

Project Title: Identification of Non-Per technetate 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 will 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 will use model technetium complexes to develop a capillary electrophoresis mass spectrometry (CEMS) technique that will be used to identify non-pertechnetate species in actual waste samples. The model technetium complexes will be 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 are too easily oxidized or show less stability in caustic media compared to the actual non-pertechnetate species in the waste.

This proposal has three major goals: (1) develop capillary electrophoresis mass spectrometry as a characterization technique, (2) separate a non-pertechnetate fraction from a waste sample and identify the non-pertechnetate species in it by CEMS, and (3) synthesize and

We have been working on understanding the electrospray ionization mass spectrometry of rhenium complexes as surrogates for technetium complexes. Rhenium compounds are chemically analogous to technetium compounds but are non-radioactive. This allows us to work at a faster rate because we do not have to isolate the instrument in a controlled area or decontaminate it after using it. We have done some direct injections of rhenium compounds into an electrospray mass spectrometer (Finnigan LCQ spectrometer). We have studied seven rhenium compounds to date: rhenium bisoxotetrapyridine $[(\text{ReO}_2(\text{py})_4)^+]$, perrhenate (ReO_4^-), rhenium gluconate $[\text{ReO}(\text{gluconate})_2]^{3-}$, $[\text{Me}_4\text{N}][\text{ReO}(\text{SCH}_2\text{CH}_2\text{S})_2]$, $[\text{Bu}_4\text{N}][\text{ReO}(\text{OCH}_2\text{CH}_2\text{S})_2]$, $[\text{Me}_4\text{N}][\text{ReS}(\text{SCH}_2\text{CH}_2\text{S})_2]$, and $[\text{Me}_4\text{N}][\text{ReO}(\text{OCH}_2\text{CH}_2\text{S})_2]$. The first compound was run in the positive ionization mode while the rest were run in the negative ion mode. The spectra were taken with sample concentrations of 50 ng/L in DI water, at a flow rate of 5 $\mu\text{L}/\text{min}$. The spectra are stable for many minutes. The spectrum of $[(\text{ReO}_2(\text{py})_4)^+]$ is shown in Figure 1. The parent ion isotopic envelope is clearly seen at 534 Daltons (Da), for this complex. The peaks at 455, 377, and 298 Da are due to the sequential losses of pyridine (MW=79 Da). Each set of peaks shows the approximate isotopic pattern expected for the rhenium complex, with natural isotopes at 185 and 187 Da, 33 and 67% relative abundance.

Initial spectra for a direct injection of the rhenium gluconate sample looked relatively clean. Unfortunately, the major peaks observed were gluconate and perrhenate (verified by running the perrhenate sample). This rhenium compound has run poorly due to either instability of the compound itself or to instability of the compound to the ionization process (electrospray). Yet, the ionization performance of this system is soft enough to keep bradykinin intact (a peptide of MW=1060 Da). In order to determine the instability question we prepared the related thio and thio/alkoxide complexes listed above to see if there is a trend toward greater instability as the number of oxygen donors increase. Figures 2 and 3 show the mass spectra for the complexes $[\text{Me}_4\text{N}][\text{ReO}(\text{SCH}_2\text{CH}_2\text{S})_2]$, and $[\text{Bu}_4\text{N}][\text{ReO}(\text{OCH}_2\text{CH}_2\text{S})_2]$. The former complex is quite stable in the negative ion mode showing no measurable breakup of the salts' anion. The latter complex's spectrum (which is actually a reaction mixture) shows three interesting peaks at 355,

