ANL/CSE-13/45

Recovery of Mo for Accelerator Production of Mo-99 Using (γ,n) Reaction on Mo-100

Chemical Science and Engineering Division

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Recovery of Mo for Accelerator Production of Mo-99 Using (γ,n) Reaction on Mo-100

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CONTENTS

1 INTRODUCTION 1

2 MOLYBDENUM PRECIPITATION 3

2.1 Precipitation of Mo Using Nitric Acid 3
2.2 Precipitation of Mo Using Acetic Acid, Ethanol, and a Mixture of the Two 6

3 SUMMARY 12

4 REFERENCE 13

FIGURES

1 Molybdenum Cycle from the Disk Production through the Recycle 2

2 Potassium-Concentration Dependence on Number of HNO_3 Washes after Precipitation of Mo from 0.2 g-Mo/mL Solution of K_2MoO_4 in 5 M KOH 4

3 Concentrations of Selected Elements in the Mo Product after Nitric Acid Precipitation and Washes 5

4 Fine Mo Precipitate Forms when Acetic Acid Is Used to Precipitate Mo; Fine Mo Precipitate also Forms when Using Nitric Acid Wash after Acetic Acid 7

5 Photographs of Mo Oxide Powders Obtained after Mo Recovery from K_2MoO_4 Solution in 5 M KOH Compared to Commercial MoO_3 Powder, on the Left 10

6 XRD Spectra of Dried Samples Obtained after Mo Recovery, and Spectra of the Same Samples after Heating to 620°C 11

7 Photographs of Dried Samples Obtained after Mo Recovery, and the Same Samples after Heating to 650°C in Air 11

TABLES

1 Mo Losses and Removal of Potassium for Different Reagents Used to Precipitate Mo 6

2 Removal of Potassium, and Mo Losses per Step 8

TABLES (Cont.)

3 Purification Steps for Removing Potassium from 1 mL of K_2MoO_4 Solution in 5 M KOH 9

4 Purification Steps for Removing Potassium from K_2MoO_4 Solution in 5 M KOH 10

RECOVERY OF Mo FOR ACCELERATOR PRODUCTION OF Mo-99 USING (γ,n) REACTION ON Mo-100

1 INTRODUCTION

Technetium-99m is a widely used radiopharmaceutical. Its parent, Mo-99, is produced worldwide to supply this important isotope. One means to produce Mo-99 is by bombarding a Mo-100 target with an electron beam from a linear accelerator; the γ/n reaction on Mo-100 produces Mo-99. After dissolving Mo-100 enriched disks in hydrogen peroxide, the solution is converted to potassium molybdate (0.2 g-Mo/mL) in 5 M KOH. After milking the Tc-99m in the TechneGen generator over a period of 7-10 days,, the molybdenum solution needs to be treated to recover valuable Mo-100 for production of sintered Mo disks. However, during the production of Mo-99 by (γ, n) reaction on the Mo-100 target, several byproducts are formed. Therefore, recycling Mo will require the conversion of K_2MoO_4 in 5 M KOH solution to MoO_3 powder, and purification from other metals present in the Mo solution. The starting Mo-100 enriched material contains less than 20 mg of potassium in 1 kg of molybdenum (<20 ppm). However, after dissolving the irradiated Mo-100 target in hydrogen peroxide and converting it to K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL), the solution contains about 1.8 kg of potassium per kilogram of molybdenum. The most challenging separation for this recovery step is purifying molybdenum from potassium. One requirement to facilitate the acceptance of the recycled material by the U.S. Food and Drug Administration (FDA) is that the impurities in the recycled material need to be at or below the levels present in the starting material. Therefore, the amount of potassium (K) in purified MoO_3 powder should be below 20 ppm; this will require a decontamination factor for removal of K to be ~1×10^5. Such a low K-contamination level will also prevent the production of large amounts of K-42 during irradiation of Mo-100. Based on economic concerns (due to the significant cost of enriched Mo-100) recycling Mo requires the conversion of K_2MoO_4 in a 5 M KOH solution to MoO_3 powder with high Mo recovery yields (>98%). A general scheme for the molybdenum cycle from disk production through recycle of the spent Mo solution is shown in Figure 1.

Argonne National Laboratory (Argonne) and Oak Ridge National Laboratory (ORNL) are cooperating with NorthStar Medical Technologies, LLC (NorthStar) in this program, which is funded by the National Nuclear Security Administration's (NNSA's) Global Threat Reduction Initiative. In this effort, development of the recovery of Mo from the spent TechneGen solutions as MoO_3 is one of Argonne's responsibilities. Recovered MoO_3 powder is shipped to ORNL for reduction and the production of new sintered Mo disks. After the production of Mo disks from recovered Mo material, the disks are dissolved at Argonne to confirm the consistency of their dissolution rates.

