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Challenges and Solutions for Handling and Characterizing Alkali-Tc-Oxide Salts

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ABSTRACT

Though not often discussed explicitly in literature, sample handling and preparation for advanced characterization techniques is a significant challenge for radiological materials. In this contribution, a detailed description is given of method development associated with characterization of highly radioactive and, in some cases, hygroscopic oxides of technetium. Details are given on developed protocols, fixtures, and tooling designed for x-ray and neutron diffraction, x-ray absorption, Raman spectroscopy, magic angle spinning nuclear magnetic resonance, and electron paramagnetic resonance. In some cases multiple iterations of improved sample holder design are described. Lessons learned in handling Tc compounds for these and similar characterization methods are discussed.

INTRODUCTION

Italian researcher Perrier and Segre first isolated Technetium (element 43) in 1937 [1]. Since its discovery it has found uses in the medical [2], steel [3], and low temperature conduction [4] fields. It has been identified in the spectrum of stars [5, 6]; research which led to the discovery of solar production of heavy elements. In the field of inorganic chemistry, it is the only unstable transition metal, sharing chemical properties with rhenium and chromium [7].

It is the radioactive nature of Tc, particularly the soft beta emitting ⁹⁹Tc, which has made analysis of the element and associated compounds challenging. Unlike most other transition metals, the handling and analysis of Tc-bearing compounds is complicated and usually requires the issuing of special permits and expensive modifications to all ready expensive and often rare

analytical instrumentation. Additionally, carefully planned procedures and experimental protocols are usually required to be prepared and approved before any experiment can be conducted with the isotope. Experiments on Tc compounds, particularly some Tc oxides, can be further complicated by their strongly hygroscopic and friable natures. As a result of these challenges, there are now only a small number of labs internationally that are actively conducting research on ^{99}Tc .

Research on Tc, although limited, is important as Tc is being produced daily for the radiopharmaceutical industry, and is a significant component of most nuclear wastes. Within the last few decades there has been a significant increase in research efforts to learn how best to store and dispose of Tc for these purposes [8-16]. Coupled with these efforts has been a push for advanced analyses of Tc bearing materials using state-of-the-art equipment [12, 17-23]. X-ray absorption fine structure (XAFS) has been utilized to investigate the near-field structures of Tc in both crystals and soft matter. Neutron diffraction has provided insight into the effect of ligands on crystal field distortions, and solid-state nuclear magnetic resonance (NMR) has been used to clarify a half-century old debate on the oxidation state of fundamental Tc oxides.

Accompanying this research has been the development of methods on how to safely and properly prepare Tc samples for these instruments, and how to design sample environments that are durable (*i.e.*, “radiation hard”), prevent diffusion of water into the samples, and provide effective containment. that provide radiation shielding. These aspects have generally not been described in research publications. Dissemination of this information is necessary, particularly as the Nuclear Energy Institute has estimated that 39% of the nuclear workforce (which has been primarily responsible for the creation of these methods) will be eligible for retirement by 2018 [24]. Most procedures and protocols take years of research and development and sizeable budgets to be produced, and their loss could drastically delay further research efforts in the field. The focus of the work herein, then, is to document some of the development efforts on methods for handling and characterization of Tc compounds.

EXPERIMENTAL METHODS

Tc utilized in these studies was obtained from Oak Ridge National Laboratory. Processing, synthesis, and purification of alkali-Tc-oxide salts has been previously described [17]. Conversion of alkali pertechnates to higher-order alkali-Tc-oxides was completed under dry conditions because the final compounds were determined to quickly absorb atmospheric water [18]. The reversion of the compounds from the desired chemistry back to an alkali pertechnetate was accompanied by a change in color, from yellow to white. Therefore, a cursory visual analysis of a compound could be made to determine if and where the Tc-containing sample had significantly reverted to its precursor form.

All samples were stored and loaded into sample holders under dry and inert conditions to avoid moisture-driven transformations. A layer of containment that was easily disposable was used during the handling and loading of samples into holders as the powders were friable, and therefore a significant dispersion hazard. Inexpensive plastic glove bags filled with 99.99% N_2 gas (Linde), were placed inside a radioactive materials fume hood to meet this requirement. The bag was taped to the floor of the fume hood. Special sample holders and tools were designed to fit and be workable within the bags’ dimensions. A set of primary and secondary gloves were required for fume hood entry. An additional set of gloves was placed over the glovebags’ gloves for better dexterity.

