

Research Article

The Fission-Based ^{99}Mo Production Process ROMOL-99 and Its Application to PINSTECH Islamabad

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An innovative process for fission based ^{99}Mo production has been developed under Isotope Technologies Dresden (ITD) GmbH (former Hans Wälischmiller GmbH (HWM), Branch Office Dresden), and its functionality has been tested and proved at the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad. Targets made from uranium aluminum alloy clad with aluminum were irradiated in the core of Pakistan Research Reactor-1 (PARR-1). In the mean time more than 50 batches of fission molybdenum-99 (^{99}Mo) have been produced meeting the international purity/pharmacopoeia specifications using this ROMOL-99 process. The process is based on alkaline dissolution of the neutron irradiated targets in presence of NaNO_3 , chemically extracting the ^{99}Mo from various fission products and purifying the product by column chromatography. This ROMOL-99 process will be described in some detail.

1. Introduction

The present sources of molybdenum-99 (^{99}Mo ; $T_{1/2} = 66\text{ h}$) are research reactors by neutron-induced fission of ^{235}U , which results in high-specific activity ^{99}Mo , or using the (n, γ) nuclear reaction with ^{98}Mo (natural Mo or enriched $^{98}\text{Mo} = 24\%$), resulting in low-specific activity ^{99}Mo . Generally, the specific activity of molybdenum produced by fission is more than 1000 times higher than that obtained by (n, γ) process. The almost universal means by which technetium-99m ($^{99\text{m}}\text{Tc}$; $T_{1/2} = 6\text{ h}$) is made available for clinical applications is from the elution of generators containing high-specific activity fission-based ^{99}Mo .

The first chemical process for separation of fission ^{99}Mo was described by the Brookhaven group, USA [1]. In this process the target (93% enriched U-235 alloyed with Al) was dissolved in 6 M nitric acid catalyzed by mercuric nitrate. In the former Zentralinstitut für Kernforschung (ZfK) Rossendorf,

a fission-based ^{99}Mo separation technology became operationally ready in 1963 which was actually the basis of the first fission-based $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator in Europe. Metallic natural uranium pellets were used as target material and the dissolution of the irradiated U-pellets was done with concentrated HCl. Quartz and glass apparatus was used in chemical processing, and yield of ^{99}Mo was $\sim 70\%$ [2]. In 1980, this process was replaced by the AMOR process (AMOR: Anlage zur Mo Production Rossendorf), developed in the same institute [3]. The AMOR process made use of original fuel elements of the RF-reactor as qualified target which was dissolved in HNO_3/Hg . Batch-wise adsorption at Al_2O_3 and sublimation technique were used for separation and purification of the ^{99}Mo . This process was in operation until the shut-down of the Rossendorf Research Reactor in 1991.

Another small-scale production process for fission ^{99}Mo was proposed by the Rossendorf group in which natural uranium as uranium oxide was used as target material [4]. This procedure was particularly interesting for those which

do not dispose of enriched nuclear fuel material. Approximately 400 g of uranium oxide enclosed in irradiation cans are dissolved in nitric acid after irradiation for 100 hrs at a neutron flux of $5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in a research reactor. The separation of ^{99}Mo from the fuel-fission product solution is performed by ion exchange with alumina in a chromatography column. Final purification includes the repeated chromatography separation and subsequently a sublimation stage.

Based on their own long-term experiences and considering international achievements in ^{99}Mo production, scientists of the Radio-Isotope department of the former Rossendorf institute ZfK designed a new process for fission-based ^{99}Mo production named ROMOL-99 [5–7]. The basic principles of this process are as follows (see also the flow scheme, Figure 1).

- (i) The dissolution of the UAlx/Al-clad targets shall be performed in a mixture of NaOH/NaNO₃ without H₂ generation, under reduced pressure conditions.
- (ii) The Xe shall be trapped cryogenically after passing a gas treatment line.
- (iii) The NH₃ generated in the dissolving process shall be separated prior to Mo separation.
- (iv) The radioiodine shall be separated prior to ^{99}Mo separation as well.
- (v) During dissolving process nitrite is generated which shall be eliminated prior to the ^{99}Mo separation.

