

Project Title: Identification of Non-Perchnetate Species in Hanford Tank Waste, Their Synthesis, Characterization, and Fundamental Chemistry

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Research Objective: Technetium, as pertechnetate (TcO_4^-), is a mobile species in the environment. This characteristic, along with its long half-life, (^{99}Tc , $t_{1/2} = 213,000$ a) makes technetium a major contributor to the long-term hazard associated with low level waste (LLW) disposal. Technetium partitioning from the nuclear waste at DOE sites may be required so that the LLW forms meet DOE performance assessment criteria. Technetium separations assume that technetium exists as TcO_4^- in the waste. However, years of thermal, chemical, and radiolytic digestion in the presence of organic material, has transformed much of the TcO_4^- into unidentified, stable, reduced, technetium complexes. To successfully partition technetium from tank wastes, it will be necessary to either remove these technetium species with a new process, or reoxidize them to TcO_4^- so that conventional pertechnetate separation schemes will be successful.

This research attempted to use model technetium complexes to develop a capillary electrophoresis mass spectrometry (CEMS) technique to identify non-pertechnetate species (TcN) in actual waste samples. The model technetium complexes would have been used as standards to establish the operational parameters for CEMS for the types of technetium compounds we speculate are in the waste. Development of this technique is critical to resolving the non-pertechnetate problem since many of technetium complexes (i.e. EDTA type complexes) originally speculated to be in the waste were too easily oxidized or show less stability in caustic media compared to the actual non-pertechnetate species in the waste.

This proposal had three major goals: (1) develop CEMS as a characterization technique, (2) separate a TcN fraction from a waste sample and identify the TcN species in it by CEMS, and (3) synthesize and characterize bulk quantities of the identified TcN species and study their ligand substitution and redox chemistry. The transition plan for this work would have been to use

the fundamental chemistry of the identified TcN species to develop efficient oxidation or separation methods for the TcN species in an actual waste matrix.

Meeting the major goals of this project and the transition plan would have enabled the development of separation and/or the feed adjustment chemistry that would efficiently remove technetium from the waste and enable DOE to fulfill its tank waste remediation mission. However, DOE has decided not to include technetium partitioning in the Hanford Waste Treatment and Immobilization Plant because it was not technically feasible. We hope that our discovery of the TcN species, attempts to oxidize them, and these EMSP projects have facilitated DOE's decision not to build a separation facility that would only be partially successful in separating technetium (the TcO_4^- fraction) from Hanford waste. This decision may save the taxpayers several hundreds of millions of dollars.

Research Progress and Implications: This report summarizes the work during months 21 through 32 of a 36-month project. The Project Goals, General Workscope, and Objectives for each of the Fiscal Years of this project are outlined in Table 1. We did not meet our objective "Develop a Capillary Electrophoresis/Mass Spectrometry (CEMS) Technique for Identifying TcN Species" because samples containing more than 1000 cpm could not be brought into the facility that housed the CEMS. This is the activity contained in ~ 0.1 mL of 2.5×10^{-6} M TcO_4^- solution. Straight injections of permanganate solutions into the MS established a detection limit of 1×10^{-5} M for the MnO_4^- ion. This is an order magnitude better than what is reported in the literature (G. R. Agnes and G. Horlick, *Applied Spectroscopy*, **48**, 655, 1994). Similarly we established a detection limit of 5×10^{-8} M for the ReO_4^- ion. Based on these data we estimated the detection limit for TcO_4^- to be about of 5×10^{-6} M. The facility activity restriction thus required us to develop a MS method at the detection limit, an impossible task! Needless to say we were never able to see a pertechnetate or technetium gluconate ion signals when working at such low concentrations. Developing a CEMS method would require even higher concentrations. Lastly, the technetium fraction we separated from AN-107, even though we have removed >99% of the gross activity, contains residual activity that is an order magnitude greater than the technetium activity. The facility restriction has forced us to consider XAS (XANES/EXAFS) for identifying the TcN species. Because EXAFS requires species at $\sim 10^{-3}$ M for structural characterization we need to separate the technetium fraction from a significant amount of Hanford waste and concentrate it to a small volume to make this technique feasible. This work will be done in collaboration with Wayne Lukens at Lawrence Berkeley Laboratory.