All equipment that went into the glove bag was dried to the extent possible. Tools and equipment that could be baked (beakers, spatulas, crucibles, mortar and pestle, and so on) were dried at 105°C for an hour or more, then taken into the bag while still warm. One set of tools was dedicated to preparing Tc samples, and were not used with other radioactive materials. This removed the possibility of contaminating samples with additional radiation sources, which could complicate obtaining approval to transport samples to analytical facilities. All samples were pulverized inside the glove bag using a small ceramic mortar and pestle into a free-flowing powder. Pulverizing was carefully performed to minimize any phase transformations, as these are undesirable.

During the work, the inside of the bag and the surface of the equipment was periodically wiped with dry towels to control radioactive particles. Once samples were loaded and sealed into analysis holders, all surfaces of the containers, reusable tools, and the walls of the glove bag were repeatedly wiped with damp towels to remove and check for unwanted radioactive contamination. Most Tc compounds produced in these experiments were water soluble, and could be easily removed from unwanted areas by a damp towel. Dry towels were less efficient at removing Tc contamination from surfaces. When possible, removed Tc was recovered so it could be recycled and used in later experiments. After swipes of an object showed no activity on a hand-held Geiger-Müller survey instrument, the object could be removed from the bag and placed in the fume hood.

After removal from the glove bag, hygroscopic samples were placed in a sealed container with a few grams of desiccant, such as molecular sieve. Samples that were to be sent out for analyses were only removed from the holder and hood a few hours prior to being shipped, and were sealed in new, plastic bags and checked by wet and dry swipes before being removed from the hood. A final layer of containment, and a final set of wet and dry swipes was completed before sealing in a sturdy shipping box.

Sample holder materials and sealing compounds/methods were evaluated over the course of experimentation. Many common sealing compounds, such as certain types and brands of epoxy and most tapes, were found to be inadequate at keeping the holders water-tight. Some sealers, particularly two-part epoxies, were found to contain water which ruined the samples. In most cases, multiple layers of sealing materials and a minimum of two layers of containment were required to seal the holders. However, even these materials often showed degradation with time and exposure to the samples' moderate levels of radiation.

Samples holders were developed for the analysis of the hygroscopic higher-order Tc oxides by neutron diffraction, solid-state NMR, EPR, Raman, XAFS, and XRD. Details are provided below on each analysis methods sample holder design.

Figure 1. Special sample holder filling containers (left) and glove bag, and multi-glove rad hood protocols (right)

Considerations for Non-dispersibility

Samples holders had to enclose and seal in the radioactive samples, keeping them from dispersing into the environment. Although all samples were shipped overnight to non-local facilities for analyses, the holders were often tested for longer-term containment capabilities. Often a sample would be loaded a few days to a week prior to analysis, and then checked once or twice daily to ensure no material had leaked.

X-ray diffraction

Capillary XRD samples were loaded with crushed sample powders (~15 μg) in the glove bag. The capillaries (Borokapillaren, 0.5 mm diameter, 0.01 mm wall thickness, Charles Supper Co.) were broken to length and sealed with Parafilm®, which was capped with a layer of epoxy. This holder was then placed inside a Kapton® sleeve, and both sides of the sleeve were sealed shut by epoxy, and the glue was taped over with Kapton® tape. Other options for XRD include hemispherical top airtight specimen holders (Bruker) if water intrusion is a problem and a relatively larger amount of sample can be used. Other standard methods which are not as good due to eventual radiation-induced degradation and water ingress include Kapton® tape placed over powder holders. Various other methods have been previously reviewed [25].

Neutron diffraction

Initial neutron diffraction analyses of alkali pertechnetate salts, samples were sealed in a 1 mm thick- walled fused quartz tubes to ensure no breakage occurred during shipping and handling. The large diameter tube (~8 mm inner diameter) allowed 200-400 mg of sample to be loaded, resulting in typical radioactivities per sample of >1 mCi (>37 MBq). Loading was completed by placing a smaller diameter glass tube into the holder, and tapping the powder sample through this tube and into the bottom of the sample holder. Loading the sample in this manner ensured that no powder adhered to the sides of the sample holder, the presence of which may interfere with the flame sealing procedure. The thick walls of the tubes made flame sealing the ends difficult, resulting in uneven glass ends. It was found that this caused excessive amorphous backgrounds, particularly with small sample volumes. However, it was also seen that the background signature was easier to fit well, and thus resulted in lower chi-squared for the low volume, high background sample data fits [17].

