

MOEX – Solvent Extraction Approach for Recycling Enriched $^{98}\text{Mo}/^{100}\text{Mo}$

Material

**Peter Tkac, M. Alex Brown, Abdul Momen, Kent E. Wardle⁺, Jacqueline M. Copple,
George F. Vandegrift**

Argonne National Laboratory, Nuclear Engineering Division, Argonne, IL 60439, USA

Abstract

Several promising pathways exist for the production of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ using enriched ^{98}Mo or ^{100}Mo . Use of Mo targets require a major change in current generator technology, and the necessity for an efficient recycle pathway to recover valuable enriched Mo material. High recovery yields, purity, suitable chemical form and particle size are required. Results on the development of the MOEX– molybdenum solvent extraction – approach to recycle enriched Mo material are presented. The advantages of the MOEX process are very high decontamination factors from potassium and other elements, high throughput, easy scalability, automation, and minimal waste generation.

Introduction

Technetium-99m, the daughter of ^{99}Mo , is the most used medical isotope with more than 40 million nuclear medicine procedures every year. Currently, the majority of ^{99}Mo is produced by fissioning of ^{235}U in nuclear reactors because of very high fission yield (6.1%) and high thermal neutron fission cross section [1]. However, the majority of reactors currently used for production of medical isotopes have been in operation for several decades. As an example, the

⁺ Currently at TerraPower, LLC, Bellevue, WA 98005, USA.

Chalk River reactor in Canada, which provides ~40% of the world's supply of ^{99}Mo , was commissioned in 1957, and will cease production in October of 2016. Currently, the majority of the US supply of ^{99}Mo is produced from the Chalk River reactor and is provided by Nordion (Canada) [1]. One of the conclusions from the recent report by National Academies [2] is that there is a substantial (>50 percent) likelihood of severe ^{99}Mo - $^{99\text{m}}\text{Tc}$ supply shortages after October 2016, when Canada stops supplying ^{99}Mo .

Several other technologies were recently proposed for production of this important medical isotope. There has been much attention recently in the direct production of $^{99\text{m}}\text{Tc}$ using $^{100}\text{Mo}(p,2n)^{99\text{m}}\text{Tc}$ by cyclotrons [3-7], due to their availability in many countries worldwide. Current feasibility studies demonstrate the possibility of producing 70 Ci (1Ci=37GBq) of $^{99\text{m}}\text{Tc}$ in two 6-h bombardments using medium-energy cyclotrons at 200 μA and 30-12 MeV (1.8 kW) [8-11]. Another alternative is production of ^{99}Mo by the $^{100}\text{Mo}(\gamma,n)^{99}\text{Mo}$ reaction [12-20] using an electron accelerator. Recent irradiation performed at Argonne National Laboratory (Argonne) [19-20] in collaboration with Los Alamos National Laboratory and supported by the National Nuclear Security Administration's Office of Material Management and Minimization (NNSA M³) produced several-Ci quantities of ^{99}Mo using ^{100}Mo -enriched sintered Mo targets. Production yields achieved were up to 3.6 mCi/kW-h-g for 99% enriched ^{100}Mo [19-20]. Yet another alternative production of ^{99}Mo is by neutron capture in a reactor using enriched ^{98}Mo targets by the $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ reaction. Production of ^{99}Mo by a neutron capture requires a large target due to low neutron cross section, and typical yield with natural Mo in the thermal flux of a research reactor (5×10^{13} n/cm²·s) is ~0.8 Ci/h of ^{99}Mo per 500 g of target, while high flux reactors with >95% enriched ^{98}Mo can produce ~32 Ci/h of ^{99}Mo for the same size of Mo target [8, 21]. A potential US domestic supplier, NorthStar Medical Technologies, LLC (NorthStar), is

planning to start the production of ^{99}Mo in 2017 by a neutron capture process at the University of Missouri Research Reactor with a capability of 100 6-day Ci/week (~ 455 Ci of ^{99}Mo at the end of the irradiation) and later ramping the production to up to 3000 6-day Ci to meet 50% of current US demand. Another pathway that NorthStar plans to use for production of ^{99}Mo is the photonuclear reaction $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$ from the irradiation of enriched molybdenum targets by an electron accelerator.

Although the efficiency of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ produced by these alternative routes is lower compared to fission-made $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$, their main advantage is minimal start-up cost, commercial availability, fast post-irradiation processing due to significantly less-complex purification schemes, far less highly radioactive waste, and much easier licensing procedures. On the other hand, use of Mo targets requires a major change in the generator technology to accommodate the high concentration of Mo. In a conventional $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator system, Mo is absorbed on an alumina column, and Tc is eluted using a saline solution. One of the concepts to adapt this technology for low specific activity Mo is to use a larger alumina column to effectively retain a higher amount of Mo. However, this requires more saline solution to elute the Tc, leading to decreases in radioactivity concentration, which without a further concentration step might not be suitable for many radiopharmaceutical preparations. To solve this problem, Chakravarty et al. [22] used nanocrystalline $\gamma\text{-Al}_2\text{O}_3$ sorbent and reported sorption capacity of up to 0.2 g-Mo/g, which is ~ 10 times higher than regular acidic alumina columns used in current generators. Another way of achieving separation of Tc from Mo is using solvent extraction, where alkaline Mo solution is contacted with methyl ethyl ketone. While Mo stays in the aqueous phase, Tc is extracted into an organic phase. However, substantial follow-on steps are required to recover Tc from the organic phase [23-24]. Another approach for recovery of Tc is to use zirconium

molybdate gel. The gel is prepared by reaction between MoO_3 and ZrOCl_2 , and Tc is eluted by a saline solution [25].

NorthStar's generator system (RadioGenix[®]) uses monomethylated polyethylene glycol covalently bound to polystyrene support (ABEC resin) [26], which is highly selective for Tc from highly alkaline solutions. ABEC resin was also used to separate Tc from Mo by Gagnon [27] and Bénard et al. [4]. AnaLig Tc02 TEVA[®] resin has also been used [4]. The variety of alternative production pathways and the availability of various Mo/Tc generator technologies for low specific activity ^{99}Mo make non-fission ^{99}Mo production a very viable option for many potential small- or large-scale producers.