The basic parameters of this process has been developed with modern nonradioactive analytical techniques by the IAF-Radioökologie GmbH Dresden, while the active testing and optimization of the process has been carried out at PINSTECH Islamabad under supervision of the German scientists. In this paper the chemical process of the ROMOL-99 technology will be described in some detail.

2. Materials and Methods

All chemicals were purchased from E. Merck (Germany) and were of guaranteed reagent grade (GR) or analytical reagent (AR) grade. Al₂O₃ (90 active acidic for column chromatography, 70–230 mesh ASTM) was used. Silver-coated alumina was freshly prepared at institute. Organic anion-exchange resin was purchased from BioRad, USA.

The non-radioactive development work was performed using uranium-free Al-plates (purchased from PINSTECH) having the same composition as the material used for the original targets.

Tracer experiments were performed using ^{131}I tracer activities which were taken from the PINSTECH routine ^{131}I production, and the ^{99}Mo tracer was taken from the routine PAKGEN $^{99\text{m}}\text{Tc}$ generator production (^{99}Mo imported from South Africa).

2.1. Irradiation of Target. Qualified HEU/Al alloy clad with high purity aluminum target plates [8] were irradiated for 12–18 h at a neutron flux of $\sim 1.5 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ inside the

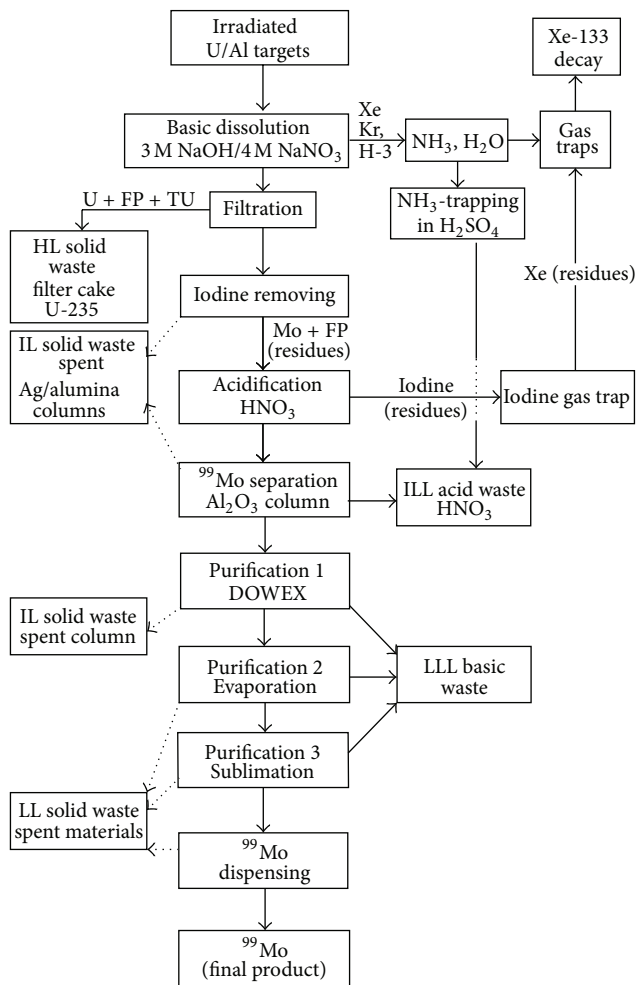


FIGURE 1: Process flow scheme of the ROMOL-99 process.

core of the Pakistan Research Reactor-1 (PARR-1). After 24 h cooling, the irradiated target plates were transferred to the $^{99}\text{Molybdenum}$ Production Facility (MPF) for separation of ^{99}Mo from the uranium, actinides, and fission products. For the warm test runs, targets were irradiated for short times at lower flux density, but the target composition was identical with those for production runs. The irradiation conditions were chosen in a way that the total activity inventory for the development work was of the order of 4 GBq.

