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Iso-polyoxomolybdates for the Recovery of Molybdenum from Alkaline Solutions

Chemical Sciences and Engineering Division

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ISO-POLYOXOMOLYBDATES FOR THE RECOVERY OF MOLYBDENUM FROM ALKALINE SOLUTIONS

1 INTRODUCTION

Technetium-99m is a widely used radioisotope for single-photon emission computed tomography (SPECT) imaging because of its ideal characteristics such as a sufficiently short half-life (6 hr) and single gamma emission (140 keV). SPECT utilizes gamma emissions from select radioisotopes such as ^{99m}Tc to collect multiple 2D images that can later be combined into 3D images that map the interior of a patient. Such images provide insight to diseases that will help doctors cure certain ailments. Currently, there is no domestic U.S. supply of ^{99m}Tc, which is a decay product of ^{99}Mo.

Argonne National Laboratory with the National Nuclear Security Administration's (NNSA) Global Threat Reduction Initiative (GTRI), in partnership with commercial entities like NorthStar Medical Technologies, LLC (NorthStar), are developing technologies for the domestic production of ^{99}Mo for nuclear medicine while minimizing civilian use of highly enriched uranium (HEU). One such method is the photonuclear reaction ^{100}Mo(γ,n)^{99}Mo. The targets, enriched-^{100}Mo pressed and sintered Mo-powder disks, represent a large investment, and therefore, ^{100}Mo must be recycled.

Processing irradiated ^{100}Mo disks results in a highly alkaline solution (~5 M KOH) of K_2MoO_4 which is used in the RadioGenix™ system to separate ^{99m}Tc from $^{99/100}$Mo. Once separated, the ^{100}Mo is recycled. To reuse ^{100}Mo, NorthStar will require that recycled materials meet the purchase specifications of the original material. Therefore, the ^{100}Mo must be isolated, washed of any impurities (e.g., K^+), and reduced back to metallic disks for future irradiations. The initial concentration of potassium in the 5 M KOH solution of K_2MoO_4 is in the range of 1.82×10^6 mg K^+ per kilogram Mo, while the final concentration of K^+ required is <100 mg K^+ per kilogram Mo. There are several possible methods to achieve this, from ion exchange columns to precipitation methods. Since the final form of Mo must be a solid, we chose to pursue a precipitation purification method.

Early transition metals, like Mo, readily form polyoxometalates (POMs). Many structures of POMs exist from the isopolyoxometalates ($[M_xO_y]^{n-}$, Figure 1) to heteropolyoxometalates ($[AM_xO_y]^{n-}$, where A = Si^{IV}, Ge^{IV}, P^V, or As^V, Figure 2). These POMs can be soluble in aqueous or organic solutions depending on the counter ion chosen [1]. For example, tetrabutylammonium hexamolybdate(VI) ($[(n\text{-}C_4H_9)_4N]_2[Mo_6O_{19}]$ or $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$) is insoluble in water but soluble in organics like acetone or acetonitrile. These compounds can be precipitated from aqueous solutions and isolated as pure materials by means of filtration. Once isolated, iso-POMs can be reduced under high temperatures and hydrogen atmosphere to give pure metallic starting materials. This study targets the $[M_6O_{19}]^{2-}$ moiety.

