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Non-pertechnetate Technetium Sensor Research and Development

March 2017

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Executive Summary

Several significant uncertainties remain regarding the understanding and modeling of the fate and speciation of technicium-99 (99 Tc) in Hanford waste tanks, glass, and low-temperature waste forms. A significant (2% to 25%) fraction of the 99 Tc in the water-soluble portion of the tank waste may be present as one or more non-pertechnetate species that have not been identified and, to date, cannot be effectively separated from the wastes. The objective of this task is to provide a sensor specifically tuned to detect the Tc(I)-carbonyl species believed to constitute the main fraction of the non-pertechnetate form of technetium. Direct measurement of the Tc(I)-carbonyl species will help reduce the uncertainties in the modeling of the fate and speciation of 99 Tc in Hanford tanks and waste forms.

This report summarizes work performed in FY2016 sponsored by the Department of Energy's Office of Environmental Management that demonstrates the protocol for using fluorescent Tc(I)-tricarbonyl complex as a means to detect the non-pertechnetate species within tank waste solutions (assuming the non-pertechnetate species are Tc(I)-tricarbonyl complexes) (Gerdes and Schneider 2016). The protocol was optimized with respect to ligand concentration, solvent choice, reaction temperature and time, and was demonstrated for Tc-carbonyl measurement in solution and simulated waste matrices. This report also summarizes the synthesis and high-yield preparation of the low-valence technetium species, $[Tc(CO)_3(H_2O)_3]^+$, which will be used as the technetium standard material for the demonstration of the non-pertechnetate species in actual Hanford wastes. Initial planning assumed the availability of actual Hanford tank waste for use in this project, but this material was not made available in FY2016. This work culminated in the quantitation of Tc(I)-tricarbonyl within a Hanford waste simulant, using a standard addition method for measurement.

Key outcomes from FY2016

FY2016 saw the development of a protocol for the non-pertechnetate sensing based on technetium complexes. This accomplishment advances the sensor concept by the development and demonstration of the protocol for the quantitative detection of Tc(I)-tricarbonyl by fluorescence measurement. This work benefitted from the Re-based testing used in optimizing the pretreatment protocol in past years, which was adapted to Tc in the present work.

The key outcomes were:

- 1. Synthesis of the Tc starting material in high yield. The systematic synthesis and high-yield preparation of the Tc(I)-tricarbonyl complex, [Tc(CO)₃(H₂O)₃]⁺, has been optimized. This complex is a convenient technetium standard material for the non-pertechnetate species for use in simulated tank waste measurements. The synthesis and characterization of this complex, starting from a convenient source of technetium, ammonium pertechnetate, is described herein.
- 2. Characterization of Tc-carbonyl complexes. Several non-pertechnetate complexes of technetium prepared as starting materials and for use as sensor probes were characterized using various standard analytical methods. The analytical methods include ⁹⁹Tc nuclear magnetic resonance (NMR), x-ray crystallography, UV-vis absorption spectroscopy and fluorescence spectroscopy. The characterized complexes include Tc(CO)₃(phen)Br, Tc(CO)₃(bpy)Br, [Tc(CO)₃(H₂O)₃]⁺, [Tc(CO)₃(bpy)(H₂O)]⁺.

- 3. **Detection Limits of Tc-carbonyl complexes**. To achieve the desired detection limits, fluorescent molecules are needed because fluorescence-based detection methods are many orders of magnitude more sensitive than other optical techniques, such as absorbance. Concentration-dependent fluorescence measurements of the Tc(CO)₃(phen)Br and [Tc(CO)₃(bpy)(H₂O)]⁺ complexes were performed, as well as their rhenium analogues with detection limit in the nano-Molar range, well below the Tc(I) concentration anticipated in waste.
- 4. **Protocol for Tc-carbonyl sample pretreatment and measurement**. Details of the general protocol for pretreatment of waste samples containing non-pertechnetate were optimized in previous years' work. The general strategy for converting the $Tc(CO)_{3}^{+}$ species in tank waste into the fluorescent probe molecule for detection and quantitative measurement was successfully demonstrated on technetium samples.
- 5. Selective partitioning and in-situ pretreatment within ion-exchange polymer thin film. To increase selectivity and enhance detection limits, an ion-selective film was used in conjunction with the optical measurement of the Re(I)-carbonyl analogue to the Tc(I) complex. The detection of [Re(CO)₃(H₂O)₃]⁺ within the ion-selective film was performed by initially flowing a solution containing the Re(I) species over the selective film, followed by a pretreatment solution containing the sensitizing ligand (bpy).
- 6. Analytical protocol for quantification for non-pertechnetate. The quantitative measurement of Tctricarbonyl analyte was demonstrated within a waste simulant using the standard addition method for analysis. In this method, a series of waste simulant samples containing an initial amount of Tctricarbonyl was spiked with a known amount of $[Tc(CO)_3(H_2O)_3]^+$ standard solution in increasing concentrations. From the fluorescence measurements of these solutions, the original 'unknown' Tccarbonyl concentration was then determined. The results from the standard addition method compared well to the 'unknown' concentration, yielding a concentration of 1.48×10^{-5} M versus 1.91×10^{-5} M (29% difference) for the detection of Tc-tricarbonyl complex.

In summary, in FY2016 a demonstration of the sensor protocol for quantifying Tc(I)-tricarbonyl complex in simulated waste was completed.

This report fulfills the following FY2016 Milestone:

March 31, 2017: Demonstrate sensor concept by quantifying Tc(I)-tricarbonyl within actual Hanford tank waste.

Format: PNNL formal report.

Acronyms and Abbreviations

BASi	Bioanalytical Systems, Inc.
Вру	2,2' bipyridine
CV	cyclic voltammogram
Dcbbpy	4, 4'-dicarbomethoxy-2, 2' bipyridine
Dmbpy	4, 4'-dimethyl-2, 2' bipyridine
Dmebpy	4, 4'-dimethoxy-2, 2'-bipyridine
DMF	dimethyl formamide
DOE	U.S. Department of Energy
DOE-EM	U.S. Department of Energy Office of Environmental Management
Dtbbpy	4, 4'-di-tert-butyl-2, 2'-bipyridine
EMSP	Environmental Management Support Program
FY	fiscal year
ITO	indium tin oxide
IUPAC	International Union of Pure and Applied Chemistry
LOD	limit of detectionNMR nuclear magnetic resonance
OTE	optically transparent electrode
PEP	Pretreatment Engineering Platform
Phen	1,10-phenanthroline
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RPL	Radiochemical Processing Laboratory
SEC	spectroelectrochemical
UV-vis	ultraviolet-visible light spectrum
WRPS	Washington River Protection Solutions
WWFTP	WRPS Waste Form Testing Program

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1.0 Background

The fate of technetium-99 (⁹⁹Tc), a Hanford Nuclear Reservation tank waste constituent, is a major River Protection Project flowsheet uncertainty. The key driver to this flowsheet uncertainty is associated with the Integrated Disposal Facility Performance Assessment ⁹⁹Tc risk determinations. Previous attempts to remove ⁹⁹Tc from the Hanford tank waste using an ion-exchange process specific to pertechnetate (TcO₄⁻, shown in Figure 1.1) were only partially successful due to the presence of other valence and complexed forms of ⁹⁹Tc in some of the tank waste supernatants. In fiscal year 2014 (FY2014), we reviewed prior work regarding the nature and extent of this non-pertechnetate, alkaline-soluble technetium in the Hanford waste tanks (Serne et al. 2014; Rapko et al. 2013). As noted in the 2014 report, prior work had presented evidence of a Tc(I)-tricarbonyl-type compound as a non-pertechnetate species present in tank waste, the parent Tc(I)-tricarbonyl-tris-aquo compound [(Tc(CO)₃(H₂O)₃]⁺, Tc(I)-tricarbonyl as shown in Figure 1.1. Under tank waste conditions, the Tc(I)-tricarbonyl species will not be the tris-aquo complex, and is expected to react with constituents within the waste by forming the [Tc(CO)₃(O)₃]ⁿ⁻ complex, wherein (O)₃ represents a multidentate ligand binding to the metal center, such as from any gluconate or citrate present within the waste. In this report, the generalized formula for the [*fac*-Tc(CO)₃(O)₃]ⁿ⁻ complex will be referred to as the Tc(I)-carbonyl species and/or written as Tc(CO)₃⁺.

