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**Recovery of Technetium and Iodine from the
PYRO-B Process**

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**Accelerator Transmutation of Waste Program
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Abstract

The Accelerator Transmutation of Waste (ATW) program was being developed to determine the feasibility of separating and transmutating the transactinides (Pu-Cm) and long-lived fission product (^{99}Tc and ^{129}I) from spent LWR fuel. Several types of ATW fuels have been suggested to transmute the Pu-Cm fraction including a TRU-Zr metal alloy dispersed in a Zr metal matrix. A pyrochemical process, PYRO-B, has been conceived to process this fuel. Two long-lived fission products, ^{99}Tc and ^{129}I , need to be removed and recovered from this process for subsequent transmutation. It is assumed that iodine can be removed trapped from the PYRO-B process off gases by conventional means and will not be discussed in this report. Thus, this report describes the initial experiments to determine how to recover technetium. Because of the low oxygen potential in the ATW fuel, technetium will most probably be incorporated into a noble metal alloy consisting of Tc, Ru, Rh, Pd, and Mo. This alloy may be robust to the PYRO-B process. Dissolution and roasting experiments to separate Re from a simulant alloy consisting of Re, Ru, Rh, Pd, and Mo are described. Because the free energy of formation of TcCl_4 is not known, there is a chance that this species may form in the PYRO-B process. For this reason we report our efforts to synthesize TcCl_4 in order to measure its thermodynamic properties.

Introduction

The Accelerator Transmutation of Waste (ATW) program is being developed to determine the feasibility of separating and transmutating the transactinides (Pu-Cm) and long-lived fission product (^{99}Tc and ^{129}I) from spent LWR fuel. The separated transactinides would be processed and fabricated into an ATW fuel while the technetium and iodine would be fabricated into elemental and salt type targets, respectively. This approach would help with the disposal of spent commercial fuel. In addition, since the residual waste after ATW treatment will have much lower levels of these long-lived species this process may improve the performance and acceptability of geologic disposal of nuclear waste. A roadmap for the Accelerator Transmutation of Waste (ATW) was submitted to Congress in 1999.¹ This document gave an overall view of the ATW concept and program.

The ATW fuel requirements² have been delineated as the following: (1) ATW fuel and targets must be fabricable with remote processes, (2) ATW fuel and target forms must be compatible with fuel recycle processes, (3) the blanket fuel must maintain the fissile material in a predictable configuration and location in the transmuter, (4) the blanket fuel must provide robust containment for fission products, and (5) the blanket fuel must retain a coolable geometry during operation. Several types of fuels have been suggested to meet these requirements including a TRU-Zr metal alloy dispersed in a Zr metal matrix. The zirconium metal matrix may constitute 50-70% of the weight of the fuel.³ Because of the large amount of zirconium in the fuel, a pyrochemical process, PYRO-B, was conceived to process the irradiated fuel. Figure 1 shows a flow diagram for

the PYRO-B process.³ The initial step chlorinates and volatilizes ZrCl₄. Although technetium forms a volatile chloride (TcCl₄, sublimes at 300°C) the thermodynamic data does exist for the formation of this compound. For this reason this report includes a section on our efforts to prepare TcCl₄ in order to study its thermodynamic properties. However, since the chlorinating agent CdCl₂ used in the process has such a large negative free energy (-343 kJ/mole)⁴ it is unlikely that the formation of TcCl₄ from Tc and CdCl₂ will occur:



This speculation is based on the free energy of formation of rhenium chloride compounds that are generally less than 200 kJ/mole.⁵

The literature describes the formation, dissolution, and physical properties of the noble metal inclusions (Mo, Tc, Ru, Rh, and Pd) that form in nuclear fuels during burn up.⁶⁻¹² The formation is dependent on the oxygen potential in the fuel. Their size is a function of the density of the fuel. Since ATW fuels will have lower oxygen potentials than LWR-UO₂ fuels, it is expected that the noble metal alloy content in ATW fuels will be quite high. In fact, the alloy may contain all of the technetium produced in the transmutation process. The PYRO-B process is not expected to oxidize these materials or chlorinate the alloy or the elemental forms of these metals. The alloy will therefore follow the cadmium pool in Figure 1. Distillation of cadmium will leave the alloy for further processing by an unknown method represented by the black box in Figure 1 labeled "Technetium Separation". Several methods are being considered. Roasting in air will take temperatures in excess of 1500° C. Reaction with ozone may be just as difficult, both of these processes will probably have to include some additional separation of technetium from other volatile oxides (mostly molybdenum oxides). Dissolution of the noble metal alloy in nitric acid is kinetically slow and a function of the surface area of the particles.^{8,12} We are looking at some methods that may enhance the dissolution rate. Dissolution would then allow a number of separation methods to be used. Whatever the case the goal is to recover >95% of the technetium from the process.

