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## Synthesis and Characterization of 5- and 6- Coordinated Alkali Pertechnetates

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### ABSTRACT

The local chemistry of technetium-99 (<sup>99</sup>Tc) in oxide glasses is important for understanding the incorporation and long-term release of Tc from nuclear waste glasses, both those for legacy defense wastes and fuel reprocessing wastes. Tc preferably forms Tc(VII), Tc(IV), or Tc(0) in glass, depending on the level of reduction of the melt. Tc(VII) in oxide glasses is normally assumed to be isolated pertechnetate  $\text{TcO}_4^-$  anions surrounded by alkali, but can occasionally precipitate as alkali pertechnetate salts such as  $\text{KTcO}_4$  and  $\text{NaTcO}_4$  when Tc concentration is high. In these cases, Tc(VII) is 4-coordinated by oxygen. A reinvestigation of the chemistry of alkali-technetium-oxides formed under oxidizing conditions and at temperatures used to prepare nuclear waste glasses showed that higher coordinated alkali Tc(VII) oxide species had been reported, including those with the  $\text{TcO}_5^-$  and  $\text{TcO}_6^-$  anions. The chemistry of alkali Tc(VII) and other alkali-Tc-oxides is reviewed, along with relevant synthesis conditions.

Additionally, we report the attempts to make 5- and 6-coordinate pertechnetate compounds of K, Na, and Li, i.e.  $\text{TcO}_5^-$  and  $\text{TcO}_6^-$ . It was found that higher coordinated species are very sensitive to water, and easily decompose into their respective pertechnetates. It was difficult to obtain pure compounds, but mixtures of the pertechnetate and other phase(s) were frequently found, as evidenced by x-ray absorption spectroscopy (XAS), neutron diffraction (ND), and Raman spectroscopy. Low temperature electron paramagnetic resonance (EPR) measurements showed the possibility of Tc(IV) and Tc(VI) in the  $\text{Na}_3\text{TcO}_5$  and  $\text{Na}_5\text{TcO}_6$  compounds as well. Preliminary structure identification is obtained by ND on  $\text{K}_5\text{TcO}_6$  and  $\text{Na}_5\text{TcO}_6$ .

It was hypothesized that the smaller counter cation would result in more stable technetates. To confirm the synthesis method,  $\text{LiReO}_4$  and  $\text{Li}_5\text{ReO}_6$  were prepared, and their Raman spectra match those in the literature. Subsequently, the Tc versions  $\text{LiTcO}_4$  and  $\text{Li}_5\text{TcO}_6$  were synthesized and characterized by ND, Raman spectroscopy, XANES and EXAFS. The  $\text{Li}_5\text{TcO}_6$  was a marginally stable compound that appears to have the same structure as that known for  $\text{Li}_5\text{ReO}_6$ . Implications of the experimental work on stability of alkali technetate compounds and possible role in the volatilization of Tc are discussed.

## INTRODUCTION

A long-term objective in  $^{99}\text{Tc}$  waste management is to obtain a clear understanding of the oxidation states and chemistry of  $^{99}\text{Tc}$  during nuclear waste vitrification using state-of-the-art analytical equipment. Vitrification is the process of immobilizing nuclear waste in glass. Currently there are  $\sim 239,000\text{ m}^3$  of waste at Hanford held in tanks awaiting processing and vitrification at the Waste Treatment and Immobilization Plant, which is currently being constructed [1]. Successful immobilization of this waste will result in the production of both Low Activity Waste (LAW) and High Level Waste (HLW) glasses. Steel canisters containing these glasses will be interred in either an on-site repository (LAW) or in a yet undefined geological repository (HLW). Currently, the DOE has estimated that  $\sim 90\%$  of the Tc held in the tanks at Hanford will be immobilized in the LAW glasses, but alternate scenarios have been suggested where  $\sim 50\%$  of the Tc will end up in HLW. Successful incorporation and stabilization of Tc into these waste glasses is critical due to the radionuclide's long half-life (ca.  $2.1 \times 10^5$  y), and its high mobility in aqueous environments under oxidizing conditions [2]. One of the major barriers to meeting the immobilization goal is the high volatility of Tc at vitrification temperatures ( $\sim 1150^\circ\text{C}$ ), which results in low Tc retention in the glass [3]. Recent research has suggested a possible mechanism for Tc volatilization from the glass melt [4]. However, further research into the chemistry of the species involved in this mechanism, and their end products is still needed. Data collected on these oxide species provide valuable insight into the mechanism of Tc volatilization during vitrification, and may provide a method to increase Tc waste loading into waste glasses. As a result, fundamental insights into the chemistry of Tc-containing oxides will be gained, which will be useful to the international radiochemical community dealing with  $^{99}\text{Tc}$ .

### Valence states in Tc

Previous investigations into the oxidation state and chemistry of Tc during LAW vitrification has shown Tc(VII), probably in the form of alkali pertechnetate, is the prevalent form of Tc throughout the process [3]. Lower oxidation states of Tc, such as Tc(IV), may also be present during vitrification [5]. However, due to the overall oxidizing conditions of the waste feed, almost all the lower valent Tc species are expected to be oxidized to Tc(VII) during vitrification. Raman studies of glasses with a typical LAW composition containing high concentrations of Tc,  $>1000$  ppm by mass, have suggested that the most likely forms of Tc in glass will be potassium pertechnetate,  $\text{KTc(VII)O}_4$ , sodium pertechnetate,  $\text{NaTc(VII)O}_4$ , or dissolved pertechnetate anion,  $\text{Tc(VII)O}_4^-$  [6]. One challenge in the incorporation of Tc(VII) into the glass is its high volatility at moderate temperatures. Baumgartner [7] has reported that up to 65% of Tc can volatilize from a borosilicate melt at  $1100^\circ\text{C}$ , and Hanford glass is to be melted at  $1150^\circ\text{C}$ . The mechanism by which this volatilization occurs is not well understood. Recent studies have suggested that Tc may volatilize faster if Cs is present and this is also affected by sulfates in the glass feed [8].

In reviewing the literature, two publications were rediscovered that describe a rare set of higher order, 5- and 6- coordinate pertechnetates, including  $\text{Na}_3\text{TcO}_5$  and  $\text{Na}_5\text{TcO}_6$  [9, 10]. These compounds do not contain the tetrahedral, 4-coordinate pertechnetate ( $\text{Tc(VII)O}_4^-$ ) ion that is normally associated with Tc bearing glasses. Instead, they contain  $\text{Tc(VII)O}_6^{5-}$  and  $\text{Tc(VII)O}_5^{3-}$ .

ions, respectively. Expected chemical representations of Tc(VII) oxyanions are shown in Figure 1.

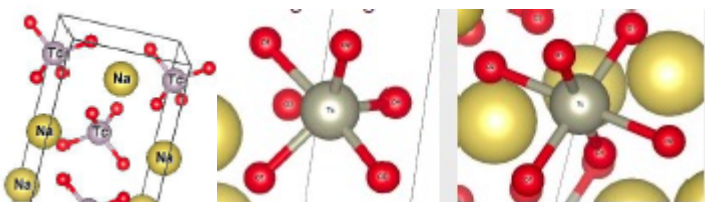


Figure 1. Potential Tc(VII) local structures for Tc in oxide glass (left: NaTcO<sub>4</sub>, middle: Na<sub>3</sub>TcO<sub>5</sub>, right: Na<sub>5</sub>TcO<sub>6</sub>).