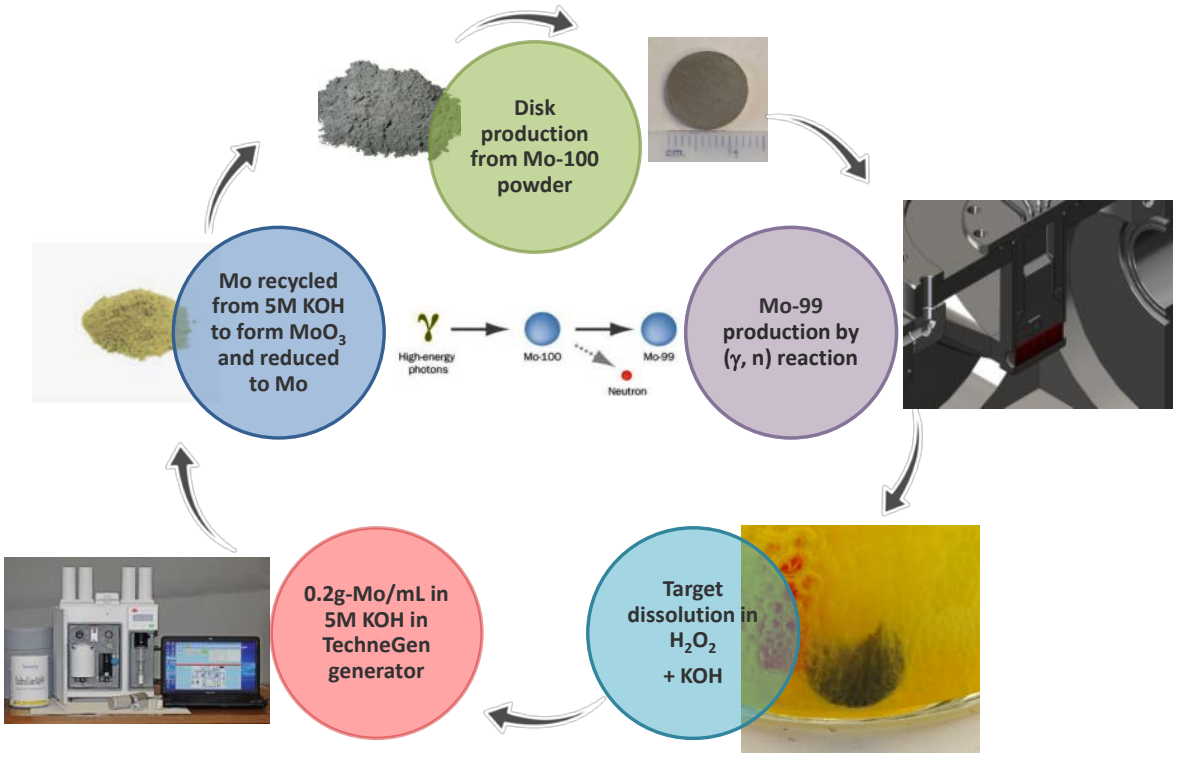

FIGURE 1. Molybdenum Cycle from the Disk Production through the Recycle

2 MOLYBDENUM PRECIPITATION

Precipitation of Mo was performed by acidifying a solution of K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL) with glacial acetic acid (AcA), ethanol (EtOH), or a mixture of both. Experiments were also performed with concentrated nitric acid. The Mo precipitate was then repeatedly washed with concentrated acetic and/or nitric acid, re-dissolved in ammonium hydroxide, and again precipitated and washed several times with acetic and/or nitric acid. After a final wash, the precipitate was re-dissolved and analyzed for K content using a K-ion-selective electrode and/or inductively coupled plasma mass spectrometry (ICP-MS). The recovery of Mo was determined using a Mo-99 tracer or, for non-radioactive experiments, using ICP-MS.

To precipitate Mo from K_2MoO_4 solution in 5 M KOH, KOH is neutralized by adding concentrated acid; further addition of acid leads to the formation of MoO_3 precipitate:

$$KOH + HA \leftrightarrows KA + H_2O, \qquad \text{(eq. 1)}$$

$$K_2MoO_4 + 2\ HA \leftrightarrows MoO_3\downarrow + 2\ KA + H_2O, \qquad \text{(eq. 2)}$$

where HA is acetic acid or nitric acid. The reactions are likely more complex; the Mo(VI) oxide is hydrated, and various mixed K-Mo species are also formed.

Molybdenum in 5 M KOH can also be precipitated by adding ethanol, since potassium molybdate is insoluble in ethanol:

$$K_2MoO_4 + KOH + CH_3CH_2OH \leftrightarrows K_2MoO_4\downarrow + CH_3CH_2OK + H_2O. \qquad \text{(eq. 3)}$$

Due to the oxidation of ethanol by nitric acid, and the possible formation of explosive ethyl nitrate, washing with AcA must follow any step involving ethanol before nitric acid is added. Alternatively, ethanol can be evaporated before the addition of nitric acid.

