# FINAL REPORT
# U.S. Department of Energy

## Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste

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**Executive Summary:** The project goal was to understand the fundamental chemistry of technetium complexes that might be formed in a Hanford tank waste environment with the types of organic ligands available in the waste. Normally, the dominant technetium species in aqueous media is anionic pertechnetate ($TcO_4^-$). Technetium is also capable of forming covalent bonds with a variety of other ligands in technetium oxidation states ranging from -I to VII.[1] In order to produce these lower valent technetium complexes from $TcO_4^-$, strong reducing agents (i.e. $Sn^{2+}$, $HSO_3^-$) are required.[2] These reductions must be performed in the presence of complexing agents to prevent formation and precipitation of $TcO_2$.

Toste has accounted for greater than 80% of the total organic carbon found in a Hanford complexant concentrate tank supernate.[3] The identified organic compounds include chelating agents (EDTA) and chelator decomposition fragments (IDA). Other major organic species in the waste include oxalate, glycolate, and citric acid. The formation of technetium complexes with these types of ligands has been reported.[2, 4-9] Thus there are many potential ligands for lower oxidation states of technetium if pertechnetate is reduced in the tanks. Radiolysis at high pH produces solvated electrons which are strong reductants ($E° = 2.86$ V) for metal ions having a reduction potential less than this; this would include the redox potentials for technetium.[10] Multiple single electron reductions could bring technetium to the V, IV, and III states and make it available for stabilization by complexants. Alternatively, chemical degradation of organics in the tanks could cause technetium reduction.[11]

With this as a background we have attempted to synthesized and characterize technetium complexes with the following ligands: ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-diacetic acid (EDDA), iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), N-(2-hydroxyethyl)ethylenediamine-triacetic acid (HEDTA), oxalate, glycolate, citrate, and gluconate, ethhylenediamine (en), diethylenetriamine (detn), and triethylenetetraamine (tetn). These preparations proved to be quite difficult as the products were often not clean and required extensive chromatographic separation. The pure products were often only soluble in water and could not be separated as single crystals. XAS was thus the primary means of determining structures. The XAS data that we were able to obtain indicated some similarity to structures in the literature but often our products were more complex. Attempts to synthesize the same complexes in base were unsuccessful because of a strong tendency to decompose to $TcO_2$ and/or oxidize to $TcO_4^-$. The synthesized complexes also when placed in base also decomposed or oxidized. In addition, dilute solutions of the complexes also appear to convert to other product. In some cases there is a slow conversion to pertechnetate. The one exception to the above observations is a gluconate complex that does form in base but also will change over time to some other species. Unfortunately there are no data that that this PI can find that show gluconate in a tank waste sample. Nitrido complexes are stable in base but it is difficult at this point to develop a mechanism for their formation. The compexity of the technetium chemistry we observed only add to the importance of understanding these complexes and how they relate to the non-pertechnetate species in tank waste.

**Summary of Relevance, Impact and Technology Transfer.** This work shows that we still do not know what the non-pertechnetate species are. This leads once again to ask the question what are the non-pertechnetate species that exist in the tanks that are so stable and hard to separate. Identifying the non-pertechnetate species and understanding their chemistry may be important if future risk assessments of the Hanford site become more stringent. The project's impact was beneficial to improving our capabilities in technetium synthetic work and structural analysis.

**Collaborative Work:** This project had two collaborations. The first was a subcontract with Professor Kenneth R. Ashley at Texas A&M University-Commerce. His work centered on trying to understand the nature of the non-pertechnetate species in Hanford waste. Initially, this PI wanted his research to be more along the lines of a synthetic effort. However, as we began to have problems forming technetium complexes that showed any significant stability under caustic condition I requested that he try to learn more about the nature of the non-pertechnetate species in some Hanford waste samples. His efforts showed that the non-pertechnetate species were stable under a wide pH range. In addition he was developing a separation procedure for these species that was leading a separation of ~50% of the non-pertechnetate fraction when this project ended.

The second collaboration was with David Blanchard at Pacific Northwest National Laboratory (PNNL). He was supposed to do the X-ray Absorption Spectroscopy (XAS) on our technetium samples at the Stanford Synchrotron Radiation Laboratory (SSRL) and do the X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) analysis of the data. This effort was particularly important to the success of the project because the technetium complexes proved very difficult to separate cleanly and to form single crystals. This was our chief method of obtaining structural information on the complexes. Unfortunately, for this PI, Dave was caught in some larger programmatic problems and was not able to fully analyze the last and best set of data. This PI has been trying to recover from this situation by enlisting expertise in XAS at Los Alamos National Laboratory (LANL) before the project report is due.