### Literature review of alkali Tc oxide synthesis

In the following discussion, only Tc compounds with valence >4 will be described. Technetium forms a number of oxyanions of Tc(V, VI, and VII) with varying numbers of oxygen ligands that have been documented to exist in the solid phase. Due to the hazards surrounding their synthesis, these are not well documented in the literature. They can be made by heating a solid pertechnetate with an excess of an alkali hydroxide or alkali carbonate to several hundred degrees Celsius, under conditions similar to a glass melt. These compounds readily hydrolyze under humid conditions, reverting to their respective alkali pertechnetates. Additionally, they readily dissolve in water to form TcO<sub>4</sub><sup>-</sup>; their solubilities decrease as a function of counter cation size, . The preparation and properties of these higher order pertechnetates were detailed in two publications from 1965 [9, 11].

**Chemical Properties of Pertechnetates.** Alkali pertechnetates are generally described as stable under atmospheric conditions, and intrinsic properties have been reported for most of the compounds. For example, KTcO<sub>4</sub> melts at 540°C and begins to sublime ~1000°C [12]. Its solubility is between that measured for KMnO<sub>4</sub> and KReO<sub>4</sub>. Pertechnetate solids have been reported for nearly all simple cations, and NH<sub>4</sub>, Cs, and Ag compounds have been identified to be isostructural with their rhenium analogues [13].

While most of the alkali pertechnetates have no reported hydrated species, a tetrahydrated form of NaTcO<sub>4</sub> has been reported by German and co-workers [14], as well as multiple hydrates of LiReO<sub>4</sub> [15], which are assumed to be analogous to LiTcO<sub>4</sub>. Most other alkali pertechnetates have been found to be anhydrous, which can be considered an indication of their relative thermal stability. Impure pertechnetates have been reported to decompose, but little is known about the mechanism of decomposition or the impurities that cause decomposition.

**Preparation and Properties of TcO<sub>5</sub><sup>3-</sup> and TcO<sub>6</sub><sup>5-</sup>.** These compounds can be prepared by heating a solid pertechnetate salt with a stoichiometric amount of alkali metal oxide to several hundred degrees Celsius in a stream of oxygen [9]. Tc(VII) compounds can be prepared in pure form by carefully measuring the reactants.

1.  $2\text{Li}_2\text{O} + \text{LiTcO}_4 \rightarrow \text{Li}_5\text{TcO}_6$  (250-450°C)
2.  $2\text{Li}_2\text{CO}_3 + \text{LiTcO}_4 \rightarrow \text{Li}_5\text{TcO}_6$  (600-650°C)
3.  $\text{Na}_2\text{O} + \text{NaTcO}_4 \rightarrow \text{Na}_3\text{TcO}_5$  (250-450°C)
4.  $2\text{Na}_2\text{O} + \text{NaTcO}_4 \rightarrow \text{Na}_5\text{TcO}_6$  (250-450°C)
5.  $\text{K}_2\text{O} + \text{KTcO}_4 \rightarrow \text{K}_3\text{TcO}_5$  (250-450°C)

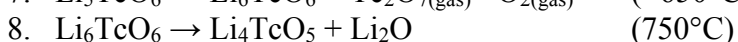
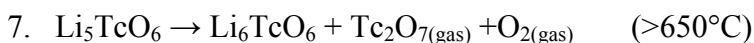
Attempts were made by Keller and colleagues [16] to synthesize  $\text{Li}_3\text{TcO}_5$  and  $\text{K}_5\text{TcO}_6$ ; however, those experiments were not successful. The colors of the solid compounds were reported to be brown. Peacock has suggested that this coloring is the result of a disturbance in the tetrahedral symmetry of the Tc anion. The brown color, or more precisely a red/pink color, is expected, as the first absorption peak of  $\text{TcO}_4^-$  is at 286 nm, which lies in the UV, just above the visible region of the electromagnetic spectrum [17]. A slight perturbation in the geometry of the structure may result in a reddish compound. Interesting, this is the same phenomena predicted to possibly cause the red coloration of solid  $\text{HTcO}_4$  [18, 19]. If these compounds form in a glass melt, they may disappear due to reaction with atmospheric moisture when the cooled melt is sampled and crushed for analysis.

Keller and Wassilopoulos [11] report that the Mg, Sr, and Ba compounds of the 5- and -6 coordinate pertechnetates are more thermally stable than the Mg, Sr, and Ba salts of 4- coordinate pertechnetate. They are made analogously to the Li, Na, and K compounds.



The compounds  $\text{Ba}_5(\text{TcO}_6)_2$  and  $\text{Ca}_5(\text{TcO}_6)_2$  are reported to be stable to  $850^\circ\text{C}$ , and  $\text{Ba}_3(\text{TcO}_5)_2$  is reported to be stable to  $1180^\circ\text{C}$ .

**Tc(VI) oxyanions.** The Tc(VII) compounds are reported to decompose to Tc(VI) compounds at higher temperature [9].



The decomposition temperatures exceed the glass vitrification temperature. Therefore, when combined with the previous mechanisms (equations 1-5), these two mechanisms could be part of the overall process for the thermal decomposition of pertechnetates. Since the Hanford LAW glass melts are expected to be strongly alkaline, the pertechnetates could be converted by reaction with  $\text{Na}_2\text{O}$  into  $\text{TcO}_5^{3-}$  and  $\text{TcO}_6^{5-}$ , which then could thermally decompose to  $\text{Tc}_2\text{O}_7$ ,  $\text{TcO}_6^{6+}$ , and  $\text{TcO}_5^{4+}$ . The Tc(VI) compounds may be thermally stable at the temperature of a glass melt. Although research has not been completed on this aspect of the melt chemistry, it may be that if  $\text{CsTcO}_4$  is formed during melting, then these pathways won't occur, and the production of gaseous  $\text{Tc}_2\text{O}_7$  may be reduced. Lowering of Tc volatility by the addition of Cs to the melt has been previously reported by Bibler et al {Bibler, 1999 #584}. Work by Range and co-workers has shown that when  $\text{CsReO}_4$ , which is isostructural to  $\text{CsTcO}_4$ , is heated above  $470^\circ\text{C}$  an  $\alpha$ -form of the compound is made. This behavior is unlike that of Na and K pertechnetates, which have a single polymorph.

$\text{Li}_4\text{TcO}_5$  is stable to at least  $900^\circ\text{C}$ . Like the Tc(VII) oxyanions, these Tc species are hypothesized to be sensitive to atmospheric moisture, and could quickly revert to pertechnetate salts if present at the surface of a sample when it is exposed to a humid atmosphere. Keller and Kanellakopoulos [9] report that the Tc(VI) compounds dissolve in water to give a pink solution (the same color as  $\text{TcO}_4^{2-}$ ), which disproportionates to  $\text{TcO}_4^-$  and  $\text{TcO}_2 \cdot n\text{H}_2\text{O}$  (the same behavior as  $\text{TcO}_4^{2-}$ ). These Tc(VI) oxyanions are probably quite sensitive to atmospheric moisture and

may quickly disappear from the surface of the sample when it is dissected and crushed. The simple Tc(VI) anion  $\text{TcO}_4^{2-}$  is known to be extremely sensitive to moisture [20].

**Pentavalent Compounds.** The tetravalent and pentavalent oxyanions were reported to be made by reduction of higher oxidation states with technetium metal, not by thermal decomposition of higher oxidation states. If the V and IV oxidation states cannot be made by thermal decomposition, then the most likely oxidation state in glass is VI and VII.



$\text{Li}_3\text{TcO}_5$  disproportionates above  $1000^\circ\text{C}$  to  $\text{Li}_4\text{TcO}_5$ , Tc metal, and  $\text{LiTcO}_4$ . Keller and Kanellakopoulos [9] claimed that  $\text{NaTcO}_3$  could be made by disproportionation, but the paper is unclear about the conditions of its formation and its overall stability. They report that it is stable to  $800^\circ\text{C}$  in the absence of excess  $\text{Na}_2\text{O}$ , but disproportionates to IV and VII in the presence of excess  $\text{Na}_2\text{O}$ .