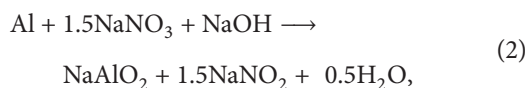
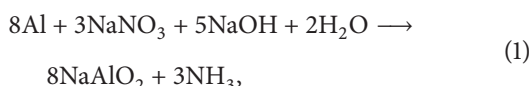
2.2. Process Control and Quality Control. Gamma ray spectroscopy high-purity Ge detector (Canberra Series 85 multi-channel analyzer) was used to determine the activity balance during all process steps and for the determination of radionuclide impurities in the final ^{99}Mo product. This concerns mainly ^{131}I and ^{103}Ru , ^{132}Te . Beta counting of ^{89}Sr and ^{90}Sr was done by a liquid scintillation analyzer (Tri-Carb 1900 TR, Packard Canberra Company) after separation by ion-exchange and precipitation with the aid of carrier. Contamination of alpha emitters was done with the α -counter (UMF-200). Radiochemical purity of [^{99}Mo] molybdate was determined by means of paper chromatography with a

mixture of hydrochloric acid, water, ether, and methanol (5 : 15 : 50 : 30) as mobile phase. The chemical purity was occasionally determined after decay by optical emission spectrometry (Optima 3300XL, Perkin Elmer). It was used for the determination of toxic elements such as Cr, Co, As, Sn, Cd, Pb, and U; the detection limits in ppm were 2, 5, 5, 5, 1, 5, and 2, respectively.

The final ^{99}Mo product was dispensed and assayed by means of a calibrated ionization chamber. Radioactivity concentration (MBq/cm^3) was calculated by dividing the total product activity by the final volume of the product solution. All required nuclear data were taken from NuDat 2.5 [9].

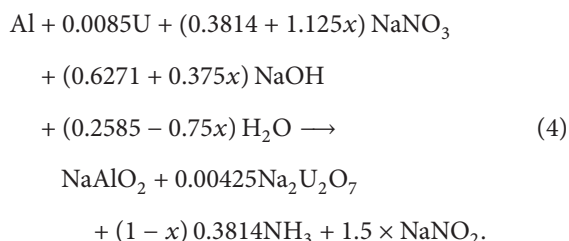
3. Results and Discussion

3.1. The Dissolving Process. When dissolving the target plates in the solvent, 3 M NaOH/4 M NaNO_3 , 3 reactions must be considered leading to different reaction products as follows:



The most important is reaction (1), where the Al reduces the nitrate ion down to NH_3 . Close to the end of the dissolving process the nitrate is reduced only to nitrite (2). This fraction is of the order of 10 to 15%. The theoretically possible reduction (3) generating hydrogen is nearly suppressed. Gas chromatographic determination of hydrogen in the off-gas from the dissolving process did not show any signal for H_2 , meaning, the upper limit for H_2 generation is <2% and is therefore without any danger.

Under the conditions that x represents the mass unit of the target matrix that undergoes to nitrite formation and consequently $(1 - x)$ represents the mass units of the target matrix that undergoes under NH_3 formation, we obtain the “master equation” for dissolving the targets following:



The value x , representing the fraction of the aluminum that is dissolved under nitrite formation, ranges between $0.1 < x < 0.16$.

The solvent volume needed for the process is determined by the solubility of the sodium aluminate (NaAlO_2) which is 2.1 M/L corresponding to 57 g/L Al. Furthermore, the Na concentration should be kept as high as possible, in order to reach safely the saturation concentration for the precipitate

$\text{Na}_2\text{U}_2\text{O}_7$. A high nitrate concentration is needed for avoiding the formation of hydrogen, while the viscosity of the solution should be suitable for easy filtration. We found a composition of 3 M NaOH/4 M NaNO_3 as most suitable for the dissolving process.