Experimental

Chemical reagents were obtained from Aldrich. A noble-metal alloy of Mo-Rh-Ru-Pd-Re was prepared by weighing out the appropriate amount of Rh, Pd, Ru and Re powders and placing them into a weighed Mo foil envelope. The envelope was then placed into an arc melter chamber and inerted with argon gas. The initial arc melting of the envelope lost ~8% of the powders. Two re-melts of the initial alloy melt gave a nice shiny button. The button was machined to produce < 2-mm chips of material.

Dissolution experiments were carried out on a hot plate in open beakers. Roastings of the alloy were performed by placing the chips in a Coors porcelain crucibles or boat. Muffle furnace roastings were done at 900°C in a Thermolyne benchtop furnace at ambient static air conditions. Tube furnace roasting were performed with a Lindeberg Blue M furnace capable of holding a 1" diameter tube. These roastings were done with a low flow rate of air (oil free) passing through the tube. Experiments were done either at 900°C or in 100°C steps from 400 to 900°C, each step lasting ~8 hours. Elemental

analysis of the chip surfaces were performed by the surface scientist in C-SIC. Powder pattern x-ray analysis was performed by the C-SIC crystallographer.

Results and Discussion

Noble Metal Alloy Experiments

A simulant to mimic the noble-metal (Mo-Rh-Ru-Pd-Tc) inclusions found in spent fuel was based on data by McEachen.¹³ The mixture chosen represents the composition, in weight percents, of the inclusions found in a CANDU fuel immediately after discharge after a burn up of 7.93 MWd/kgU: Tc (10.81%), Ru (32.71%), Rh (5.59%), Pd (12.01%), and Mo (38.87%). The CANDU composition approximated the best available estimate for the alloy expected in ATW fuel at the time of the simulant preparation. We have subsequently obtained a calculated estimate of the noble metal content in the ATW fuel expected to be processed by the PYRO-B process.¹⁴ A simulant alloy containing Re (6.4%), Ru (23.6%), Rh (8%), Pd (17.7%), and Mo (44.3%) should be used in future experiments.

Rhenium metal was substituted for technetium in the alloy preparation because the arc melter was a dedicated non-radioactive apparatus. Rhenium is also a VIIA transition metal and is a chemical analogue of technetium. This statement is generally true, especially when the chemical behavior being compared does not involve oxidation state changes. The preparation of the alloy with rhenium as a surrogate for technetium is probably acceptable. However, subsequent chemistry on the alloy may need to account for the differences in the chemistries of these two elements.

The initial arc melting of the molybdenum envelope containing the powders of the other four elements appeared to be quite violent, the powders spewed from the envelope as soon as the arc ruptured the envelope. The final alloy button weighed 8% less than theoretical. In the future this alloy should be made totally from foils. All the metals, except ruthenium, can be obtained from Aldrich as foils. Ruthenium rod can be obtained from Goodfellow Corporation (Berwyn, PA). Wrapping all the foils around the rod and performing at least three melting cycles will definitely result in a cleaner operation and should give a product that has a more definite bulk composition.

Accounting for a proportionate loss of the powders the estimated theoretical composition of the alloy is Re (10.6%), Ru (31.4%), Rh (5.3%), Pd (10.6%), and Mo (42%). The surface metal content of the < 2-mm noble metal alloy chips were determined on two samples. A surface analysis technique was chosen because the alloy was quite inert to aqueous dissolution techniques (see below). Table 1 shows the data and the

Table 1. Surface Analysis of Noble Metal Alloy Chips.

	Mo	Re	Ru	Rh	Pd
Analysis 1	32.0	5.0	50.0	7.0	6.0
Analysis 2	51.7	12.1	14.0	7.6	14.5
Ave \pm STD	41.9 \pm 13.9	8.6 \pm 5.0	32 \pm 3	7.3 \pm 0.4	10.3 \pm 6.0
Theoretical	42	10.6	31.4	5.3	10.6

averages. The averages have large errors but are more or less consistent with the theoretical percentages expected from the synthesis.