## EXPERIMENT

### Synthesis

Synthesis in the Radiological Processing Laboratory at Pacific Northwest National Laboratory was performed to attempt creation of reported compounds:  $\text{Na}_3\text{TcO}_5$ ,  $\text{Na}_5\text{TcO}_6$ ,  $\text{K}_3\text{TcO}_5$ ,  $\text{K}_5\text{TcO}_6$ , and  $\text{Li}_5\text{TcO}_6$ . These compounds are very sensitive to decomposition by water, and may not have been pure. Initial results confirmed these suspicions, in that the respective 4-coordinate pertechnetates were found as a part of the samples.

Preparation of  $\text{Tc(VII)O}_6^{5-}$  and  $\text{Tc(VII)O}_5^{3-}$  alkali salts began with the production of the corresponding alkali pertechnetates, detailed elsewhere [4]. Once purified, recrystallized, and dried to a constant weight, these salts were then mixed with stoichiometric amounts of standardized, KHP (NIST, 2% phenolphthalein in anhydrous ethanol as indicator) alkali hydroxide or carbonate solutions in oxidized nickel crucibles. Firing of the nickel crucible was necessary because it provided the interior of the vessel with a thin layer of protective nickel oxide, which, when placed in contact with the caustic hydroxide solutions at elevated temperatures, would not appreciably react. Most batches were calculated to produce gram quantities of product. The addition of the hydroxide solution to the salt formed a slurry that was slowly dried to a solid mass on a hot plate set to  $\sim 200^\circ\text{C}$ . This process was completed in a fume hood, and done slowly with a loose fitting oxidized Ni cover to prevent the radioactive material inside the crucible from being ejected out of the vessel. Once the reactant mass had dried, an oxidized nickel lid was placed over the top crucible, and it was transferred to a muffle furnace preheated to  $450^\circ\text{C}$ . During transfer from the hot plate to the furnace, the sample was placed into a secondary containment vessel with a layer of desiccant in the bottom. The sample was heated in the oven for 30-60 min, depending on the size of batch being synthesized, to allow reaction with the salts and excess alkali. The initial colors of the final samples were bright yellow for the Na and Li compounds and bright orange to red for the K compounds, which faded to a gray or yellow-gray color after a few moments. The intensities of the colors decreased as soon as the samples were removed from the oven. Immediately upon removal from the oven, the sample was placed back into the same secondary containment container that had desiccant.

## General considerations for analysis

About ¼ of all samples, particularly those made early in the study, liquefied before they could be measured. Thus, special handling and sample loading techniques were developed for all analysis methods. For instance, adjustments had to be made for sample holder filling protocols so that powders could be loaded in a glove bag backfilled with an inert atmosphere (99.99% pure N<sub>2</sub> gas from Linde). Additionally, prior to loading, any container to be in direct contact with the sample was placed in an evacuated chamber over a strong desiccant to remove most of the water that may have been adsorbed onto its surface. Once packed and sealed, containers were externally checked for radioactive contamination, and then placed into a secondary holder containing fresh desiccant. The samples were held in this containment until just prior to sample analysis or to shipping. Even sealed containers previously successfully used for acquisition of Raman data on Tc samples were found to be inadequate, as the sealing material had sufficient moisture to hydrolyze the new Tc compounds, and were inappropriate for higher levels of activity (beta-decay degradation of seals for ~50 µCi or 1.85 MBq samples).

EPR was obtained on ..... Samples for electron paramagnetic resonance (EPR) were .....

X-ray absorption spectroscopy (XAS) data was obtained at Stanford Synchrotron Radiation Lightsource at beamline 11-2. Powdered samples were sealed between two layers Kapton tape, and mounted in an aluminum XAS sample holder. The holder was further heat sealed plastic pouches for purposes of radiological containment. X-rays were monochromatized using a double crystal monochromator with Si (220),  $\phi = 90$  crystals. The second crystal was detuned by 50% to reduce the harmonic content of the beam. Data was obtained in transmission using Ar-filled ion chambers. Raw data were converted to spectra corrected for detector dead time using the software packages SixPack {Webb, 2005 #154} and Athena {Ravel, 2005 #93}. Extended X-ray absorption fine structure (EXAFS) spectra were fit using Artemis {Ravel, 2005 #93} with theoretical scattering functions calculated using Feff8. The X-ray absorption near-edge structure (XANES) spectra were fit using the locally written program 'fites.' The standard spectra used are TcO<sub>4</sub><sup>-</sup>, and Tc<sup>4+</sup> gluconate (as surrogate for octahedral Tc<sup>4+</sup>).

Neutron scattering experiments were performed at the Nanoscale-Ordered Materials Diffractometer (NOMAD) at the Spallation Neutron Source at Oak Ridge National Laboratory [21]. Powdered samples (200 – 400 mg) were flame sealed in fused quartz (~1 mm wall thickness) NMR tubes to prevent dispersibility of the >1 mCi (>37 MBq) of each powder. Neutron diffraction data was collected over a Q range of 0.04 to 50 Å<sup>-1</sup> at room temperature. The total duration of the data collection for each sample was ~10 h, taken in ~20 min intervals and summed to reduce noise. Refinements of alkali pertechnetate diffraction patterns were performed in General Structure Analysis System (GSAS) using EXPGUI [22] starting with lattice parameters and positions of previously reported rhenium-based analogous structures.

Raman was obtained on a Horiba high-resolution confocal inverted-stage microscopic Raman spectrometer (LabRam HR8000) with 1800 grooves/mm diffraction grating, using a Nikon Eclipse Ti microscope. For sample containment, a polystyrene “membrane box” (Ted Pella) was modified by removing a circular opening on top which was replaced with an epoxied quartz window through which scattered Raman light could be collected. A circular Teflon washer was epoxied to the inside surface of the quartz window to create a containment for the particles of Tc-containing oxide. Laser excitation was provided by a Quantum Laser MPC-3000, which delivered ~20 mW at 532 nm with a spot diameter of ~1 µm. Spectra were recorded with a Peltier-cooled Horiba Synapse charge-coupled device (CCD) detector with a 1024×256 pixel

array. The spectrometer was calibrated using a Hg pen lamp and an amorphous Si wafer for frequency verification. Spectral resolution of the system, as described, was  $1.8 \text{ cm}^{-1}$  /pixel with a laser spot size of  $1.1 \text{ }\mu\text{m}$ . The spectrometer position was  $950 \text{ cm}^{-1}$ , allowing data collection from  $1750$  to  $\sim 50 \text{ cm}^{-1}$ . The number of spectral acquisitions, count times, and the diameter of the confocal iris were varied to maximize the signal-to-noise ratio of spectra for each sample.

## RESULTS

### Electron Paramagnetic Resonance

Electron Paramagnetic Resonance (EPR) was utilized to determine whether even oxidation state  $^{99}\text{Tc}$  species were present in the samples. Low temperature data was acquired in addition to room temperature data to reduce spectral noise and improve resolution. Preliminary temperature-dependent EPR data was obtained on the early generations of  $\text{Na}_5\text{TcO}_6$ ,  $\text{Na}_3\text{TcO}_5$ , and  $\text{K}_3\text{TcO}_5$  (see Figure 2). EPR on  $\text{K}_3\text{TcO}_5$  suggested no half-integer spins of Tc, consistent with the Raman spectra showing only  $\text{KTcO}_4$  for this synthesis. Both Na samples, however, showed evidence of  $S=1/2$  species, probably Tc(VI), in the medium temperature range ( $50$ - $120 \text{ K}$ ), and  $S=3/2$  species, probably Tc(IV), at low temperature ( $<20 \text{ K}$ ). The local environment of the  $S=1/2$  species is considerably different between the two Na compounds, however (see Figures 3 and 4). These results suggested that an unknown mechanism was operating that was causing the reduction within the Na compounds.