Washing steps are repeated until satisfactory purification factors are achieved. This usually requires about 30–40 mL of concentrated HNO_3 per milliliter of K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL). After a final purification step, wet MoO_3 precipitate is slowly heated to remove residual HNO_3 and water. The dry MoO_3 precipitate usually has a yellowish color, but white and blue powders were also obtained. Dried Mo oxide powder is sent to ORNL for reduction to Mo metal.

2.1 PRECIPITATION OF Mo USING NITRIC ACID

Precipitation of molybdenum using nitric acid needs to be performed very carefully due to a very strong neutralization reaction between a strong acid and base. Purification of Mo from K after multiple washes with nitric acid is shown in Figure 2. Experiments with multiple washes were performed in separate batches. About 91% of the total K is removed in the first step; ~8%

of the K is removed in the second wash. An additional two washes remove ~1% of K. More than eight washes with nitric acid are required to achieve the desired purification from K (25 ppm).

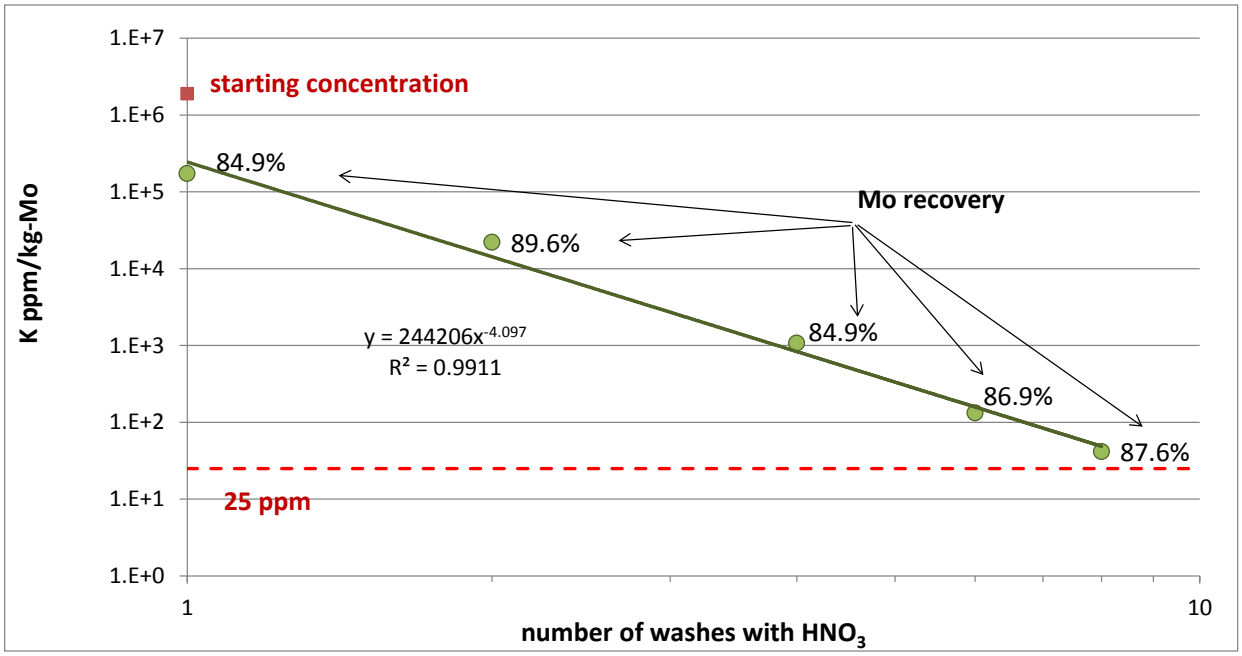

FIGURE 2 Potassium-Concentration Dependence on Number of HNO_3 Washes after Precipitation of Mo from 0.2 g-Mo/mL Solution of K_2MoO_4 in 5 M KOH

As seen in the data shown in Figure 2, the recovery of Mo using nitric acid is below 90%, which is not acceptable. Data indicate that most of the Mo is lost in the first step, and additional losses during multiple washing steps are not very significant. Since the experiments were performed in separate batches total Mo recoveries vary in the range of 84.9-89.6%.