Two general methods were investigated for recovering technetium (or rhenium) from the noble metal alloy. Dissolution of the alloy and subsequent separation of technetium by extraction or anion exchange was the first method investigated. The alloy was quite resistant to dissolution attempts. Sequential exposure to hot concentrated nitric acid, nitric acid/H₂O₂, and hot aqua regia (HCl/HNO₃ mixtures) over three days only dissolved 5.7% of the alloy. These reagents are known to dissolve the separate components of the alloy except ruthenium. This inertness of the alloy is consistent with the actual noble metal inclusions found in spent fuel. Kleykamp has shown that 0.15 to 1.5 μm inclusions will take 8 hours to dissolve in hot 7 M nitric acid.^{8,12} Thus, it is not surprising that these large chips used in this study were slow to dissolve.

Roasting the noble metal chips in a muffle furnace at 900°C volatilizes 33.4% of the alloy in 8 hours. Another sample roasted for 24.5 hours only lost 35.4% of its weight. The roasting reduced the surface molybdenum content from 42% to 18% in 8 hours and to 10% after 24.5 hours. Rhenium also showed a reduced surface concentration after the muffle furnace treatment. All the other elements show increased surface concentrations.

Table 2. Surface Analysis of Noble Metal Alloy Chips After Burning in a Muffle Furnace

	Mo	Re	Ru	Rh	Pd
8 hours	18.0	5.0	45.0	18.5	13.5
24.5 hours	10.0	6.5	52.0	16.0	15.5
Ave \pm STD	41.9 \pm 13.9	8.6 \pm 5.0	32 \pm 3	7.3 \pm 0.4	10.3 \pm 6.0
Theoretical	42	10.6	31.4	5.3	10.6

Based on the initial composition of the alloy and the trends in Table 2, most of the gross weight loss observed for the alloy was due to molybdenum, and to a lesser extent rhenium, volatilizations. Information in the literature on the oxygen partial pressure for the formation of the oxides of these metals and their volatilities suggest that MoO₃ (sublimation 1153°C) was the major species lost during roasting.^{13,15} Thermodynamically, TcO₂ (or ReO₂) is the next most favorable oxide to form.^{13,15} If conditions are oxidizing enough, Tc₂O₇ (or Re₂O₇) may form which is quite volatile (bp 316°C, Re₂O₇, 360°C). Selective condensation of the volatile molybdenum and technetium oxides might be a way to separate and recover technetium. Alternatively, the vapors can be dissolved into an aqueous solution and technetium separated anion exchange and/or precipitation techniques.

Chips that have been roasted at 900°C (see below) are somewhat more reactive to the dissolution procedure discussed above; 20% of the roasted alloy dissolved. The combination of roasting and dissolution left 54% of the alloy.

Roasting the chips in a tube furnace with a low flow of air passing over the chips promotes the formation of volatile oxides. In addition, the flowing, confined, gases can deposit the oxides, perhaps preferentially, on the cooler regions of the tube down stream from the hot zone. Figure 2 shows a picture of the down-stream portion of the tube after roasting the chips at 900°C for 4 hours. There are obvious zones of different material

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

←(1) ↑(1) ↑(2)

Figure 2. ↑Down-stream section of tube. The black arrow points toward the hot region of the tube. The red arrow indicates where a ring of white crystals of MoO_3 deposited. The green arrow indicates the edge of the furnace.

QuickTime™ and a
Photo - JPEG decompressor
are needed to see this picture.

Figure 3. Ring of MoO_3 .

Table 3. Surface Analysis of Noble Metal Alloy Chips After Burning in a Tube Furnace at 900°C for 4 hours.

	Mo	Re	Ru	Rh	Pd
8 hours	8.5	5.5	65.0	17.0	4.0
Ave ± STD	41.9 ± 13.9	8.6 ± 5.0	32 ± 3	7.3 ± 0.4	10.3 ± 6.0
Theoretical	42	10.6	31.4	5.3	10.6

being deposited as the gases exit the high thermal regions of the furnace. Since 94% of the weight of the chips volatilized the deposits represent all five elements in the alloy. One phase of molybdenum separated very cleanly from the colorful mirror deposits. Figure 3 shows a ring of white crystals that deposited where the red arrow in Figure 2 indicates. X-ray analysis of the crystals showed that they were MoO₃. Surface analysis on the recovered roasted chips (Table 3) shows that surface concentrations of molybdenum, rhenium, and palladium dropped during the roasting while rhodium and ruthenium increased. Thus the residual chip material probably consists mainly of these two elements.