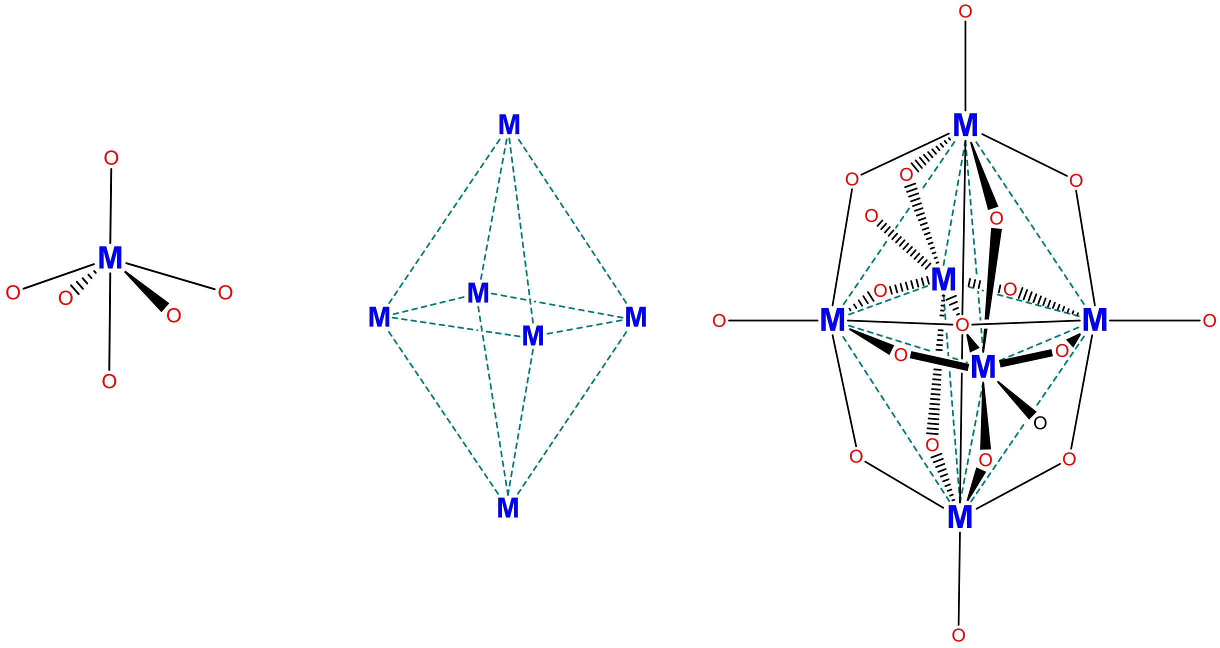

FIGURE 1 Structural Representations of $[M_6O_{19}]^{2-}$, an Isopolyosometalate. Metal centers are denoted by "M"; and oxygen atoms are "O". Left: distorted octahedral environment around metal center, the basic building block of the full structure. Middle: general arrangement of metal centers within full structure. Right: full structure, in which oxygen atoms occupy space on each of the edges seen in the middle figure, and a single oxygen is in the middle of the structure.

Molybdenum will precipitate as $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ when $[MoO_4]^{2-}$ is heated in acidic conditions in the presence of $n\text{-}Bu_4NBr$. This compound has been characterized as indefinitely stable when stored in a desiccator [1]. It has been shown that thermal decomposition of $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ will result in the loss of the organic groups at temperatures around 300 ^{o}C and the rest of the compound will reduce to MoO_2 after 500 ^{o}C [2,3]. The metal can be achieved at higher temperatures under a hydrogen atmosphere. These attributes make iso-POMs attractive for the purpose of recycling Mo. Herein, we report strides taken towards recycling Mo by iso-POM precipitation.

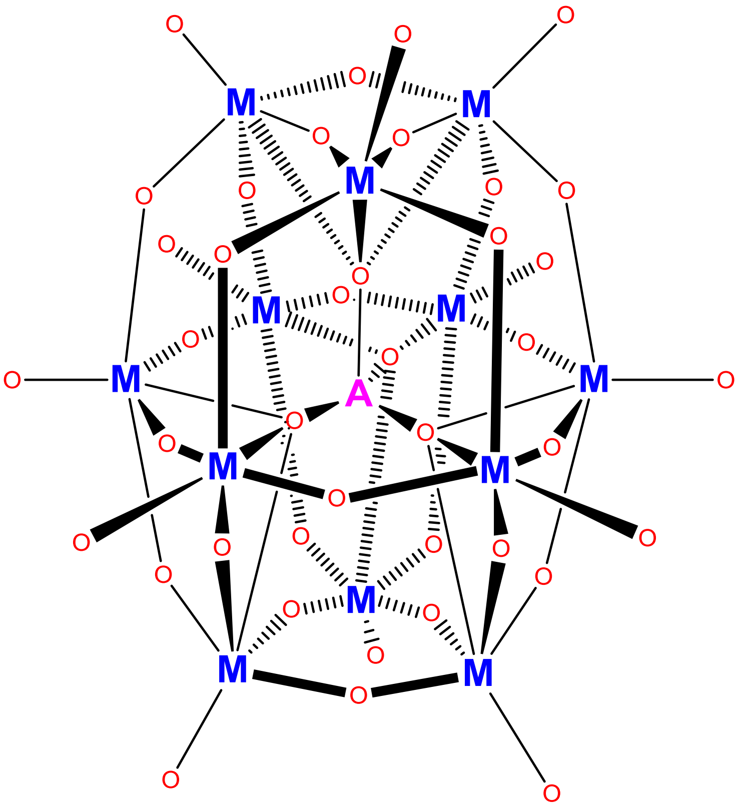

FIGURE 2 Structural Representations of $[AM_{12}O_{40}]^{n-}$, a Heteropolyoxometalate. A central heteroatom is denoted by "A"; metal centers are denoted by "M"; and oxygen atoms are "O".