We also looked at purification from many other metals that could be present in the target as impurities or produced during irradiation of Mo-100 enriched targets. Major impurities present in the starting target material include Na, Ca, K, Fe, and Cu; two main side-reaction products are Zr and Nb. Therefore, the focus was on purification from those metals, but we looked at others as well. A mixture of elements representing alkali metals, alkali-earth metals, transition metals, metalloids, and nonmetals was added to a starting solution of K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL) with an initial concentration of approximately 50 ppm (50 mg/kg-Mo). It should be noted that this concentration is significantly higher than the actual level of impurities present in the starting material. This mixture of elements was added as a small aliquot of three mixed ICP-MS standards. As seen in Figure 3, the starting concentration of some metals (Na, Ca, Rb, Al, Si, P, Cd, and W) was higher than 50 ppm due to their presence in the natural MoO_3 used for this study. On the other hand, some metals precipitated when added to the 5 M KOH solution. Major metals present in the precipitate were Mg, Cr, Mn, Fe, Co, Ni, Sr, Ag, Ba, Ta, and Hg.

The precipitate was removed by filtration. The data also indicate that about 30% of starting Nb concentration was removed from the solution. The gray bars in Figure 3 indicate the starting measured concentration, and symbols show the concentration after HNO_3 washes.

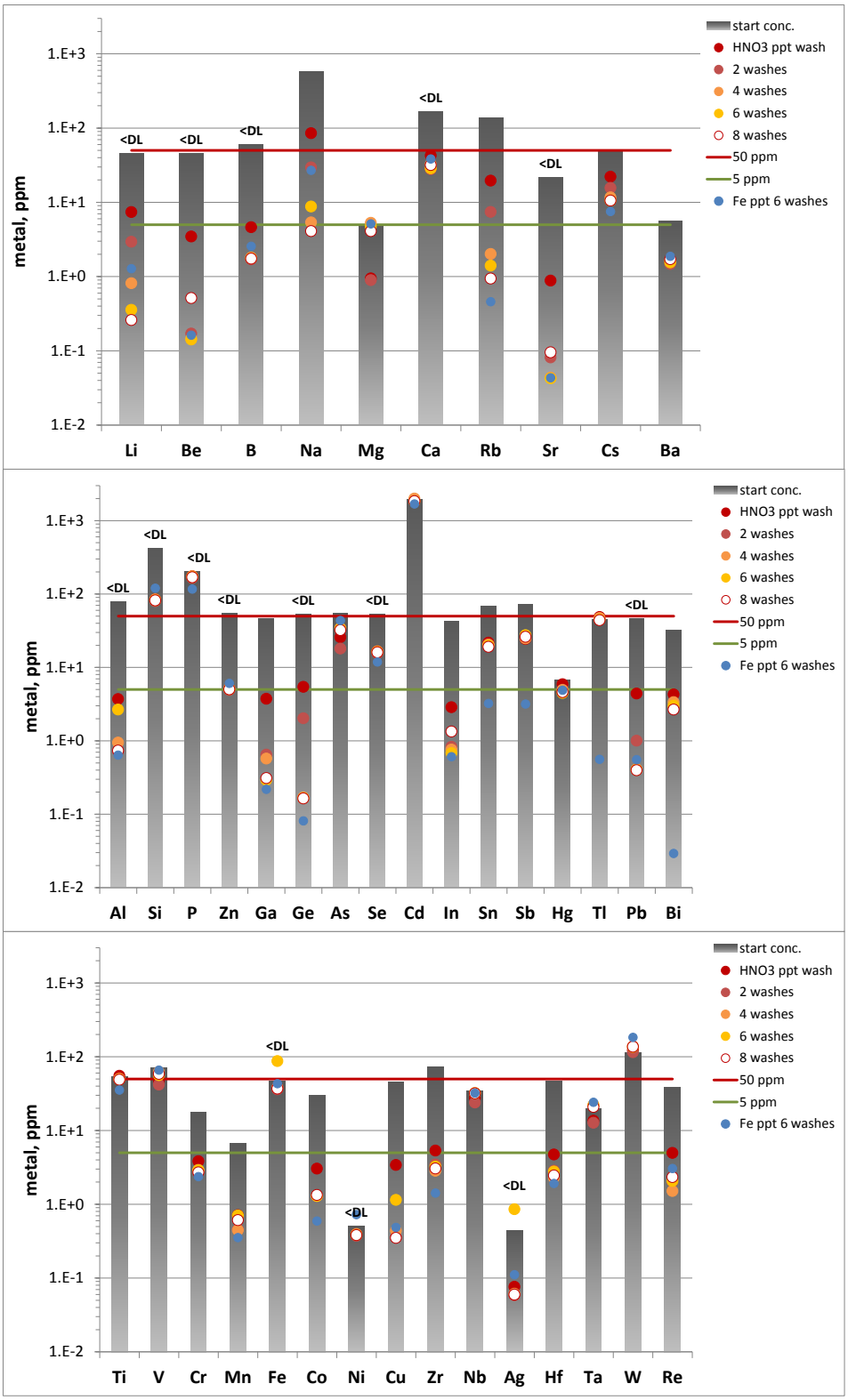

FIGURE 3 Concentrations of Selected Elements in the Mo Product after Nitric Acid Precipitation and Washes

Data in Figure 3 show that all main impurities that are present in the starting material are effectively removed by nitric acid, except for Cd, Ti, Tl, V, Nb, Ta, and W that are not effectively removed by HNO_3 washes. However, from the latter only Nb is problematic since it is a major side reaction product. Although approximately 30% of Nb was removed with the initial precipitate that formed in KOH, soluble Nb species were not effectively removed by washing the Mo oxide precipitate with nitric acid.