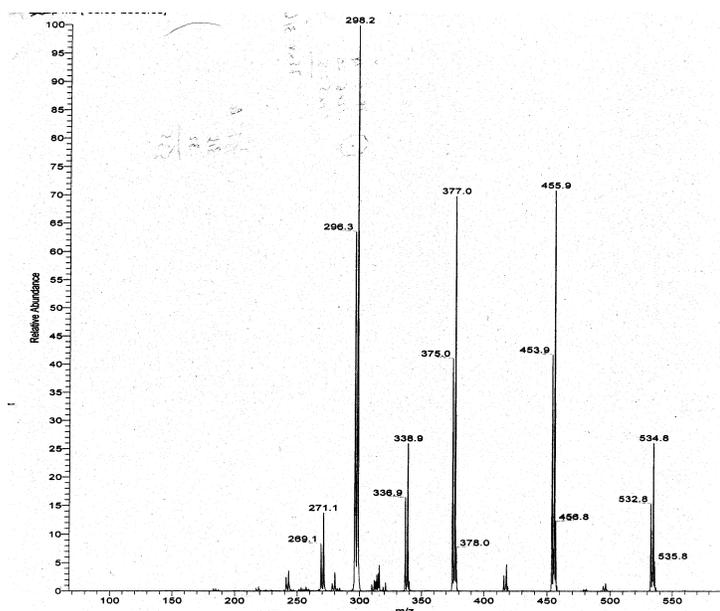


Figure 1. Mass Spectrum of $[\text{Re}(\text{O})_2(\text{py})_4]^+$ by Direct Injection.

5-6-02-S2_020506163842 #1 13-225 RT: 3.30-6.59 AV: 1.13 SM: 7G NL: 1.83E5
T: -p ms [150.00-2000.00]

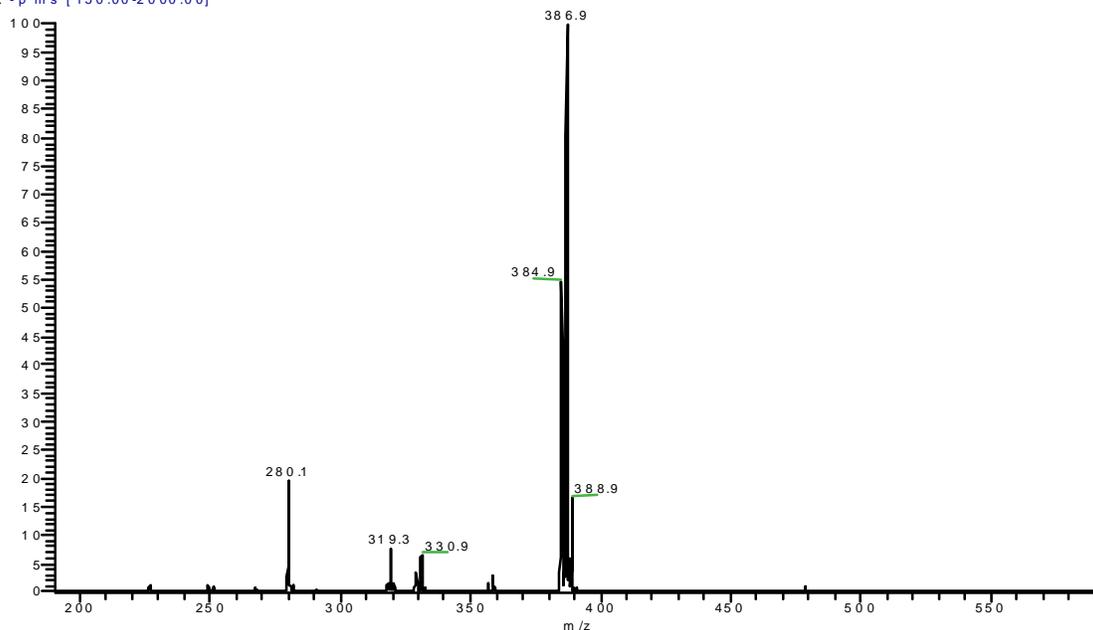


Figure 2. [Me₄N][ReO(SCH₂CH₂S)₂] 1.6 mg in 1.6 ml MeOH/H₂O/HAc (1.0/0.55/0.05), Negative Mode.

5-6-02-S5 #51-92 RT: 1.48-2.69 AV: 42 SM: 7G NL: 4.77E4
T: -p ms [150.00-2000.00]