2 EXPERIMENTAL

Molybdenum was precipitated by using a modified procedure from Inorganic Syntheses [1] that involves the following reaction:

$$6K_2MoO_{4(aq)} + 10HCl_{(aq)} + 2(n\text{-}C_4H_9)_4NBr_{(aq)} \rightarrow$$

$$[(n\text{-}C_4H_9)_4N]_2[Mo_6O_{19}]_{(s)} + 10KCl_{(aq)} + 2KBr_{(aq)} + 5H_2O_{(l)} \qquad \text{(Eq. 1)}$$

A solution of $K_2MoO_{4(aq)}$ (0.2 g-Mo/mL in 1 mL of 5 M KOH) was neutralized by slow addition of HCl (6 M, 1 mL) and further acidified by slow addition of HCl (6 M, 1 mL). A solid formed on contact with the second addition of acid and dissolved upon stirring. The solution yellowed after addition of ~1.5 mL of HCl and precipitated upon complete addition. A solution of tetrabutylammonium bromide [$(n\text{-}C_4H_9)_4NBr$ or Bu_4NBr: 0.092 g/mL, 1.2 mL] was then added. Precipitation of the solution increased. Stirring became difficult, so the solution was diluted with 10 mL of H_2O. The resultant slurry was heated at 75-80 ^{o}C with stirring for ~45 min. During this period, the white solid turned yellow. The suspension was then allowed to cool to room temperature. The slurry was transferred to a centrifuge tube and diluted with water (10 mL).

The sample was centrifuged, and the solution decanted onto a fine-porosity glass-fritted funnel. The solution was passed through the funnel; the filtrate was saved for analysis. Water (10 mL) was added to the centrifuge tube, and the solution was mixed by vortex mixing for several minutes and then centrifuged. The solution was again passed through the funnel, and the filtrate was collected for analysis. This process was repeated five times. The solid became more and more flocculent with each wash and would not compact with centrifugation. Flocculent solid that did not settle was collected on the fritted funnel. Upon completion of the wash steps, the yellow product was dissolved in boiling acetone, passed through the fritted funnel (dissolving the previously collected solid), and collected. A fine white solid was left on the frit. This solid is most likely another polymolybdate that precipitated upon initial acidification of the solution. The white solid was dissolved from the frit with NH_4OH (10 mL) and collected separately from the yellow product. Evaporation of the solvents gave crystalline $(Bu_4N)_2[Mo_6O_{19}]$ and white byproduct (Figure 3). Samples were weighed and then prepared for analysis.

Inductively coupled plasma-mass spectrometry (ICP-MS) was performed under acidic aqueous conditions. Water-insoluble $(Bu_4N)_2[Mo_6O_{19}]$ was decomposed with NH_4OH and H_2O_2 over several days. Because complete dissolution of the solid was difficult, the ICP-MS data for the recovery of Mo were poor. This problem will be discussed in more detail in the next section.

The semi-dissolved samples were then diluted with water and two aliquots from each sample ($(Bu_4N)_2[Mo_6O_{19}]$ and white byproduct) were taken. The first aliquots were acidified and then submitted for analysis. Molybdenum was extracted from the second aliquots with tributyl phosphate (TBP). Low potassium concentrations in the presence of high Mo concentrations can be determined after Mo was extracted into 30% TBP from ~5 M HCl according to a procedure developed earlier [4,5]. The aqueous layer was collected and submitted for ICP-MS analysis.

FIGURE 3 Photograph of Solids Isolated from Method 2: Hydrolysis Product (left), $(Bu_4N)_2[Mo_6O_{19}]$ (middle), and $(Bu_4N)_2[Mo_6O_{19}]$ and Hydrolysis Product Combined (right)

This experiment was repeated (no extraction was performed) using ^{99}Mo spiked solutions to verify the Mo recovery.