In the second iteration, neutron diffraction samples were placed in 5 mm outer diameter fused quartz NMR tubes (0.38 mm wall thickness, Wilmad 509-PP-7QTZ) that were flame sealed at both ends to a final 25-50 mm in length. Lessons learned on handling allowed thinner walled tubes to be used, which also were easier to seal. The tubes had to be made of an amorphous material so that the diffraction pattern of the tube did not interfere with the diffraction pattern of the compound inside. The tubes, once loaded following the same protocol as above, were slowly evacuated prior to being flame sealed. After the lessons learned about the effects and durability of epoxy for these kinds of samples it was decided that a safer method of sample closure for the neutron diffraction experiments would be flame sealing. Flame sealing was performed with an propane-oxygen torch in a radiological fume hood. Care was taken not to heat the samples during sealing, and the tube was frequently checked to make sure it remained cool during the sealing process. Approximately 30 – 200 mg of the Tc compound was placed in each tube, with particle size ~75 μm . For the beamline used, filling the tube to a height of 8 mm is ideal to take advantage of the whole beam.

For neutron diffraction analysis, the powder-filled tubes were held between two rubber bars inside a metal sample holder, and the bottom of the tube, where the powder was located, was placed facing the neutron beam. Longer tubes were made for the second set of sample analyses to allow for better sample alignment within the diffraction chamber.

Figure 2. Neutron diffraction holders. First generation (left) and second generation (center); tool used to sieve the samples to $<75\ \mu\text{m}$ and load the NMR tubes (right).

X-ray absorption

XAFS samples were crushed powders that had been thoroughly mixed with boron nitride powder to achieve a necessary dilution ratio for XAFS analysis. The sample holder consisted of a dry metal or TeflonTM rectangular frame (2 x 2-4 cm) that had an oblong window ($\sim 3 \times 10\ \text{mm}$) in the middle. The frames were taped on one side, covering the hole and edges, with Kapton® (polyimide) tape and then the sample was loaded into the window until the window was filled. A second piece of Kapton® was then placed over the window to seal in the powder. Another layer of Kapton® was adhered on either side of the holder. The holders were smeared and counted to determine if any contamination was present. If contaminated, the holders were wiped down until no contamination was detected. The holder was heat-sealed inside a Mylar® (polyethylene terephthalate) bag, which counted as secondary containment. These bags were then attached to a larger metal frame (typically aluminum) with the windows of the sample holders being aligned to the windows of frame. Samples prepared this way could be measured in both fluorescence and transmission XAFS modes. Early versions of this procedure used Mylar® backed tape to seal in the samples, but was found to contain too much water, and the samples decomposed after a few days of contact. Dilution of the samples with boron nitride and sealing with Kapton® helped mitigate this issue. Typical radioactivity of each sample was $\sim 43\ \mu\text{Ci}$ (1.59 MBq). This sample holder design was usable for analyses at both SSRL and APS.

Figure 3. X-ray absorption holders. Completed assembly (left) and loaded for beamline (right)

Raman spectroscopy

Confocal (microscopic) Raman analyses of synthesized technetium (Tc) containing glasses and oxides required their encapsulation in containers to prevent dispersal of radioactive particles. A simple, preliminary, design of a sample holder was made from a polystyrene “membrane box” modified to present a quartz window through which scattered Raman light could be collected. These boxes consist of two halves, each with a plastic membrane stretched across their inner surfaces. The boxes were inexpensive and were considered “one time use” containers. Membrane boxes (Ted Pella Inc.) were easily adapted to the encapsulation of the Tc-containing materials. The membrane boxes were machined on a lathe to remove a ~18 mm circular opening on one side of the two-piece box. A ~25 mm square quartz window was then epoxied to the outside surface of the membrane box to cover the ~18 mm opening on the one side of the box. Attaching the quartz window to the outside of the box allowed for a larger working distance on the inverted stage confocal Raman microscope. Once the epoxy had cured the membrane was removed from the “window” side of the two-piece box. A ~12 mm circular TeflonTM washer, with approximately a ~3 mm central hole, was epoxied to the inside surface of the quartz window to create a well for the sample. This well was essential to providing enough particles within the viewing area of the confocal Raman microscope using varying magnification microscope objectives. After the sample was placed in the center of the TeflonTM washer a second quartz window was epoxied to the top of washer, sealing the Tc between the two quartz windows. The two halves of the membrane box were then sealed together with vinyl tape around the periphery. The assembled box and sample was placed upside down on the inverted stage microscope for analyses. The scattered Raman light was collected in a 180° backscatter geometry. Spectra were acquired from approximately 10 to 20 particles, or 10 to 20 spots on glasses, and evaluated for consistency of spectral bands and band intensities before averaging. The averaged spectra were analyzed for agreement with published spectra of Tc-containing oxides or glasses as available.