Several significant uncertainties remain regarding the understanding and modeling of the fate and speciation of 99 Tc in Hanford waste tanks, glass, and low-temperature waste forms. A significant (2% to 60%) fraction of the 99 Tc in the water-soluble portion of the tank waste may be present as a non-pertechnetate species that has not been identified and cannot currently be effectively separated from the wastes. The objective of this task is to develop a sensor specifically tuned to detect the Tc(I)-carbonyl species believed to constitute the main fraction of the non-pertechnetate form of technetium. Direct measurement of the Tc(I)-carbonyl species will help reduce the uncertainties in the modeling of the fate and speciation of 99 Tc in Hanford tanks and waste forms.

This report describes the research undertaken to further the development of a sensor designed specifically to quantitatively measure the non-pertechnetate species within Hanford tank wastes. The goal of this work was to design a sensor specific to the primary compound of interest, the Tc(I)-tricarbonyl compound.

The work scope covered in this report was supported by the U.S. Department of Energy's Office of Environmental Management (DOE-EM). This work was performed under Contract DE-AC05-76RL01830, in accordance with *Test Plan TP-EMSP-0020, Rev. 0.0 "Technetium Management – Hanford Site (FY 2016)"*. Work was performed at Pacific Northwest National Laboratory (PNNL) under *Test Instruction TI-EMSP-0022 "FY 2016 Task 2. Non-Pertechnetate Sensor Research and Development"*, and at the University of Cincinnati under *Test Instruction TI-EMSP-0024 "FY 2016 Task 2. Non-Pertechnetate Sensor Research and Development"*, and at the University of Cincinnati under *Test Instruction TI-EMSP-0024 "FY 2016 Task 2. Non-Pertechnetate Sensor Research and Development, University of Cincinnati"*. The work described in this report was assigned the technology level "Applied Research." All staff members contributing to the work received proper technical and quality assurance training prior to performing work under the aforementioned Test Plans and Test Instructions.



Figure 1.1. Structures of Pertechnetate (TcO_4^-) , and Technetium(I)-tricarbonyl-tris-aquo Cation, $[(Tc(CO)_3(H_2O)_3]^+$

1.1 Quality Assurance

This work was conducted as part of PNNL Project 54042 under the Technetium Management Program, with funding from the U.S. Department of Energy Office of Environmental Management.

All research and development (R&D) work at PNNL is performed in accordance with PNNL's laboratory-level Quality Management Program, which is based on a graded application of NOA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. In addition to the PNNL-wide quality assurance (OA) controls, the OA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for the work. The WWFTP QA program consists of the WWFTP Ouality Assurance Plan (OA-WWFTP-001) and associated OA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work. The WWFTP OA program is based on the requirements of NOA-1-2008, *Quality Assurance Requirements for Nuclear* Facility Applications, and NQA-1a-2009, Addenda to ASME NQA-1-2008 Quality Assurance Requirements for Nuclear Facility Applications, graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2, "Guidance on Graded Application of Quality Assurance (OA) for Nuclear-Related Research and Development." Preparation of this report and performance of the associated experimental work were assigned the technology level "Applied Research" and were conducted in accordance with procedure QA-NSLW-1102, Scientific Investigation for Applied Research. All staff members contributing to the work have technical expertise in the subject matter and received OA training prior to performing quality-affecting work. The "Applied Research" technology level provides adequate controls to ensure that the activities were performed correctly. Use of both the PNNL-wide and WWFTP OA controls ensured that all client QA expectations were addressed in performing the work.

2.0 Introduction

The form of the non-pertechnetate technetium complex in some Hanford tank supernatants has been documented to be the $[Tc(CO)_3(O)_3]^{n-}$ (where $(O)_3$ is a multidentate ligand, such as glycolate, citrate, or oxalate) (Lukens et al. 2004; Serne et al. 2014; Rapko 2014). While the $[Tc(CO)_3(O)_3]^{n-}$ and related complexes are not readily detected optically, we proposed to convert the $Tc(CO)_3^+$ species into a fluorescent complex that would be detectable at the concentrations found in tank waste.

The direct reaction of $[Tc(CO)_3(O)_3]^{n-}$ with bidentate and tridentate ligands has been established under conditions (neutral and basic pH, at room temperature, saline) suitable for radiotherapeutic applications (Alberto 2005; Alberto et al. 2001; Alberto et al. 1998). By changing the nature of the entering ligand groups to bipyridine (bpy), phenanthroline (phen), or functionalized bpy and phen ligands, we propose to convert the $[Tc(CO)_3(O)_3]^{n-}$ complex into optically emissive complexes with the formula $[Tc(L-L)(CO)_3(H_2O)]^+$ according to the scheme shown below. The list of entering bidentate ligands (L-L) includes dtbbpy¹, dmbpy², dmebpy³, bpy, dcbbpy⁴, and phen.

$$[Tc(CO)_{3}(H_{2}O)_{3}]^{+} \xrightarrow{L \cap L} [Tc(CO)_{3}(H_{2}O)(L \cap L)]^{+}$$
⁽¹⁾

A range of Re(I) complexes, based on the Re(I)-tricarbonyl core, have previously been shown to be emissive (Richter et al. 1996), and are used in our work as a non-radioactive surrogate for the Tc(I)tricarbonyl system. Based on our previous years' work under this program, we have prepared and demonstrated that $[Tc(L-L)(CO)_3(H_2O)]^+$, where L-L is the bidentate ligands, bpy and phen, form fluorescent complexes. The emission quantum yields were sufficiently high to allow for the detection limits in the nano-Molar range to be measured, indicating the suitability of these compounds for the sensitive detection of the Tc(I)-tricarbonyl form of technetium.

In our past work under separate funding sources, and in collaboration with the University of Cincinnati, we developed and demonstrated a selective optical sensor for the luminescent Tc(II) complex $[Tc(dmpe)_3]^{2+}$, composed of a selective polymer film that concentrates the technetium complex within the spectroelectrochemical compartment of the sensor. After the technetium complex is absorbed into the polymer film, the cell is activated electrochemically and the $[Tc(dmpe)_3]^{2+}$ complex is modulated between the Tc(I) (non-emissive) and the Tc(II) (emissive) redox states. The recorded luminescent emission was demonstrated to be proportional to technetium concentration, linear over five to six orders of magnitude in concentration, and with a detection limit at the nano-Molar level (Chatterjee et al. 2011).

This task seeks to convert the non-emissive $[Tc(CO)_3(O)_3]^{n-}$ complexes into the emissive $[Tc(L-L) (CO)_3(H_2O)]^+$ complex, followed by the fluorescence mode detection of these new species. Further selectivity can be obtained by the separation and pre-concentration within an ion-exchange

¹ 4, 4'-di-tert-butyl-2, 2'-bipyridine

² 4, 4'-dimethyl-2, 2' bipyridine

³ 4, 4'-dimethoxy-2, 2'-bipyridine

⁴ 4, 4'-dicarbomethoxy-2, 2' bipyridine

polymer film. This report details the experimental work performed during FY2016 to accomplish these goals.

2.1 Concept for Detection of Non-pertechnetate Form of Technetium

The general strategy for the selective detection of $Tc(CO)_{3}^{+}$ in solution is the conversion of the complex into a fluorescent form, followed by the optical measurement of the emission signal. To achieve the desired detection limits, fluorescent molecules are needed that can reasonably be detected at nano-Molar concentrations. To achieve added selectivity, reversible electrochemistry can be used. The introduction of electrochemistry to the process will allow 1) change in the technetium oxidation state to create/quench fluorescence; 2) modulated electrochemical-induced fluorescence (on/off) signal; and 3) modulation (change) of the signal of technetium to distinguish it from the constant fluorescence arising from interfering species.

The general steps for demonstrating the fluorescence-based concept for detection of the Tc(I)-tricarbonyl species are shown in Figure 2.1. They include adding the non-emissive $[Tc(CO)_3(H_2O)_3]^+$ complex to a tank waste simulant with the formation of the $[Tc(CO)_3(O)_3]^{n-}$ complex, wherein (O)₃ represents a multidentate ligand binding to the metal center, such as from any gluconate or citrate in the waste. The final step is the addition of the pretreatment solution, which includes the incoming bidentate ligand (such as bpy or phen) with the concomitant formation of the fluorescent probe complex, $[Tc(CO)_3(L-L)(H_2O)]^+$.