Samples of $(Bu_4N)_2[Mo_6O_{19}]$, the white byproduct, and a mixture of the two products were sent to Oak Ridge National Laboratory (ORNL) for thermal gravimetric analysis (TGA) combined with differential thermal analysis (DTA). ORNL used a TA Instruments Q600 TGA/DTA to run the samples. Analysis of the pure $(Bu_4N)_2[Mo_6O_{19}]$ sample (16 mg) was performed twice where it was heated at a rate of 2^{o}C/min in an argon atmosphere and again in a 4% H_2 in argon atmosphere.

3 RESULTS AND DISCUSSION

Initial attempts at preparing and washing $(Bu_4N)_2[Mo_6O_{19}]$ included isolation of natural Mo as $(Bu_4N)_2[Mo_6O_{19}]$ on a glass-fritted funnel, followed by washing the solid on the funnel. Recoveries by mass were very good (>90%); therefore, ^{99}Mo-spiked trials were conducted while awaiting ICP-MS results. These trials were conducted prior to execution of the centrifugation/filtration method (described in the experimental section). Washes for these samples were conducted on fritted funnels. These trials determined that 99-100% of the Mo was recovered overall. An average of 55% was collected in the $(Bu_4N)_2[Mo_6O_{19}]$ acetone fraction, and 45% was isolated in the NH_4OH fraction. The discrepancy observed between mass yields and gamma counting yields is from loss of material on the frit (powder) and the chemical form of the material (i.e., $[Mo_6O_{19}]^{2-}$, $[Mo_7O_{24}]^{6-}$, etc.) complicating yield calculations. This method only used five wash steps and will need to be repeated by the newly modified procedure.

In later trials, we followed the method described in the experimental section. It has been noted that acidification of the starting solution must be slow to avoid formation of undesirable solids. Polymolybdates such as $[Mo_7O_{24}]^{6-}$ will precipitate when aqueous solutions of molybdate are treated with acid, and the pH is lowered to or below 6 [1,6]. Other polymolybdate ions containing 8 and 36 molybdenum atoms can also form by further lowering the pH or increasing the acid concentration. These reactions are represented by the following equations [6]:

$$7\,[MoO_4]^{2-} + 8\,H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4\,H_2O \qquad \text{(Eq. 2)}$$

$$8\,[MoO_4]^{2-} + 12\,H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6\,H_2O \qquad \text{(Eq. 3)}$$

$$36\,[MoO_4]^{2-} + 64\,H^+ \rightleftharpoons [Mo_{36}O_{112}]^{8-} + 32\,H_2O \qquad \text{(Eq. 4)}$$

The end point of the acid addition during the POM synthesis was just after the solution becomes yellow. If more acid was added to the solution, precipitation of Mo occurred. While the yield of $(Bu_4N)_2[Mo_6O_{19}]$ decreased, this did not affect the Mo recovery yields. The precipitated Mo was still recovered; it simply made the final clean-up more intensive. During final recovery, $(Bu_4N)_2[Mo_6O_{19}]$ was dissolved from the fritted funnel in boiling acetone. The other material (presumably a potassium-polymolybdate) was insoluble in acetone and was dissolved in base (NH_4OH).

ICP-MS data from the filter wash method demonstrated that washing was not sufficient. Molybdenum recoveries were >90%; however, the K content (800-20000 mg-K/kg-Mo) was far above the desired levels (<100 mg-K/kg-Mo). The wash method was insufficient because of the inherent nature of the material: $(Bu_4N)_2[Mo_6O_{19}]$ caked on the frit, and sufficient washing was nearly impossible. Attempts to break the solid up and achieve sufficient mixing led to splashing and loss of material.

A more efficient method was employed in later trials. The solid was centrifuged; the solution was decanted onto a filter and filtered; the solid was washed with water; this solution was mixed by vortex; and the washing process repeated. This allowed for adequate washing and little to no loss of material. The ICP-MS data for five washes are shown in Table 1. The data are given as averages over several small-scale trials.

This data show that, after five washes, >94% of potassium is removed, and ~3% Mo is lost. The most significant loss of Mo occurs with the initial filtration of the product, suggesting that the Mo does not completely react or the product has begun decomposing. The percent of Mo lost decreases over the first two washes; therefore, it is more likely that the initial loss of Mo is from incomplete reaction. However, the product may start to decompose after the third wash, as the percent of Mo lost slowly increases as the number of washes increases. Another possibility for the increased loss of Mo over time is that unreactive Mo is trapped within an aggregate solid and is washed out as these aggregates disperse. The desired product, $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$, initially forms as large clumps and, upon repeated washing with water, breaks into flocculent particles.