Work on the second goal, "Develop a Method to Separate TcN Fractions from Hanford Waste Samples", has been quite successful and also revealing about the nature of the species we are trying to identify. We have used several methods to separate the technetium fraction from the gross activity ($^{90}\text{Sr}/^{90}\text{Y}$) in the waste. Initial experiments with AN-107 tank waste studied the effect of pH on cation separations. It is suspected that protonating the chelating ligands (polyaminocarboxylates, i.e. EDTA) that bind cations such as $^{90}\text{Sr}^{2+}$ causes the ligand to release the strontium so that it can be sorbed by the cation resin. Although successful at low pH, this approach runs the risk of altering the TcN species that exist in the caustic tank waste. Thus we developed a new procedure using Zn^{2+} that allows us to do the cation separations without acidifying the sample. The Zn^{2+} ion has a larger stability constant with EDTA than Sr^{2+} , $\log K = 16.5$ vs. $\log K = 8.74$. If Zn^{2+} were added to the waste solution, it is possible that the Zn^{2+} could displace EDTA type ligands chelating Sr^{2+} and allow the strontium to be sorbed by the Na^+ form of the cation resin. Little or no pH change would be expected from the metathesis reaction.

Table 1. Workscope objectives and Goals

Workscope →

FY1 Objectives	FY2 Objectives	FY3 Objectives	Project Goals
Run model Re/Tc complexes on CE/MS	Run a TcN fraction from AN-107 on CE/MS	Run other TcN fractions from AN-107 on CE/MS	Develop a Capillary Electrophoresis/Mass Spectrometry (CEMS) Technique for Identifying TcN Species
Optimize the separation of a TcN fraction from AN-107	Separate other TcN fractions from AN-107	Other envelope C post-Superlig 639 effluents	Develop a method to separate TcN fractions from Hanford waste samples
Scoping chemistry on Re/Tc gluconate and alkoxide complexes	Synthesize and characterize ID'ed TcN compounds	Study the redox and ligand substitution chemistry of the compounds	Synthesize, characterize, and develop the chemistry of the identified TcN species

Application of this procedure has allowed us to remove ~99% of the gross activity from the sample; the Zn^{2+} procedure is effecting a decontamination from the gross activity in the waste that is equivalent to adjusting the pH to ~1. Thus we get the equivalent decontamination with a much lower probability of altering the TcN species identity. However the procedure loses 13-18% of the technetium, which suggests that a cationic species is being removed. Lukens at Berkeley has re-examined the 1995 PNNL XANES data and concluded that the Tc(IV) oxidation state assignment for the non-pertechnetate species could be interpreted as a Tc(I). Lukens speculated that $Tc(CO)_3^+$ complex could be in the waste. Our cationic losses support this speculation.

Because of the restrictions on activity at the mass spectrometry facility we used size exclusion chromatography to remove residual activity from the cation column effluents to separate the various non-pertechnetate fractions from each other. This work showed at least two major technetium fractions, TcO_4^- and TcN. Unfortunately, the activity levels remained too high for use and we had significant loss of our TcN fraction. The unlikely prospect of identifying the TcN species by CEMS has required us to pursue XANES and EXAFS to determine the oxidation state and obtain structural information on these species. The latter technique requires $\sim 10^{-3}$ M concentration of the species. To meet this we are isolating and concentrating a technetium fraction derived from 146 mL of AN-107 (3.4×10^{-5} M total Tc, 60% non-pertechnetate). We are removing the gross activity by Zn^{2+} /cation exchange and the inert salts (40% by weight in the waste) by precipitation with ethanol. Figure 1 compares the liquid scintillation spectra of AN-107, the purified technetium fraction, and a ^{99}Tc standard. The AN-107 spectrum is dominated by the $^{90}Sr/^{90}Y$ beta decay. Below 40 keV the technetium fraction is dominated by ^{63}Ni while above 200 keV there is some residual $^{90}Sr/^{90}Y$ activity. Comparing the ^{99}Tc standard to the 40-200 keV region of the technetium fraction shows that technetium is present. Gamma counting the