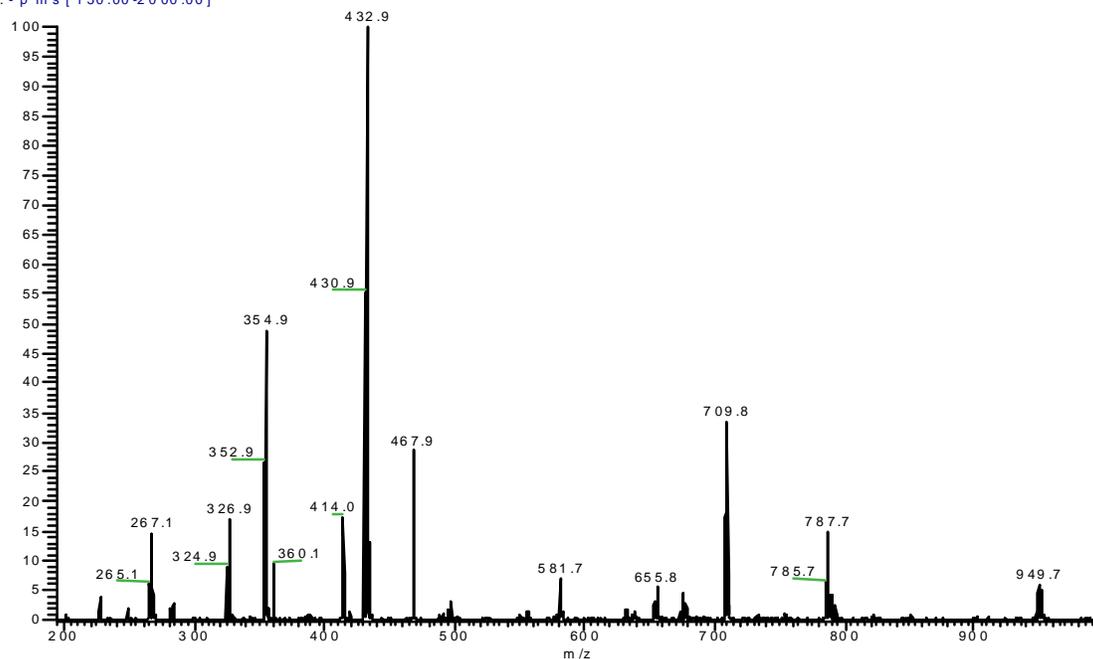


Figure 3. [Bu₄N][ReO(OCH₂CH₂S)₂] solution 100 ml in 1.5 ml MeOH/H₂O/HAc (0.9/0.55/0.05), Negative Mode.

433, and 710 Da. The first peak is the salts' anion while the most intense peak appears to be an $\text{ReO}(\text{OCH}_2\text{CH}_2\text{S})_3$ species that probably has one ligand binding in a bidentate mode and two ligands coordinating just through the sulfur. The latter peak appears to be a $[(\text{ReO}(\text{OCH}_2\text{CH}_2\text{S}))_2(\mu\text{-OCH}_2\text{CH}_2\text{S})_2]$ dimer. This more complex spectrum for this complex would seem to verify our hypothesis that there is a trend toward greater instability as the number of oxygen donors increases. However, subsequent work with technetium alkoxide complexes has revealed that the reaction conditions used to prepare the rhenium gluconate complex may have also contributed to its instability.

An extensive study of technetium alkoxide type complexes was begun. Alkoxide complexes are being investigated because they seem to be more stable in base than any other type of complex that might exist in Hanford waste, including EDTA type complexes. Based on the results to date they also seem more stable than the analogous rhenium complexes. In addition, we have confirmed that ~1300 tons of sugar, gluconate, and tartaric acid were used for denitrating B plant post PUREX acidic raffinates. Addition of these compounds brought the residual nitric acid concentration down to 1 M before these solutions were made caustic. We are preparing a number of alkoxide complexes. The alkoxide ligands being investigated are sugar, gluconate, mannitol, tartrate, ethylene glycol, butanol, 1,4-butanediol, 1,3-propanediol, pinacol, 1,2-cyclohexanediol, formaldehyde, oxalic acid, glycolic acid, acetol, 2,3-butanediol, and glycerol.

To date most of the work has been with gluconate. A technetium gluconate complex formed at 10^{-2} M NaOH with excess ligand and reductant. The complex oils out from the reaction mixture by adding a ten-fold excess of ethanol. The product is insoluble in all solvents except water. The UV-Visible spectrum of the isolated oil is shown in Figure 4. There is relatively strong peak at 506 nm and a weak peak at ~600 nm. A strong absorbance occurs at ~300 nm. Spectra taken during the reaction were used to estimate the extinction coefficient of the technetium gluconate complex's 506-nm peak. Assuming a complete reaction and a monomeric species then $\epsilon = 652 \text{ M}^{-1} \text{ cm}^{-1}$. If a dimer was formed then the coefficient would be twice this or $1305 \text{ M}^{-1} \text{ cm}^{-1}$. These extinction coefficients are much higher than that of the known Tc(V) alkoxide complexes, bis(1,2-ethanediolato)oxotechnetium(V), which has a weak ($\epsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}$) peak at 535 nm (Davison et al. *Inorganic Chimica Acta*, **128**, p.161, 1987). If the gluconate complex is a dimer the extinction coefficient would be in the range ($600\text{-}1800 \text{ M}^{-1} \text{ cm}^{-1}$) of the alkoxide dimers complexes formed under radiolysis (Lukens et al. *Environ. Sci. & Technol.* 2002). These radiolysis dimers had peaks at 495 nm. Further characterization (XAS, NMR, IR, etc.) of the gluconate complex is needed to verify its structure.