A second tube furnace experiment was tried where the temperature was raised by 100°C incrementally from 400 to 900°C. This was done in order to fractionate the volatile species coming off the alloy. Each roasting was for 8 hours. Table 4 shows the surface analysis analytical data for chips removed after the 600, 700, and 900°C steps. These data are also plotted in Figure 4. After the 400°C roasting step the chips are tarnished, not heavily oxidized. After roasting at 500°C the chips have lost their metallic sheen and shows obvious oxidation. At this point there is a blue green film and a light gray film depositing just down stream of the thermal zone. After the 600°C step the blue green film has become more pronounced and the chips are heavily oxidized. After roasting at 700°C the chips have some white crystalline material on them and there is a ring of white crystals depositing in the tube similar to that shown in Figure 3. However the position of the ring is still within the thermal zone. After the 800°C step the white crystals have migrated 3" down stream and have maintain their disk configuration. The white crystals were recovered at this point. The chips at this point look very charred. After roasting at 900°C the chips are almost a powdery black material.

The most dominant characteristic in Figure 4 is the molybdenum curve. The surface concentration of this element maximizes at 700°C, the temperature at which there were crystals of MoO₃ are forming on the alloy. This observation is consistent the work of Matui et. Al. who observed rapid weight losses when roasting molybdenum metal and

Table 4. Surface Analysis of Noble Metal Alloy Chips from a Sequential Roasting from 400-900°C.

	Mo	Re	Ru	Rh	Pd
600°C	57.8	5.8	2.4	2.7	31.3
700°C	68.6	8.3	4.8	2.8	15.5
900°C	27.6	6.4	26.3	22.5	17.2
Ave ± STD	41.9 ± 13.9	8.6 ± 5.0	32 ± 3	7.3 ± 0.4	10.3 ± 6.0
Theoretical	42	10.6	31.4	5.3	10.6

a Mo, Ru Pd alloy at 700°C.¹⁶ The increase in the surface molybdenum concentration before this temperature is a result of it migrating to surface and probably concentrating there as an oxide before volatilization.¹⁶ At higher temperatures the molybdenum concentration falls as it is depleted from the alloy by volatilization. Consequently, the surface concentrations of rhodium and ruthenium rise which probably indicates that these elements are not volatilizing; they are becoming the dominant surface elements. Palladium's behavior appears more complex and is inconsistent with the literature.^{13,15,16} At 600°C the surface concentration of this element is 31%, up substantially from its initial concentration of 10%. Although data are lacking below 600°C, the shape of the curve suggests that a plume of palladium comes off between 400 and 700°C; this plume may be responsible for the blue green and light gray films depositing during these stages of the roasting. However, like ruthenium and rhodium the surface concentration of palladium starts to rise from 800 to 900°C. This suggests that the residual palladium may be a different species than the volatile form or it forms a stable phase with the residual elements.

Rhenium's behavior is almost flat from 600 to 900°C and the surface concentration is not significantly different than its initial concentration. If rhenium is supposed to act like technetium then this behavior is contrary to what is expected based on the calculations of Matui and Naito.¹⁵ Providing that the technetium (or in this case