Figure 2.1. Concept Protocol for the Detection of the Tc(I)-tricarbonyl Form of Technetium and its Nonradioactive Rhenium-based Surrogate

If greater sensitivity and selectivity are required, an additional step can be introduced. This is shown schematically in Figure 2.2. Once the probe complex, $[Tc(CO)_3(L-L)(H_2O)]^+$, is formed, it can partition into a selective ion-exchange film attached to the sensor platform. Once in the membrane, the complex can be monitored through both electrochemistry and fluorescence detection.



Figure 2.2. Concept for the Selective Partitioning and Electromodulation Detection of Tc(CO)₃⁺

3.0 Experimental

The methodology for the detection of a technetium complex is based on the formation of a fluorescent Tc(I) complex with the general formula $[Tc(L-L)(CO)_3(H_2O)]^+$ from the non-emissive $[Tc(CO)_3(O)_3]^{n-}$ complex. Re(I) analogues to the technetium system were used in the initial testing for the sensor concept. The Tc-carbonyl and Re-carbonyl complexes targeted are also electroactive, which allows for the application of a spectroelectrochemical technique as a method of detection. This section describes the synthesis of the technetium and rhenium compounds, as well as a summary of the analytical instrumentation used to support materials characterization.

3.1 Preparation of Complexes

The general strategy for the synthesis of technetium-tricarbonyl complexes of the general formula $Tc(L-L)(CO)_3Br$ and $[Tc(L-L)(CO)_3(H_2O)]^+$ is shown in Figure 3.1. As depicted, a convenient starting material is $Tc_2(CO)_{10}$, which can be reacted with elemental bromine to form the Tc(I) complex $Tc(CO)_5Br$. Reaction of $Tc(CO)_5Br$ with a bidentate sensitizing ligand (such as bpy) forms $Tc(L-L)(CO)_3Br$, shown in the top right of Figure 3.1. The complex $Tc(CO)_5Br$ can also be reacted with water to form the bromide salt of the Tc(I)-aquo complex, $[Tc(CO)_3(H_2O)_3]^+$. This Tc(I)-tricarbonyl compound can in turn be reacted with a bidentate ligand to form the final desired product $[Tc(L-L)(CO)_3(H_2O)]^+$, shown in the bottom right of Figure 3.1. In general, there can be a variety of entering sensitizing ligands, as shown in Figure 3.2. In the past, Re(I)-carbonyl analogues were used to model their technetium analogues. The following paragraphs give details of the preparation of each of the complexes used in this study.



Figure 3.1. General Synthesis for [Tc(L-L)(CO)₃(H₂O)]⁺



Figure 3.2. Ligands Used for the Preparation of $[Tc(L-L)(CO)_3(H_2O)]^+$ and $Tc(L-L)(CO)_3Br$ Complexes: 2,2'-bipyridine (bpy); and 1,10'-phenanthroline (phen)

Chemicals and Materials. Table 3-1 provides the names, purities, and suppliers of the chemicals and solvents used in this work. The optically transparent electrodes were 10 mm \times 40 mm \times 1.1 mm indium tin oxide (ITO) coated on glass (20 Ω /sq., 150-nm ITO layer on Corning 1737F glass substrate; Thin Film Devices, Anaheim, CA). Aqueous solutions were prepared with deionized water (D2798 Nanopure system; Barnstead, Boston, MA).

Chemical	Supplier
 dirhenium decacarbonyl (98%) 	
■ 2,2'-bipyridyl (≥99%)	
• $1,10'$ -phenanthroline ($\geq 99\%$)	
■ bromine (≥95%)	
■ dichloromethane (anhydrous, ≥99.8%)	
• diethyl ether (anhydrous, $\geq 99.0\%$)	Sigma Aldrich
 acetonitrile (anhydrous, 99.8%) 	Sigilia Aldrich
■ 2-proponal (≥95%)	
• toluene (anhydrous, 99.8%)	
• <i>N</i> , <i>N</i> -dimethylformamide (anhydrous, 99.8%)	
• Nafion (5 wt.% in lower aliphatic alcohols and water	
15 to 20% water)	
rhenium pentacarbonyl bromide (98%)	Strem Chemicals
methanol (\geq 99.8%) acetic acid, glacial (\geq 99.7%)	Fisher
carbon tetrachloride (≥99%)	ACROS Organics

Table 3-1. Chemicals Used Without Further Purification and Their Suppliers

Simulant preparation: Hanford waste supernatant simulant was prepared as described in Levitskaia et al (2014) Levitskaia Tatiana et al. (2014).

Re(**CO**)₅**Br.** Approximately 7 mmol Re₂(CO)₁₀ was added to a round-bottomed flask, to which 50 mL of dichloromethane was added. The solution was stirred to ensure all starting material dissolved. In a separate beaker, 2 - 3 mL of Br₂ was dissolved in approximately 20 mL of dichloromethane. The Br₂ solution was added, dropwise, to the flask containing Re₂(CO)₁₀ until the light brown/orange color persisted. The solution was stirred for 5 minutes to ensure the color remained. The solvent was then removed using rotary evaporation. The product remaining was a fine, white powder, usable as-is without further purification. A similar method was mentioned in previous articles (Lazarova et al. 2004; Salignac et al. 2003; He et al. 2005).

 $[\mathbf{Re}(\mathbf{CO})_3(\mathbf{H}_2\mathbf{O})_3]\mathbf{Br}$. Approximately 1.2 mmol $\mathbf{Re}(\mathbf{CO})_5\mathbf{Br}$ was added to a round-bottomed flask, to which 20 mL of DI water was added. The starting material did not dissolve in room-temperature water. The solution refluxed for at least 24 hours at 100 °C. Periodically, the condenser was rinsed as the starting material deposited at the bottom of the condenser. Upon completion of the reflux, the solvent was removed using rotary evaporation. The product remaining was a white solid, which was stored for use (Lazarova et al. 2004; Salignac et al. 2003; He et al. 2005).

General Re(L-L)(CO)₃**Br synthesis.** Approximately 1 mmol Re(CO)₅Br was added to a round-bottomed flask, to which 40 mL of toluene was added. The temperature controller was turned on to begin heating the solution. More solvent was added, as necessary, to ensure all of the Re(CO)₅Br was dissolved before ligand addition. Approximately 1.1 mmol of the ligand (bpy or phen) was added to the flask. A color change was observed immediately upon ligand addition. The solution refluxed for approximately 5 hours at 70 °C. The solution was then allowed to cool back to room temperature. The sample was filtered and rinsed with diethyl ether. The product was dried and stored for use.

General [Re(L-L)(CO)₃(H₂O)]Br Synthesis. Approximately 1 mmol [Re(CO)₃(H₂O)₃]Br was added to a round-bottomed flask, to which 40 mL of methanol was added. The temperature controller was turned on to begin heating the solution. More solvent was added, as necessary, to ensure all of the $[Re(CO)_3(H_2O)_3]Br$ was dissolved before the ligand addition. Approximately 1.1 mmol of the ligand (bpy or phen) was added to the flask. A color change was observed immediately upon ligand addition. The solution refluxed for approximately 5 hours at 65 °C. The solution was then allowed to cool back to room temperature. If no precipitate was observed, the solvent was removed using rotary evaporation. If the precipitate was observed, the sample was filtered and rinsed with diethyl ether. The product was dried and stored for use.

 $Tc_2(CO)_{10}$. The technetium decacarbonyl was made by reaction of ammonium pertechnetate and carbon monoxide in a Parr bomb. Approximately 0.4 grams (2.2 mmol) of ammonium pertechnetate was suspended in 30 mL of toluene in a glass vessel (70 mL volume) inside a Parr reaction bomb. The bomb was sealed, sparged with CO for 20 minutes, then pressurized to about 1300 psi at room temperature. The temperature was then raised to 200 °C and left for 40 hours.

The solution was centrifuged to remove the toluene-insoluble material, then evaporated to several milliLiters total volume, which led to the formation of crystals of $Tc_2(CO)_{10}$. Brown material remained dissolved in the toluene. The crystallized $Tc_2(CO)_{10}$ was isolated by decanting off the brown solution and then was recrystallized by placing it in several milliLiters of clean toluene, warming the toluene to 60 to 80 °C to dissolve the crystals, then cooling it in an ice bath. Nearly colorless crystals were obtained.