We also tested a co-precipitation technique using ferric hydroxide to see whether it helps to improve purification from Nb. Precipitated ferric hydroxide was removed by centrifugation. The solution containing Mo was than precipitated and washed six times with HNO_3. Nevertheless, co-precipitation with Fe was not effective for removal of Nb; this could be due to relatively high Nb concentration (~1 mM) used in this experiment. According to Steinberg (1963), tracer Nb should strongly adsorb on many precipitates. However, removal of trace Nb produced during irradiation has to be performed before the precipitation of Mo because tracer Nb is unstable in acid solution in the absence of complex forming anions, and it tends to deposit on glassware or could co-precipitate with Mo. An upcoming experiment will examine the purification of Nb obtained in tracer concentration in irradiated Mo disks at the linac. Another possible option for separation of Nb from Mo is ion exchange.

2.2 PRECIPITATION OF Mo USING ACETIC ACID, ETHANOL, AND A MIXTURE OF THE TWO

Another way to precipitate Mo from K_2MoO_4 solution in 5 M KOH to add acetic acid, ethanol, or a mixture of the two (eqs. 2 and 3). Table 1 compares Mo losses and removal of K in the precipitation step using different reagents. Mo losses in nitric acid are due to the formation of soluble Mo species, while in other cases it is mostly due to the presence of fine precipitate, which remain suspended in solution. When a mixture of ethanol and AcA is used, Mo losses in the precipitation step are very low. Figure 4 contains photographs of precipitates following centrifugation, which form after addition of AcA or an AcA mixture with ethanol. Fine precipitate that forms in acetic acid can be removed by filtration or can be collected after allowing the sample to sit for few minutes following centrifugation.

TABLE 1 Mo Losses and Removal of Potassium for Different Reagents Used to Precipitate Mo

Reagent Used to Precipitate Mo[a]	Mo Lost	K Removed
AcA	0.2–2%	70–77%
EtOH	~0–0.2%	~42%
4:1 EtOH:AcA	0.05–0.4%	~40%
HNO3	8–20%	~90%

[a] AcA = acetic acid; EtOH = ethanol.

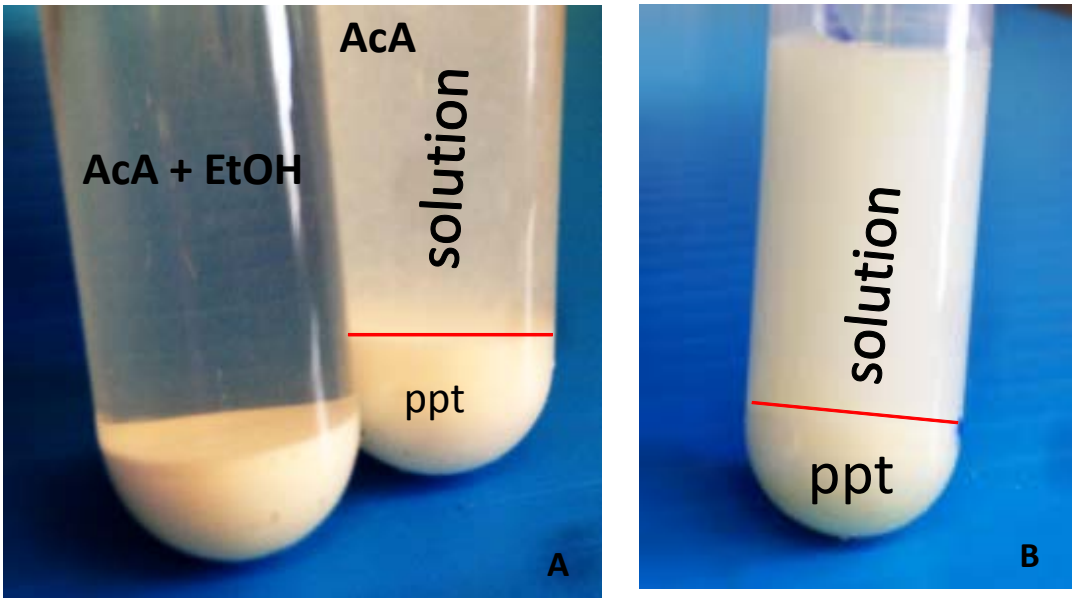

FIGURE 4 (A) Fine Mo Precipitate Forms when Acetic Acid Is Used to Precipitate Mo (This can be avoided if acetic acid is mixed with ethanol); (B) Fine Mo Precipitate also Forms when Using Nitric Acid Wash after Acetic Acid