The dissolving process is strong exothermic (close to 600 kcal are generated for dissolving 100 g Al), and in addition the dissolving speed increases with the second power of the temperature. Thus, the reaction is self-accelerating. Following the experiences collected in Dresden (IAF) and PINSTECH, the control of the dissolving process is easy and safely possible by short heating and cooling pulses. With these techniques one can easily adjust the dissolving temperature at around 70–80°C. Furthermore, the process can be performed at slightly reduced pressure conditions (see Figure 2). The dissolving process is performed in a special, dissolving vessel, equipped with heater and cooling jacket.

3.2. NH_3 Distillation. Since the iodine shall be removed from the process solution using a silver-coated column material, the NH_3 is recommended to be eliminated because it has potential to influence the efficiency of the iodine removal at the Ag-coated column. The simplest way to separate the NH_3 is the distillation from strong basic solution. Preliminary experiments have shown that 150–200 mL distilled volume is sufficient. This volume can be distilled off from the target solution within about 20 minutes. In the production runs, the distilled NH_3 is trapped in 5 N H_2SO_4 solution.

3.3. Filtration. The precipitate that is formed during the dissolving process is composed of mainly 2 components: the sodium diuranate and in addition the nonsoluble hydroxides, oxides or carbonates of several alloying metals of the Al-matrix that are coprecipitated together with the $\text{Na}_2\text{U}_2\text{O}_7$. Based on analytical data of the Al-matrix material used for the target preparation, the following quantities for the precipitate should be expected (Table 1).

Assuming a density of the precipitate of $4.4 \text{ g}/\text{cm}^3$ (based on ~30% porosity) and the uranium in the form of $\text{Na}_2\text{U}_2\text{O}_7 \times 6 \text{H}_2\text{O}$, one would obtain a precipitate volume of $\sim 2.37 \text{ cm}^3$, which corresponds to a filter bed thickness of $d \leq 1.5 \text{ mm}$.

The target element uranium after dissolution must be present exclusively in the chemical form of $\text{Na}_2\text{U}_2\text{O}_7$ because it is well known that uranium species of lower oxidation stage absorb ^{99}Mo and consequently lower the production yield. Dissolving the same targets alone in NaOH or KOH (without NaNO_3) [10], an additional oxidation process (usually H_2O_2) is required to reach the oxidation stage of +6 for both of the U and the Mo.

As shown from the crystallographic analysis, the target element uranium was found after our ROMOL-99 dissolving process straight as sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) in the precipitate (Figure 3) without any further treatment.

The time needed for filtration is mainly determined by the surface area and the porosity of the used filter plate and the filter cake, the viscosity of the solution and the filtration pressure. The filter plate consists of a 3 mm thick metallic (INOX) sinter plate with a porosity of $\sim 30 \mu\text{m}$. The cold

