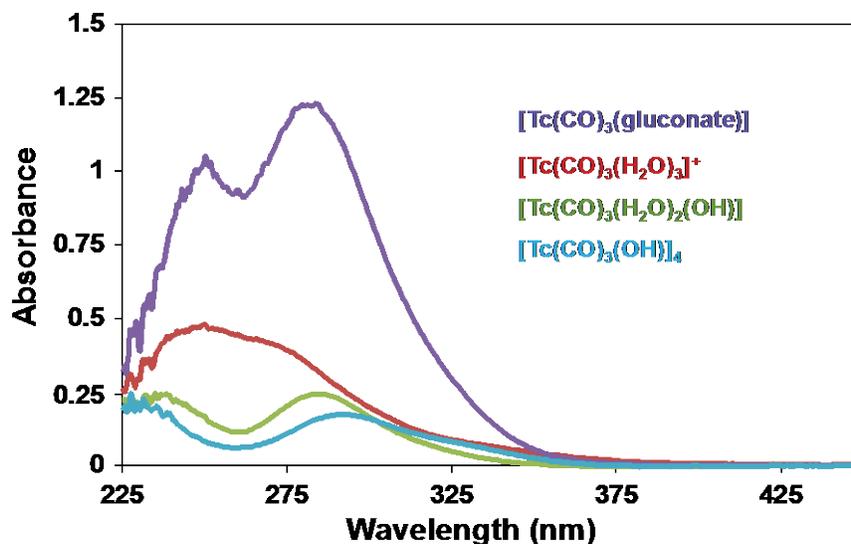


Figure 6. UV spectra of aqueous solutions of $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ in 0.25 M potassium gluconate/0.7 M NaOH, $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ in 0.2 M HCl, $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_2(\text{OH})]$ at pH = 14, and $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ at pH = 8. Spectral are not normalized to technetium concentration.

Time stability of the $[\text{Tc}(\text{CO})_3]^+$ species

Table 2 summarizes time conversion of the $[\text{Tc}(\text{CO})_3]^+$ species to TcO_4^- assessed by using ^{99}Tc NMR. All solutions were air-stored in the borosilicate glass containers without light protection.

Table 2. Aerial stability of the $[\text{Tc}(\text{CO})_3]^+$ species with time.

Time elapsed	Percent fraction		
$[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ in 0.2 M HCl			
	$[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$		TcO_4^-
3 hours	0.77		0.23
5 days	0.65		0.35
10 days	0.33		0.67
$[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_2(\text{OH})]$ at pH = 13.5			
	$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$		TcO_4^-
30 min	0.84		0.16
14 days	0.70		0.30
30 days	0.66		0.34
$[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ in 0.7M NaOH			
	$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_3]$	$[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$	TcO_4^-
2 hours	0.75	0.1	0.15
6 hours	0	0.5	0.5
14 days	0	0.38	0.62
30 days	0	0.35	0.65

As it evident from Table 2, gradual oxidation of all monitored $[\text{Tc}(\text{CO})_3]^+$ species to TcO_4^- with time was observed. Surprisingly, the stability of the mono-hydroxo derivative was found to be greater than that of the parent $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ species. During the preparation of the $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex in 0.7M NaOH matrix, the mixture contained $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ at a significantly larger concentration than the gluconate complex. Pertechnetate constituted about 15% of the total Tc in this solution. Six hours post solution preparation, $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ was completely converted to about equal amounts of $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ and TcO_4^- . The percent fraction of $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex gradually decreased with time due to the oxidation to Tc(+7) and formation of TcO_4^- . After 30 days, about 30% of $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ decomposed.

DISCUSSION/CONCLUSION

Extensive experimentation testing various synthetic procedures to best obtain analytical quantities of the $[\text{Tc}(\text{CO})_3]^+$ species indicated that it is not feasible to obtain $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ complex in the aqueous media under alkaline conditions because of the incomplete reduction of TcO_4^- to $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ rather than to the $[\text{Tc}(\text{CO})_3]^+$ species, and because of extensive product hydrolysis and its re-oxidation to TcO_4^- . We currently believe that the most viable option is to use $[\text{Tc}(\text{CO})_3\text{Cl}_3]^{2-}$ as a stable and reliable source of Tc(I) that can be easily converted to $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ as needed. It was observed that two-step reductive synthesis of $[\text{Tc}(\text{CO})_3\text{Cl}_3]^{2-}$ involving first reduction of TcO_4^- from Tc(+7) to Tc(+5) and isolation of $[\text{Bu}_4\text{N}][\text{TcOCl}_4]$ compound followed by its reduction to Tc(+1) in the form of $[\text{Tc}(\text{CO})_3\text{Cl}_3]^{2-}$ offers a better yield and more favorable product purification procedure than does the one-pot reduction of Tc(+7) to Tc(+1). It should be noted that during this two step reductive synthesis, any $[\text{Tc}(\text{CO})_4\text{Cl}_2]^-$ co-product formed will exchange two Cl- groups and mobile *trans*-CO group [10] for water, generating the same $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ species.