**Research Objectives:** The ultimate goal of this project is to separate technetium from Hanford tank waste. Our prior work with Hanford waste has shown that a large portion of the technetium in some tanks is not pertechnetate ($TcO_4^-$) and is not easily oxidized to it.[12-21] This has serious repercussions for technetium partitioning schemes because they are designed to separate this chemical form. Rational attempts to oxidize these species to $TcO_4^-$ for processing or to separate the non-pertechnetate species themselves would be facilitated by knowing the identity of these complexes and understanding their fundamental chemistry. Tank characterization work has not yet identified any of the non-pertechnetate species. However, based on the types of ligands available and the redox conditions in the tank, a reasonable speculation can be made about the types of species that may be present.[3] Thus, this project was synthesizing relevant model complexes of Tc(III), Tc(IV), and Tc(V) that may form under tank waste conditions. The complexes were to be characterized and used as standards for characterizing the non-pertechnetate species in actual waste using instrumental techniques such as XAS and subsequent EXAFS and XANES analysis. We had hoped to study the redox chemistry of the technetium complexes so that more efficient and selective oxidative methods can be used to bring the tank non-pertechnetate species to $TcO_4^-$ for processing purposes. We were to study the ligand substitution chemistry of the synthesized complexes, which could be used to develop separation methods for non-pertechnetate species. Understanding the fundamental chemistry of these technetium complexes hopefully will enable technetium to be efficiently removed from the Hanford tank waste and help DOE to fulfill its remediation mission.

## Experimental Methods

**General:** All water used was 18-MΩ water (Millipore, Bedford, MA). Except where noted, chemicals were reagent grade and were obtained from either Aldrich Chemical Co. or Fisher Scientific and were used without further purification. An Ocean Optics model SD 2000 UV-VIS spectrometer was used to measure the adsorption spectra of the technetium complexes. Atlantic Microlab, Inc. (Norcross, GA) performed chemical analysis for C, H, and N. Technetium-99 concentrations were made using a calibrated Packard 2200 liquid scintillation counter. The XAS measurements were performed on ~0.01M technetium samples at the Stanford Radiation Laboratory (SSRL).

**Pertechnetate anion preparation and assay techniques: CAUTION:** $^{99}$Tc is a weak β-emitter. Radiation from the amount of material used in these is experiments are completely absorbed by the glass walls of the reaction vessels. Even so all operations hare been carried out in specially designed laboratories suitable for handling gram quantities of technetium. Ammonium pertechnetate, $NH_4TcO_4$, was obtained from Oak Ridge National Laboratory. This material, which should be white, was black; indicating it had undergone radiolytic autoreduction to $TcO_2$. This mostly black solid was purified by hydrogen peroxide oxidation in ammonium hydroxide and metathesized with NaOH to produce $NaTcO_4$.

Liquid scintillation counting (LSC) of $^{99}$Tc was performed using a Packard Model 2200 CA Tri-Carb® Liquid Scintillation Analyzer instrument, which has a counting efficiency of 98% for $^{99}$Tc ($\beta^-$ = 292 keV, branching ratio = 100%). The counting solution (cocktail) was prepared in 25 mL polyethylene scintillation vials by taking the desired volume (V) of the sample, (6.0 mL–V) of water, and 14.0 mL of Ultima Gold™ A/B scintillation liquid (Packard). The cocktails were analyzed using an energy window of 0–200 keV, which encompasses >99.9% of the activity in the $^{99}$Tc spectrum. The number of counts-per-minute (cpm) for each sample and for several background samples (bkg) were recorded. The net cpm of $^{99}$Tc in the sample was converted to nanograms (ng) $^{99}$Tc by equation (1):

$$\underline{{}^{99}\text{Tc (cpm)} \qquad + \qquad 98} \qquad = \qquad {}^{99}\text{Tc ng} \qquad\qquad (1)$$

This equation was derived from a calibration curve established with an Amersham $^{99}$Tc standard (Amersham Corporation, Arlington Heights, IL).

**Preparation of Technetium complexes**: The preparation of the complexes were adaptations of the procedures in the literature described by several major author, Baldas[1], Burgi[6], Linder.[7, 8] All reaction were carried in water at a < 5 mmol scale. The reactions were done at room temperature or if required with slight warming. Rigorous anaerobic conditions were not used but the reactions were done in capped vial with a nitrogen purge. Typical preparations are given below. Complexes were prepared using ligands such as ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-diacetic acid (EDDA), iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), N-(2-hydroxyethyl)ethylenediamine-triacetic acid (HEDTA), oxalate, glycolate, citrate, and gluconate, ethhylenediamine (en), diethylenetriamine (detn), and triethylenetetraamine (tetn).

**Preparation of Tc(EDDA) (2):** $NaTcO_4$ (0.356 g, 1.915 mmol) was added to 10 mL of 0.1 M NaOH containing $NaHSO_3$ (0.329 g, 3.16 mmol) and ethylenediaminediacetic acid (EDDA, 0.675 g, 3.84 mmol). The capped solution was stirred for 2-3 days. During which time the solution went from colorless to pale orange and eventually to dark red. The product was precipitated by adding ethanol, filtering and washing with a 4:1 ethanol:water solution. The product does not sorb onto Sephadex®-CM-25 (Aldrich) but does stick to Sephadex®-QAE-A25 (Aldrich) indicating it is anionic complex. Purification was achieved by loading an aqueous solution of the product onto a 1 x 50-cm Sephadex®-G-10 column and eluting with water; the product was evaporated to dryness. Chemical analysis found: Tc, 17.40%; C, 19.38%; H, 3.91%, N, 7.78%. Calculated for $[Tc_2EDDA_3]_n$: Tc, 28%; C, 30.5%; H, 2.4%, N, 11.9%. IR (nujol, $cm^{-1}$): 3100-3600 (s,b), 1598 (s), 1403 (sh), 1378 9sh), 1338 (m), 1243 (w), 1125 (vw), 1008 (m), 958 (w), 913 (w), 851 (sh). UV-VIS ($H_2O$; $\lambda_{max}$, nm ($\varepsilon$, L $mol^{-1}$ $cm^{-1}$)): 384 (5504), 485 (2650), 522 (2515).