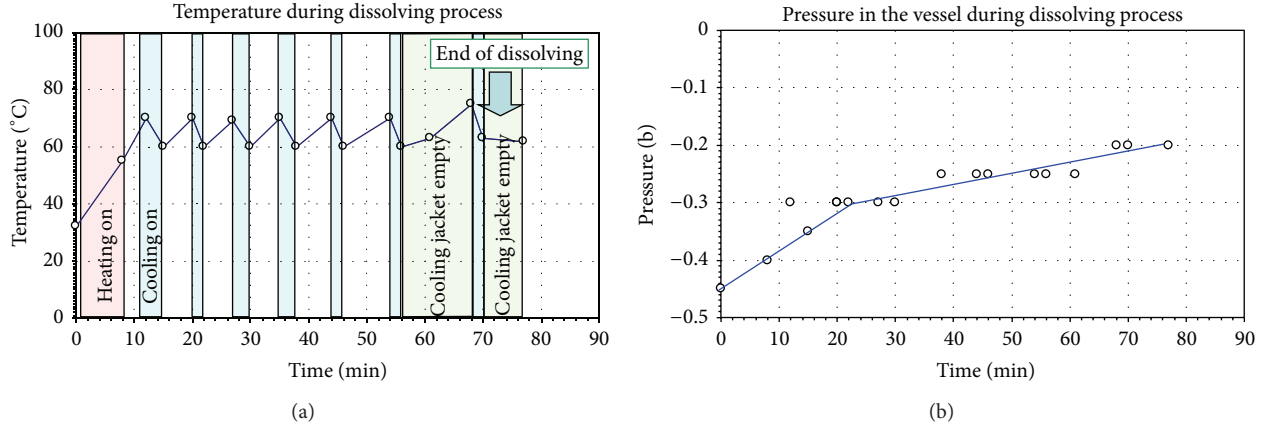


FIGURE 2: Temperature gain during controlled dissolving process (a) and the pressure situation during the dissolving process (b).

TABLE 1: Composition of the target material and the related composition of the precipitate after the dissolving process.

Alloying element	Content (%) of Al-weight)	Content in (mg) for 3 targets	Precipitated species	Precipitate in (mg) for 3 targets
Fe	0.14	128,8	$\text{Fe}(\text{OH})_2$	207.14
Mn	0.002	1,84	$\text{Mn}(\text{OH})_2$	3.03
Si	0.01	9,20	SiO_2	19.33
Ca	0.16	147,2	CaCO_3	950.43
C	0.1	92	C	92.00
U	5.16	5100	$\text{Na}_2\text{U}_2\text{O}_7$	6814.85

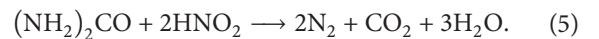
and hot runs showed that first of all the precipitate can be filtrated from the target solution with the above given alloying components, and in addition sufficient filtration speed (200–300 mL/min) is achieved in 10–20 min at a temperature of around 50°C.

3.4. Iodine Removal. In order to minimize the risk of iodine release in later production steps and waste, the adsorption on silver is the most promising approach for trapping the radioiodine before the ^{99}Mo is separated. During the production process, we have to deal with ^{132}I (2.3 h half-life, daughter of ^{132}Te), ^{133}I (20.8 h half-life), and ^{131}I (8.02 d half-life). Freshly prepared silver-coated Al_2O_3 material has shown to be the most appropriate material; this material has been prepared according to the Wilkinson et al. method [11]. The iodine removal process is performed by controlled filtration of the filtrated target solution over a column filled with this material. The flow rate needs to be controlled. Since the optimal flow rate for high iodine trapping efficiency is identical with the speed for introducing the basic target solution into the strong acid reaction vessel (next process step); there is no technological separation of both steps, thus, while transferring the basic solution into the nitric acid for acidification the radioiodine is removed simultaneously. The transfer process lasts for about 60–90 minutes. The efficiency

for iodine trapping has been determined to be >98%. The Ag-column also traps a good fraction of the Ru (see Figure 4); ^{99}Mo could not be detected within a detection limit of 3%.

3.5. Acidification and Nitrite Destruction. For the main separation step—the separation of the ^{99}Mo from the process solution after iodine removal— Al_2O_3 column chromatography has been selected. Molybdate is adsorbed from weak HNO_3 -acid media at Al_2O_3 (this principle is used in the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ -generator technology). Thus, the strong basic process solution needs to be acidified. This is not an easy step, since the Al-concentration is high. An anion-exchange process, as it is used in cases where only NaOH or KOH is involved for dissolving the targets under H_2 generation, is not possible due to the high NO_3^- concentration. Many test experiments have been performed in order to determine the optimal conditions for this step. When introducing strong basic aluminate solution into strong acid HNO_3 solution in the first step, $\text{Al}(\text{OH})_3$ is precipitated. This hydroxide needs to dissolve immediately, otherwise it may transmute into nonsoluble configurations which may create problems in the further production steps. When the basic solution is introduced with moderate speed (50–70 mL/min) under strong mixing, one observes first a thick white precipitate that is redissolved relatively fast. Due to neutralization heat the solution is warming up. In order to bring the solution to boil additional heating is required.