Precipitation of K_2MoO_4 from 5 M KOH solution using ethanol is a viable option for KOH removal. However, several washes are needed to completely remove KOH, and in order to purify molybdenum from K, acetic or nitric acid has to be used to precipitate Mo as an oxide. Due to the oxidation of ethanol by nitric acid, and possible formation of explosive ethyl nitrate, washing with AcA must follow any step involving ethanol before adding nitric acid. When a fine precipitate forms after using the AcA wash, it can be collected if the sample is allowed to sit for a few hours. Additional centrifugation can eliminate Mo losses significantly.

Another stage where the fine precipitate forms is when switching from an AcA wash to a nitric acid wash (Figure 4). In this case, the precipitate cannot be easily removed by centrifugation, and the sample has to sit for several hours. In some cases, we also looked at re-dissolving the Mo precipitate, which is obtained after AcA or an AcA mixture with ethanol, in ammonium hydroxide followed by precipitation with AcA. Table 2 shows the data for Mo losses, percent of K removed per step, and the possibility for formation of a fine precipitate containing Mo.

After centrifugation, it is important to let the samples sit for at least a few minutes to observe the formation of a fine precipitate in the solution. This usually happens when acetic acid is used to neutralize the basic Mo solution (KOH, NH_4OH), or when nitric acid is used after AcA (Table 2). Therefore, the data for Mo losses in Table 2 represent the range that was observed; the lower number illustrates Mo losses after a clear solution was obtained and higher numbers represent Mo losses when the solution containing Mo fine particles was decanted. Additional washes with nitric acid do not contribute to Mo losses very significantly; however, they are important to bring the concentration of K in the Mo product below 25 ppm.

TABLE 2 Removal of Potassium, and Mo Losses per Step

Step	Reagent	K Removed	Mo Loss	Solution[a]
Mo ppt	AcA[b,c]	70–77%	0.2–2%	Cloudy
Wash 1	AcA	10–15%	<1%	Clear
Wash 2	HNO_3[c]	5–10%	0–15%	Cloudy
Dissolution	H_2O+NH_4OH	–	–	Clear
Precipitation	AcA[c] precipitation	0–5%	0–3%	Cloudy
Wash 3	HNO_3[c]	<0.5%	0–15%	Cloudy
Wash 4	HNO_3	<0.1%	0–2%	Clear
Wash 5	HNO_3	<0.1%	<0.5%	Clear

[a] Cloudy = contains fine Mo precipitate; clear = might contain soluble Mo species.

[b] AcA = acetic acid.

[c] Fine precipitate can form after centrifugation.

The best Mo recoveries are usually obtained when AcA or an AcA-ethanol mixture are used for Mo precipitation, followed by a few acetic acid washes and several nitric acid washes. This is illustrated in Table 3 for small-scale experiments where very good Mo recoveries were obtained.

Although K impurities in the Mo product were above 25 ppm, additional washing steps with nitric acid should remove the remaining K, as shown in Figure 2. After a final washing step, Mo precipitate is dried and weighed. Usually yellowish Mo powder is obtained; however, white and blue colored powders are sometimes obtained (Figure 5). It should be noted that color of the final Mo powder may differ even if the same purification procedure was used. Different colors of Mo powder could be due to the presence of small amounts of lower-oxidation-state Mo (Mo blue) or different contents of water. Partial reduction of Mo occurs when Mo precipitate is heated to remove any residual HNO_3.During this process nitric acid could partially decompose to nitrogen dioxide and nitric oxide. The presence of small amounts of reagents in the final Mo product may also contribute to the color differences.

Several scaled-up experiments with 8–28 g of Mo (30–140 mL of 0.2 g-Mo/mL in 5 M KOH) were performed with various purification schemes. Table 4 shows a summary of purification steps, K content in the Mo product, and Mo recovery.

Very good recovery was obtained when AcA was used for Mo precipitation. After each precipitation step, and when switching from AcA to nitric acid, the sample was allowed to sit for several hours to eliminate Mo losses. Very good purification from K (<25 ppm) was obtained for samples when AcA or an AcA mixture with ethanol was used for precipitation. The starting concentration of K in Mo samples 66 and 67 (obtained after dissolution of ORNL-sintered Mo disks) before adding KOH was 35 ppm. The concentration of K in recovered Mo oxide powders (66 and 67) was below its starting concentration.