As mentioned above, determination of the Mo physically recovered is difficult. Recovery determination by mass is complicated because there is the potential for several different forms of Mo, and determination by ICP-MS is plagued by the robust nature of the product. Because the $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ product is slowly decomposed by basic or acidic solutions, complete dissolution of the material for ICP-MS is challenging. During decomposition of $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$, a great deal of solid is left undissolved. The recovery of Mo shown in Table 2 is not an accurate representation of the true recovery. A much more accurate method for the determination of the recovery of Mo as $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ is to use a spike of Mo-99 during the synthesis. These results demonstrate >99% recovery of Mo. The ICP-MS data in Table 2 report the amount of K^+ left in the final product (0.09%).

TABLE 1 ICP-MS Data of Washing Solutions. ICP-MS data reported with 10% uncertainty. Percentages based on 0.193 g Mo and 0.351 g K in the starting solution.

Sample	Mass of Mo (g)	% Mo Loss	Mass of K (g)	% K Removed
Initial filtrate	2.79E-03	1.45	2.79E-01	79.49
Wash 1	5.71E-04	0.30	4.50E-02	12.82
Wash 2	3.18E-04	0.16	5.68E-03	1.62
Wash 3	5.98E-04	0.31	8.62E-04	0.25
Wash 4	7.74E-04	0.40	2.68E-04	0.08
Wash 5	1.02E-03	0.53	2.19E-04	0.06
Totals	6.07E-03	3.15	3.31E-01	94.31

TABLE 2 ICP-MS Data for the Recovered Product of (n-$Bu_4N)_2[Mo_6O_{19}]$ and Mo Byproduct. ICP-MS data reported with 10% uncertainty. Percentages are based on 0.193 g Mo and 0.351 g K in the starting solution.

Sample	Mass of Mo (g)	% Mo Recovered	Mass of K (g)	% K Left
POM	5.33E-02	27.62	3.03E-04	0.09
Byproduct	5.16E-02	26.74	3.58E-03	1.02

The data show that slightly over 25% of the Mo is recovered as the byproduct. This is an accurate measure of the byproduct, as it was completely dissolved for these analyses. The amount of potassium that stays with the byproduct suggests that it is an insoluble potassium salt of Mo. Further work needs to be performed to optimize the formation of (n-$Bu_4N)_2[Mo_6O_{19}]$ and minimize the formation of the byproduct. The byproduct most likely forms from over-acidification of the starting solution. Therefore, the pH of the starting solution (K_2MoO_4) is of critical importance, since the basic solution must first be neutralized and then acidified with HCl. The yield of the desired product may be increased and the byproduct decreased by introducing the Bu_4NBr at different points during the synthesis, such as prior to neutralization, after neutralization, or just before complete acidification. This action may promote formation of (n-$Bu_4N)_2[Mo_6O_{19}]$ even if the solution is over-acidified. Another parameter to vary would be at what point the solution is heated to 80 ^oC.

The TGA/DTA results for the trials with pure argon and 4% H_2 in argon atmospheres are shown in Figures 4 and 5, respectively. In argon, the sample began to lose weight at 280 ^oC with four total regions of weight loss. When the atmosphere was changed to 4% $H_{2(g)}$ in $Ar_{(g)}$, a similar trace was observed. The only major difference was a single higher temperature weight loss at 569 ^oC.