**Preparation of Tc(gluconate):** This complex was prepared by a method similar to the literature.[22] Sodium pertechnetate (0.214g, 1.15 mmol), sodium gluconate (2.511g, 11.5 mmol), sodium sulfite (0.272 g., 2.16 mmol) were dissolved in 0.10 M NaOH (Note: Stannous chloride can also be used as a reductant). Each solution was then added in succession to a 20 mL glass vial. The total volume was approximately 12 mL and the final pH of the reaction mixture was 12. Within two days, the solution became pale pink and got progressively darker over the next two weeks. The product does not sorb onto Sephadex®-CM-25 (Aldrich) but does stick to Sephadex®-QAE-A25 (Aldrich) indicating it is anionic complex. Purification was similar to that described for the Tc(EDDA) complex. The pink product UV-VIS has a $\lambda_{max}$ at 516 nm. The reaction also works well in 2,5 M NaOH.

**Preparation of Tc(N)(IDA):** All the nitrido technetium complexes were prepared from $TBA[Tc(N)Cl_4]$.[9,23] $TBA[Tc(N)Cl_4]$ (0.057 g, 0.086 mmol) in acetone was mixed with an excess of iminodiacetic acid (0.057 g, 0.43 mmol) in water. The solution immediately turned orange then red. After 30 minutes the solution is colorless with a red precipitate. The red solid was dissolved in water and purified on G-10. The same reaction performed under slightly basic conditions gives a yellow product.

## Results

Because polyaminocarboxylate ligands are known to exist in Hanford tank waste our first set of technetium complexes we prepared were those with these types of ligands. These were initially prepared using methods similar to those found in the literature. A typical procedure involved the sulfite reduction of pertechnetate under mildly acidic to neutral conditions. Each complex was precipitated from aqueous solutions by the addition of ethanol. After dissolving in water, the complexes were purified using size exclusion chromatography (Sephadex G-10). The products were generally only soluble in water which made it difficult to form crystals. Attempts to form crystals of the compound with various counter cations ($Cs^+$, $Sr^{2+}$, $Ba^{2+}$, $NH_4^+$, PPN) were unsuccessful using a variety of techniques including vapor diffusion of ethanol into an aqueous solution of the product or solvent layering techniques.[24] The IR data and chemical analysis generally indicated a significant amount of waters of hydration in the dried products.

Polyaminocarboyxlate technetium complexes are known to form a dimeric structure, $[(L)Tc(\mu\text{-}O)_2Tc(L)]^{n-}$, with technetium in the +4 oxidation state. Complexes have been prepared using ligands such as EDTA (ethylenediaminetetraacetic acid), EDDA (ethylenediamine-N,N'-diacetic acid), IDA (iminodiacetic acid), NTA (nitrilotriacetic acid), DTPA (diethylenetriaminepentaacetic acid) and oxalate.

The first complex synthesized was a Tc(EDTA) (**1**) complex. This complex has been synthsized by Burgi[6] and Linder.[7,8] Similar crystal structures were obtained by both groups showing the complex to be a technetium (IV) dimer, $[(EDTA)Tc(\mu\text{-}O)_2Tc(EDTA)]^n$. Other chracterization data were different; both preparations showed a UV-VIS band at ~500 nm but with quite different extinction coefficients (ε, L $mol^{-1}$ $cm^{-1}$), 4200 and 2000, respectively. Our complex, a brownish-purple material, had an exticion coefficient of 640 L $mol^{-1}$ $cm^{-1}$. Our XANES data showed the complex was a Tc (IV) species but the EXAFS data said it was a dimer bridged by a single oxygen, a μ-O bridge. In addition the complex contained three EDTA ligands. Our $[Tc(\mu\text{-}O)Tc(EDTA)_3]$ complex may have 1 or 3 EDTA ligands that bridges the Tc atoms. Linder also prepared an EDTA dimer with a single bridging μ-O group that had a UV band at 622 nm with an extinction coefficient of only 450 L $mol^{-1}$ $cm^{-1}$.[8] What these differences suggest is that slight variations in reaction conditions can lead to quite different results. In addition, the complexes may be able to convert between each other.