All alternative routes for large production of ^{99}Mo , as well as the cyclotron-driven direct production of $^{99\text{m}}\text{Tc}$ mentioned above, require use of enriched ^{98}Mo or ^{100}Mo for efficient production. Enriched molybdenum (>95% enriched ^{100}Mo) currently costs \$850-3000 per gram [28], although the price for kilogram quantities is likely lower. Due to this high cost, potential manufacturers require ways to efficiently recycle it. Recently, there has been much attention given to recycling pathways to recover valuable enriched Mo material. Bénard et al. [4] and Gagnon et al. [27] reported 85 and ~87% recovery yields, respectively. Recently, we reported a process for recycling enriched Mo material from highly alkaline spent generator solution (SGS, RadioGenix[®] from NorthStar) using a precipitation technique with ~95% total recovery yields [29]. However, the process is labor-intensive, and is challenging for automation. The process was performed with up to 260 g of Mo material and can be scaled up for processing of up to 400 g of Mo.

Besides high recovery yields, an equally important aspect of developing a recycling method is to have a suitable particle size of recycled Mo powder that is suitable for production of recycled Mo

targets that have high enough theoretical density and good dissolution characteristics for quick post-irradiation processing. If very fine Mo powder is used for production of sintered Mo targets, high theoretical density disks can be manufactured by the classic sinter-press technique [30]. However, depending on sintering temperatures used for the production of Mo disks, the dissolution rates can be severely affected, leading to prolonged dissolution times [30-32]. On the other hand, having a very coarse Mo powder material can lead to lower theoretical densities of pressed targets and/or the requirement to mill the material into desired particle size or further processing steps that could lead to some losses of enriched material.

Here we report our results on a very efficient way to recycle enriched Mo from highly alkaline solutions (2 M K_2MoO_4 in 5 M KOH) that is currently being considered for separation of Tc from low specific activity Mo. The process can be easily automated and used with several-hundred gram batches, or applied for small-scale processing mostly relevant for producers of ^{99m}Tc using cyclotrons. Very high recovery yields and separation factors for potassium were achieved, and obtained Mo material has suitable particle size distribution that can be directly used for reduction to Mo metal and used for production of Mo targets.

Experimental

Small-scale solvent extraction experiments were performed to determine optimal conditions for effective extraction of high Mo concentrations. Two diluents for tri-*n*-butyl phosphate (TBP) were investigated in this work: a solution of 50% TBP (by volume) in 1-octanol and 30% TBP in tetrachloroethylene (TCE) were used for all extraction experiments. Diluents were chosen to prevent the formation of 3rd phase in TBP, which occurred when *n*-dodecane was used. Before its use, the TBP solvent was pre-equilibrated with an aqueous phase containing HCl in the same

concentration as that used in the extraction experiment. Distribution ratios, defined as equilibrium concentration in the organic phase divided by the equilibrium concentration in aqueous phase, were measured in batch experiments; samples were vigorously agitated in extraction vials using a vortex mixer with an equal aqueous and organic volume under ambient temperature conditions (20°C). After agitation, the phases were separated using centrifugation, and aliquots from both organic and aqueous phases were taken to measure equilibrium concentrations of the metal ion using a NaI detector (Wizard with RiaCalc WIZ program 3.6 software with energy discrimination of 700–900 keV) or a HPGe (Ortec) detector. For tracer studies, ⁹⁹Mo was provided from a TechneLite generator (Lantheus) that had been eluted with ammonium hydroxide. Distribution ratios for experiments performed without ⁹⁹Mo tracers, or for other elements, were determined using ICP-MS. To determine the organic HCl concentration, typically a 1 mL aliquot of the organic phase (contacted with equal volumes of organic and aqueous phase three times) was titrated using Methrom 836 Titrando using standardized sodium hydroxide solution in a mixture of ethanol in water. All titrations were performed in duplicate. Large-scale extraction experiments with up to 4.5 L of aqueous phase were also performed. Mixing was performed in a large HDPE bottle, and phase separation was performed using a 5 L separatory funnel. Solvent extraction was usually performed in two steps; in the first contact ~3.5-4 L of organic phase was contacted with ~4.5 L of ~0.35 M Mo in 5 M HCl. Then, aqueous solution from the first extraction was contacted with 1 L of TBP solution. Organic phases were then combined and scrubbed using 4 M HCl. In this process, Mo lost during scrub was not recovered. The organic phase containing Mo was then stripped with NH₄OH.

A surrogate for spent Tc generator (RadioGenix) feed was prepared by dissolution of MoO₃ in KOH or by dissolution of natural sintered Mo disks in hydrogen peroxide and addition of KOH

to make 200 g-Mo/L in 5 M KOH. Surrogate generator solution was then acidified by HCl to make various Mo and HCl concentrations. The hydrochloric acid used for extraction experiments and NH₄OH used to strip Mo from TBP were trace metal grade. All other chemical reagents used in this work were of analytical-reagent-grade purity and were used without further purification. All aqueous solutions were prepared with deionized water with a resistivity $\geq 18 \text{ M}\Omega \text{ cm}$.

Results and discussion

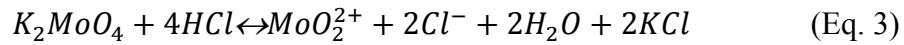
Trace Mo and HCl extraction by TBP

Distribution ratios of Mo using ⁹⁹Mo tracer from various HCl concentrations for 50% TBP/1-octanol and 30% TBP/tetrachloroethylene (TCE) are presented in Figure 1. While distribution ratios, D(Mo), for the TBP/TCE system remain more or less constant at $[\text{HCl}] > 5 \text{ M}$, significant decreases in Mo extraction with increasing HCl concentrations above 5 M are observed for the 50% TBP/1-octanol system. This is due to lower extraction of HCl by TBP/TCE system compared to TBP/1-octanol. The plot of $[\text{HCl}]_{\text{org}}$ vs. $[\text{HCl}]_{\text{aq}}$ is presented in Figure 2 for both diluents; upon contact of 30% TBP in TCE with 5 M HCl, the organic concentration of HCl is $\sim 0.064 \text{ M}$, while for 50% TBP in 1-octanol the organic concentration of HCl is $\sim 0.96 \text{ M}$.