The recrystallized $Tc_2(CO)_{10}$ was further purified by sublimation. The slightly tan $Tc_2(CO)_{10}$ was dissolved in toluene and then evaporated into the bottom of a glass sublimation apparatus. The air was pumped out to the extent possible (the ultimate pressure of the oil-less pump is 2 to 3 Torr), dry ice and ethanol were placed in the cold finger, and the bottom of the sublimator was warmed in a water bath at 90 °C. A white frost of $Tc_2(CO)_{10}$ slowly formed on the cold finger over a period of many hours. The sublimed product was rinsed off the cold finger with toluene and the toluene evaporated. The sublimed product now was pale yellow. The yellow color was removed by one final recrystallization from diethyl ether. The solid was dissolved in a minimum of diethyl ether at room temperature and then reduced in volume by evaporation over a stream of nitrogen gas to a minimal volume of liquid. The liquid was then removed by transfer pipette and the solids air dried. The final product was colorless.

 $Tc(CO)_5Br$. To make $Tc(CO)_5Br$, 0.1167 g of $Tc_2(CO)_{10}$ (0.244 mmol) was dissolved in 60 mL of dichloromethane; then 0.7 mL (13.7 mmol) of bromine dissolved in dichloromethane was added. This mixture stood overnight, covered to keep air out. The next morning, a precipitate (presumably $Tc(CO)_5Br$) had formed, leaving a clear orange solution (the color of bromine). The solution was decanted from the precipitate and evaporated under flowing dry nitrogen at room temperature, forming a dark orange material. The precipitate, which was pale orange, was recrystallized from dichloromethane to attempt to improve its purity. The final product was still pale orange, perhaps still contaminated with a small amount of the orange side product. The pale orange product was then recrystallized from toluene, which worked much better than dichloromethane. Subsequent preparations used fresh bromine, which yielded a $Tc(CO)_5Br$ product free from this orange impurity. No further effort was expended to identify the orange impurity. The final product was pale grey and the orange residue was a dark non-crystalline mass.

 $Tc(phen)(CO)_3Br. Tc(CO)_3(phen)Br was prepared by reacting Tc(CO)_5Br with 1,10'-phenanthroline. The pale grey Tc(CO)_5Br (39 mg) (0.123 mmol) was dissolved in 10 mL ethanol, then added to an equimolar amount of phen dissolved in 10 mL ethanol. No apparent reaction occurred initially, but the solution turned pale yellow after about 10 minutes. The ethanol was evaporated at room temperature. The Tc(CO)_3(phen)Br was dried to a yellow free-flowing powder with a few orange crystalline solids. The product was redissolved in dimethylforamide and stored in dimethylformamide for future use.$

 $Tc(bpy)(CO)_3Br. Tc(CO)_3(bpy)Br$ was prepared by reacting $Tc(CO)_5Br$ with 2,2'-bipyridyl. The pale grey $Tc(CO)_5Br$ (44 mg) (0.139 mmol) was dissolved in 10 mL acetonitrile, to which an equimolar amount of bpy was added. No apparent reaction occurred immediately, but the solution turned faint orange after about 30 minutes. The acetonitrile was evaporated at room temperature. The $Tc(CO)_3(bpy)Br$ dried to a yellow-crystalline solid. The product was stored in acetonitrile for future use.

 $[Tc(CO)_3(H_2O)_3]Br. [Tc(CO)_3(H_2O)_3]Br was prepared by the reaction of Tc(CO)_5Br with water at room temperature. Approximately 10 mL HBr (1 µmol, pH 4) was added to 50 mg of Tc(CO)_5Br (0.157 mmol) in a 20 mL boroaluminosilicate vial, and allowed to react for 5 hours at room temperature, resulting in a colorless solution containing the <math>[Tc(CO)_3(H_2O)_3]^+$ product. The product was stored in a pH-4 HBr solution for later use.

 $[Tc(CO)_3(bpy)(H_2O)]Br. [Tc(CO)_3(bpy)(H_2O)]Br was prepared by the reaction of <math>[Tc(CO)_3(H_2O)_3]Br$ (0.157 mmol) with a molar equivalent amount of 2,2'-bipyridyl (bpy) in an aqueous solution containing HBr (1 µmol, pH 4). The mixture was allowed to react overnight at room temperature. The yellow product adhered to the edges of the reaction vessel, as seen in Figure 3.3. The colorless solution was removed from the reaction vessel and the yellow product was dissolved and recrystallized from acetonitrile.



Figure 3.3. Photograph of [Tc(CO)₃(bpy)(H₂O)]Br Suspension in Aqueous Solution Containing HBr

3.2 Instrumentation

Solution Absorption and Emission Spectroscopy. UV-visible absorbance measurements were completed using an Ocean Optics DH-MINI- deuterium tungsten halogen light source and a FlameTM spectrometer with OceanView software in 1 cm cuvettes. Emission spectra were recorded using a Horiba Jobin Yvon FluoroMax Plus-C spectrofluorometer equipped with a 150 W ozone-free xenon lamp, single Czerny Turner excitation spectrometer blazed at 330 nm, and a single Czerny Turner emission spectrometer blazed at 500 nm. Emission spectra were corrected for instrumental response. The emission measurements of rhenium complexes prepared in situ were collected using an InSpectrum 150 spectrometer-CCD, using SpectraSense data-acquisition software. A 404-nm laser source was used for excitation. Signal integration times were typically 999 msec using a 2-mm slit width using a 600-gr/mm grating blazed at 500 nm.

Spectroelectrochemistry. Fluorescence-based spectroelectrochemical (SEC) experiments were performed using a thin-film flow cell. The body of the flow cell is made of black Delrin with a 4-mm \times 20 mm oval well to accommodate ~0.4 mL solution. The cell is attached to a 4-in. \times 4-in. base to allow for convenient mounting. The top of the cell has three holes, two for the attachment of Teflon tubing for a solution inlet and outlet, and one for the platinum wire (auxiliary electrode), affixed with epoxy. The platinum wire is protected on the outside of the cell with plastic tubing and exposed at the end to allow for contact with the potentiostat leads. The side of the cell body has a hole for the fixture of the Ag/AgCl reference electrode. An ITO glass slide, which serves at the optically transparent working electrode, was placed at the well opening with a 51-µm-thick Teflon spacer. Electrical contact to the ITO slide was provided by linear spring finger arrays (Laird Technologies), mounted on each side of the cell body. A Schott SF6 coupling prism (Karl Lambrecht) was mounted on one end of the ITO slide using high-viscosity refractive index standard fluid (Cargille, n = 1.51) to span the prism/ITO slide gap. Two Delrin pieces, one with an oval hole (0.25 in. \times 0.75 in.) and the other with a circular hole (i.d. = 0.5 in),

were used to fasten the ITO slide onto the flow cell and hold the prism in place. The optical components include a 405-nm laser from Power Technology Incorporated directed through an optical fiber. The light is focused by a microscope lens and attenuated through the coupling prism into the OTE. A collection fiber is positioned at the backside of the OTE, directly over a reflection point. The signal is collected with an InSpectrum 150 spectrometer-CCD using SpectraSense data-acquisition software. Signal integration times were typically 999 ms using a 2-mm slit width for a 600-grooves-per-mm grating blazed at 500 nm. The electrochemical components included 1a Princeton Applied Research 237A (EG&G) potentiostat with Corrware software v3.3b from Scribner Associates. (Andria et al. 2009; Kaval et al. 2003)

Technetium-99 NMR spectroscopy. The NMR sample solutions were placed in capped polytetrafluoroethylene (PTFE)/fluorinated ethylene propylene (FEO) copolymer sleeves (Wilmad), which were inserted into 5- or 10-mm glass NMR tubes to provide secondary containment for the radioactive liquid. Technetium-99 NMR data were routinely collected at 67.656 MHz on a Tecmag Discovery spectrometer equipped with a 10-mm broadband Nalorac probe as described elsewhere (Cho et al. 2004) at the RPL at PNNL. An aqueous solution of 10-mM TcO₄⁻ was used as a ⁹⁹Tc chemical shift reference, and all chemical shift data are quoted relative to TcO₄⁻ (Franklin et al.).

X-ray data collection. Crystal structure and x-ray data were collected using a Bruker D8 VENTURE diffractometer by MoK α radiation. The initial unit cell was determined using the APEX2 program package. Data integration was performed using SAINT, and SADABS was used to determine the numerical absorption correction. Subsequent data reduction, structure solution, and refinement were carried out using the SHELXTL program. The structure was solved by direct methods and defined on F² by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. The dimensions of the Tc(CO)₃(bpy)Br crystal were 0.235 mm × 0.178 × 0.054 mm. The dimensions of the Re(CO)₃(bpy)Br crystal were 0.20 mm × 0.28 × 0.29 mm.