Mo recovery for samples where HNO_3 was used is consistent with the data obtained for small-scale experiments, which were usually below 90%. Purified samples were dried and sent to ORNL for reduction to Mo powder and production of new Mo sintered disks.

TABLE 3 Purification Steps for Removing Potassium from 1 mL of K_2MoO_4 Solution (0.2 g-Mo/mL) in 5 M KOH

Step	Reagent Used[a]
	Sample 59
Precipitation	5 mL EtOH
Wash 1	5 mL EtOH
Wash 2	5 mL EtOH
Wash 3	5 mL EtOH
Wash 4	5 mL AcA
Wash 5	5 mL AcA
Wash 6	5 mL HNO_3
Dissolution	2 mL DIW +1 mL NH_4OH
Precipitation	6 mL AcA
Wash 7	5 mL HNO_3
Wash 8	5 mL HNO_3
Wash 9	5 mL HNO_3
Wash 10	5 mL HNO_3
Wash 11	5 mL HNO_3
Mo Recovery	99%
K ppm	103
	Sample 60
Precipitation	5 mL 4:1 EtOH/AcA
Wash 1	5 mL 4:1 EtOH/AcA
Wash 2	6 mL AcA
Wash 3	5 mL AcA
Wash 4	5 mL HNO_3
Dissolution	2 mL DIW +1 mL NH_4OH
Precipitation	6 mL AcA
Wash 5	5 mL HNO_3
Wash 6	5 mL HNO_3
Wash 7	5 mL HNO_3
Wash 8	5 mL HNO_3
Wash 9	5 mL HNO_3
Mo recovery	96.7%
K ppm	96

[a] AcA = acetic acid; DIW = deionized water; EtOH = ethanol.

FIGURE 5 Photographs of Mo Oxide Powders Obtained after Mo Recovery from K_2MoO_4 Solution (0.2 g-Mo/mL) in 5 M KOH Compared to Commercial MoO_3 Powder, on the Left

TABLE 4 Purification Steps for Removing Potassium from K_2MoO_4 Solution (0.2 g-Mo/mL) in 5 M KOH[a]

Sample 66 50 mL K_2MoO_4 (0.2 g-Mo/mL) in 5 M KOH	Sample 67 42 mL K_2MoO_4 (0.2 g-Mo/mL) in 5 M KOH	Sample 80 140 mL K_2MoO_4 (0.2 g-Mo/mL) in 5 M KOH
260 mL AcA	200 mL 4:1 EtOH/AcA	560 mL HNO_3
200 mL AcA	200 mL 4:1 EtOH/AcA	500 mL HNO_3
200 mL HNO_3	240 mL AcA	510 mL HNO_3
100 mL DIW + 50 mL NH_4OH	100 mL DIW + 50 mL NH_4OH	510 mL HNO_3
240 mL AcA	240 mL AcA	525 mL HNO_3
200 mL AcA	200 mL AcA	520 mL HNO_3
200 mL HNO_3	200 mL HNO_3	530 mL HNO_3
200 mL HNO_3	200 mL HNO_3	530 mL HNO_3
100 mL DIW +50 mL NH_4OH	100 mL DIW +50 mL NH_4OH	–
240 mL AcA	200 mL AcA	–
200 mL HNO_3	200 mL HNO_3	–
200 mL HNO_3	200 mL HNO_3	–
200 mL HNO_3	200 mL HNO_3	–
200 mL HNO_3	200 mL HNO_3	–
200 mL HNO_3	–	–
Mo recovery: 99%	Mo recovery: 82%	Mo recovery: 86.1%
K: 20.8ppm	K: 20.8ppm	K: 189.3ppm

[a] AcA = acetic acid; DIW = deionized water; EtOH = ethanol.

X-ray diffraction (XRD) analysis confirmed that the main Mo species present in the product is MoO_3. In general, dried samples obtained after purification showed some amount of the hexagonal hydrated MoO_3 phase. Some peaks for this phase, which do not overlap with peaks for the orthorhombic phase, are indicated by red lines in Figure 6. These peaks could point to the presence of hydrated Mo species such as $HMo_{5.35}O_{15.75}(OH)_{1.6} \cdot 1.7H_2O$ or hydrated oxide $MoO_3 \cdot 0.55H_2O$. These peaks disappear after heating the samples to more than 600°C, and XRD spectra confirm the presence of only orthorhombic MoO_3.

Photographs of Mo powders before and after heating are shown in Figure 7. Weight losses are mostly due to dehydration of Mo oxide; however, some loses may be due to MoO_3 volatility at higher temperatures.