The epoxy gave off water vapor as it cured, which made it unsuitable for a number of Tc compounds. Also, samples containing relatively high levels of radioactivity, ~50 μCi (1.85 MBq), caused epoxy seals in membrane boxes to degrade within a few weeks. This led to the design of a threaded metal sample holder which consisted of front and rear fused silica windows, an O-ring, a TeflonTM washer, a cylindrical housing, and a threaded compression plug. The samples were sealed by the threaded plug compressing the O-ring between the windows, which removed the need for use of glues or tapes. To fill a mount, the front window is placed in the housing, then an O-ring is placed on the window, with a small TeflonTM washer inside the O-ring. The sample is then placed inside the TeflonTM washer using a special funnel that kept the rest of the housing clean. The rear window is then placed on the O-ring and the back is screwed on using the wrench. The sample contacts only the silica windows and the TeflonTM washer. No epoxy or tape is used, and the mount can be easily assembled in an inert atmosphere inside a glove bag. After the mount is assembled and brought out into room air, the O-ring keeps atmospheric moisture away from the sample. The mount can be disassembled to retrieve and recycle the technetium compound inside. The mounts can be re-used indefinitely, with new O-rings.

Figure 4. Raman spectroscopy holders. Generation one membrane box (left). Generation two tooling including metal housing with fused silica windows, washers, and housing back plug (center) in exploded view, shown in (right) inside the carrying container with housing plug wrench and funnel. The completed Raman holder (right) is shown inside its TeflonTM carrying holder (cap removed) designed for secondary containment during transport and storage.

Nuclear magnetic resonance

For magic angle spinning (MAS), solid-state NMR (MAS ss-NMR) experiments, $\sim 75 \mu\text{g}$ of powder ($\sim 100 \mu\text{Ci}$ or 3.70 MBq of radioactivity) were packed into a specially designed Torlon® (polyamide-imide) solid state-NMR insert that fit into a commercial 3.2 mm PENCIL style (Agilent or Revolution NMR) zirconia NMR rotors. The use of the insert was three-fold. First, it provided a strong, unbreakable secondary layer of containment for the Tc powders. This was a necessary feature as the samples were spun at 18 kHz, and the inserts had to be able to withstand a rotor “crash” where the zirconia holder may break. Second, it could be easily handled and cleaned (by placing in simmering water for a few hours). Cleaned inserts were found to contain no dispersible Tc on their surfaces nor material contamination on the inside, and could be reused multiple times before being discarded. Third, the inserts allowed for powders to be loaded in the NMR rotors without the need to stabilize the powders into a solid mass. Addition of stabilizers, e.g., encapsulation of powders in epoxy, were believed, based on previous experience with hydrated glues, to add a layer of chemical complexity, including hydrating previously dried products, which could complicate the NMR results. Special NMR tools, which could also be cleaned and reused multiple times, were designed to allow for careful incremental packing of the insert. Imbalances in the insert due to heavier loading of material in one section of the insert could lead to a rotor crash and needed to be avoided.

Figure 5. MAS-NMR tooling and sample holders (left) and final inserts for rotors (right)

Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) was performed using the NMR inserts as sample holders, ensuring that spectra for both techniques were collected on the identical sample. However, the spectra displayed a background arising from free radicals present in the insert material. An alternative holder for EPR consisting of a 3.15 mm inner diameter FEP (fluorinated ethylene propylene copolymer) sleeve (Wilmad) that could be capped and sealed was subsequently used to obtain background-free spectra for comparison. In both cases, either the FEP tube or the NMR insert was subsequently inserted and sealed into a 5.0 mm outer diameter quartz screw-cap EPR tube (Wilmad), both as a second layer of containment and for compatibility with the Oxford Cryostat use in the experiments.

DISCUSSION AND CONCLUSIONS

In all cases, it took two or three iterations of design and testing before an acceptable and radiologically durable sample holder for each analytical method was achieved. Considerations regarding non-dispersability, adsorbed surface water content, radiation-hardness, and non-reactivity to sample materials were needed for each holder. Additionally, the holders could not interfere with data acquisition processes. Because of the radioactivity of the samples, it generally took 3 to 5 times longer at each loading step (i.e., loading samples into holders and holders into instruments) than it would have required with non-radiological sample. This development process, however, would have taken much longer if it were not for input and guidance provided by the radiation protection technicians, instrument scientists, sample environment support staff, and radioanalytical scientists who consulted and collaborated on this research.

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