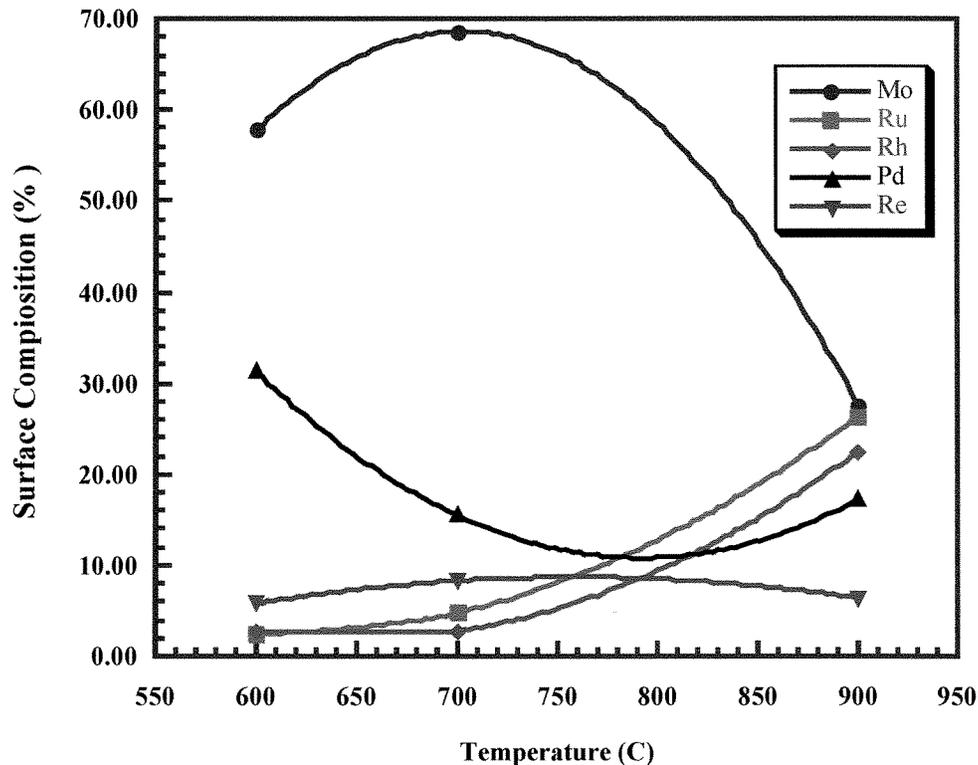


Figure 4. Surface Concentrations of the Five Elements During the Stepped Tube Reaction.

rhodium) is oxidized in the alloy then this element should volatilize as Tc_2O_7 at temperatures $<400^\circ C$. The rhodium result may indicate that rhodium is not easily oxidized in the alloy.

Attempted Synthesis of $TcCl_4$

The goal of the project was to synthesize $TcCl_4$ via a milder route than previously used methods. The more common method is to reduce NH_4TcO_4 to the metal under a stream of hydrogen gas.¹⁷ The metal is then reacted with chlorine gas at $200-400^\circ C$ in a sealed vial. The final product is then sublimed in a stream of chlorine gas to give dark red needle shaped crystals. Tc_2O_7 has also been reduced in the presence of CCl_4 at $400^\circ C$ in a sealed glass tube to give $TcCl_4$.¹⁸

We looked at four separate approaches to produce $TcCl_4$ under mild conditions. The first was to remove the triphenylphosphines of $TcCl_4(PPh_3)_2$ with a Lewis Acid. $TcCl_4(PPh_3)_2$ is easily synthesized from NH_4TcO_4 and triphenylphosphine in hydrochloric acid and ethanol.¹⁹ Presumably, Lewis Acids could coordinate triphenylphosphine stronger than technetium thereby, scavenging the phosphines from the $TcCl_4(PPh_3)_2$ and generating $TcCl_4$. We tried a variety of Lewis Acids without any significant results. In a couple of reactions, a dark green product is produced but there was no evidence for the production of $TcCl_4$. Another method for removing phosphines from transition metals is to use another transition metal precursor with a high affinity for phosphine, i.e., a soft metal.²⁰ Therefore, we tried to react $TcCl_4(PPh_3)_2$ with $Ni(cod)_2$ (cod = cyclooctadiene) and $PdCl_2$. Again, there was no evidence for the formation of $TcCl_4$. These experiments are shown in Figure 5.

Typical experiment:

A 100 mL Schlenk flask was charged with $TcCl_4(PPh_3)_2$ (0.142 g, 0.186 mmol.) and BF_3 (12% in MeOH, 0.25 mL) in methanol (25 mL). The solution was refluxed overnight under argon. No changes in color were observed to indicate the formation of $TcCl_4$.

In the second synthetic route into $TcCl_4$, we tried to scavenge the oxygen atoms from $(Bu)_4NTcO_4$ and TcO_2 with diphosgene (a phosgene precursor) in a chlorinated ionic liquid. Phosgene is known to scavenge oxygen from transition metal complexes.²¹ The general idea was to remove the oxygens from $(Bu)_4NTcO_4$ or TcO_2 in a solvent that contained chloride ions that could coordinate the metal. There was no evidence for the formation of $TcCl_4$ under these conditions.