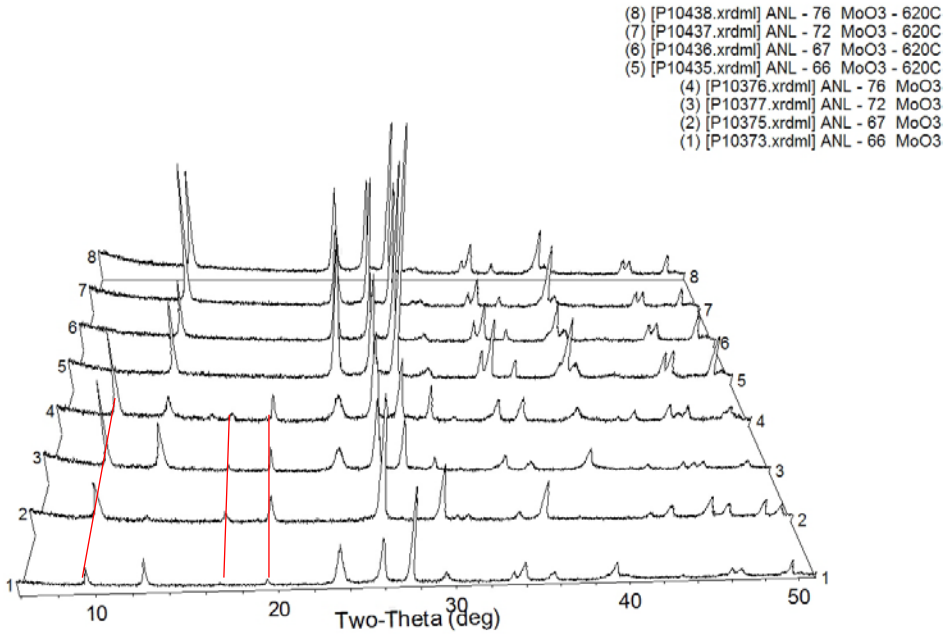

FIGURE 6 XRD Spectra of Dried Samples Obtained after Mo Recovery (1–4), and Spectra of the Same Samples after Heating to 620°C (5–8)

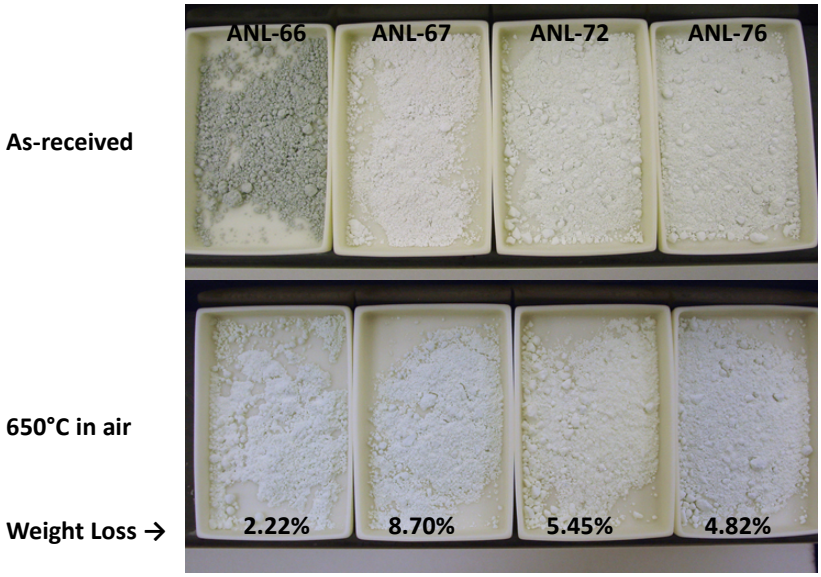

FIGURE 7 Photographs of Dried Samples Obtained after Mo Recovery (top row), and the Same Samples after Heating to 650°C in Air (bottom row)

3 SUMMARY

Data for Mo purification obtained in small-scale experiments and experiments with several grams of Mo clearly show that when Mo is precipitated using nitric acid, Mo recovery is usually below 90%, which is not acceptable. On the other hand, when AcA is used Mo recoveries are very good. Another advantage of using AcA for precipitation of Mo is that the neutralization reaction is not as energetic as when HNO_3 is used.

Future experiments will focus on optimizing the steps in order to simplify the purification process while maintaining high purification factors and high Mo recovery. This might be achieved by using AcA for the precipitation of Mo, and HNO_3 for washing the Mo oxide precipitate.

We also plan to look at the purification of Nb during the Mo-recovery process. Irradiated Mo disks where Nb is produced as a side reaction product will be used after dissolution in hydrogen peroxide and conversion to 5 M KOH.

Once optimum conditions are found for Mo purification from K and side reaction products, multiple experiments will be performed with up to 400 g of Mo per batch. We will also perform experiments with natural Mo targets irradiated and dissolved at the Missouri University Research Reactor (MURR).

4 REFERENCE

Steinberg, E.P., 1963, *Radiochemistry of Zirconium and Niobium*, Los Alamos National Laboratory.

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