Extraction with high Mo concentration

Solvent extraction is an effective way for separation of Mo; however, most of the recent studies performed used relatively low Mo concentration [33-37], which is not very suitable for processing large quantities of Mo. TBP is a well-refined extraction solvent used in reprocessing of used nuclear fuel and can handle high concentrations of metal with good kinetics. Molybdenum does not extract by TBP from nitric acid [37]; however, due to complexing properties of chloride toward molybdenyl ion (MoO_2^{2+}), high concentrations of Mo can be

processed by TBP. Up to 0.45 M Mo solutions in HCl were prepared by acidifying a highly alkaline solution of ~2 M K_2MoO_4 in 5 M KOH (SGS) with HCl. Conversion of molybdate into molybdenyl species occurs as described by Eq. 3.



According to Eq.3 (KOH not shown), four moles of HCl are consumed per one mole of Mo. At the same time, a significant amount of KCl may precipitate, if the final concentrations of Mo and HCl are high enough that the solubility limit for KCl is reached. From ~5 M HCl, very high distribution ratios were obtained by TBP with >95% recoveries for 30% TBP in TCE and up to 0.35 M Mo, and >97% with 50% TBP in 1-octanol for 0.45 M Mo (Table 1). Such a high extraction recoveries allow for high throughput and ability to process large quantities of Mo. It should be noted that extraction of potassium from these conditions is very low and distribution ratios, $D(K)$, were usually <0.01.

Stripping of Mo from TBP

It was determined that NH_4OH is very effective in stripping Mo from TBP. Nearly quantitative removal of Mo from the organic phase can be achieved in a single contact with NH_4OH (Table 2). It was determined that NH_4OH can effectively strip Mo from the organic phase with close to 100% recoveries in just one step. Different ratios of NH_4OH (as 22% NH_3) to TBP were also investigated for stripping. It was determined that ~0.3 M Mo in TBP can be effectively stripped at a 2.5:1 (TBP: NH_4OH) ratio. At a 5:1 ratio, Mo partially precipitates, which is due to neutralization of alkaline strip solution by H^+ from the TBP phase and reaching the Mo solubility limit.

Due to complex changes in speciation of molybdenum during the stripping stage, where the molybdenyl cation (MoO_2^{2+}) is converted to ammonium heptamolybdate (AHM – $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot x\text{H}_2\text{O}$) under highly alkaline conditions, the kinetics of stripping Mo from TBP with NH_4OH were also investigated. Molybdenum was extracted from an aqueous solution containing 0.3 M Mo and 5 M HCl by 30% TBP in TCE. The organic phase containing Mo was then stripped with 11.9 M NH_4OH with O/A=1(organic to aqueous phase ratio). It was demonstrated that >99.8% of Mo was stripped into the aqueous phase after 5-20 seconds; however, cloudiness in the organic phase was observed even after centrifugation. This is due to incomplete stripping of Mo from the organic phase and the presence of a very low concentration ($2-6 \times 10^{-4}$ M Mo) as solid AHM. Longer mixing times of 40-60 seconds allow for complete separation of both phases even without centrifugation and lead to clear phases. The organic Mo concentration after 40-second contact was found to be 1.2×10^{-4} M Mo.

The strip solution from the molybdenum solvent extraction (MOEX) process is evaporated using rotary evaporation, and a white crystalline product containing mixture of AHM and NH_4Cl is obtained. Due to its corrosive properties, ammonium chloride needs to be removed before reduction to Mo metal. To selectively remove NH_4Cl from the mixture, the difference in solubility of AHM and NH_4Cl in ethanol was utilized. While AHM is considered to be not soluble in ethanol, the low solubility of NH_4Cl in ethanol (~6 g/L) allows for selective removal of NH_4Cl . Use of 80% ethanol in water was found to be even more efficient in selective removal of NH_4Cl . Based on the results obtained from batch experiments, the following flowsheet was proposed for recovery of Mo using solvent extraction (Figure 3). The alkaline solution of ~2.1 M K_2MoO_4 in 5 M KOH (SGS) is acidified with hydrochloric acid to make a solution of ~0.35 M Mo in 5 M HCl. During this step, a significant amount of potassium is removed by reaching the

solubility limit of KCl. The resulting solution is then contacted with the TBP solvent, which extracts molybdenum but does not extract potassium. Although extraction of potassium is very low, some presence of K due to partial phase carryover is removed using a scrub section with 4-5 M HCl. Molybdenum is then stripped from the TBP by using ammonium hydroxide. This solution is then evaporated, which precipitates molybdenum as ammonium heptamolybdate (AHM: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot x\text{H}_2\text{O}$) and ammonia as ammonium chloride (NH_4Cl). The solid is washed with 80% ethanol (EtOH), which dissolves the NH_4Cl away from the AHM. It was experimentally confirmed that recovered AHM can be reduced directly to Mo metal by a two-stage reduction process in a hydrogen atmosphere [38].

Results from six large-scale extraction experiments are summarized in Table 3. A total of ~880 g of Mo was processed in these six batches. Usually, about 75-80% of K is removed during the acidification step, when SGS is combined with HCl. After two extraction steps (see experimental section), the Mo strip solution usually contains <0.05% of the original amount of K, and the content of K in the AHM product after ethanol wash is <0.01% from its original concentration in SGS. The average recovery yield from the MOEX recycle process is $97.2 \pm 2.4\%$. It should be noted that Na is also being removed by this method; therefore, this process could also be applied to Mo/Tc SGS streams containing Mo in highly alkaline NaOH.

Data in Table 3 show that a significant presence of P in the strip solution was observed, which is due to phase carryover and some solubility of TBP in the aqueous strip solution. However, it should be noted that the final wash of the solid AHM and NH_4Cl mixture with ethanol removes phosphorous below detection limits. Moreover, further removal of potassium is achieved in this step as well. It is worth noting that tin has a very similar extraction behavior as molybdenum, and will not be removed from molybdenum by the MOEX process. This is especially obvious for

Sample 2 (Table 3), which was obtained by dissolution of Mo disks using 50% H₂O₂ stabilized with tin. Therefore, if peroxide is used for dissolution of irradiated Mo targets, no Sn-stabilized peroxide should be used. Similarly tungsten is not being removed, and its content in enriched Mo target should therefore be low, otherwise several tungsten side-reaction products can be formed by the (γ, n) reaction on ¹⁰⁰Mo such as ¹⁸⁷W, ¹⁸⁵W, and ¹⁸¹W. On the other hand, good extraction behavior of tungsten from HCl by TBP could be used for recycling of enriched ¹⁸⁶W that is used for the production of ¹⁸⁸Re medical isotope in a ¹⁸⁸W/¹⁸⁸Re generator. About 50% of the recycled AHM material had a particle size >149 μ m, ~40% were 149-74 μ m, and ~10% were <74 μ m. More than 95% of all particles were >44 μ m. A small batch of recycled AHM material was reduced to Mo metal at Oak Ridge National Laboratory. Reduction of the AHM material led to ~25-30% decrease in size of obtained Mo particles, and pressed and sintered Mo disks had good dissolution rates [30].