4.0 Results and Discussion

Section 4.0 summarizes the use of fluorescence measurements for the detection of the non-pertechnetate (Tc-tricarbonyl) complexes in solution and in film. This section details the application of the protocol used to prepare the fluorescent technetium species directly from the non-emissive species contained within the waste. Section 4.1 describes the characterization studies performed to determine which technetium species would be synthesized. Section 4.2 shows the fluorescence measurements of Tc-tricarbonyl species as well as their rhenium analogues and the limit of detection for these compounds. Section 4.3 provides details of the pretreatment steps used for preparing the emissive Tc-tricarbonyl species using complexes in aqueous solution. Section 4.4 gives details of the standard addition experiment and the measurement of the Tc-tricarbonyl complex from simulated waste solution. Section 4.5 highlights pretreatment, spectroscopic, and spectroelectrochemical detection of Re-tricarbonyl species within an ion-selective polymer film environment used as surrogates for their technetium analogues.

4.1 Characterization of Tc-tricarbonyl Complexes

All synthesized Tc-tricarbonyl species were characterized using varoius spectroscopic techniquies, including ⁹⁹Tc NMR, x-ray crystallography, absorption, and fluorescence. Table 4-1 contains the chemical shift values (ppm) for the various ⁹⁹Tc NMR resonances; the respective spectra are shown in Figure 4.1. The Tc(CO)₃(phen)Br species exhibits a shift at -1115 ppm, with a small peak at 0 ppm that is assigned to the Tc(VII) complex, $[TcO_4]^-$ (pertechnetate). The Tc(CO)₃(bpy)Br species shows a peak at -1096 ppm. The $[Tc(CO)_3(H_2O)_3]^+$ species displays a peak at -869, very near the literature value of -868 ppm (Mikhalev 2005). The $[Tc(CO)_3(bpy)(H_2O)]^+$ species shows four ⁹⁹Tc resonances at -1041, -1092, -1095, and -1154 ppm. Due to the possibility of ionization and nature of the solvent coordination to Tc, these assignments remain uncertain.

Compound	Solvent	Chemical shift, ppm (this work)	Chemical shift, ppm (literature)
Tc(CO) ₃ (phen)Br	DMF	-1115	
Tc(CO) ₃ (bpy)Br	CH ₃ CN	-1096	-1078
$[Tc(CO)_{3}(H_{2}O)_{3}]^{+}$	HBr (pH=4)	-869	-868
$[Tc(CO)_3(bpy)(H_2O)]^+$	CH ₃ CN	-1041, -1092, -1095, -1154	

Table 4-1. Results of ⁹⁹Tc NMR Measurements for Various Tc(I) Complexes



Figure 4.1. Technetium-99 NMR Spectra for Various Tc(I) Complexes

The structure of $Tc(CO)_3(bpy)Br$ was confirmed using x-ray diffraction analysis. Photographs of $Tc(CO)_3(bpy)Br$ and $Tc(CO)_3(bpy)Br$ crystals are shown in Figure 4.2A and Figure 4.2C. Their corresponding molecular structures are shown in Figure 4.2B and Figure 4.2D, with corresponding atom numbering schemes. Selective relative bond lengths and angles are presented in Table 4-2.



Figure 4.2. (A) Photograph and (B) Molecular Structure of Tc(CO)₃(bpy)Br; (C) Photograph and (D) Molecular Structure of Re(CO)₃(bpy)Br; bpy = 2,2'-bipyridyl

	M(CO) ₃ (bpy)Br	
	M = Tc	$\mathbf{M} = \mathbf{R}\mathbf{e}$
	Distan	ces (Å)
M(1)-C(11)	1.917(3)	1.908(11)
M(1)-C(12)	1.918(3)	1.906(13)
M(1)-C(13)	1.927(4)	1.856(17)
M(1)-N(1)	2.175(2)	2.168(9)
M(1)-N(2)	2.171(2)	2.162(8)
M(1)-Br(1)	2.6308(4)	2.5833(15)
O(2)-C(11)	1.139(4)	1.152(14)
O(3)-C(12)	1.139(4)	1.152(15)
O(1)-C(13)	1.111(4)	1.21(2)
	Angle	es (°)
C(11)-M(1)-C(12)	89.20(15)	89.5(5)
C(11)-M(1)-C(13)	90.76(14)	89.5(6)
C(12)-M(1)-C(13)	89.49(13)	89.6(6)
N(2)-M(1)-N(1)	75.37(9)	75.0(3)
C(11)-M(1)-Br(1)	89.75(10)	93.2(4)
C(12)-M(1)-Br(1)	91.42(10)	90.8(4)
C(13)-M(1)-Br(1)	178.96(10)	177.2(5)
N(2)-M(1)-Br(1)	84.63(7)	84.2(2)
N(1)-M(1)-Br(1)	86.83(7)	86.6(2)
O(1)-C(11)-M(1)	178.7(3)	178.9(12)
O(2)-C(12)-M(1)	179.4(3)	178.3(12)
O(3)-C(13)-M(1)	176.5(3)	175.4(16)

Table 4-2. Selected Bond Distances (Å) and Angles (°) for Tc(CO)₃(bpy)Br and Re(CO)₃(bpy)Br; bpy = 2,2'-bipyridyl

Both $Tc(CO)_3(bpy)Br$ and $Tc(CO)_3(phen)Br$ absorb light at 365 nm, as shown in Figure 4.3. The excitation and emission spectra for both species is shown in Figure 4.4. Excitation spectra show peaks at 397 nm and 380 nm for $Tc(CO)_3(bpy)Br$ and $Tc(CO)_3(phen)Br$, respectively. $Tc(CO)_3(bpy)Br$ emits light at 575 nm and $Tc(CO)_3(phen)Br$ at 560 nm.

The non-pertechnetate Tc(I) species anticipated to be present in tank waste lack a spectroscopic signature that is easily distinguishable from other species also found in the waste. Figure 4.4A shows the absorbance spectra of $[Tc(CO)_3(H_2O)_3]^+$ before and after the addition of a sensitizing ligand. The $[Tc(CO)_3(H_2O)_3]^+$ species is transparent in solution over the region of 300 nm to 900 nm. After the addition of a sensitizing ligand, the newly formed $[Tc(CO)_3(bpy)(H_2O)]^+$ species absorbs light at 355 nm. Though this species absorbs light, using absorbance as a detection technique has the disadvantages of low sensitivity and selectivity. When measuring absorbance, every species that absorbs light will be observed in the wavelength range of measurement. Also, the target species in a sample would have to be in a high enough concentration to be detected. Fluorescence signals can be better detected in the presence of

interfering species and at lower concentrations, well below the concentration of non-pertechnetate technetium in tank waste. Figure 4.5B shows the excitation and emission spectra of the fluorescent $[Tc(CO)_3(bpy)(H_2O)]^+$ species. The complex excites at 415 nm and emits light at 573 nm, summarized in Table 4-3. The high selectivity and sensitivity of the fluorescence signal of the $[Tc(CO)_3(bpy)(H_2O)]^+$ species will be beneficial for detection of the non-pertechnetate technetium species in a real waste sample.



Figure 4.3. Absorbance Spectra of Tc(CO)₃(L-L)Br; (A) bpy = 2,2'-bipyridyl and (B) phen = 1,10'-phenanthroline



Figure 4.4. Excitation and Emission Spectra of $Tc(CO)_3(L-L)Br$, where L-L is (A) bpy = 2,2'-bipyridyl and (B) phen = 1,10'-phenanthroline. Excitation spectra are represented by dashed lines. Emission spectra are represented by solid lines.