As said before, we also have nitrite in the system, which is recommended to be destroyed. Simultaneously with the acidification process the nitrite is reduced with urea under nitrogen formation according to



In test experiments, this gas generation looked like very fine silk. This gas generation is mixing the solution only a little, because of the microscopic fine bubbles, this effect is by far insufficient; additional strong stirring is required. The complete nitrite destruction and the re-dissolving of the primary precipitated hydroxides require refluxing under stirring for one additional hour after complete solvent transfer.

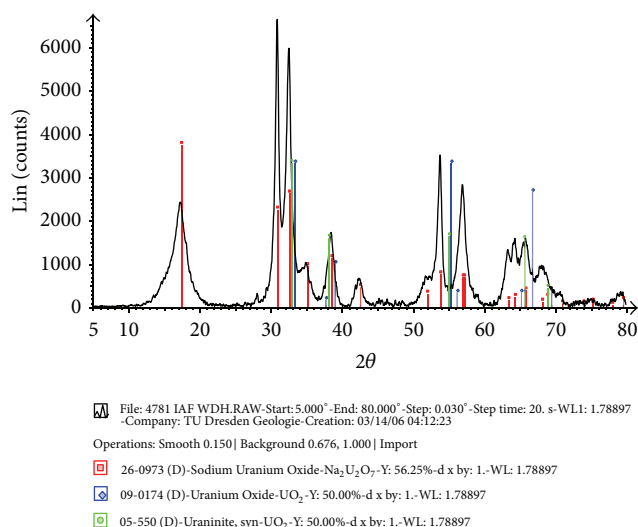


FIGURE 3: X-ray diffraction patterns of the uranium precipitate that show only the reflections of $\text{Na}_2\text{U}_2\text{O}_7$ and excluded other uranium species to be present. This X-ray diffractogram was performed by TU Dresden/Geologie.

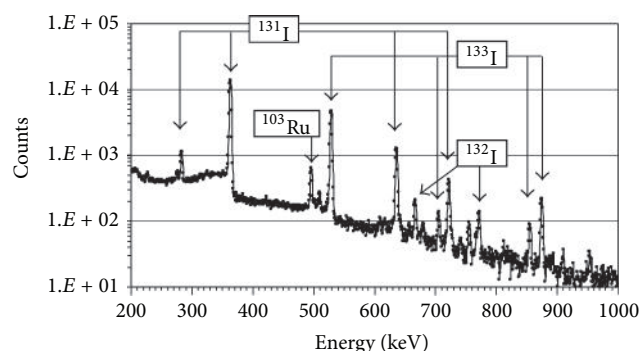


FIGURE 4: Gamma spectrum of the Ag-coated Al_2O_3 column after passing the filtrated target solution. The measurement was done from large distance. Only gamma signals from iodine radionuclides and Ru could be identified.

The reaction gases of this acidification process and in addition a slight carrier gas flow release also remain volatile iodine species (from iodine residue and decay of Te-parent nuclides) and radio Xe (mainly from ^{133}I -decay). The radio iodine is retained in a gas adsorption trap filled with Ag-IONEX. This is a Zeolite exchange material that adsorbs at $T > 100^\circ\text{C}$ volatile inorganic and organic iodine species that is widely used in fuel reprocessing process for decontamination of acid off-gases. After passing the IONEX filter, off-gas from the acidification process that still may contain some Xe is introduced into the gas process line for further treatment.

When the nitrogen formation and iodine release is finished, the solution is cooled down to room temperature and is ready for the Al_2O_3 column process.