Automation of MOEX process

For full-scale processing of several hundred grams of Mo per day, development of an automated recycle process is very important. Annular centrifugal contactors have been used for automated solvent extraction processes for several decades, mostly as part of nuclear fuel cycle research and development at U.S. Department of Energy facilities [39]. However, due to the corrosiveness of hydrochloric acid, stainless steel contactors cannot be used; therefore, a plastic (acrylic), 3D-printed, multi-stage centrifugal contactor (2-cm diameter) designed by Argonne [40] was tested. Several multi-stage contactor runs were performed to date with a focus on the compatibility of the plastic contactor body with chemicals used in the MOEX process, and to test the complex chemistry of the proposed extraction process. It appears that use of TCE as the

diluent may have clear benefits to the hydraulic operation of the contactors. Because of its high density, this diluent increases the efficiency of physical separation and, consequently, the throughput that can be achieved. Experiments that are currently underway demonstrate the feasibility of an automated extraction route for the Mo-recycling process with fully plastic (housing and rotor) 3D-printed centrifugal contactors. The results from this study are very positive, and detailed experimental results will be presented in separate publication.

Conclusion

Batch experiments performed using a TBP solvent showed that molybdenyl chloride can be extracted from a wide range of aqueous HCl concentrations. Very high extraction yields can be obtained with up to ~0.45 M Mo. Extracted Mo can be effectively stripped from the organic phase using ammonium hydroxide. Low distribution ratios for K and Na allow for very high separation factors with very good recovery yields (~97%). Recovered ammonium heptamolybdate has a good distribution of particle size that is suitable for a direct conversion to Mo metal for production of Mo metal targets.

Acknowledgment

Authors wish to thank Yifen Tsai (Argonne National Laboratory) for performing ICP-MS analyses and Rick Lowden (Oak Ridge National Laboratory) for reduction of recycled material and production of sintered Mo disks.

Work supported by the U.S. Department of Energy's NNSA Office of Material Management and Minimization, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

References

[1] National Research Council of the National Academies. (2009) Medical Isotope Production without Highly Enriched Uranium; The National Academies Press: Washington, DC.

[2] The National Academies of Sciences, Engineering, Medicine. (2016) Molybdenum-99 for Medical Imaging; The National Academies Press: Washington, DC.

[3] Morley, T.; Gagnon, K.; Schaffer, P.; Asselin, E.; Zeisler, S.; McQuarrie, S.; Kovacs, M.; Wilson, J.; Benard, F.; Ruth, T. (2011) Cyclotron production of technetium radioisotopes. *J. Nucl. Med.*, 52: 291.

[4] Benard, F.; Buckley, K.R.; Ruth, T.J.; Zeisler, S.K.; Klug, J.; Hanemaayer, V.; Vuckovic, M.; Hou, X.; Celler, A.; Appiah, J.P.; Valliant, J.; Kovacs, M.S.; Schaffer, P. (2014) Implementation of multi-curie production of Tc-99m by conventional medical cyclotrons. *J. Nucl. Med.*, 55: 1017–1022.

[5] Eslami, M.; Kakavand, T. (2014) Simulation of the direct production of Tc-99m at a small cyclotron. *Nucl. Instr. Met. Phys. Res. B*, 329: 18–21.

[6] Dick, D. (2014) Diversification of Mo-99/Tc-99m supply. *J. Nucl. Med.*, 55: 875–876.

[7] Manenti, S.; Holzwarth, U.; Loriggiola, M.; Gini, L.; Esposito, J.; Groppi, F.; Simonelli, F. (2014) The excitation functions of Mo-100(p, x)Mo-99 and Mo-100(p,2n)Tc-99m. *Appl. Radiat. Isot.*, 94: 344–348.

[8] Lagunas-Solar, M.C. (1991) Cyclotron production of NCA 99mTc and 99Mo, an alternative non-reactor supply source of instant ^{99m}Tc and $^{99}\text{Mo}/^{99m}\text{Tc}$ generators. *Int. J. Rad. Appl. Instrum. A*, 42: 643–657.

[9] Takacs, S.; Tarkanyi, F.; Sonck, M.; Hermanne, A. (2002) Investigation of the $^{nat}\text{Mo}(p,x)^{96}\text{m}\text{g}\text{Tc}$ nuclear reaction to monitor proton beam: new measurements and consequences on the earlier reported data. *Nucl. Instrum. Methods Phys. Res. B*, 198: 183–196.

[10] Guérin, B.; Tremblay, S.; Rodrigue, S. (2010) Cyclotron production of $^{99}\text{m}\text{Tc}$: an approach to the medical isotope crisis. *J. Nucl. Med.*, 51: 13N–16N.

[11] Pillai, M.R.A.; Dash, A.; Knapp, F.F. (2013) Sustained Availability of $^{99}\text{m}\text{Tc}$: Possible Paths Forward. *J. Nucl. Med.*, 54: 313–323.

[12] Bennett, R.G.; Christian, J.D.; Petti, D.A.; Terry, W.K.; Grover, S.B. (1998) A system of $^{99}\text{m}\text{Tc}$ production based on distributed electron accelerators and thermal separation. *Nucl. Technol.*, 126: 102–121.

[13] Sabel'nikov, A.; Maslov, O.D.; Molokanova, L.G.; Gustova, M.V.; Dmitriev, S.N. (2006) Preparation of ^{99}Mo and $^{99}\text{m}\text{Tc}$ by $^{100}\text{Mo}(\gamma,n)$ photonuclear reaction on an electron accelerator, MT- 25 microtron. *Radiochem.*, 48: 191–194.

[14] Avagyan, R.; Avetisyan, A.; Kerobyan, I.; Dallakyan, R. (2014) Photoproduction of Mo-99/Tc-99m with electron linear accelerator beam. *Nucl. Med. Biol.*, 41:705–709.