Compound	Excitation, nm	Emission, nm
Tc(CO) ₃ (bpy)Br	397	575
Tc(CO) ₃ (phen)Br	380	560
$[Tc(CO)_3(bpy)(H_2O)]^+$	415	573

Table 4-3. Excitation and Emission for Tc(I) species



Figure 4.5. (A) Absorbance Spectra of $[Tc(CO)_3(H_2O)_3]^+$ and $[Tc(CO)_3(bpy)(H_2O)]^+$; (B) Excitation and Emission Spectra of $[Tc(CO)_3(bpy)(H_2O)]^+$, bpy = 2,2'-bipyridyl

4.2 Detection Limit Measurements of Tc-tricarbonyl Complexes in Aqueous Solution

To achieve the desired detection limits, fluorescent molecules are needed because fluorescence-based detection methods are many orders of magnitude more sensitive than other optical techniques, such as absorbance. Concentration-dependent fluorescence measurements of the $Tc(CO)_3(phen)Br$ and $[Tc(CO)_3(bpy)(H_2O)]^+$ complexes were performed, as well as those of their rhenium analogues. Figure 4.6 shows the concentration profiles of $Tc(CO)_3(phen)Br$ and $[Tc(CO)_3(bpy)(H_2O)]^+$. Based on these data, the detection limit for each complex was calculated using Equation 2 (Long and Winefordner 1983).

$$LOD = \frac{k * S_b}{m},\tag{2}$$

where LOD is the limit of detection, k is a numerical constant, m is the slope of the linear region of the plot, and s_b is the standard error for the blank measurements. In accord with the International Union of Pure and Applied Chemistry (IUPAC) recommendations (IUPAC 1978), a k value of 3 was applied, which corresponds to a 99.87% confidence level. The LOD values are summarized in Table 4-4. The LOD values for the technetium complexes are higher than those of their rhenium analogues, yet still in the nano-Molar range. The LOD values are also lower than the concentrations of the Tc-tricarbonyl complex

in tank waste, estimated to be in the 10 to 60 μ M range (Serne et al. 2014). The difference between the LOD values of the technetium species and those of their respective rhenium analogues can be attributed to the sensitivity of the fluorescent Tc-tricarbonyl complex to prolonged light exposure. The photograph in Figure 4.7 shows [Tc(CO)₃(bpy)(H₂O)]⁺ before (left) and after (right) irradiation for emission measurements.



Figure 4.6. Concentration emission profiles for various Tc-tricarbonyl species and their Re analogues: (A) Tc(CO)₃(phen)Br collected at 400 nm excitation; (B) Re(CO)₃(phen)Br collected at 405 nm excitation; (C) [Tc(CO)₃(bpy)(H₂O)]⁺ collected at 415 nm excitation; and (D) [Re(CO)₃(bpy)(H₂O)]⁺ collected at 404 nm excitation

	LOD, nM		
Compound	M = Tc	M = Re	
M(CO) ₃ (phen)Br	676	10.6	
$[M(CO)_3(bpy)(H_2O)]^+$	210	17	

Table 4-4. Experimental LOD Values for $M(CO)_3(phen)Br$ and $[M(CO)_3(bpy)(H_2O)]^+$ Complexes,
(M = Re and Tc)



Figure 4.7. Photograph of [Tc(CO)₃(bpy)(H₂O)]⁺ Before (left) and After (right) Irradiation

4.3 Pretreatment Solution and Sample Preparation

The general strategy for converting the $Tc(CO)_3^+$ species in tank waste into the fluorescent probe molecule for detection and quantitative measurement is shown in Figure 4.8. In this figure, the $[Tc(CO)_3(H_2O)_3]^+$ can react directly with the incoming sensitizing ligand contained within the pretreatment solution to yield the fluorescent molecule for quantitative measurement. For the demonstration of the quantitative measurement of the Tc-tricarbonyl complex within a waste matrix, the original $[Tc(CO)_3(H_2O)_3]^+$ complex can be added to a waste simulant to form the organic complexed form of the Tc-tricarbonyl species depicted as the $[Tc(CO)_3(O_1)(O_2)(O_3)]^n$ complex. The reaction of this complex with a pretreatment solution of suitable composition allows for several factors to occur simultaneously:

- 1. The introduction of an excess of incoming sensitizing ligand, L-L, to ensure that all the $[Tc(CO)_3(O_1)(O_2)(O_3)]^n$ species converts to that fluorescent probe;
- 2. The solubilization of the formed fluorescent Tc-tricarbonyl-ligand complex, allowing for ease of measurement; and
- 3. The dilution of the original matrix to diminish the competition of other organic ligands within the tank waste matrix.

The final intended product is the $[Tc(CO)_3(L-L)(H_2O)]^+$ complex. Depending on the solvent used in the pretreatment solution, the technetium complex may substitute the aquo ligand resulting in the general formula $[Tc(CO)_3(L-L)(X)]^+$, where $X = H_2O$, CH₃CN, or CH₃OH.



Figure 4.8. General Strategy for Converting the Tc(CO)₃⁺ Complex into the Fluorescent Probe Module Using the Pretreatment Solution

The initial simulated waste solution for testing the fluorescence-based method of Tc-tricarbonyl detection is based on the Pretreatment Engineering Platform (PEP) supernatant simulant composition (Levitskaia Tatiana et al. 2014). Table 4-5 contains the composition of the various components. This fairly simple waste simulant was chosen for its high alkalinity, high ionic strength characteristics, and the presence of oxalate as a potential complexant for the Tc-tricarbonyl species. Future tests will contain increasing amounts of other organic complexants, including citrate and gluconate.

Table 4-5.	Composition of	the Simulated Waste	Used with the Tc	c-tricarbonyl Detection and
	Demonstration.	Simulant is based on	PEP supernatant	simulant composition.

Component	Chemical Formula	Concentration (g/L)
Sodium oxalate	$Na_2C_2O_4$	1.9
Aluminum nitrate (60 % solution)	Al(NO ₃) ₃ ·9H ₂ O	78 (60 % solution of Al(NO ₃) ₃ ·9H ₂ O)
Sodium phosphate	$Na_3PO_4 \cdot 12H_2O$	25
Sodium sulfate (anhydrous)	Na ₂ SO ₄	25
Sodium nitrate	NaNO ₃	104
Sodium hydroxide (50 % solution)	NaOH	104 (50 % solution of NaOH)
Sodium nitrite	NaNO ₂	35
Sodium carbonate (anhydrous)	Na ₂ CO ₃	58.57

Demonstration of Pretreatment Protocol for Measurement of $[Tc(CO)_3(H_2O)_3]^+$ **.** A schematic illustrating the general step-by-step methodology for the measurement of $[Tc(CO)_3(H_2O)_3]^+$ in solution is shown in Figure 4.9. The pretreatment solution (0.125 M bpy in acetonitrile) is spiked with increasing amounts of $[Tc(CO)_3(H_2O)_3]^+$ in water solution (Step 2). The mixture is allowed to react for 10 min. at room temperature, followed by optical measurement of the fluorescent signal (Step 3).



Figure 4.9. Schematic Showing the Steps to Measure Tc-tricarbonyl Species in Solution. The strategy is to demonstrate the measurement in water solution (Step 2) and in simulated waste (Step 1).

Demonstration of bpy/Acetonitrile Pretreatment Solution with $[Tc(CO)_3(H_2O)_3]^+$ in Water. Following the approach shown in Figure 4.9, successive 10-µL aliquots of $[Tc(CO)_3(H_2O)_3]^+$ in HBr (pH = 4) were added to a pretreatment solution containing 0.125 M bpy in acetonitrile, then allowed to react for 10 min. at room temperature (Step 2). The fluorescence measurements of these solutions were measured and are shown in Figure 4.10A. The plot of maximum emission versus the concentration of the Tc-tricarbonyl in the pretreatment solution is shown in Figure 4.10B. The lower concentration ranges on the maximum emission versus concentration are linear, and were used to determine the LOD for this solution. The LOD value using this protocol is 220 nM, very similar to the 210-nM LOD value of the concentration emission profile of the target species (Figure 4.6C).



Figure 4.10. Pretreatment of $[Tc(CO)_3(H_2O)_3]^+$ in Water Using the Pretreatment Protocol with 0.125 M bpy in Acetonitrile: (A) Fluorescence measurement of solutions containing variable concentrations of $[Tc(CO)_3(H_2O)_3]^+$ in water; (B) max emission vs. concentration curve. The equation of the line is $Y = 1.4 \times 10^9 \text{ X} - 9022$ and $R^2 = 0.973$.

4.4 Standard Addition of Tc-tricarbonyl Standard in Simulated Waste Sample

This section describes the use of the standard addition method to determine the amount of Tc-tricarbonyl complex within a sample of simulated waste. In this demonstration, a simulated waste solution containing a given amount of the Tc-tricarbonyl compound is prepared. The initial amount of Tc-tricarbonyl within the simulated waste sample was 1.48×10^{-5} M in $[Tc(CO)_3]^+$. The simulated waste sample containing $[Tc(CO)_3]^+$ was treated according to protocol described in Figure 4.9. The simulated waste sample was added to a pretreatment solution containing 0.125 M bpy in acetonitrile (Step 1). The supernatant for the resulting suspension was then divided into several sub-samples, to which known amounts of $[Tc(CO)_3(H_2O)_3]^+$ standard were added (Step 2). The individual samples, with increasing amounts of added standard, were then measured by performing a fluorescence measurement (Step 3).