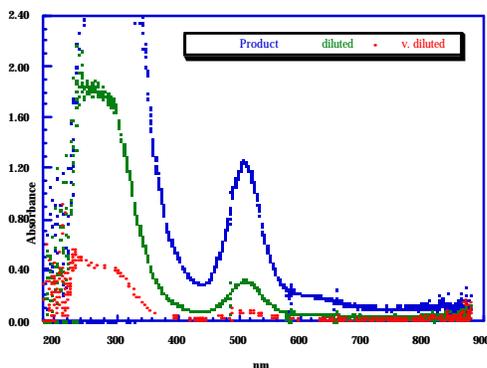


Figure 4. Technetium Gluconate Complex in Water.

The gluconate complex is quite stable in a basic (pH 12) solution. No attenuation of the intensity of UV-Visible spectrum of the complex was noted over 19 days. Addition of the complex to various buffers results in a slight shift of the spectra to lower wave lengths (503 nm). After 5 days the pH 4 and pH 9.18 spectra shift to longer wave lengths indicating possible substitution of the buffer anions (pH 4, phthalate and pH 9.18, borate) for the gluconate ligand.

Because the complexes appear to be impossible to crystallize we were concerned about the purity of the complexes. We have recently used thin layer chromatography (TLC: cellulose or silica gel) developed with either water or acetone to examine the purity of the complexes. Detection of the radiological species on the chromatogram is done with a Bioscan Imaging Scanner AR-2000. Figure 5 shows the results for a technetium gluconate reaction mixture developed on silica with water. Development is from left to right with an initial setting at 50 mm. Since pertechnetate and the gluconate complex are water-soluble they both move with the solvent front in water. Since there is no residual peak at the initial point no TcO_2 was formed in the reaction. Figure 6 shows the chromatogram developed in acetone, a solvent that pertechnetate is soluble in but the gluconate complex is not. Since no activity migrated with the solvent front all the pertechnetate was consumed in the reaction to form the gluconate complex.

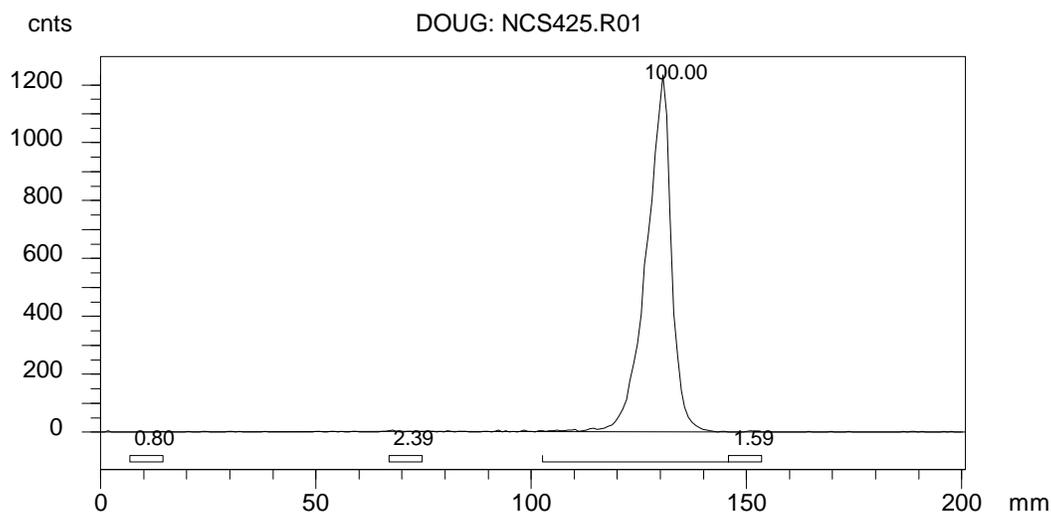


Figure 5. Tc-Gluconate Reaction Mixture Developed on Silica with Water.