[15] Starovoitova, V.N.; Tchelidze, L.; Wells, D.P. (2014) Production of medical radioisotopes with linear accelerators. *Appl. Radiat. Isot.*, 85: 39–44.

[16] Dale, G.; Chemerisov, S.; Vandegrift, G.; Tkac, P.; Woloshun, K.; Bach, H.; Heath, C.; Kelsey, C.; Bowers, D.; Gelis, A.V.; Jonah, C.; McCrady, R.; Olivas, E.; Hurtle, K.; Pitcher, E.; Romero, F.; Tuzel, W.; Giola, J.; Tomei, T.; Wheat, R.; DeCroix, M.; Warren, D.; Dalmas, D.; Romero, B.; Harvey, J.T. (2010) Global threat reduction initiative (GTRI) accelerator production of ^{99}Mo , LA-UR-11-, 2010 Report; Los Alamos National Laboratory: Los Alamos, NM.

[17] Roberts, A.D.; Geddes, C.G.R.; Matlis, N.; Nakamura, K.; O'Neil, J.P.; Shaw, B.; Steinke, S.; van Tilborg, J.; Leemans, W.P. (2015) Measured bremsstrahlung photonuclear production of Mo-99 (Tc-99 m) with 34 MeV to 1.7 GeV electrons. *Appl. Radiat. Isot.*, 96: 122–128.

[18] Pellerin, E.; Ogbomo, K., Barnard, J.; Saunders, C.; Mangera, K. (2012) Evaluation of radionuclidic profiles of molybdenum-99 from accelerator transmutation of natural and Mo-100 enriched molybdenum. *J. Nucl. Med.*, 53: 1485.

[19] Chemerisov, S.; Bailey, J.; Heltemes, T.; Jonah, C.; Gromov, R.; Makarashvili, V.; Tkac, P.; Rotsch, D.; Virgo, M.; Vandegrift, G.F. (2016) Unpublished results.

[20] Chemerisov, S.; Bailey, J.; Heltemes, T.; Jonah, C.; Gromov, R.; Makarashvili, V.; Tkac, P.; Rotsch, D.; Virgo, M.; Vandegrift, G.F. (2016) Unpublished results.

[21] Munze, R.; Hladik, G.; Bernhard, G.; Boessert, W.; Schwarzbach, R. (1984) Large Scale Production of Fission Mo-99 by Using Fuel Elements of a Research Reactor as Starting Material. *Int. J. Appl. Radiat. Isot.*, 35: 749–754.

[22] Chakravarty, R.; Ram, R.; Dash, A.; Pillai, M.R. (2012) Preparation of clinical-scale $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ column generator using neutron activated low specific activity ^{99}Mo and nanocrystalline $\gamma\text{-Al}_2\text{O}_3$ as column matrix. *Nucl. Med. Biol.*, 39: 916–922.

[23] Tachimori, S.; Amano, H.; Nakamura, H. (1971) *J. Nuc. Sci. Technol.*, 8: 357–362.

[24] Baker, R.J. (1971) A system for the routine production of concentrated technetium-99m by solvent-extraction of molybdenum-99. *Int. J. Appl. Radiat. Isot.*, 22: 483–485.

[25] Osso, J.A.; Lima, A.L.V.P.; da Silva, N.C.; Nieto, R.C.; de Velosa, A.C. (1998) Preparation of a Gel of Zirconium Molybdate for Use in the Generators of $^{99}\text{Mo}-^{99\text{m}}\text{Tc}$ Prepared with ^{99}Mo

Produced by the $^{98}\text{Mo}(\text{n}, \gamma) ^{99}\text{Mo}$ Reaction. International Meeting on Reduced Enrichment for Research and Test Reactors, October 18-23, 1998, Sao Paulo, Brazil.

[26] Rogers, R.D.; Griffin, S.T.; Horwitz, E.P.; Diamond, H. (1997) Aqueous biphasic extraction chromatography (ABECTM): uptake of pertechnetate from simulated Hanford tank wastes. *Solv. Extr. Ion Exch.*, 15: 547–562.

[27] Gagnon, K.; Wilson, J.S.; Holt, C.M.B.; Abrams, D.N.; McEwan, A.J.B.; Mitlin, D.; McQuarrie, S.A. (2012) Cyclotron production of $^{99\text{m}}\text{Tc}$: recycling of enriched ^{100}Mo metal targets. *Appl. Radiat. Isot.*, 70: 1685–1690.

[28] Gumiela, M.; Dudek, J.; Bilewicz, A. (2016) New Precipitation Method for Isolation of $^{99\text{m}}\text{Tc}$ from Irradiated ^{100}Mo Target. *J. Rad. Nucl. Chem.*, DOI: 10.1007/s10967-016-4967-2.

[29] Tkac, P.; Vandegrift, G.F. (2016) Recycle of Enriched Mo Targets for Economic Production of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ Medical Isotope without Use of Enriched Uranium. *J. Rad. Nucl. Chem.*, 308: 205–212.

[30] Tkac, P.; Rotsch, D.A.; Chemerisov, S.D.; Bailey, J.L.; Krebs, J.F.; Vandegrift, G.F. (2016) Unpublished results.

[31] Tkac, P.; Vandegrift, G.F.; Harvey, J.; (2013) Dissolution of sintered Mo disks, Report ANL/CSE-13/19; Argonne National Laboratory: Argonne, IL.

[32] Tkac, P.; Vandegrift, G.F. (2014) Dissolution of sintered Mo disks, Report ANL/CSE-14/26; Argonne National Laboratory: Argonne, IL.

[33] Hung, L.; Hertz, A.; Hartmann, D.; Charton, F.; Boutin, O. (2016) Supercritical CO₂ extraction of molybdenum-ligand complexes from sulfuric solutions, *J. of Supercritical Fluids*, 111: 97–103.

[34] Zhang, X.; Ning, P.; Cao, H.; Zhang, Y. (2016) Measurement and Modeling for Molybdenum Extraction from the $\text{Na}_2\text{MoO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ System by Primary Amine N1923. *Ind. Eng. Chem. Res.*, 55: 1427–1438.

[35] Mandal, S.; Mandal, A.; Lahiri, S. (2013) Species dependent extraction of Mo-99, *J. Radioanal. Nucl. Chem.*, 295: 861–863.