Something about what is known/published for EPR assignments for Tc-99.

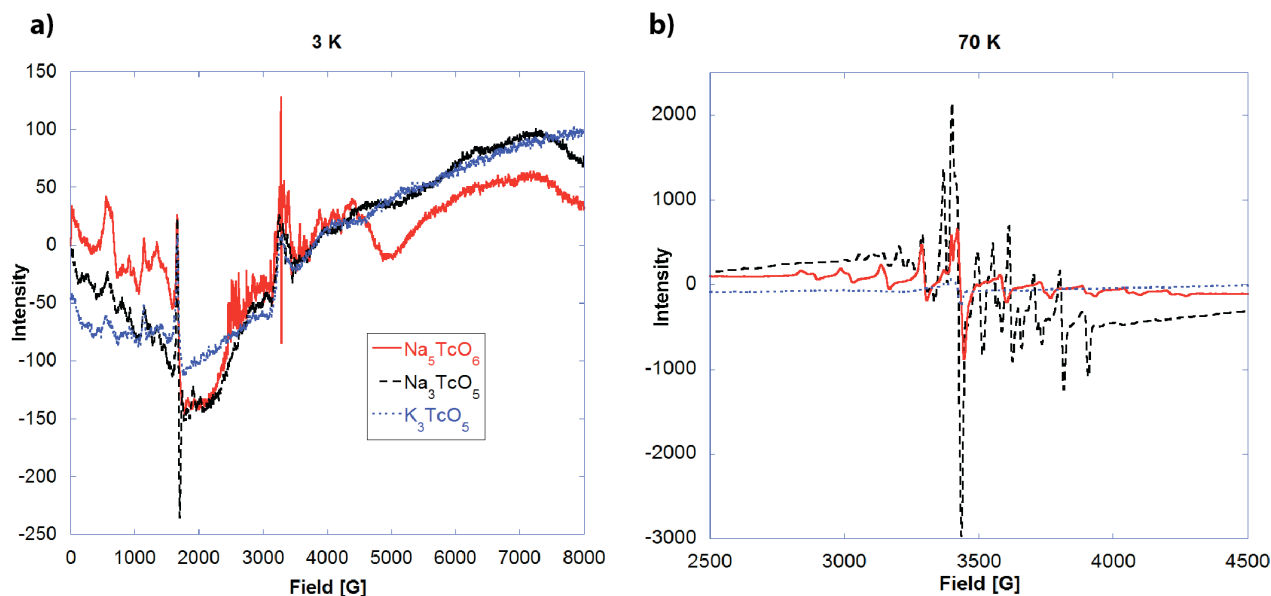


Figure 2: EPR spectra of measured technetates at 3 K and 70 K. At 3 K,  $\text{Na}_3\text{TcO}_5$  and  $\text{Na}_5\text{TcO}_6$  show evidence of Tc(IV), while  $\text{K}_3\text{TcO}_5$  showed no signal. At 70 K,  $\text{Na}_3\text{TcO}_5$  and  $\text{Na}_5\text{TcO}_6$  show evidence of a spin  $1/2$  nucleus, which could be Tc(II) or Tc(VI), but in very different environments, while  $\text{K}_3\text{TcO}_5$  showed no signal. These experiments are performed in parallel-



mode EPR, which is only sensitive to integer spins or highly coupled species, where  $\Delta S=2$ . The half-field peak is from a defect, not from Tc.

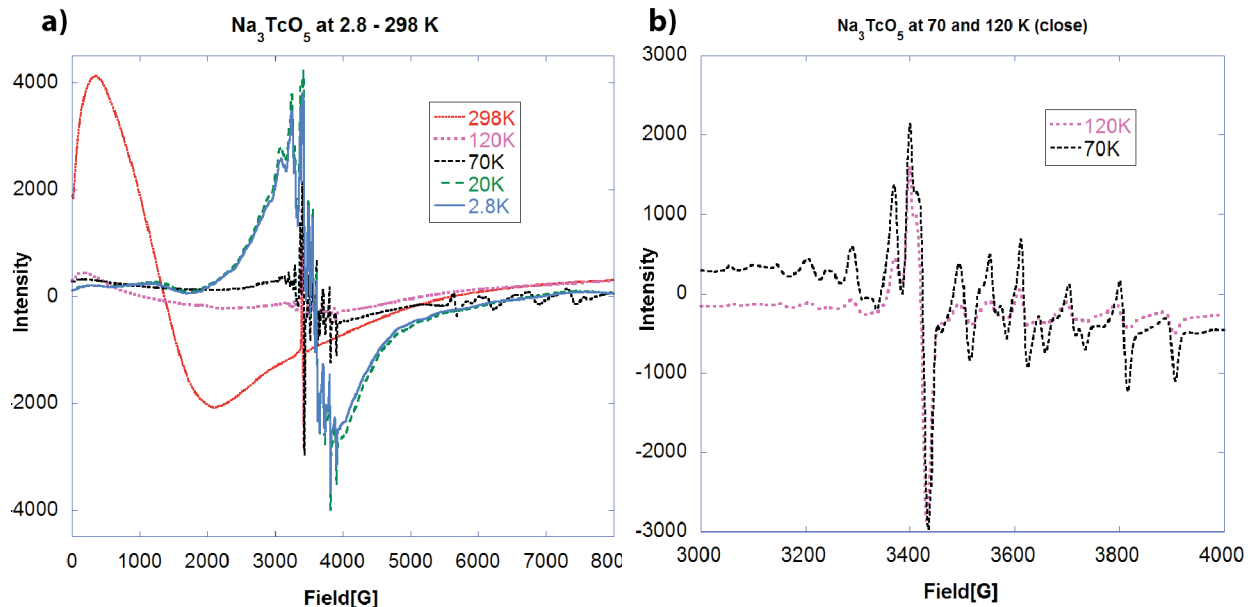


Figure 3: EPR spectra of  $\text{Na}_3\text{TcO}_5$  as a function of temperature. These spectra are from normal-mode EPR.

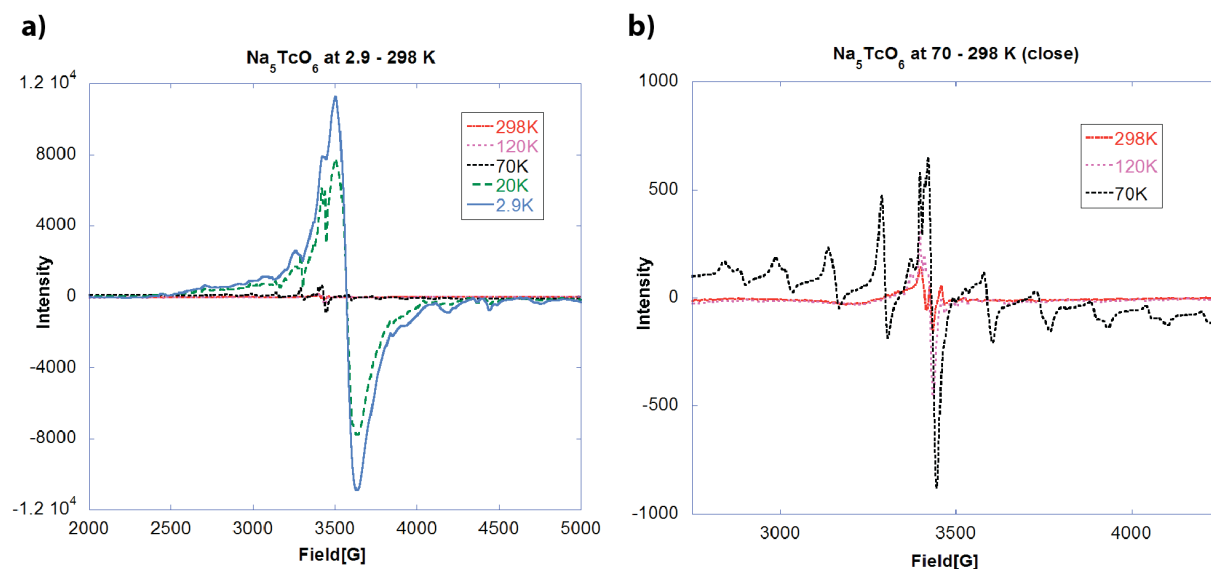


Figure 4: EPR spectra of  $\text{Na}_5\text{TcO}_6$  as a function of temperature. These spectra are from normal-mode EPR.