Experiments were performed to determine if reduced, soluble technetium complexes could be formed from TcO_4^- under alkaline conditions without using external radiation, reductants, or catalytic metals to reduce the TcO_4^- . Sodium hydroxide solutions (2 M) containing a ligand (1M) and TcO_4^- (0.01 M) were stored at room temperature for four days under either dark or light conditions. Analysis of the solution by the TLC/Bioscan technique showed that carbohydrates/sugars or compounds with both a carboxylic acid and a hydroxyl group can reduce TcO_4^- to form reduced, soluble, technetium complexes. Complexes are formed under both dark and light conditions, which rules out photolysis as a cause of the reaction. However, ligands with only carboxylic acid groups or three hydroxyl groups or less do not show significant, if any amount of reduced, soluble technetium complexes being formed. Ligands containing both carboxylic acid groups and nitrogen atoms such as EDTA show mixed results, only small amounts of complexes being formed but the complexes seemed to be unstable and difficult to

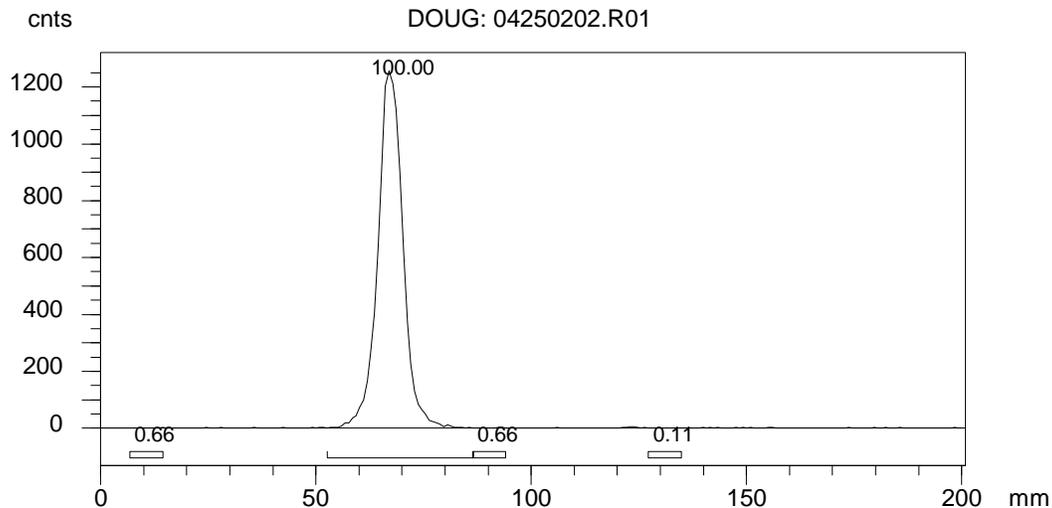


Figure 6. Tc-Gluconate Reaction Mixture Developed on Silica with Acetone.

analyze. This latter result is consistent with previous observations that EDTA type complexes of technetium are not stable in a caustic medium.

The UV-VIS spectrum of the gluconate reaction has weak band at 507 nm ($\epsilon = 20\text{-}40 \text{ M}^{-1} \text{ cm}^{-1}$). Assuming the reaction is complete, the weak band at 507 nm ($\epsilon = 20 \text{ M}^{-1} \text{ cm}^{-1}$) is much weaker than those observed by Lukens et al. (Environ. Sci. & Technol. 2002) who performed a similar experiment with a ^{60}Co source. These low extinction coefficients suggests that the complex a Tc(V) gluconate complex similar to the known bis(1,2-ethanediolato)oxotechnetium(V), which has a weak ($\epsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}$) peak at 535 nm (Davison et al. *Inorganic Chimica Acta*, **128**, p.161, 1987). Since gluconate has both polyalcohol and carboxylate functionalities we tested mannitol and acetate separately. Mannitol reacted within 4 days while no reaction has been observed for acetate in this time. Thus it appears that some of the reagents used in Hanford processing for denitration are reductants for pertechnetate in their own right.

Planned Activities

We will start to optimize the separation of a non- TcO_4^- fraction from an actual Hanford waste sample, AN-107, this summer. We will also run model technetium complexes on CE/MS this summer. The General Workscope and Objectives for each of the Fiscal Years of this project are outlined in the table above. We plan to present several papers or posters at the spring ACS meeting.

Information Access

One Page Adobe Acrobat File attached.