Two endothermic transitions without associated weight losses occur at 182 and 188^oC. This effect could be associated with phase changes in the structure of (n-$Bu_4N)_2[Mo_6O_{19}]$. The major onset of mass loss begins near 280^oC. Decomposition of the material does not begin until 350^oC. At this point, the structure loses two n-Bu_4N^+ and four oxygen atoms, as reported in the literature [2,3]. The material continues to decompose in a second process between 600 and 800^oC, which would correspond to the loss of more oxygen atoms. It seems that $H_{2(g)}$ facilitates the decomposition that begins at ~ 400 ^oC. The data reported by ORNL demonstrate a final weight loss of 54.6% (45.4% remaining) and do not correspond to full reduction to Mo. The total loss would be 57.8% with 42.2% remaining. Lowden and Montgomery at ORNL have shown that MoO_3 can be reduced to metallic Mo by heating to 550°C at 10°C/min and then to 750°C at 1°C/min to allow time for conversion of MoO_3 to MoO_2. The heating is then continued at 2°C/min to 1100°C. The furnace is held at temperature for an hour before cooling to room temperature. Lowden and Montgomery have noted that complete reduction of MoO_2 occurs at the end of the furnace run. During ORNL's TGA/DTA analysis, heating (n-$Bu_4N)_2[Mo_6O_{19}]$ at 10 ^oC/min resulted in large volume expansion of the material. Therefore, larger containers or lower heating rates must be used.

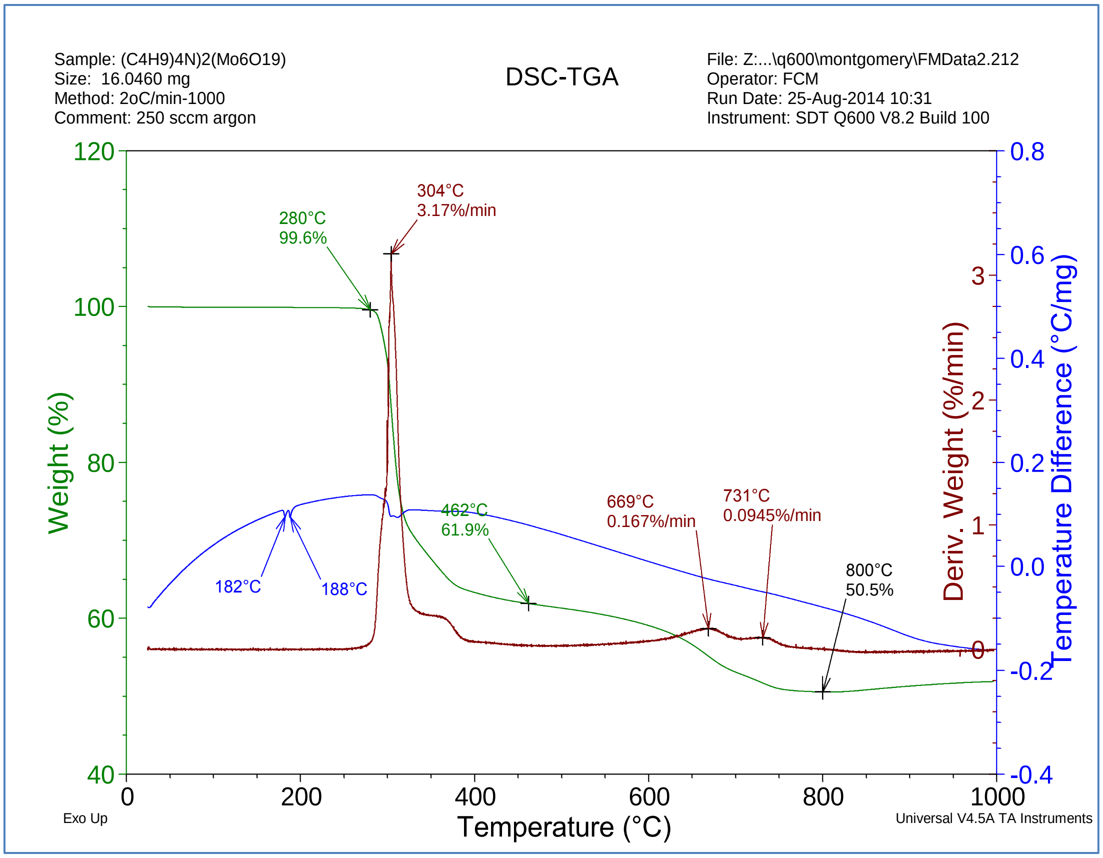

FIGURE 4 TGA/DSC Trace for $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ in $Ar_{(g)}$ Atmosphere. Heating rate: 2 ^{o}C/min; gas flow rate: 250 sccm. Curves supplied by personal communication with Richard Lowden and Fred Montgomery at ORNL.