### X-ray Absorption

X-ray absorption measurements were performed on some of the samples, and EXAFS spectra were obtained for  $\text{K}_3\text{TcO}_5$  and  $\text{Li}_5\text{TcO}_6$ . The  $\text{K}_3\text{TcO}_5$  sample was a roughly rectangular chunk of

material measuring approximately 1 mm × 1 mm × 6 mm sealed inside two layers Kapton tape. The data itself is not completely reliable and may suffer from pinhole effects. An improvement to mounting methods has been since made to the process (i.e. for Li<sub>5</sub>TcO<sub>6</sub> described below), and includes the crushing and mixing of the radioactive powder with dried boron nitride before being placed into the XAS holder.

For modeling K<sub>3</sub>TcO<sub>5</sub> in Feff8, the crystal structure of Na<sub>3</sub>OsO<sub>5</sub> was used [23] with Os replaced by Tc. Three different models were tried: 1) four equidistant oxygen neighbors (TcO<sub>4</sub><sup>-</sup> structure), 2) one short oxygen bond and four longer ones (square pyramid), and 3) two short oxygen bonds and three longer one (trigonal bipyramid). The quality of the fit is determined from the reduced  $\chi$ -squared value ( $\chi$ -squared divided by the number of degrees of freedom). Despite the average quality of the data, the results are unequivocal – the best model consists of four oxygen neighbors at 1.71 Å with a single longer Tc-O distance of 2.03 Å. This could be either a mixture of Tc(VII) and Tc(IV) in a ratio of ~6:1 or one or more Tc(VII) species. The best fit values are given in Table 1 and the corresponding fit is illustrated in Figure 5. The results of the model testing are given in Table 2. The parameters given in Table 1 provide the best fit by a wide margin. The same model with two different Debye-Waller parameters gives basically the same result. The model with three short and two long Tc-O distances has a small reduced  $\chi^2$  value, but has unrealistic Debye-Waller parameters.

The Li<sub>5</sub>TcO<sub>6</sub> sample was a roughly rectangular chunk of material measuring approximately 1 mm × 1 mm × 6 mm sealed inside two layers Kapton tape. For modeling in Feff8, the Li<sub>5</sub>ReO<sub>6</sub> structure [24] was used with Re replaced with Tc. Three models were tested: 1) Six equidistant oxygen bonds, 2) four long oxygen bonds and two shorter oxygen bonds, and 3) two long oxygen bonds, two intermediate bonds, and two short oxygen bonds. The best model for the Li<sub>5</sub>TcO<sub>6</sub> data consisted of four oxygen neighbors at 1.73 Å, and hence suggests the compound measured was LiTcO<sub>4</sub> and not Li<sub>5</sub>TcO<sub>6</sub>.

Whether the EXAFS results for K<sub>3</sub>TcO<sub>5</sub> are due to just Tc(VII) or a mixture of Tc(VII) and Tc(IV) can potentially be determined by XANES spectroscopy. The XANES spectrum of the sample is shown in Figure 6 along with a fit using a combination of the XANES spectra of TcO<sub>4</sub><sup>-</sup> and Tc(IV) gluconate. The latter is the surrogate for the structure of Tc(IV) in octahedral symmetry with oxygen neighbors, which would be the structure of Tc(IV) in this system. As shown in Figure 6, the combination of the spectra of TcO<sub>4</sub><sup>-</sup> and Tc(IV) gluconate does not reproduce the observed spectrum. Therefore, it is likely that the spectrum and EXAFS results correspond to one or more Tc(VII) species rather than a mixture of Tc(IV) and Tc(VII). It is likely that the sample contains only Tc(VII), but the Tc-O distances are not consistent with a single species. The 1.71 Tc-O distance is almost certainly due to just pertechnetate. If the species were five coordinate, the Tc-O distance should be considerably longer. The 2.03 Å Tc distance is typical of octahedral Tc(IV), and is a bit longer than the 1.9 Å average Re-O distance in octahedral Li<sub>5</sub>ReO<sub>6</sub> [25] or La<sub>3</sub>ReO<sub>8</sub> [26]. This distance may be ascribed to octahedral Tc(VII). This sample is likely a mixture of tetrahedral KTcO<sub>4</sub> and octahedral K<sub>5</sub>TcO<sub>6</sub> as previously described for Bi<sub>28</sub>Re<sub>2</sub>O<sub>49</sub> [27]. XANES spectra collected on various K-Tc(VII)-O samples are also shown in Figure 6.

Linear combination fitting of the Li<sub>5</sub>TcO<sub>6</sub> XANES suggests only Tc(VII) environments are present in the sample. However, its spectrum is different than that of the synthesized LiTcO<sub>4</sub> (see Figure 7). XANES spectra of various Na-Tc(VII)-O samples are also shown in Figure 7.

**Table 1:** Parameters for best model of the EXAFS spectrum of  $K_3TcO_5$ . Fit range was  $3 < k < 14$ ,  $1 < R < 2$ ; # of independent points = 8.8; # of parameters = 4; R\_factor = 0.017

Neighbor	# of Neighbors	Distance ( $\text{\AA}$ )	$\sigma^2$ ( $\text{\AA}^2$ )
O	4	1.72(1)	0.0031(4) <sup>b</sup>
O	1	2.03(3)	0.0031(4) <sup>b</sup>

a)  $S_0^2=0.9$  (fixed),  $\Delta E=15(3)$

b) Debye-Waller parameters constrained to be equal

**Table 2:** Parameters for best model of the EXAFS spectrum of  $Li_5TcO_6$ . Fit range was  $2 < k < 13.5$ ,  $1 < R < 5$ ; # of independent points = 32.7; # of degrees of freedom = 34.7; # of parameters = 19; R\_factor = 0.047. Data collected in transmission.