[36] Maiti, M.; Lahiri, S. (2010) Separation of ^{99}Mo and $^{99\text{m}}\text{Tc}$ by liquid– liquid extraction using trioctylamine as extractant. *J. Radioanal. Nucl. Chem.*, 283: 661.

[37] Tkac, P.; Paulenova, A. (2008) Speciation of Molybdenum (VI) in Aqueous and Organic Phases of Selected Extraction Systems. *Sep. Sci. Technol.*, 43: 2641–2657.

[38] Lowden, R.A.; Nunn, S.D.; Kiggans Jr., J.O.; Parten, R.J.; Bryan, C.D. (2015) Powder Metallurgy Fabrication of Molybdenum Accelerator Target Disks, Report ORNL/TM-2014/238; Oak Ridge National Laboratory: Oak Ridge, TN.

[39] Bernstein, G.; Grosvenor, D.; Lenc, J.; Levitz, N.A. (1973) A High-Capacity Annular Centrifugal Contactor. *Nucl. Technol.*, 20: 200–202.

[40] Wardle, K.E. 3D Printed Modular Centrifugal Contactors and Method for Separating Moieties Using 3D Printed Optimized Surfaces. US Patent Application 20,160,184,735, March 10, 2016.

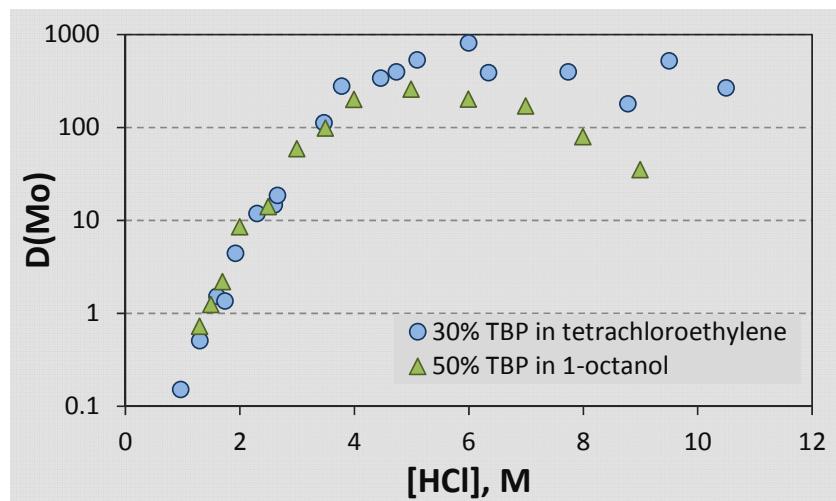
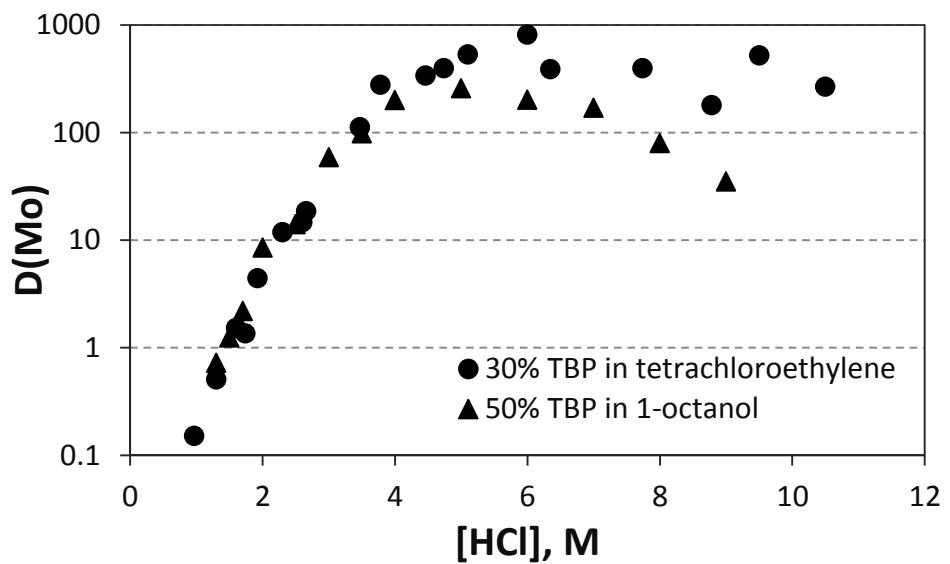


Figure 1. Distribution ratios of trace Mo(VI) from HCl by 30% TBP in tetrachloroethylene (circles) and 50% TBP in 1-octanol (triangles).

B&W version



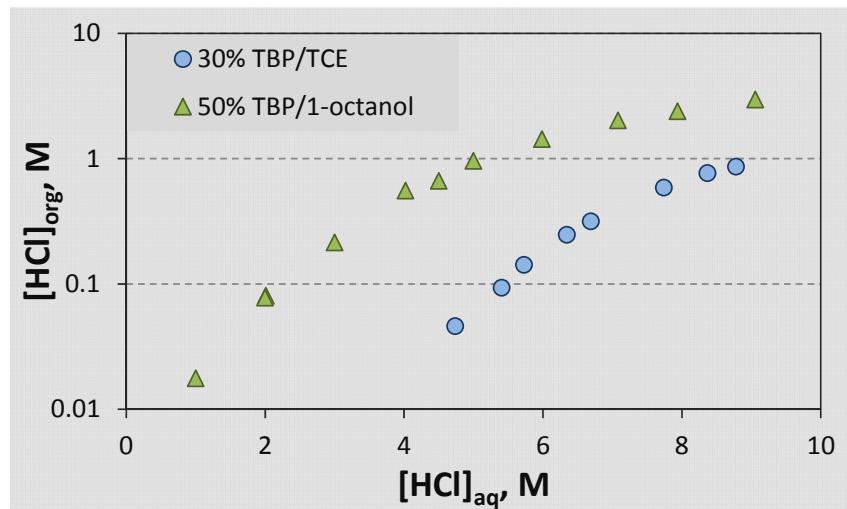
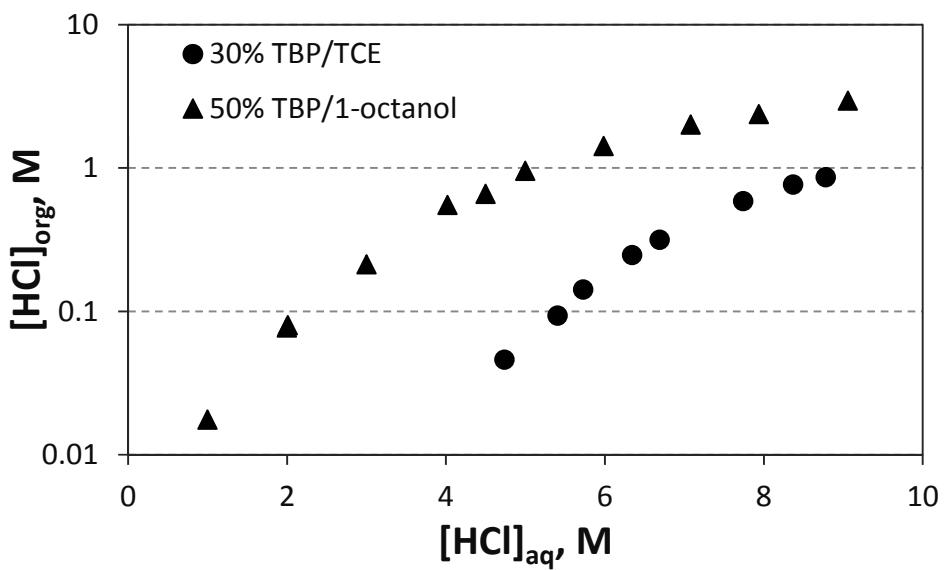