The fluorescence measurements of the various samples are shown in Figure 4.11A. The maximum emission versus the concentration of $[Tc(CO)_3(H_2O)_3]^+$ "standard" added is shown in Figure 4.11B. Based on the graphical analysis of the plot in Figure 4.11B. The calculated concentration of the "unknown" material in the original sample was determined to be 1.91×10^{-5} M. This is in agreement with the known value (as determined by liquid scintillation counting of a sample aliquot of known volume) for this original sample (1.48×10^{-5} M) and constitutes a 29% difference. This value represents one measurement. Additional replicates are planned that might yield better agreement.

Further work is still needed to determine the effects of using more complicated simulated wastes compositions, including the addition of other organic complexants and additional metals. Ultimately, testing involving the use of actual waste is planned.

"Unknown" concentration = 1.48E-05 M Calculated value by Stand Addn = 1.91E-05 M in sample



Figure 4.11. Pretreatment of $[Tc(CO)_3]^+$ in Simulated Waste Using the Pretreatment Protocol with 0.125 M bpy in Acetonitrile: (A) Emission spectra and (B) standard addition plot for pretreatment of $[Tc(CO)_3]^+$ in simulated waste. The calculated value of the unknown $[Tc(CO)_3]^+$ in simulated waste is 1.91×10^{-5} M; the actual unknown, as determined by LSC, is 1.48×10^{-5} M.

4.5 Selective Partitioning and In-situ Pretreatment within Ionexchange Polymer Thin Film

This section highlights the general strategy for the in-situ complex formation and detection of the fluorescent Tc-tricarbonyl complex within a selective film. Initial testing for this sensing platform has been conducted using the Re-tricarbonyl analogue. The flow cell sensor device is described in the spectroelectrochemistry portion of the experimental section. The sensing platform is shown schematically in Figure 4.12. The sensing platform starts with the ITO slide, which serves as the waveguide and optically transparent working electrode. The ITO is coated with a chemically selective ion-exchange polymer thin film before going into the flow cell. A structure of the polymer, Nafion, used in this study is shown in Figure 4.13. Nafion has a stable, hydrophobic Teflon backbone with terminal sulfonated groups that allow for ionic exchange with cationic species, such as the $[Re(CO)_3(H_2O)_3]^+$ species. An excitation wavelength is coupled into the waveguide (glass substrate) to monitor for change in emission intensity. A sensitizing ligand, such as bpy, is loaded into the selective ion-exchange film by flowing across the surface of the film (Step 1). The non-emissive $[Re(CO)_3(H_2O)_3]^+$ is then flowed across the film.

The species partitions into the selective film and forms a fluorescent $[Re(CO)_3(L-L)(H_2O)]^+$ complex (Step 2). A selective electrochemical potential is then applied to modulate the oxidation state of the $[Re(CO)_3(L-L)(H_2O)]^+$, effectively turning the fluorescent signal "on" and "off" (Step 3). A photograph of the fluorescent $[Re(CO)_3(L-L)(H_2O)]^+$ complex within the selective film is shown in Figure 4.14. As shown in the schematic in Figure 4.12, light is coupled into the ITO and undergoes multiple points of reflectance as it passes through the waveguide. The yellow-green spots seen in the oval window in Figure 4.14 represent the points of reflectance as the light hits the edge of the waveguide on the side of

selective film, where the fluorescent $[Re(CO)_3(L-L)(H_2O)]^+$ complex is present. One of these reflectance points is monitored for change in emission intensity. In this section, the pretreatment of $[Re(CO)_3(H_2O)_3]^+$ in a selective film is demonstrated both with and without spectroelectrochemical modulation.



Figure 4.12. Schematic of Re-tricarbonyl Pretreatment and Spectroelectrochemical Detection within a Selective Film



Figure 4.13. Structure of Nafion



Figure 4.14. A Photograph of [Re(CO)₃(bpy)(H₂O)]⁺ in Selective Film in the Flow Cell Sensing Device

Demonstration of $[Re(CO)_3(H_2O)_3]^+$ **in-situ pretreatment in selective film.** The pretreatment and fluorescence detection of $[Re(CO)_3(H_2O)_3]^+$ within a film is demonstrated in a manner similar to the schematic shown in Figure 4.12. A 1 mM solution of $[Re(CO)_3(H_2O)_3]^+$ in water is flowed across an ITO slide coated with a 25 nm Nafion film at a flow of 0.05 mL/min (Step 1). The pretreatment solution containing 0.125 M bpy in acetonitrile is then flowed across the film-coated electrode at a rate of 0.05 mL/min (Step 2). As the ligand partitions into the film, it forms the fluorescent $[Re(CO)_3(bpy)(H_2O)]^+$ complex with the Re-tricarbonyl species, and a resulting growth in emission intensity is observed (Step 3). Figure 4.15A shows the whole emission spectrum as a function of time as the fluorescent $[Re(CO)_3(bpy)(H_2O)]^+$ forms within the film. Figure 4.15B follows the peak emission versus time. While using a pretreatment solution with organic solvent is suitable for pretreatment in solution as well as short-term monitoring within film, the solvent can strip the film from the ITO slide in a system requiring extended monitoring, such as the incorporation of spectroelectrochemical modulation. An ideal system would use a pretreatment solution with aqueous solvent. Also with an aqueous solvent, the fluorescent $[Re(CO)_3(bpy)(H_2O)]^+$ complex would have a higher affinity for the film environment due to its low solubility in aqueous solvents.



Figure 4.15. Pretreatment and Spectroscopic Detection of the Pretreatment of [Re(CO)₃(H₂O)₃]⁺ with 0.125 M bpy in Acetonitrile; (A) Emission spectra vs. time and (B) peak emission vs. time at 404 nm excitation

5.0 Conclusions and Path Forward

FY2016 work developed a protocol for non-pertechnetate sensing using technetium complexes in solution and in simulated tank waste. This study advances the sensor concept by the development and demonstration of the protocol for the quantitative detection of Tc(I)-tricarbonyl, non-pertechnetate species, by fluorescent measurement. Initial planning assumed the availability of actual Hanford tank waste for use in this project, but this material was not made available in FY2016. This work culminated in the quantitation of Tc(I)-tricarbonyl within a Hanford waste simulant using a standard addition method for measurement.

5.1 Summary of Fiscal Year 2016 Work

The systematic synthesis and high-yield preparation of the Tc(I)-tricarbonyl complex, $[Tc(CO)_3(H_2O)_3]^+$, has been optimized. This complex is a convenient technetium standard material for the non-pertechnetate species for use in simulated tank waste measurements. The synthesis and characterization of this complex, starting from a convenient source of technetium, ammonium pertechnetate, is described herein.

Several non-pertechnetate complexes of technetium prepared as starting materials and for use as sensor probes were characterized using various standard analytical methods. The analytical methods include ⁹⁹Tc NMR, x-ray crystallography, UV-vis absorption spectroscopy and fluorescence spectroscopy. The characterized complexes include $Tc(CO)_3$ (phen)Br, $Tc(CO)_3$ (bpy)Br, $[Tc(CO)_3(H_2O)_3]^+$, $[Tc(CO)_3(bpy)(H_2O)]^+$.

To achieve the desired detection limits, fluorescent molecules are needed because fluorescence-based detection methods are many orders of magnitude more sensitive than other optical techniques, such as absorbance. Concentration-dependent fluorescence measurements of the $Tc(CO)_3$ (phen)Br and $[Tc(CO)_3(bpy)(H_2O)]^+$ complexes were performed, as well as of their rhenium analogues with detection limits in the nano-Molar range, well below that of the Tc(I) concentration anticipated in waste.

Details of the general protocol for pretreatment of waste samples containing non-pertechnetate were optimized in previous years' work. The general strategy for converting the $Tc(CO)_3^+$ species in tank waste into the fluorescent probe molecule for detection and quantitative measurement was successfully demonstrated on technetium samples.

In order to increase selectivity and enhance detection limits, an ion-selective film was used in conjunction with the optical measurement of the Re(I)-carbonyl analogue to the Tc(I) complex. The detection of $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ within the ion-selective film was performed by initially flowing a solution containing the Re(I) species over the selective film, followed by a pretreatment solution containing the sensitizing ligand (bpy).