3.6. Alumina Column Process. The separation of the ^{99}Mo from the acidified target solution is achieved via anion

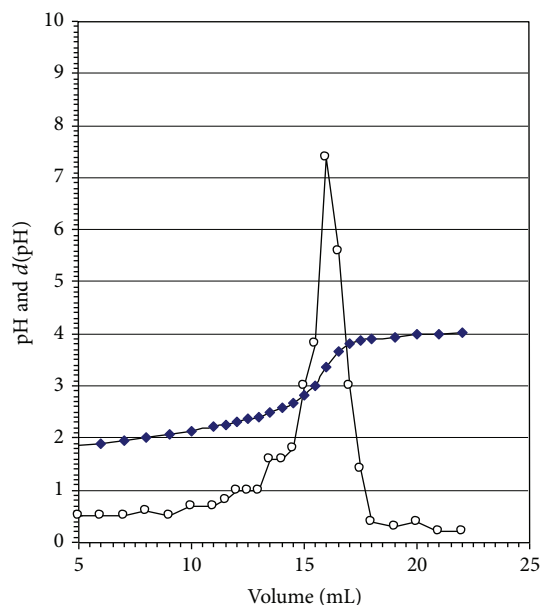


FIGURE 5: Potentiometric titration of 1 mL of the acidified target solution after nitrite destruction diluted to 100 mL with 0.100 N NaOH.

exchange chromatography using weak acid Al_2O_3 as column material. The adsorption efficiency for Mo depends mainly on the salt concentration and the acidity of the solution and not so much on the absorber material itself. For the optimization of the column parameters, the control of the free acidity in the FEED solution played an important role. Due to the high salt concentration (especially that of Al^{3+}), a direct pH-measurement is not possible. A potentiometric titration did not show the required precision (see Figure 5).

The safe and better is to dilute a sample of the solution by a factor 1 : 100 with distilled water. This solution could perfectly undergo a pH measurement with an ordinary glass electrode. The pH determined in this way was always in the region of $2.2 < \text{pH} < 2.6$, which means that the free acid concentration in the original FEED solution under practical conditions was in the range of about $0.15 < [\text{H}^+] < 0.7 \text{ M}$.

Under practical conditions, the volume of the loading solution (FEED) is around 6 L (for ~100 g target material). After the loading process, the column shall be washed with 0.5–1.0 L of 0.5 M HNO_3 , 500 mL water and then with 1500 mL 0.01 M NH_4OH . The ^{99}Mo is then eluted with up to 2000 mL of 1 M NH_4OH solution. One obtains a raw ^{99}Mo product of already $\gg 99\%$ radionuclide purity.

In order to define the optimal Al_2O_3 column parameters one needs to consider

- (i) the adsorption capacity of the exchange material Al_2O_3 ,
- (ii) the selectivity related to the separation from radioactive contaminations,
- (iii) the possible and needed loading- and elution speed which is relevant for the duration of the process.

TABLE 2: Optimal parameters for the alumina column process.

Al ₂ O ₃ column	About 50 mm × 145 mm, bottom G 3 frit
Al ₂ O ₃ weak acid material	250 g, size ~60 μm, density 1.25 mL/g, porosity 0.875
Loading process:	FEED volume ~5.8 L, 0.15 < [H ⁺] < 0.7 M, ~120 min
(1) Wash process	1000 mL 0.5 M HNO ₃ , time about 15 min
(2) Wash process	500 mL water, time about 7 min
(3) Wash process	1000 mL 0.01 M NH ₃ , time about 15 min
Liquid waste volume:	8300 mL
Elution	1000 mL 1-2 M NH ₃ , time about 30 min
Alumina column process:	Total time about 3 h.