Contrary to literature reports none of the polyaminocarboxylate complexes exhibited significant stability under caustic conditions. The observed instability of the complexes appears to a function of concentration. This is illustrated by our investigations of the Tc(EDTA) (**1**) complex. Solutions of the complex that are > 0.01 M are stable in water for months. Upon dilution to tank relevant concentrations, 5 x $10^{-5}$ M, the absorbance at 500 nm decreases to about 60% of its initial value within several days. These solutions are relatively stable compared to a slow oxidation to pertechnetate that is occurring either subsequently or concurrently to dilution. This oxidation, as expected, is dependent on the exposure to oxygen. This behavior was observed for solutions having pHs between 3 and 11. We suspect that the dimeric complexes are forming monomeric species on dilution and the monomeric species are unstable to oxidation. At even greater dilution (<< $10^{-5}$ M), such as those used in a CE-ICP-MS experiment that we tried, we observed even faster decomposition to pertechnetate. Complex equilibria between monomers, μ-O dimers, and bis (μ-O dimers) of technetium nitrido complexes have been described by Baldas.[9] In addition Linder has noted that technetium aminocarboxylate complexes freely interconvert to other species in solution which complicates their isolation and characterization.[8] This observation is conquered by this set of workers. The stability of the complexes can be enhanced by increasing the ligand concentration in solution and adding a holding reductant; conditions that mimic a tank waste environment. Further studies are needed to define the chemistry of these complexes in caustic media under these types of conditions.

At pHs > 12, the EDTA complex is converted, within 2 days, to a colorless species which is not pertechnetate. There is no oxygen dependence on this conversion. Technetium distribution coefficients between the basic solutions and Reillex™-HPQ anion exchange resin show that the $TcO_4^-$ concentration is still increasing after 50 days. Some bis (μ-O dimers) of Tc and Mn are known to under go reduction to in the presence of base. The reduced Tc complexes are highly colored and some such as the TCTA complex are quite stable. We did not observed this type of color change but at tank concentrations this may have not been observable. However the slow oxidation to pertechnetate may be indicate some similarity to the chemistry at higher concentrations.

The Tc (EDDA) complex (**2**) is a red colored material. The UV-VIS spectrum of this complex shows a band at 485 nm ($\varepsilon = 2650$) and 522 nm ($\varepsilon = 2515$) which suggests a mixture or a more complicated structure than **1**. The IR spectrum shows carboxylate coordination at 1598 $cm^{-1}$ and Tc-O-Tc bridging stretch at 791 $cm^{-1}$. The XAS data indicated a Tc(IV) complex with (μ-O) bridging groups with the technetium atoms being separated by ~3.5 Å The elemental analysis indicated a 2:3 relationship between technetium and EDDA. This combined data suggested a tetramer, $Na_4[Tc_4(\mu\text{-}O)_4(EDDA)_6]$, shown in Figure 1.

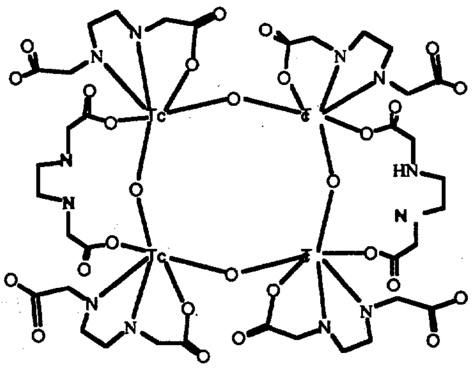

**Figure 1. Structure of the $[Tc_4(\mu\text{-}O)_4(EDDA)_6]^{4+}$.**

The two bands in the UV-Vis at 485 and 522 may reflect the presence of the two types of Tc-Tc interactions in the tetramer, the simple μ-O bridge and the combined μ-O/EDDA bridge. Complex **2** decomposes to pertechnetate in 0.67 M NaOH over two days. The Tc-EDDA complex is appears to be stable for weeks in water at concentrations >0.01 M, but unstable in water at concentrations $< 5 \times 10^{-3}$.

In the presence of IDA, a red and a blue complex ($\lambda_{max} = 518$ and 590 nm, respectively) are formed in equilibrium but could be separated and isolated by selective ethanol precipitation or size exclusion chromatography. The infrared spectrum of these complexes indicates coordination of the ligand carboxylate groups to technetium at approximately 1625 $cm^{-1}$. An observed stretch at ~1085 $cm^{-1}$ is consistent with the presence of a Tc-OH group in the red complex. The XAS data indicated that this was a Tc(IV) monomeric species, $[Tc(OH)_2(IDA_2)]^{2-}$ (**3**). The IR (748 $cm^{-1}$) of the blue complex indicate that a bis (μ-O) bridge exist between two technetium centers. The EXAFS supports a dimer structure. The blue color suggests a III/IV dimer. The elemental analysis is consistent with $Na_3[Tc_2IDA_3]\bullet5H_2O$ (**4**). The anion of **3** shown in Figure 2 also has a bridging IDA group.

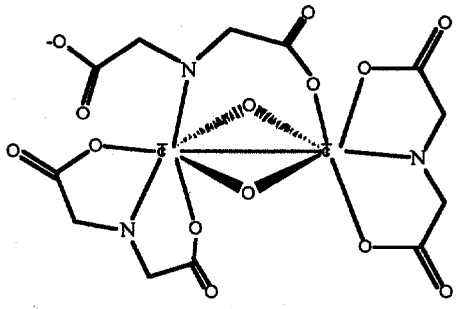

**Figure 2. Structure of $Na_3[Tc_2IDA_3]\bullet5H_2O$ (4).**

The red IDA complex at ~0.01M appears to stable in water for months but decomposes overnight in 0.67M NaOH. The blue complex is unstable in water decomposing to unknown species after several weeks. Both complexes are stabilized by adding $HSO_3^-$ and excess IDA to the solution; a situation not unlike a Hanford tank waste environment where complexant concentrations are large relative to technetium and radioloysis maintains a reducing environment.