isolated

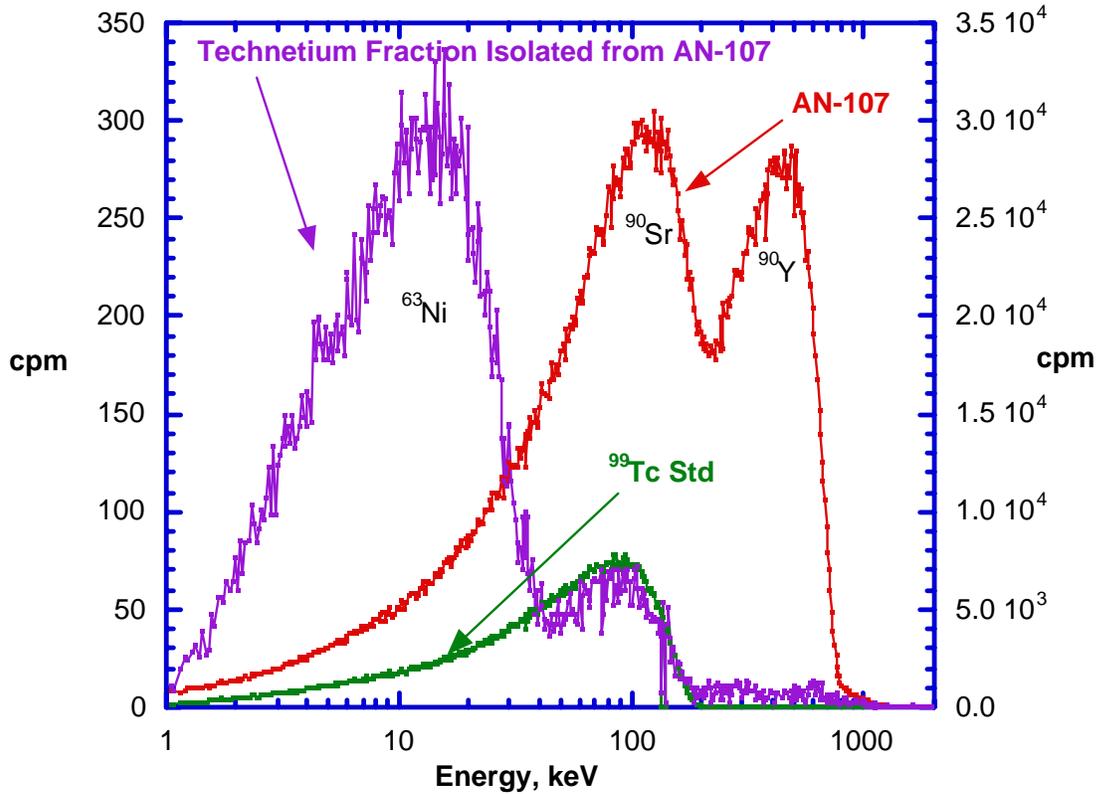


Figure 1. Liquid scintillation spectra of AN-107, a ⁹⁹Tc standard, and the technetium fraction isolated from AN-107. (The right axis applies to the ⁹⁹Tc and AN-107 spectra while the left axis applies to the technetium fraction.)

Table 2. Isotope activities in the technetium fraction isolated from AN-107

Isotope	Ci/mL (x 10 ⁻⁷)	Total Ci (x 10 ⁻⁷)	% Activity in total sample	% Activity 40-200 keV
⁶⁰ Co	0.340	31	5.1	32.3
¹⁰⁶ Ru	0.014	1.3	0.21	1.36
¹⁵² Eu	0.001	0.09	0.014	0.09
¹⁵⁴ Eu	0.016	1.5	0.25	1.56
¹⁵⁵ Eu	0.007	0.64	0.11	0.67
²⁴¹ Am	0.012	1.1	0.18	1.1
⁶³ Ni	5.600	511	84.2	
⁹⁹ Tc	0.648	59	9.7	61.5
⁹⁰ Sr/ ⁹⁰ Y	0.014	1.3	0.21	0.68

fraction shows that other isotopes are also present (Table 2) and they have beta activities in the 40-200 keV range. However, ^{99}Tc makes up ~62% of the activity in this region.

Our third project goal is to characterize, and develop the chemistry of the identified TcN species. Because of the mass spectrometry problem we obviously have not synthesized any identified species.

Planned Activities: We will be sending the isolated technetium fraction derived from AN-107 to Wayne Lukens at Lawrence Berkeley. He will perform a XANES/EXAFS experiment in July at the Stanford Synchrotron. We are starting to isolate technetium fractions from two other Hanford samples, 101-SY and 103-SY. If the technetium concentrations are high enough in these samples will also send these to Lukens for a later experiment. We plan to present several papers or posters at the spring ACS meeting in San Diego.

Information Access: Wayne W. Lukens, David K. Shuh, Norman C. Schroeder, and Kenneth R. Ashley, "Identification of the Non-perotechnetate Species in Hanford Waste Tanks, XAFS Studies of Tc(I) Carbonyl Complexes", *Environmental Science and Technology*, **38(1)**, 229 (2004).