Neighbor	# of Neighbors	Distance ( $\text{\AA}$ )	$\sigma^2$ ( $\text{\AA}^2$ )
O	4.1(6)	1.72(9)	0.0034(6)

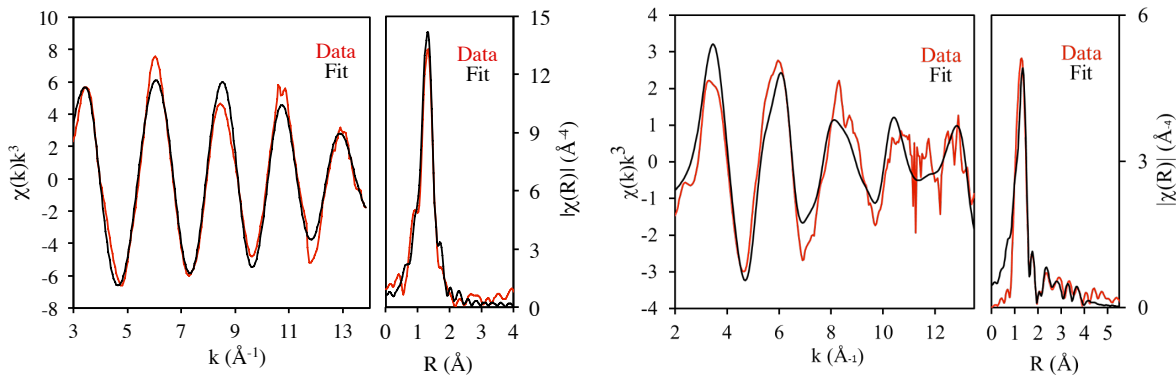
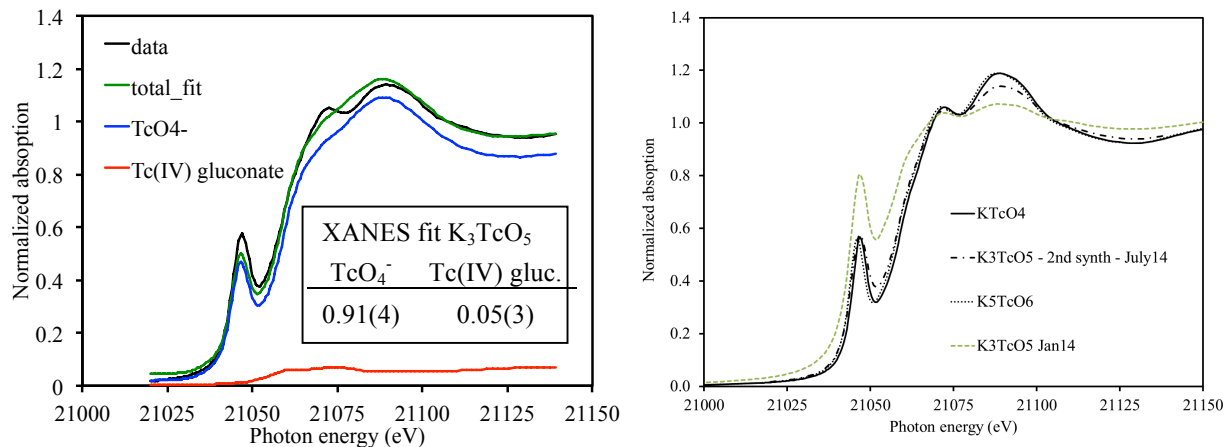


Figure 5: EXAFS spectra of  $K_3TcO_5$  (left) and  $Li_5TcO_6$  (right). In all cases the experimental data (red) is compared with the fit (black). Left section of each set is the k-space data and right section is its Fourier Transform into real space.



**Figure 6.** XANES for K-Tc(VII)-oxides. Left: XANES fit for  $K_3TcO_5$  (July 2014 synthesis); The combined spectra (green) do not reproduce experiment (black); thus, the sample is not a mixture of Tc(VII) and Tc(IV). Right: Collected XANES for  $K_3TcO_5$  (two batches),  $K_5TcO_6$ , and  $KTcO_4$ .

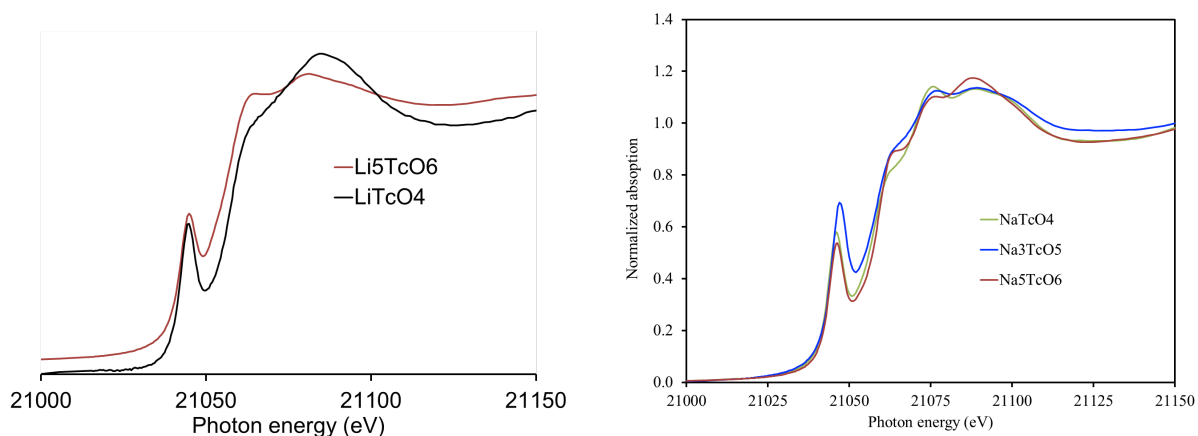


Figure 7: XANES spectra: (Left) Li-Tc(VII)-O compounds and (Right) Na-Tc(VII)-O

### Neutron Diffraction

Samples that survived transport to the Spallation Neutron Source (SNS) were  $\text{Na}_5\text{TcO}_6$ ,  $\text{K}_5\text{TcO}_6$ , and  $\text{Li}_5\text{TcO}_6$ . The diffraction patterns and attempted fits for two of the compounds are displayed in Figure 8. The materials were either a mixture of their pertechnetate counterparts and their expected chemistry, or as in the case of  $\text{Na}_5\text{TcO}_6$ , had completely degraded to pertechnetate salts. From rough Rietveld refinements, it was possible to estimate the approximate proportions of each species in the solids:  $\text{Li}_5\text{TcO}_6$  was  $\sim 64\%$  pure, and  $36\%$  lithium pertechnetate, and  $\text{K}_5\text{TcO}_6$  was  $\sim 65\%$  pure, and  $35\%$  potassium pertechnetate.

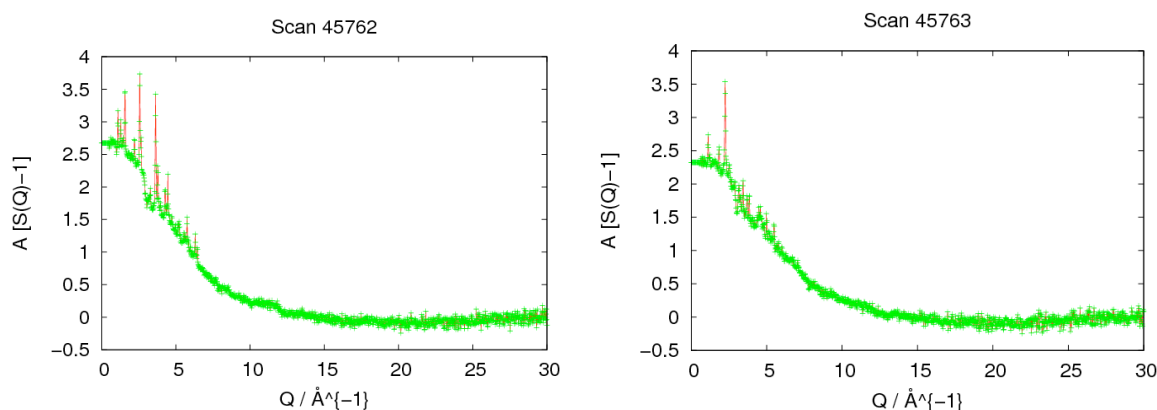


Figure 8: Neutron scattering spectrum measured for (left)  $\text{Na}_5\text{TcO}_6$  and (right)  $\text{K}_5\text{TcO}_6$ . The large backgrounds are likely due to hydrogen scattering from using excess NaOH and KOH in the syntheses.