A purple Tc-citrate complex (**5**) was also formed with a $\lambda_{max}$ = 530 nm. The IR data indicates bound carboxylates, a Tc-OH stretch at 1108 $cm^{-1}$ and a Tc-O-Tc stretch at 718 $cm^{-1}$. The XANES data show Tc(IV). The EXAFS data also indicates a number of μ-O bridges but the data is too complicated to propose a structure. Another author has suggested a convoluted trimer for a Tc citrate complex.[25] This complex is also stable for months in water but decomposes overnight in 0.5M NaOH.

The deep red Tc-glycolate (**6**) complex ($\lambda_{max}$ = 360, 518 nm) has an infrared spectrum that show carboxyl coordination to Tc at 1629 $cm^{-1}$ and a Tc-OH stretch at 1142 $cm^{-1}$. The XAS data indicate a Tc(IV) monomeric complex. A previously proposed ($[Tc(OH)_2glycolate]_2^-$) prepared by a different method is consistent with these observations. The glycolate complex decomposes over 3 days in 2 M NaOH to $TcO_4^-$ (Figure 3). The stability could be slightly enhanced by mimicking the reducing environment in the tanks with the addition of excess reducing agent and free ligand.

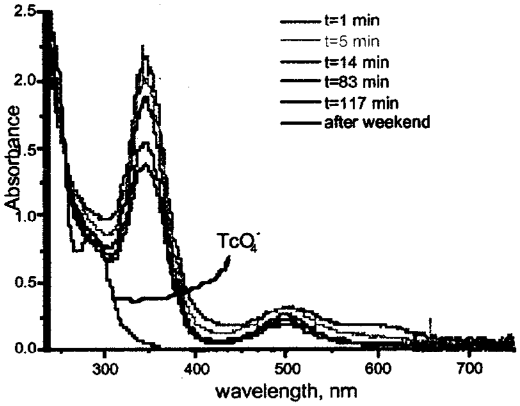

**Figure 3. Decomposition of Tc-glycolate (6) in 2 M NaOH.**

An extended series of technetium nitrido complexes were prepared using $[TcNCl_4]^-$ as a starting material. Substitution of the chlorides for a variety of ligands has been attempted under acidic and basic conditions. For each ligand (EDTA, oxalate, HEDTA, glycolate, citrate, IDA, EDDA), a scarlet red complex is formed in 0.5 M $HNO_3$, while a bright yellow complex is formed in 0.5 M NaOH. Addition of nitric acid to the yellow complex causes the rapid formation of the red complex and vice-versa. Dimeric red nitrido complexes of EDDA and EDTA with a μ-O bridge have been reported in the literature.[26,27] The red color was attributed to a transition in a linear Tc-O-Tc three-center π-bond system. The yellow complexes may either be dimeric in nature with a bis-μ-oxo bridge, or monomeric. The XANS analysis of our red Tc(N)IDA **(7)** complex does not show a K shell pre-edge peak indicative of a Tc(VI) species. The chemical shift and shape of the edge indicates that this complex is a Tc (IV) species.[28] However there are no known Tc(IV) nitrido complexes and the reaction conditions were not right for the formation of a Tc(V) nitrido complex.[9] Thus we presume the anomalous XANES data are peculiar to nitrido complexes. The EXAFS data suggests that the complex is a triangular trimeric species with bridging μ-O groups between the technetium atoms; the technetium atoms being separated by ~3.6 Å. Only one IDA ligand is attached to each Tc(N) center.

A $[TcO(gluconate)_2]^{3-}$ complex has been used as a ligand transfer ligand complex for forming technetium radiopharmaceutical complexes of a desired ligand. This technique is useful because it is competitive with $TcO_2$ formation and precipitation. This is interesting because gluconate is the initial product of sugar-based denitration processes at Hanford.[29] Unfortunately, the denitration conditions were such that gluconate was consumed in the denitration process. This PI has not seen a tank analysis that shows residual gluconate. Anyway, we have been successful using sulfite or stannous chloride as a reductant to forms a stable, reduced technetium complexes it base concentrations up to 2.5 M NaOH. This is consistent with Steigman who has shown that the Tc-gluconate complex forms readily under basic conditions (pH = 12).[22] Several other similar polyhydric complexes of technetium are also known with widely differing stabilities.[22] Although no crystallographic studies of any polyhydric complex of technetium have been reported, some structural information is available. A study of the $SnCl_2$ reduction of pertechnetate in the presence of gluconate and glucoheptonate concluded that a large family of Tc(V) compounds could be formed in dilute alkali.[22] The number of electrons taken up by pertechnetate, *n*, was 2.0 for a gluconate/technetium ratio down to 17:1 in alkaline solution but was 2.4 at a pH = 5.0 when the ratio was 110. A further iodometric titration in air resulted in an n value of 2.8. The nature of the products formed in the presence of insufficient gluconate has not been investigated. Steigman has also suggested that the carboxylic acid group is not involved in binding of the technetium to polyhydric alcohols.[22] Possible structures could include monomeric or μ-oxo dinuclear species.