This work demonstrated ^{99}Tc NMR to be the powerful method of the identification of the $[\text{Tc}(\text{CO})_3]^+$ species as they exhibit distinctly different spectra that are sensitive to the nature of the coordinating ligands. Observed ^{99}Tc NMR spectral profiles are described in Table 3.

Table 3. Summary of $[\text{Tc}(\text{CO})_3]^+$ speciation by ^{99}Tc NMR spectroscopy.

Species	Chemical shift ppm	Average half-width Hz	Stable pH range
TcO_4^-	0	40	No dependence
$[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$	-869	80	pH = 1 – 7
$[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$	-1060	90	pH = 6 to about 2M NaOH
$[\text{Tc}(\text{CO})_3(\text{OH})_2(\text{H}_2\text{O})]^-$	-1146	100	$[\text{OH}^-] > 1.8\text{M}$
$[\text{Tc}(\text{CO})_3(\text{OH})_3]^{2-}$	-1482	25	$[\text{OH}^-] > 1.8\text{M}$
$[\text{Tc}(\text{CO})_3(\text{OH})]_4$	-585	250	5 – 8
$[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$	-1230, -1247	270, 300	$[\text{OH}^-] > 0.1\text{M}$

NMR analysis using ^{99}Tc nucleus revealed important information on the hydrolysis behavior of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ ion. It was observed that $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ ion can exist only in acidic aqueous solutions and undergoes extensive hydrolysis starting at pH of about 6.8. Based on the preliminary titration results the first $\text{p}K_a$ of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ complex was obtained to be 7.75. These results are in agreement with the literature reports. Groshkov et al., 2000, who studied $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ hydrolytic behavior by potentiometric titration, observed its initial hydrolysis at pH of 5.8 – 6. Alberto et al., 1999 estimated $\text{p}K_a$ of the $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ complex

to be about 8.5.

The mono-hydrolyzed $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ species readily undergo oligomerization and form poly-nuclear colloid $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ [7, 3]. In this work we observed preferential formation of $[\text{Tc}(\text{CO})_3(\text{OH})]_4$ tetramer in the pH range of 6.8 – 7.8. At higher pH, mono-hydroxo species persists in solution, and at pH of 13 and above no formation of tetramer was observed.

In agreement with the report by Gorshkov et al., 2000 [7] who postulated the second hydrolysis product $[\text{Tc}(\text{CO})_3(\text{OH})_2(\text{H}_2\text{O})]^-$ in the highly alkaline solution with $[\text{OH}^-] > 1.5 \text{ M}$, we have found this product in the solution at $[\text{OH}^-] = 1.8 \text{ M}$ in equilibrium with the first hydrolysis product. In addition, a third product was formed, which exhibited a ^{99}Tc resonance at -1482 ppm. Speculatively it can be suggested based on the very narrow profile of this band that it corresponds to the third hydrolysis species $[\text{Tc}(\text{CO})_3(\text{OH})_3]^{2-}$ and possesses a highly symmetrical structure. Additional studies are planned to identify the composition of these species.

The formation of the $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex was demonstrated in NaOH solution. It was observed that initially mixing of $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ and Potassium Gluconate/NaOH solutions generates both $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ and $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complexes, with the former quickly converting to the Tc(I) tricarbonyl gluconate complex and pertechnetate. Similar behavior was reported by Lukens et al., 2004 [1]. The Tc-99 NMR spectrum of $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ exhibited two bands at -1230 and -1247 ppm with corresponding half-widths of 270 and 300 Hz. This result is generally consistent with the previous report [1] postulating that $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ complex had a single broad ^{99}Tc resonance at -1239 ppm and half-width of 650 Hz. We concluded that the broad ^{99}Tc resonance observed in this previous study was in fact a unresolved doublet. The presence of two ^{99}Tc resonances suggests the existence of two non-equivalent gluconate species. We speculatively assign these species to $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ and a mixed hydroxo-gluconate complex.

Time monitoring studies have indicated a limited stability of all tested species. In 10 days, 53% $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ was converted to TcO_4^- , while after thirty days, 21% $[\text{Tc}(\text{CO})_3(\text{OH})(\text{H}_2\text{O})_2]$ and 30% $[\text{Tc}(\text{CO})_3(\text{gluconate})]^{2-}$ were re-oxidized to TcO_4^- ; presumably in all cases by the oxygen in air.

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