The quantitative measurement of Tc-tricarbonyl analyte was demonstrated within a waste simulant using the standard addition method for analysis. In this method, a series of waste simulant samples containing an initial amount of Tc-tricarbonyl was spiked with a known amount of $[Tc(CO)_3(H_2O)_3]^+$ standard solution in increasing concentrations. From the fluorescence measurements of these solutions, the original "unknown" Tc-carbonyl concentration was then determined. The results from the standard addition

method compared well to the 'unknown" concentration, yielding a concentration of 1.48×10^{-5} M versus 1.91×10^{-5} M (29% difference) for the detection of Tc-tricarbonyl complex.

5.2 Path Forward for Fiscal Year 2017

FY2017 work will continue optimizing the pretreatment solution for measuring the $Tc(CO)_3^+$ class of compounds. Using Tc-tricarbonyl starting materials prepared under FY2016, we will determine the optimum method for fluorescence detection for Tc-tricarbonyl compounds using actual Hanford waste. Actual Hanford waste has been identified for this project and will be available for FY 2017. Our determination of optimum method will be based on the direct fluorescence measurement of Tc-tricarbonyl species in solution. Our FY2017 work will culminate with a demonstration of the measurement of Tc-tricarbonyl compounds using actual waste samples.

6.0 References

- Alberto R. 2005. "New Organometallic Technetium Complexes for Radiopharmaceutical Imaging." In Contrast Agents III, ed. W Krause, Vol. 252 in Topics in Current Chemistry, pp. 1-44. Springer Berlin Heidelberg.
- Alberto R, K Ortner, N Wheatley, R Schibli, and AP Schubiger. 2001. "Synthesis and Properties of Boranocarbonate: A Convenient in Situ CO Source for the Aqueous Preparation of [^{99m}Tc(OH₂)₃(CO)₃]⁺." *Journal of the American Chemical Society*. 123(13):3135-36. doi: 10.1021/Ja003932b. <Go to ISI>://000167806300023
- Alberto R, R Schibli, A Egli, AP Schubiger, U Abram, and TA Kaden. 1998. "A Novel Organometallic Aqua Complex of Technetium for the Labeling of Biomolecules: Synthesis of $[^{99m}Tc(OH_2)^3(CO)_3]^+$ from $[^{99m}TcO_4]^-$ in Aqueous Solution and Its Reaction with a Bifunctional Ligand." *Journal of the American Chemical Society*. 120(31):7987-88. doi: 10.1021/Ja980745t. <Go to ISI>://000075420100043
- Andria SE, CJ Seliskar, and WR Heineman. 2009. "Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 21. Selective Chemical Sensing Using Sulfonated Polystyrene-Block-Poly(Ethylene-Ran-Butylene)Block-Polystyrene Thin Films." *Analytical Chemistry*. 81(23):9599-606. doi: Doi 10.1021/Ac901595b. <Go to ISI>://000272084700016
- Chatterjee S, AS Del Negro, MK Edwards, SA Bryan, N Kaval, N Pantelic, LK Morris, WR Heineman, and CJ Seliskar. 2011. "Luminescence-Based Spectroelectrochemical Sensor for [Tc(dmpe)₃]^{2+/+}(dmpe=1,2-*bis*(Dimethylphosphino)Ethane) within a Charge-Selective Polymer Film." *Analytical Chemistry*. 83(5):1766-72. doi: 10.1021/Ac1030368. <Go to ISI>://000287685800040
- Cho HM, WA de Jong, BK McNamara, BM Rapko, and IE Burgeson. 2004. "Temperature and Isotope Substitution Effects on the Structure and NMR Properties of the Pertechnetate Ion in Water." *Journal of the American Chemical Society*. 126(37):11583-88. doi: Doi 10.1021/Ja047447i. <Go to ISI>://000223921800044
- Franklin KJ, CJL Lock, BG Sayer, and GJ Schrobilgen. 1982. "Chemical Applications of Technetium-99 NMR Spectroscopy: Preparation of Novel Technetium(VII) Species and Their Characterization by Multinuclear NMR Spectroscopy." *Journal of the American Chemical Society*. 104(20):5303-06. doi: 10.1021/ja00384a007.
- Gerdes K, and S Schneider. 2016. "*Technetium Management Program Plan*." Pamphlet, US DOE, Washington, DC.
- He H, M Lipowaska, X Xu, AT Taylor, M Carlone, and L Marzilli, G. 2005. "Re(CO)₃ Complexes Synthesized Via an Improved Preparation of Aqueous Fac-[Re(CO)₃(H₂O)₃]⁺ as an Aid in Assessing ^{99m}Tc Imaging Agents. Structural Characterization and Solution Behavior of Complexes with Thioether-Bearing Amino Acids as Tridentate Ligands." *Inorganic Chemistry*. 44(15):5437-46. doi: 10.1021/ic0501869.

- IUPAC. 1978. "Nomenclature, Symbols, Units and Their Usage in Spectrochemical Analysis—II. Data Interpretation Analytical Chemistry Division." Spectrochimica Acta Part B: Atomic Spectroscopy. 33(6):241-45. doi: 10.1016/0584-8547(78)80044-5. http://www.sciencedirect.com/science/article/pii/0584854778800445
- Kaval N, CJ Seliskar, and WR Heineman. 2003. "Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 16. Sensing by Fluorescence." *Analytical Chemistry*. 75(22):6334-40. doi: 10.1021/Ac0347664. <Go to ISI>://000186601500041
- Lazarova N, S James, J Babich, and J Zubieta. 2004. "A Convient Synthesis, Chemical Characterization and Reactivity of [Re(CO)₃(H₂O)₃]Br: The Crystal and Molecular Structure of [Re(CO)₃(CH₃CN)₂Br]." *Inorganic Chemistry Communications*. 7:1023-26. doi: 10.1016/j.inoche.2004.07.006.
- Levitskaia Tatiana G, A Anderson, SD Chatterjee, HM Cho, BM Rapko, JM Peterson, ED Walter, and NM Washton. 2014. Speciation and Oxidative Stability of Alkaline Soluble, Non-Pertechnetate Technetium. Report No. PNNL-23654 Rev. 0; EMSP-RPT-024 Rev. 0, Pacific Northwest National Laboratory, Richland, WA.
- Long GL, and JD Winefordner. 1983. "Limit of Detection." *Analytical Chemistry*. 55(7):A712-A24. doi: <Go to ISI>://A1983QR92600004
- Lukens WW, DK Shuh, NC Schroeder, and KR Ashley. 2004. "Identification of the Non-Pertechnetate Species in Hanford Waste Tanks, Tc(I)-Carbonyl Complexes." *Environmental Science & Technology*. 38(1):229-33. doi: 10.1021/Es034318d. <Go to ISI>://000187781800044
- Mikhalev VA. 2005. "99Tc NMR Spectroscopy." *Radiochemistry*. 47(4):319-33. doi: 10.1007/s11137-005-0097-3.
- Rapko BM. 2014. Protocol for Identifying the Presence of and Understanding the Nature of Soluble, Non-Pertechnetate Technetium in Hanford Tank Supernatants. Report No. PNNL-23180/EMSP-RPT-020, Pacific Northwest National Laboratory, Richland, WA.
- Rapko BM, SA Bryan, S Chatterjee, MK Edwards, TG Levitskaia, JM Peterson, RA Peterson, and SI Sinkov. 2013. *Investigations into the Nature of Alkaline Soluble, Non-Pertechnetate Technetium*. Report No. PNNL-22957; EMSP-RPT-018, Pacific Northwest National Laboratory, Richland, WA.
- Richter MM, JD Debad, DR Striplin, GA Crosby, and AJ Bard. 1996. "Electrogenerated Chemiluminescence .59. Rhenium Complexes." *Analytical Chemistry*. 68(24):4370-76. doi: Doi 10.1021/Ac9606160. <Go to ISI>://A1996VX78600011
- Salignac B, PV Grundler, S Cayemittes, U Frey, R Scopelliti, AE Merbach, R Hedinger, K Hegetschweiler, R Alberto, U Prinz, G Raabe, U Kolle, and S Hall. 2003. "Reactivity of the Organometallic Fac-[(CO)₃Re^I(H₂O)₃]⁺ Aquaion. Kinetic and Thermodynamic Properties of H₂O Substitution." *Inorganic Chemistry*. 42(11):3516-26. doi: 10.1021/ic0341744.
- Serne RJ, BM Rapko, and IL Pegg. 2014. Technetium Inventory, Distribution, and Speciation in Hanford Tanks. Report No. PNNL-23319, Rev.1; EMSP-RPT-022, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.

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