With this as a background, our XAS data on our pink complex was quite interesting. The XANES data showed it to be a Tc(V) species as expected. However, the EXAFS data suggested that the complex is a trimeric species with μ-O bridges between the technetium centers. The O=Tc-O-Tc=O linkage is quite unique in technetium chemistry.[30,31]

In order to obtain greater insight into the nature of the non-pertechnetate complexes in actual waste we have tried to separate the species from an actual waste sample. Figure 4 is a chromatogram of a separation performed on AN–107 using Sephadex® G10 size exclusion gel. In this experiment, 0.400 mL of AN–107 that was brought to pH 3 and passed through the column (An interesting aspect to this separation is that the non-pertechnetate species seem to be stable at pH 3!). The eluent is water. Figure 4 displays the gross $\gamma$–counts (NaI), the gross $\beta$-counts (LSC), and the net $^{99}$Tc count vs. elution volume. The total technetium analyses indicated that 60% of the technetium was coming through the gel Sephadex® column; a percentage consistent with the non-pertechnetate content of the AN-107 waste. The small pertechnetate anion stuck to the top of the column. Further development of this technique will ultimately give a sample clean enough to be analyzed by CEMS.

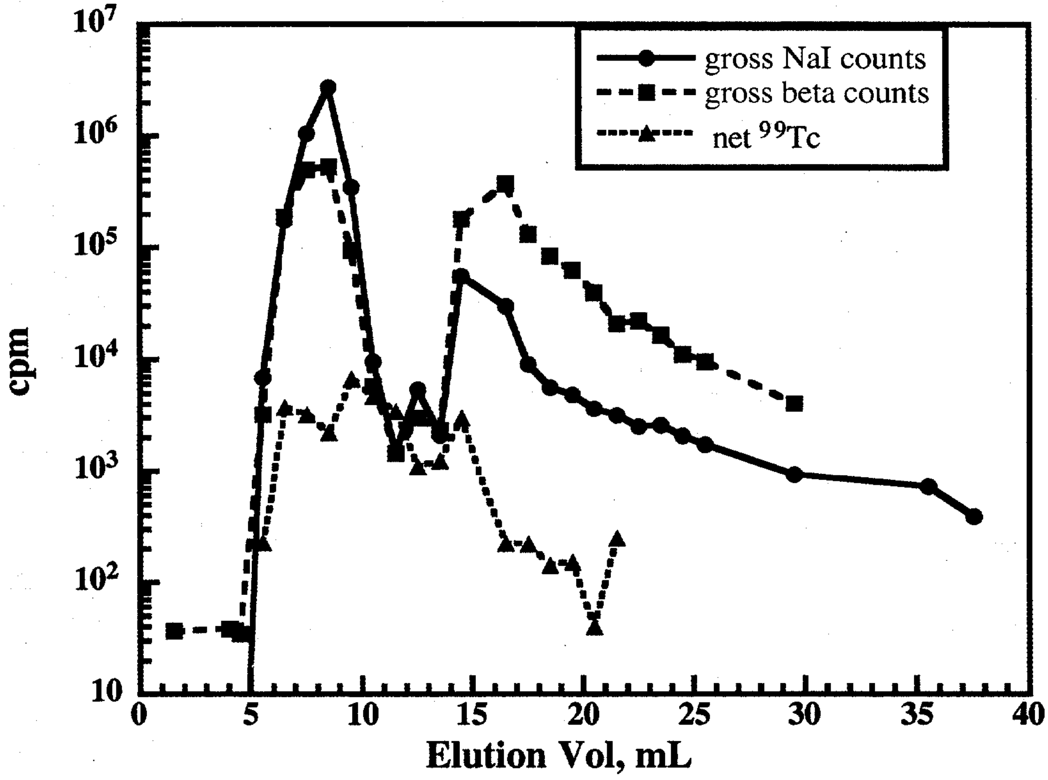

**Figure 4. Gross $\gamma$, $\beta$, $^{99}$Tc Counts vs. Elution Volume for a Chromatographic Elution of AN–107 Using Sephadex® G10.**

## Relevance, Impact and Technology Transfer:

a. **How does this new scientific knowledge focus on critical DOE environmental management problems?** The work we have done shows that many of the non-nitrido technetium complexes we prepared are not stable in caustic conditions. We prepared many different complexes under slightly acidic or neutral conditions that XAS data suggested were either Tc(IV) or Tc(V). Upon dissolution in basic solution (~0.5 M NaOH) they decomposed, over hours to days, to unknown species, $TcO_2$, or pertechnetate. The probable reason for the instability of the Tc(IV) species in base is hydrolysis to $TcO_2$.[32] Many of these experiments produced a brown or black precipitate speculated to be $TcO_2$. In addition, both oxidation states are also susceptible to oxidation as evidenced by the production of pertechnetate. This would seem to eliminate them as possible candidates for the troubling non-pertechnetate species in the Hanford waste. However, the complex chemistry in the tanks has produced many different ligand types and structures and this study could not have exhausted this list.