### Raman Spectroscopy

The collected Raman spectra for synthesized Na and K technetates are shown in Figure 9.  $\text{Na}_5\text{TcO}_6$  showed evidence of  $\text{NaTcO}_4$  and some new peaks, while  $\text{Na}_3\text{TcO}_5$  contained  $\text{NaTcO}_4$  peaks, similar peaks to  $\text{Na}_5\text{TcO}_6$ , and a few other new peaks. Measurements of  $\text{K}_3\text{TcO}_5$  showed only  $\text{KTcO}_4$ , while  $\text{K}_5\text{TcO}_6$  showed  $\text{KTcO}_4$  plus new peaks. The identities of these new peaks

could not be confirmed, as there are no published literature Raman spectra for alkali TcO<sub>5</sub> or TcO<sub>6</sub> compounds, or even comparable rhenium compounds, to our knowledge. For this reason, we attempted to make and measure the Li compounds, for which literature Raman spectra existed for the Li<sub>5</sub>ReO<sub>6</sub> and LiReO<sub>4</sub>.

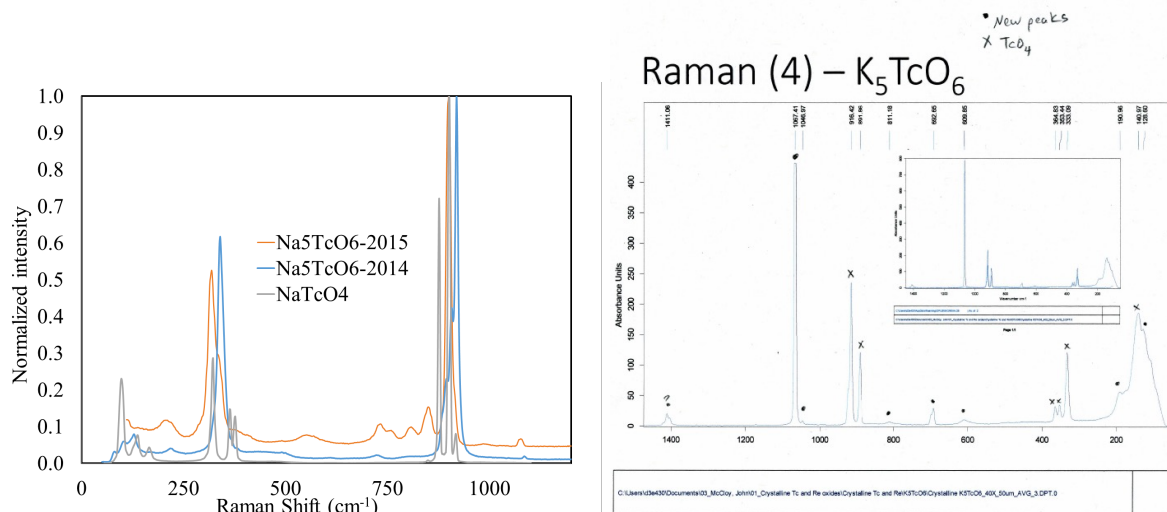


Figure 9: Raman spectra. Na technetates (left) and K technetates (right)

To establish the synthesis protocols for the Li-Tc-O compounds, both Li<sub>5</sub>ReO<sub>6</sub> and LiReO<sub>4</sub> were synthesized and their Raman spectra collected. Peaks in the Raman spectra for Li<sub>5</sub>ReO<sub>6</sub> matched literature reports [28], as did those for LiReO<sub>4</sub> [29]. The collected Raman spectra for synthesized Na and K technetates are shown in Figure 10.

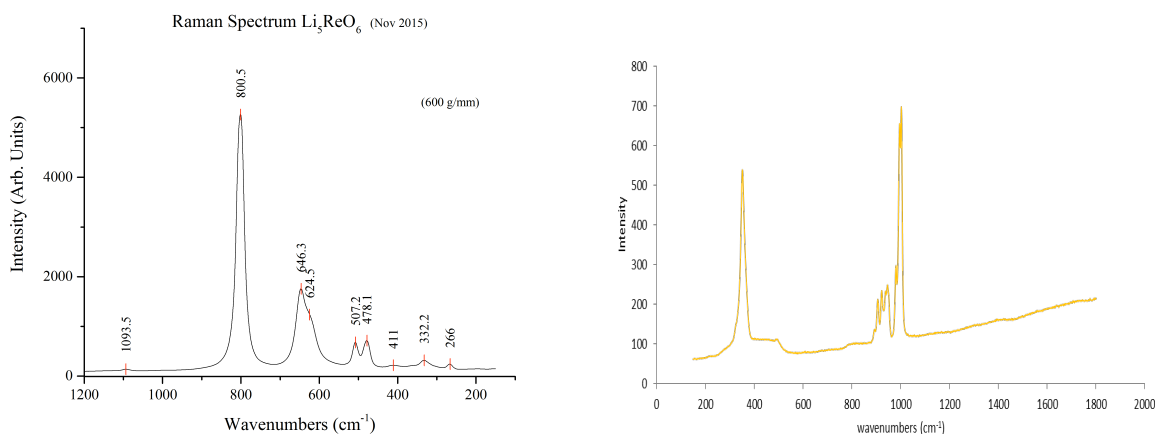


Figure 10: Raman spectrum of Li<sub>5</sub>ReO<sub>6</sub> (left) and of LiReO<sub>4</sub> (right)

Raman spectra of Li<sub>5</sub>TcO<sub>6</sub> are shown in Figure 11, emphasizing two groupings of similar spectra that were found in the samples depending on the region probed. Measured Raman spectra of LiTcO<sub>4</sub> (not shown) look considerably different than these.

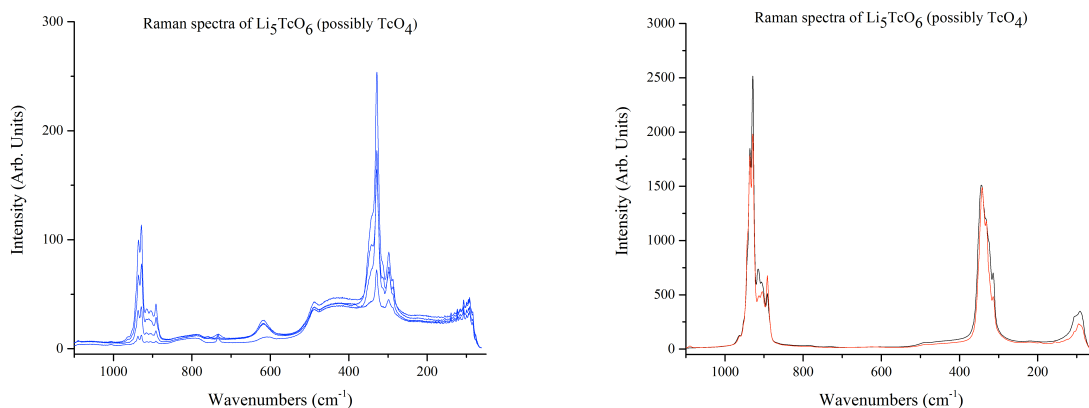


Figure 11: Raman spectra of  $\text{Li}_5\text{TcO}_6$ , showing two types of spectra acquired.

## DISCUSSION

A summary of the synthesis and characterization of 5- and 6- coordinate alkali pertechnetates is given in Table 3. Several valuable lessons and observations were made over the course of these experiments. The first was that all the higher order technetium oxides studied were determined to be deliquescent and unstable in moist atmospheres. Once the compounds became hydrated, they reverted to tetrahedrally coordinated pertechnetate species. This may be due to the distribution of bonding electrons between the Tc-O bond within each anion.