Figure 2. Plot of $[\text{HCl}]_{\text{org}}$ vs. $[\text{HCl}]_{\text{aq}}$ for 30% TBP in tetrachloroethylene (circles) and 50% TBP in 1-octanol (triangles).

B&W version



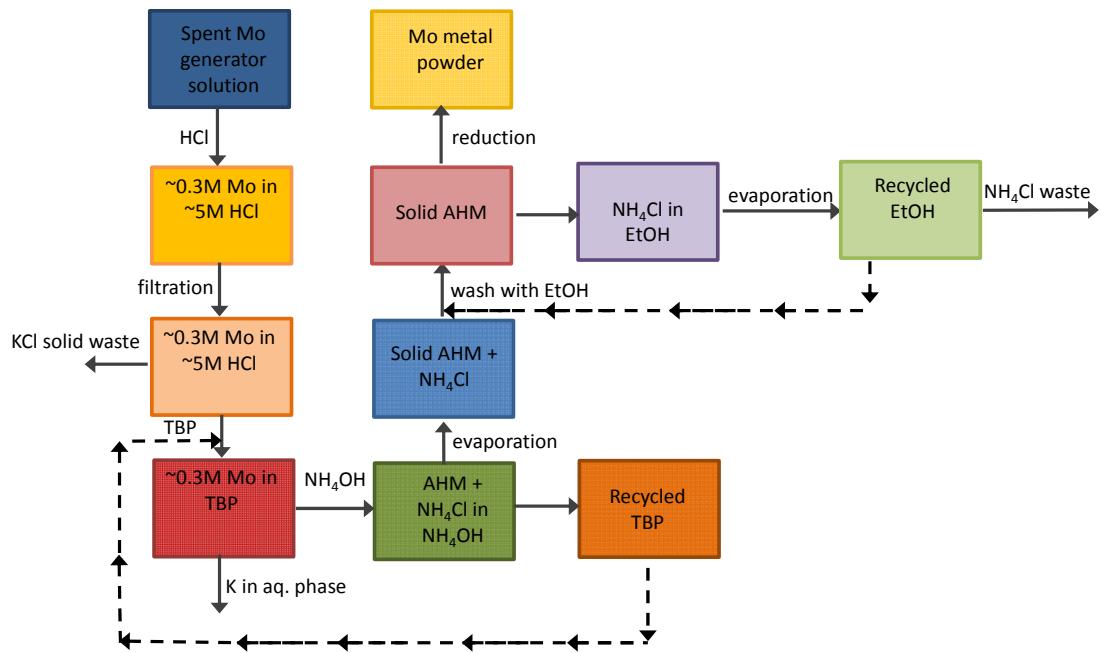


Figure 3. Scheme of Mo recycle process.

B&W version

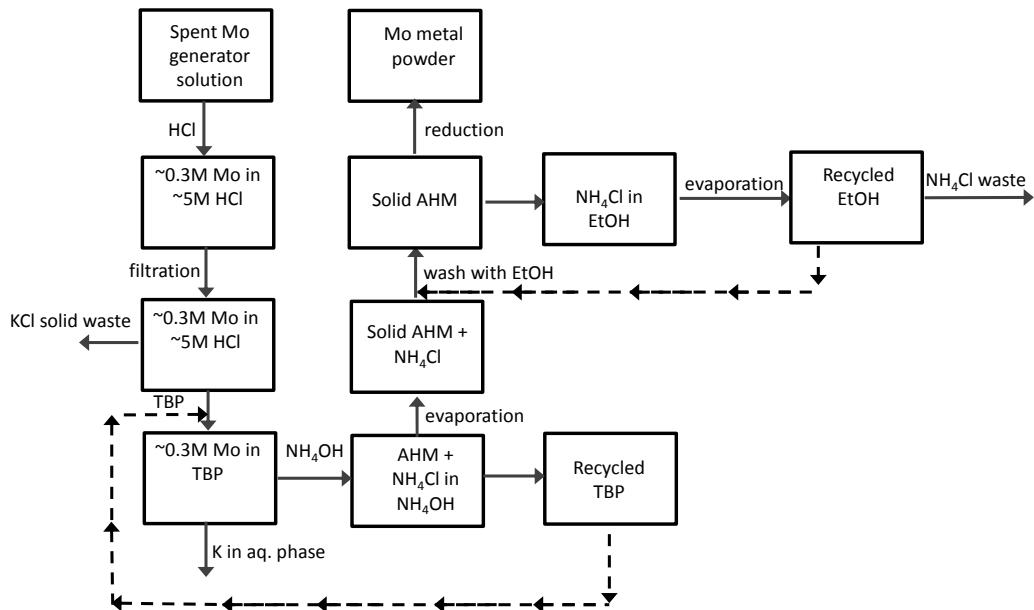


Table 1. Distribution ratios of Mo at high-Mo loading by 50% TBP in 1-octanol and 30% TBP in TCE. ICP-MS data are reported with 10% uncertainty.