Gluconate complexes are interesting because gluconate is the initial product of sugar-based denitration processes at Hanford.[29] Unfortunately, the denitration conditions were such that gluconate was consumed in the denitration process. This PI has yet to see a tank waste organic content analysis that shows gluconate or any of its lower breakdown products present. This search includes a search of the computerized Hanford Defense Waste Model prepared by Agnew et al.[33] Nitrido complexes are stable in base but it is difficult at this point to develop a mechanism for their formation. This leads once again to ask the question what are the non-pertechnetate species that exist in the tanks that are so stable and hard to separate.

b. **How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?** This work shows that we still do not know what the non-pertechnetate species are. Since these species are resistant to oxidation and proposed separation schemes they will still present a formable separations problem. The current approach at Hanford is get around the problem by requiring an over all technetium removal requirement of 80%.[34] The non-pertechnetate species will remain in the bulk of the waste that will be converted to glass chips for near surface disposal on the Hanford reservation.[35] This approach will facilitate the DOE to reduce its pretreatment costs, meet its schedule, and meet its current risk assessments. However, if future risk assessments become more stringent then the need to study this problem may require further study. At this point or preferably in anticipation of a future problem it may be beneficial to approach this problem from another point of view. This was proposed in our renewal proposal where we suggested that we separated the non-pertechnetate species and analyze them with several different techniques

c. **To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-driven applied technology development?** With nine possible oxidation states, the chemistry of technetium is very complex. Research on technetium has been largely driven by it application to medical radiopharmaceutical. The early literature on technetium complexes containing ligands similar to those in Hanford tank waste was done at much less than the millimole scale.[4,5] Thus, compounds were never isolated and there was much speculation on the type of species present. Work at larger scales by Linder[8], Burgi[6], and Davidson[7] (to name a few) produced structural information on technetium complexes containing ligands relevant to Hanford waste. Recent work is still directed at the medical radiopharmaceutical application but has an emphasis on complexes that are of a different nature than those expected in tank waste.[1,9] Thus, this work has refocused some technetium synthetic chemistry back to an important environmental that may have other application in the medical radiopharmaceutical field.

d. **What is the project's impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?** The project has given this PI, his collaborators, post-doctoral student, and other students an interesting project to work on. It has allowed LANL, the Chemistry Division, and especially the Isotope and Nuclear and Radiochemistry (C-INC) group to re-establish itself in the field of technetium synthetic chemistry. The results of this project are useful in that they can be used eliminate possibilities for the non-pertechnetate species in the tank waste. These results will be used by this PI for publications and as supporting evidence for new proposals that will use a different approach to solving the non-pertechnetate problem in the waste.

e. **Are larger scale trials warranted? What difference has the project made? Now that the project is complete, what new capacity, equipment or expertise has been developed?** No large-scale trials are warranted. The project adds to the characterization and reactivity of technetium complexes in basic media. The project will help limit the scope of future efforts to solve this problem.

f. **How have the scientific capabilities of collaborating scientists been improved?** Our collaborating scientist has become more skilled in the structure analysis of technetium compounds by EXAFS and XANES. Because of our collaborators problem of getting enough time to analyze our last data set this forced this PI to develop XAS capabilities with structural chemist within the his division. Our X-ray crystallographer has made it his mission to develop his expertise so that he can supply this service to the Chemistry Division.

g. **How has this research advanced our understanding in the area?** It has given greater insight into the nature of technetium complexes in a basic environment and gave further information about the nature and stability of the non-pertechnetate species in the Hanford waste.

h. **What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?** A different approach to this problem is warranted. We should probably stop speculating about what might be the identity of the non-pertechnetate species in Hanford waste and instead take a more analytical approach. We should try to separate the non-pertechnetate fraction from a waste sample and then develop methods like capillary electrophoresis to identify the species. We recently proposed this approach in our renewal proposal but were not funded.

i. **Have any other government agencies or private enterprises expressed interest in the project?** Lynntech, Inc. of College Station, Texas was interested in our on the oxidation of the non-pertechnetate species. They provided us with research money with a "Funds in

Agreement" to apply their proprietary oxidant to this problem. Because of this agreement, my contact at Lynntech was quite interested in our synthetic work and how the complexes we were working on might stand up to his oxidant.

**Project Productivity: Did the project accomplish all of the proposed goals? If not, why not? Was the project on schedule? Was the work plan revised? If so, describe revision.**

The project did not accomplish all it original goals. The major reason for this is that the technetium chemistry proved a lot more difficult to achieve than originally thought. The background literature that was the basis of the proposed chemistry implied greater stability for the technetium complexes in base than was observed. The inability to obtain single crystals slowed identification of the complexes. This left XAS as major way of identifying the products of our work. This is a slow process since data is only generated two times a year at the most. In addition the data analysis was not in the PI control and thus was subject to delays inflicted on our collaborator by his other pressing programmatic problems. Another factor is the ever-increasing emphasis on ES&H in today's DOE laboratory environment. This does have consequences on productivity and does begin to intimidate workers who are afraid of having contamination incidents.

**Personnel Supported:**

Norman C. Schroeder (PI, technical staff member, LANL)
Jon Bernard (post-doctoral student, LANL)
Kenneth R. Ashley (Chemistry Professor, Texas A&M-Commerce)
Dave Blanchard (technical staff member, PNNL)
Steve Conradson (technical staff member, LANL)
Brian Scott (technical staff member, LANL)
Ahn Truong (GRA summer student from Texas A&M-Commerce)
Jason Ball (chemical technician, LANL)

**Publications:**

Norman C. Schroeder, Susan D. Radzinski, Kenneth R. Ashley Anh P. Truong, Glenn D. Whitener "Feed Adjustment Chemistry for Hanford 101-SY and 103-SY Tank Waste: Attempts to Oxidize the Non-Pertechnetate Species" submitted to the *Journal of Radioanalytical and Nuclear Chemistry*.