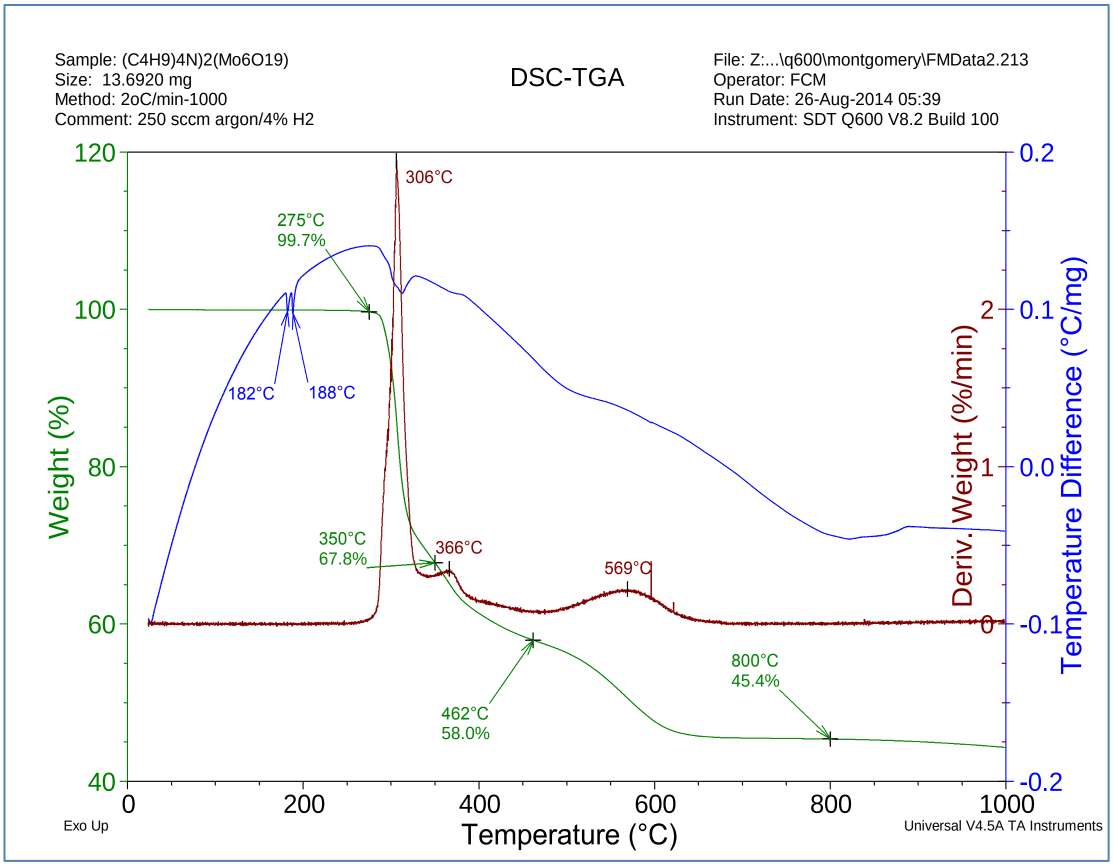

FIGURE 5 TGA/DSC Trace for (n-$Bu_4N)_2[Mo_6O_{19}]$ in 4% $H_{2(g)}$ in $Ar_{(g)}$ Atmosphere. Heating rate: 2 ^{o}C/min; gas flow rate: 250 sccm. Curves supplied by personal communication with Richard Lowden and Fred Montgomery at ORNL.

4 SUMMARY

Recovery of molybdenum as an iso-POM has been demonstrated. More work is required to optimize the formation of the desired product, $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$, and eliminate formation of insoluble potassium-containing byproducts, potassium polymolybdates. Several experiments to increase yields include probing the acidification, the point at which Bu_4NBr is added, and the temperature during reaction. Gamma counting results for Mo-99 spiked trials were much more reliable than ICP-MS results for the determination of Mo recovery. This was because the inherent robust nature of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ makes complete dissolution difficult. However, ICP-MS was very effective for the determination of Mo lost and potassium removed in each wash. ICP-MS data demonstrated that <0.1 % of the potassium remains after five washes, which corresponds to ~1570 mg K^+ per kilogram Mo (assuming 99% recovery observed from Mo-99 spiked trials). Several more washes are required to bring the potassium content to <100 mg K^+ per kilogram Mo. Thermal decomposition of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ was performed by ORNL. The compound undergoes several decomposition steps. Complete reduction of the complex was not achieved under the conditions used.

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