TBP	[Mo], M	[HCl], M	[K], M	D(Mo)
50% in 1-octanol	0.35	6.4	0.37	40.5
50% in 1-octanol	0.37	6.2	0.41	38.7
50% in 1-octanol	0.39	6.0	0.44	33.5
50% in 1-octanol	0.40	5.8	0.47	38.0
50% in 1-octanol	0.45	5.3	0.62	34.8
50% in 1-octanol	0.096	1.0	0.19	0.84
50% in 1-octanol	0.096	3.0	0.19	10.7
50% in 1-octanol	0.096	7.1	0.19	94.1
50% in 1-octanol	0.096	9.1	0.19	56.1
30% in TCE	0.28	2.0	0.56	1.0
30% in TCE	0.26	4.0	0.51	40.6
30% in TCE	0.42	5.0	0.50	10.8
30% in TCE	0.35	5.0	0.50	23.3
30% in TCE	0.27	5.0	0.50	67.3
30% in TCE	0.21	5.0	0.50	123
30% in TCE	0.17	5.0	0.50	174
30% in TCE	0.06	5.0	0.50	326
30% in TCE	0.02	5.0	0.50	421
30% in TCE	0.01	5.0	0.50	608
30% in TCE	0.07	1.0	0.1	0.07
30% in TCE	0.07	1.2	0.1	0.14
30% in TCE	0.07	2.6	0.1	5.7
30% in TCE	0.07	3.5	0.1	67
30% in TCE	0.07	4.4	0.1	206
30% in TCE	0.07	5.9	0.1	555

Table 2. Concentration of Mo in aqueous and organic phases after extraction of 0.33M Mo from 5M HCl by 30% TBP in TCE, after scrub with 3-5M HCl and strip with 3.2-11.9M NH₄OH

	Extraction		Scrub			Strip		
	5 M HCl	3 M HCl	4 M HCl	5 M HCl	11.9 M NH ₄ OH	7.6 M NH ₄ OH	4.9 M NH ₄ OH	3.2 M NH ₄ OH
[Mo] _{aq} , M	5.3×10 ⁻³	9.1×10 ⁻²	2.2×10 ⁻²	4.2×10 ⁻³	3.27×10 ⁻¹	3.27×10 ⁻¹	3.27×10 ⁻¹	3.27×10 ⁻¹
[Mo] _{org} , M	3.27×10 ⁻¹	2.36×10 ⁻¹	3.05×10 ⁻¹	3.23×10 ⁻¹	N/A	N/A	N/A	N/A

Table 3. Distribution of various elements in four different fractions of MOEX extraction process. ICP-MS data are reported with 10% uncertainty.

Sample #	Mo fraction	Concentration, ppm (mg/kg-Mo)										
		K	Na	P	Ti	Cu	Zr	Nb	Sn	Sb	Cs	W
1	SGS	1.9×10 ⁶	1.0×10 ⁴	<360	20.7	195	0.21	1.77	10.2	4.28	0.72	235
2	SGS	2.0×10 ⁶	2428	2447	29.1	6.06	1.42	5.00	1332	1.73	1.32	697
3	SGS	2.0×10 ⁶	1.1×10 ⁴	<100	23.9	4.98	<0.28	1.72	7.04	4.18	0.77	206
4	SGS	1.9×10 ⁶	1472	<370	39.4	3.07	1.31	0.92	67.2	4.64	0.49	46.7
5	SGS	1.9×10 ⁶	1.0×10 ⁴	<340	35.2	6.95	0.65	0.90	1.10	4.66	0.68	256
6	SGS	1.9×10 ⁶	1.0×10 ⁴	<340	35.2	6.95	0.65	0.90	1.10	4.66	0.68	256
1	Mo in HCl	9.7×10 ⁵	1.1×10 ⁴	<230	22.1	53.4	0.47	2.07	9.10	4.34	0.68	244
2	Mo in HCl	4.1×10 ⁵	2272	2324	41.9	7.37	1.89	5.05	1294	0.93	0.84	593
3	Mo in HCl	5.2×10 ⁵	1.1×10 ⁴	<75	36.6	5.87	0.89	2.05	21.9	3.23	0.58	201
4	Mo in HCl	4.0×10 ⁵	1550	239	28.9	2.08	1.05	1.04	69.8	4.33	0.25	41.9
5	Mo in HCl	4.2×10 ⁵	1.0×10 ⁴	<160	27.8	6.46	0.93	0.95	0.83	4.21	0.46	245
6	Mo in HCl	4.0×10 ⁵	1.0×10 ⁴	<160	27.8	6.46	0.93	0.95	0.83	4.21	0.46	245
1	Mo strip	439	20.3	5.8×10 ⁴	198	3988	0.18	1.81	20.5	3.65	0.52	176
2	Mo strip	661	123	6.8×10 ⁴	179	918	<0.78	2.46	1220	1.16	0.79	207
3	Mo strip	562	18.6	3.9×10 ⁴	122	7.27	<0.48	1.57	42.4	3.91	0.67	132
4	Mo strip	992	463	<1800	<49	<7.1	2.36	0.98	64.9	4.31	0.71	87.2
5	Mo strip	620	556	2133	<41	37.6	4.04	0.83	24.4	5.78	0.70	167
6	Mo strip	<206	556	2133	<41	37.6	4.04	0.83	24.4	5.78	0.70	167
1	AHM	68.2	22.6	<150	16.6	10.8	1.26	1.86	6.65	3.27	0.28	185
2	AHM	93.5	9.00	158	16.9	1.63	0.77	2.52	1021	0.98	0.20	494
3	AHM	57.9	19.3	<57	20.7	12.4	0.46	1.77	49.9	2.20	0.34	249
4	AHM	384	22.0	<180	30.1	1.27	4.11	0.96	75.7	2.32	0.23	88.3
5	AHM	130	45.0	<310	65.6	1.64	0.65	0.91	7.49	1.60	0.24	179

“SGS” = spent generator surrogate solution; “Mo in HCl” = aq. phase before extraction; “Mo strip” = Mo product recovered from TBP; “AHM” = ammonium heptamolybdate product after wash with ethanol.