A paper on the synthesis and XAS of technetium complexes is being worked on.

**Interactions:** Presentations at meetings, workshops, conferences, seminars, etc.

1. Norman C. Schroeder, "Oxidation, Characterization and Separation of Non-Pertechnetate Species in Hanford Wastes," Efficient Separations and Processing Crosscutting Program FY 1998 Technical Exchange Meeting, Augusta GA, March 17-19, 1998.

2. Norman Schroeder, Dustin Clark, and Jonathan Bernard, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," NMSU Mini Symposium in Environmental Chemistry, Las Cruces NM, April 18, 1998 (LAUR 98-1372).

3. Norman Schroeder, Dustin Clark, and Jonathan Bernard, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," NMSU Mini Symposium in Environmental Chemistry, Las Cruces NM, April 18, 1998 (LAUR 98-1372).

4. J. G. Bernard, D.L. Clark, N .C. Schroeder, K .R. Ashley, and A .P. Truong, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," presented at the American Chemical Society National Meeting, Boston, Aug 1998.

5. Jonathan G. Bernard, Dustin L. Clark, Jason R. Ball, Norman C. Schroeder, Kenneth R. Ashley, and A. P. Truong, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," presented to the CST visiting committee, June 1998.

6. Norman C. Schroeder, Jonathan G. Bernard, Dustin L. Clark, Jason R. Ball, Kenneth R. Ashley, Anh P. Truong, and David L. Blanchard, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," Environmental Management Science Program Workshop, July 27-30, 1998 Chicago, Ill

7. Kenneth R. Ashley, Anh P. Truong, Leah M. Arrigo, Jeffery B. Dooley, Patrycja A. Szczepaniak, Norman C. Schroeder, Glenn D. Whitener, and Susan D. Radzinski, "Oxidation of Reduced Technetium in 101-SY and 103-SY Hanford Tank Wastes," presented at the 54th Southwest Regional ACS Meeting, Baton Rouge LA, Nov 1998.

8. Norman C. Schroeder and Kenneth Ashley, "Oxidation, Characterization and Separation of Non-Pertechnetate Species in Hanford Wastes," Hanford Tank Waste Technetium Chemistry Workshop, Richland, Washington September 21-25, 1998.

9. Kenneth Ashley and Norman C. Schroeder, "Reillex-HPQ Anion Exchange Column Chromatography: Removal of Pertechnetate Ion from DSSF-5 Simulant, Resin Sustainability and Flow Studies," Hanford Tank Waste Technetium Chemistry Workshop, Richland, Washington September 21-25, 1998.

10. Jonathan G. Bernard, Eve Bauer, Norman C. Schroeder, Monique P. Richards, Rebecca M. Chamberlin, David L. Blanchard, "Technetium Chemistry in Alkaline Nuclear Waste", Gordon Conference on Inorganic Chemistry, Rhode Island, July 1999.

11. Jonathan G. Bernard, Norman C. Schroeder, Dustin L. Clark, and Kenneth R. Ashley, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," presented at the American Chemical Society National Meeting, New Orleans LA, August 1999.

12. Norman C. Schroeder, Jonathan G. Bernard, Kenneth R. Ashley, and David L. Blanchard, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," presented at the DOE/AL Review of the DOE/EM Office of Science and Technology Projects, September 1-3, 1999.

13. Kenneth R. Ashley and Norman C. Schroeder, "Separation of Pertechnetate Anion Using Reillex-HPQ Resin", Southwest Regional Meeting of the American Chemical Society, El Paso TX Oct 21-23, 1999.

14. Norman C. Schroeder, Jonathan G. Bernard, Kenneth R. Ashley, and David L. Blanchard, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," presented at the American Chemical Society National Meeting, San Francisco CA, March 26-30, 2000.

15. Norman C. Schroeder, Jonathan G. Bernard, Kenneth R. Ashley, and David L. Blanchard, "Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste," presented at EMSP Workshop, Atlanta GA, and April 25-28, 2000.

**Transitions:**

**Describe cases where knowledge resulting from your effort is used, or will be used, in a technology, technique or process improvement application. Transitions can be to entities in the DOE, other federal agencies, or industry.** The expertise in technetium synthesis established under this project may be used to help form collaboration with a private company interested in developing a technetium radiopharmaceutical project. In addition, the development of capabilities to handle gram quantities of technetium helped our group get involved in the preparation of Tc targets for the Accelerator Transmutation of Waste project.

**Patents:** None

**Future Work: What remains to be done?** A positive ID of a non-pertechnetate species separated from actual waste would be a great start. Then we could synthesize the real species and study its oxidation and separations chemistry.

**Will the project lead to future work**? It is my mission to pursue further funding on this fascinating problem.

**If so, describe the nature of the future work.** See my renewal proposal that I submitted to EMSP.

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**Feedback:** Forget the monthly reports and go to a quarterly report.