Typical experiment:

A 100 mL Schlenk flask was charged with $(Bu)_4NReO_4$ (0.1830 g, 0.3715 mmol.) and diphosgene (0.25 mL, 2.1 mmol.) in 44% EMIM- $AlCl_4$ ionic liquid. Refluxed over night under argon. Formation of red $ReCl_4$ was not observed

The third route to synthesize $TcCl_4$ was to electrochemically oxidize technetium metal or reduce $(Bu)_4NTcO_4$ to $TcCl_4$ in an ionic liquid. Two different ionic liquids were used. The first was a chloroaluminate ionic liquid that would have excess chloride anions in solution. The second ionic liquid was a pyrrolidine based ionic liquid without any

chloride present. The idea behind using the second ionic liquid was that the metal center could be either oxidized or reduced to a M(IV) center and then a chloride source could be added to form to generate the MCl_4 complex. For the majority of these experiments, rhenium was used as a surrogate for technetium. The reason for using rhenium was that the ionic liquids can be hygroscopic and are best handled in a glove box and the glove box that was accessible could not accommodate technetium. Neither the oxidation of rhenium metal nor the reduction of NH_4ReO_4 proved to generate $ReCl_4$. The results were difficult to interpret because the cyclic voltammograms (CV) of both the starting materials and the product are complicated and unknown. Reduced $(Bu)_4NTcO_4$ was used in both a chloroaluminate ionic liquid and a non-chloroaluminate ionic liquid with bubbling chlorine gas to serve as a chloride source. However, no evidence for the formation of $TcCl_4$ was observed.

Typical experiment:

A three-compartment electrochemical cell was set up in an inert atmosphere glove box with the working electrode being rhenium foil. The potential was set at +1.5 V. No formation of red color to indicated $ReCl_4$ was observed

The last synthetic route was to reduce either TcO_4^- or ReO_4^- (as a surrogate) to $TcCl_4$ or $ReCl_4$, respectively in hexachloropropene. The basis for this reaction came from known uranium chemistry where UCl_4 is prepared by heating UO_3 in hexachloropropene.²² In the uranium chemistry, the UO_3 is soluble in hexachloropropene and UCl_4 precipitates out as it is formed. Therefore, the product can be simply removed by filtration. Also, $ReCl_4$ has been prepared from $ReCl_5$ in tetrachloroethene.²³ Furthermore, $Re_2Cl_8 \cdot \text{hexachloropropene}$ has been prepared from $ReCl_5$, Re_2O_7 , $ReOCl_4$ and amorphous ReO_2 . The decomposition of $Re_2Cl_8 \cdot \text{hexachloropropene}$ in carbon tetrachloride was reported. However, in the same article the authors reported no reaction of crystalline ReO_2 or rhenium trioxide in hexachloropropene. In our case, the reaction of either TcO_4^- or ReO_4^- in hexachloropropene did not seem to produce either $TcCl_4$ or $ReCl_4$, respectively. In some cases a red solution was formed (indicative of $TcCl_4$ or $ReCl_4$) but identification and isolation of the product proved difficult or impossible.

Typical Experiment:

A 100 mL Schlenk flask was charged with $(Bu_4N)ReO_4$ (0.25 g, 0.51 mmol.) and hexachloropropene (50 mL). The solution was refluxed overnight. The solution did turn red but there was no precipitate. Because of the high boiling point the hexachloropropene the product was not separated from the solution.

Other factors proved to make this project difficult. First, the experimental sections and characterization of $TcCl_4$ and $ReCl_4$ in the literature are vague at the best. $TcCl_4$ does have a magnetic moment but the values range between 3.14-3.8 for μ_{eff} . One article does report UV/Vis data but indicated that the complexes were probably $TcCl_4(\text{solvent})_2$ and rapidly decomposed.²⁴ X-ray data are available in a couple of polymorphs-there are at least multiple polymorphs of $ReCl_4$ and $TcCl_4$.²⁵ In some reports, analysis was performed by decomposing the $TcCl_4$ and complexing the technetium using furil- α -dioxime followed by precipitation of the chloride as silver chloride. The ratio of Tc/Cl was determined to obtain the stoichiometric ratio. Second, decomposition of the $TcCl_4$ and

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