It seems that  $\text{K}_5\text{TcO}_6$  is possible to synthesize, and that  $\text{K}_3\text{TcO}_5$  either does not form or quickly decomposes to  $\text{K}_5\text{TcO}_6$  and  $\text{KTcO}_4$ . It may be that the synthesis reported by Keller of  $\text{K}_3\text{TcO}_5$  was this mixture, and that  $\text{K}_5\text{TcO}_6$  in its pure form was very difficult to stabilize due to its high reactivity with water, and resulted in Keller stating that this compound could not be formed.

A review of the crystal structures for  $\text{NaReO}_4$ ,  $\text{Na}_3\text{ReO}_5$ , and  $\text{Na}_5\text{ReO}_6$ , which according Keller *et al.* [9] are isostructural with their Tc analogues, shows that sodium perrhenate has the highest symmetry, followed by  $\text{Na}_5\text{ReO}_6$ , and then  $\text{Na}_3\text{ReO}_5$  (Table 4). These final two compounds also have more than one Re-O bond length. The lower symmetry of the two structures, and possibly their Tc analogues, may suggest that they may have a slight polarizability that could attract water molecules to the structure. Detection of possible polarizability in the structure of  $\text{NaTcO}_4$  in regards to the Tc-O bonds has been discussed elsewhere [4]. Both the XANES spectra (Figure 7) and the Raman spectra (Figure 9) of the Na-Tc(VII)-O compounds suggest that at least one higher coordinated Tc(VII) species may have been created, but it is not clear whether it is  $\text{TcO}_5$  or  $\text{TcO}_6$ . Clearly from EPR (Figures 3 and 4), at least some of the syntheses attempts resulted in some lower valent Tc, probably Tc(VI) and Tc(IV).

Li compounds, though somewhat less thoroughly studied here, appear to be somewhat easier to synthesize than the Na and K compounds. Keller reported that  $\text{Li}_3\text{TcO}_5$  could not be synthesized, so only  $\text{Li}_5\text{TcO}_6$  was attempted here, and by ND and XANES it was suggested that this compound was at least partially synthesized, and Raman and XANES spectra show considerable differences from  $\text{LiTcO}_4$ . It may be that ion size and field strength play a role in the stability of these Tc compounds.

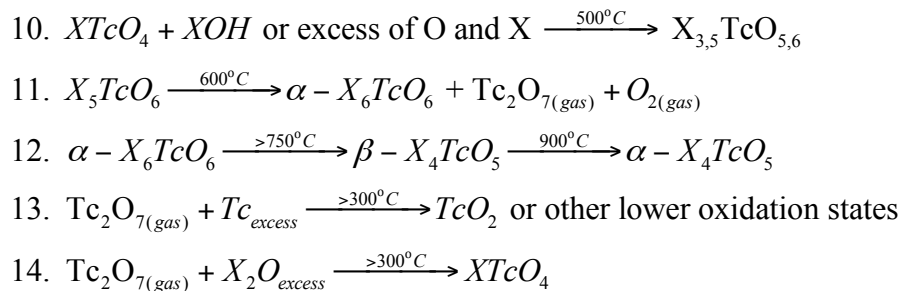
**Table 3:** Review of reported crystal structures of 7+ oxidation state technetates and rhenates, not including pertechnetate and perrhenate. (NSS, not successfully synthesized; PSS, possibly successfully synthesized; SS, successfully synthesized, as determined by neutron diffraction (ND), Raman (R), or XAS (XAS); NA, not attempted). Crystal systems and space groups listed are from the literature.

Tc/Re(VII)	Li	Ref	Na	Ref	K	Ref
$\text{TcO}_5^{3-}$	NSS	[9]	PSS $\text{TcO}_4, \text{TcO}_6$ (R)	[6]	NSS $\text{KTcO}_4$ (R) Mix of $\text{KTcO}_4$ & $\text{TcO}_6?$ (EXAFS)	[10]
$\text{ReO}_5^{3-}$	NSS	[10, 30]	NA Trigonal: $\text{P3}_1$ Trigonal: $\text{P3}_121$	[23, 30, 31]	NA	[10, 30, 32, 33]
$\text{TcO}_6^{5-}$	PSS (ND)	[10, 16]	PSS (R, XANES) Hexagonal	[6, 16, 34]	PSS Mix of $\text{KTcO}_4$ and unknown (R); Mix of $\text{KTcO}_4$ and $\text{TcO}_6?$ (ND)	[9, 10]
$\text{ReO}_6^{5-}$	SS (R) Monoclinic: $\text{C2/m}$ [24, 25] Hexagonal [35]	[10, 24, 25, 30, 35]	NA Monoclinic: $\text{C2/m}$ Orthorhombic: $\text{Fddd}$ Hexagonal	[24, 30, 34, 36]	NSS	[30]

Table 0-1 Comparison of crystallographic data on Na-Re-O compounds. Data acquired from [24, 31]. Na-Tc-O data was estimated using Vesta crystallographic software and GSAS. Due to the size of Tc, it is assumed that the unit cell volume for the Tc based compounds would be greater than that reported for the analogues Re compounds. However, the bond length may be comparable.

Compound	$\text{NaReO}_4$	$\text{NaTcO}_4$	$\text{Na}_3\text{ReO}_5$	$\text{Na}_3\text{TcO}_5$	$\text{Na}_5\text{ReO}_6$	$\text{Na}_5\text{TcO}_6$
<b>Crystal System</b>	tetragonal		trigonal (Rhombohedral)		Monoclinic	
<b>Space Group</b>	$\text{I } 41/a$		$\text{P } 31$		$\text{C } 2/m$	
<b># Bonding Oxygens</b>	4		5		6	
<b>Charge on anion</b>	-1		-3		-5	
<b>Approximate Re-O or Tc-O Bond Length (Å)</b>	1.71	1.72	1.841 1.807 1.778 1.784	1.85 1.81 1.79 1.79	1.876 1.803	1.88 1.81
<b>Relative Symmetry</b>	Highest		Lowest		Low	

Employing both linear combination and principal component analysis on XANES data collected on the glasses and Tc compounds, it was determined that one of the Tc(VII) species in the glasses may be a higher order alkali-Tc-oxide,  $X_5TcO_6$  or  $X_3TcO_5$ , where X is an alkali ion [4]. By placing these species into the context of glass melt chemistry, it was then possible to propose a set of mechanisms, based on the works of Keller, Kanellakoulos, and Sherma [9, 10], by which Tc might incorporate into glass or volatilize from the melt:



The gaseous byproduct of this reaction is technetium heptoxide,  $Tc_2O_7$ , which has been described as being highly reactive, and is able to combine with alkali to reform alkali pertechnetate or with hydrogen to form a pertechnic acid,  $HTcO_4$ , species [37, 38]. The work of Colton, Rard, and Vida has thoroughly studied the thermodynamics of  $Tc_2O_7$  [39-41]. However, little research has studied its reactivity under glass melting conditions, and there is still controversy over the structure of pertechnic acid [37].

## CONCLUSIONS

Alkali-technetium-oxide compounds were synthesized and measured with a variety of characterization techniques. It was found that the 5- and 6-coordinate pertechnetates,  $TcO_5^{3-}$  and  $TcO_6^{5-}$ , are relatively unstable and react easily with water, making characterization difficult. Nonetheless, we could show that at least impure compound of several of these oxides were produced. A proposal has been made that these Tc(VII) oxides and other obscure lower valent Tc species could play a role in volatilization of Tc from glass melters. More research is needed on synthesis and characterization of these rare and difficult radioactive compounds.

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