

# Method for Increased Accuracy of ICP-MS Detection of Potassium in Samples with High Molybdenum Content

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Chemical Sciences and Engineering Division

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# METHOD FOR INCREASED ACCURACY OF ICP-MS DETECTION OF POTASSIUM IN SAMPLES WITH HIGH MOLYBDENUM CONTENT

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## 1 INTRODUCTION

Argonne National Laboratory (ANL) is supporting development of accelerator-based production of  $^{99}\text{Mo}$  using the photonuclear reaction  $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$  with an enriched  $^{100}\text{Mo}$  target. After dissolution of irradiated Mo target disks in hydrogen peroxide, Mo is converted to potassium molybdate by addition of KOH. The highly alkaline solution of  $\text{K}_2\text{MoO}_4$  (0.2 g-Mo/mL in 5 M KOH) is loaded into the Technegen generator, where Tc is retained on an aqueous biphasic extraction chromatography (ABEC) column, while Mo passes through and is recovered for further processing. After the molybdenum is processed in the Technegen generator, the spent solution needs to be treated to recover valuable Mo-100 for future production of sintered Mo disks. Therefore, recycle of Mo will require conversion of  $\text{K}_2\text{MoO}_4$  in 5 M KOH solution to  $\text{MoO}_3$  powder that can be further reduced to Mo metal.

The starting Mo-100 enriched material contains 20-40 mg of potassium in one kilogram of molybdenum. However, after dissolving the irradiated Mo-100 target in hydrogen peroxide and converting it to  $\text{K}_2\text{MoO}_4$  in 5 M KOH (0.2 g-Mo/mL), the solution contains about 1.8 kg of potassium per kilogram of molybdenum. One requirement for the recycled Mo material is that the impurities in the recycled material be at the same or lower concentration than that present in starting material to facilitate acceptance for use of recycled Mo-100 by the U.S. Food and Drug Administration (FDA). The required purification factor for removal of potassium in purified  $\text{MoO}_3$  powder is  $\sim 1 \times 10^5$ , which would prevent production of large amounts of K-42 during the irradiation of Mo-100 disks at the low energy accelerator facility (linac). Additionally, recycle of Mo requires conversion of  $\text{K}_2\text{MoO}_4$  in 5 M KOH solution to  $\text{MoO}_3$  powder with high Mo recovery yields (>98%) due to a high cost of enriched Mo-100 material.

During FY 2013, we used a potassium selective electrode (PSE) and inductively coupled plasma mass spectroscopy (ICP-MS) to determine the concentration of potassium in the final purified-Mo product. The disadvantage of using a PSE is that both ammonium and sodium hydroxide, which are necessary to re-dissolve  $\text{MoO}_3$  precipitate, interfere with potassium detection. With ICP-MS, the detection limit for potassium is affected by the high dilution that needs to be made due to a very high concentration of molybdenum or other dissolved solids (salts such as NaOH). If the sample of recycled and purified Mo submitted for ICP-MS analysis meets the criterion for potassium concentration (20 mg-K/kg-Mo) and contains 0.2 g of Mo in 25 mL of solution (8000 mg-Mo/L), the concentration of potassium in this sample would be 160  $\mu\text{g/L}$ . However, the maximum

concentration of total dissolved solids (TDS) that can be loaded into our ICP-MS instrument is 80-100 mg/L. To achieve this concentration, the solution must be diluted by  $\geq 80$  times, which reduces the concentration of potassium to  $\sim 2$   $\mu\text{g/L}$ . Since the detection limit for potassium under these conditions using ICP-MS is  $\sim 10$   $\mu\text{g/L}$ , Mo has to be selectively removed from the sample matrix for potassium analysis. This separation can be achieved by solvent-solvent extraction. It has been reported that 30% tri-*n*-butyl phosphate (TBP) effectively extracts a relatively high Mo concentration (0.02 M) from 5 M HCl [Tkac and Paulenova, 2008]. Under strong acidic conditions, the extraction process involves this reaction:



## 2 RESULTS AND DISCUSSION

To test this procedure, we began by dissolving  $\sim 0.65$  g of  $\text{MoO}_3$  ( $\sim 0.43$  g of Mo) in  $\text{NH}_4\text{OH}$ . Potassium was added as KCl followed by addition of concentrated HCl (Optima) to yield 5 M HCl. The starting concentration of Mo was  $\sim 0.09$  M. An aliquot of this solution was taken and submitted for ICP-MS analysis to determine the Mo and K concentration before Mo extraction. Another aliquot was contacted with 30% TBP in *n*-dodecane pre-equilibrated with 5 M HCl (organic-to-aqueous ratio of 1:1) and mixed vigorously by vortex for 4 min. After extraction, phases were separated by centrifugation. The aqueous phase was contacted with another portion of TBP (1:1), mixed for 4 min, centrifuged, and then submitted for ICP-MS to determine the concentration of potassium after extraction of Mo.

Table 1 presents the concentration of potassium in the aqueous solution before and after extraction of Mo by TBP, as determined by ICP-MS. The data clearly show that Mo can be effectively removed from the aqueous phase without affecting the concentration of potassium.

Table 1. ICP-MS results of Mo and K concentrations before and after extraction of Mo by 30% TBP.

Sample	K, mg/L	Mo, mg/L
Aqueous phase before extraction	3.53	8680
Aqueous phase after extraction	3.49	ND

ND = not detected.

The starting Mo-100 enriched material contains a low concentration of potassium (20-40 mg-K/kg-Mo). To analyze the concentration of potassium in the starting material used for production of Mo-99, we dissolved  $\sim 2.4$  g of Mo-100 enriched sintered disks in 30% hydrogen peroxide, evaporated the solution to dryness, and converted it to  $\text{MoO}_3$  powder by additional heating. Then,  $\sim 0.3$  g of  $\text{MoO}_3\cdot x\text{H}_2\text{O}$  powder enriched with Mo-100 was re-dissolved in ammonia. Next, the solution was converted to 5 M HCl by adding concentrated HCl (Optima) and was submitted for ICP-MS to determine the potassium

concentration. A portion of the solution was contacted with TBP to selectively remove Mo as described above, and was analyzed by ICP-MS at different dilutions.

Table 2 gives the ICP-MS results from aqueous solution before and after extraction of Mo. These results show that selectively removing Mo by solvent extraction allows performing ICP-MS analysis at very low dilutions, which increases the detection limit for potassium.

Table 2. Concentrations of Mo and K determined by ICP-MS before and after extraction of Mo-100 from solution.

<b>Sample</b>	<b>K, mg/L</b>	<b>Mo-100, mg/L</b>
Before extraction	-	6960
After extraction		
DF=10	0.291	ND
DF=5	0.284	ND
DF=5	0.275	ND
DF=2	0.291	ND
<b>Average</b>	<b>0.283</b>	-
<b>STDEV</b>	<b>0.008</b>	-
<b>Mg-K/kg-Mo</b>	<b>40.7</b>	-

DF = dilution factor; STDEV = standard deviation.

### 3 SUMMARY

When a sample of MoO<sub>3</sub> is re-dissolved in ammonium hydroxide and converted to 5 M HCl, selective extraction of Mo by 30% TBP significantly reduces the TDS concentration in samples for ICP-MS, and allows quantification of potassium concentration at very low levels.

### 4 REFERENCE

Tkac, P.; Paulenova, A., 2008, Speciation of molybdenum (VI) in aqueous and organic phases of selected extraction systems, *Separation Science and Technology* **43**: 2641–2657.