The capacity of Al₂O₃ for Mo adsorption is known to be ~30 mg Mo/g Al₂O₃ column material. In test experiments using 50 mL of model-target solutions containing a Mo-concentration of 20–33 mg Mo/L and columns with 2 g Al₂O₃ column material (0.7 × 5.6 cm column dimension) using a flow rate of 7 cm/min corresponding to 2.7 mL/min the Mo could be adsorbed with an average yield of >90%. Thus, in these experiments only a small fraction (1.5–2.5%) of the capacity of the exchanger has been utilized. This corresponds to 0.5–0.8 mg Mo/g Al₂O₃. Based on this data one would need for processing of 3 target plates theoretically 140 g of Al₂O₃ corresponding to 152 mL Al₂O₃ for the separation process.

For defining the column dimensions one needs to find a compromise between the needed amount of the Al₂O₃ material and reasonable high applicable elution speed. Furthermore one has to consider losses due to irreversible bound Mo with increasing Al₂O₃ quantities. Assuming the following practical conditions:

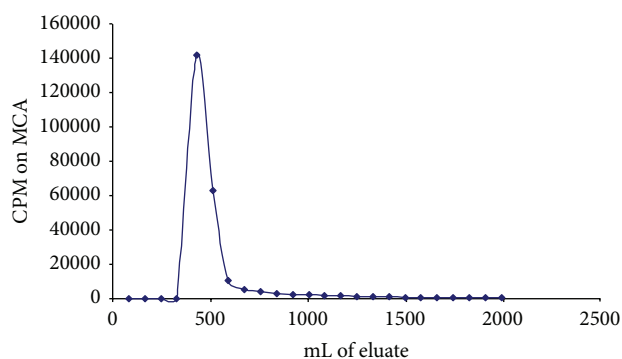
- (i) the total volume of liquids that has to pass the column is ~11 L composed from 5.8 L acidified target solution, 3.3 L wash solutions, and 2.0 L elution volume,
- (ii) the linear filtration speed is 7 cm/min (50 mL/min for loading and eluting and 80 mL/min washing),
- (iii) the diameter of the column shall be 5 cm,

one obtains a volume flow speed of 137 mL/min under practical conditions.

Considering the previous determined 140 g or 152 mL Al₂O₃ absorber material, one would obtain an absorber bed height of 7.8 cm. If one increases the dimensions by at least a factor 2 for compensating not optimal conditions, the length of the Al₂O₃ column becomes 15.6 cm filled with 304 mL Al₂O₃ absorber material.

During the commissioning, it has been demonstrated that a 250 g alumina column bed is acceptable which corresponds to a column bed volume of about 275 mL. Table 2 summarizes the Al₂O₃ column process parameters.

Using the parameters shown in Table 2, the profile for eluting the ⁹⁹Mo from the Al₂O₃ column has been performed. As seen in Figure 6, the ⁹⁹Mo is eluted in a relatively sharp peak and 1000 mL of 1.0 M NH₃ solution is sufficient.

FIGURE 6: Elution profile for ⁹⁹Mo elution from the Al₂O₃ column with 1 M NH₃ using the parameters shown in Table 2.

The ⁹⁹Mo retention at the column using model solutions was practically 100%, and the ⁹⁹Mo recovery was measured to be 91.2%.

The Al used in the target material contains some quantities of Si. It is well known that Si forms very unpleasant nonsoluble Mo Si-species which may cause dramatic losses in the ⁹⁹Mo yield. Certain limited quantities of Mo-carrier can help solving this problem. The other way around would be to elute the Al₂O₃ column with higher-concentrated NH₃ (2 M instead of 1 M) or with NaOH.

3.7. DOWEX-1 Column Process. Molybdenum in its anionic form MoO₄²⁻ is adsorbed directly from the ammonia solution eluted from the Al₂O₃ column at strong basic anion exchange resins as DOWEX-1 (configuration OH⁻). The distribution coefficients has been determined to be $K_D = 270$ for adsorption from 1 M NH₄OH and $K_D = 0.8$ for the desorption with 1 M (NH₄)₂CO₃ solution.

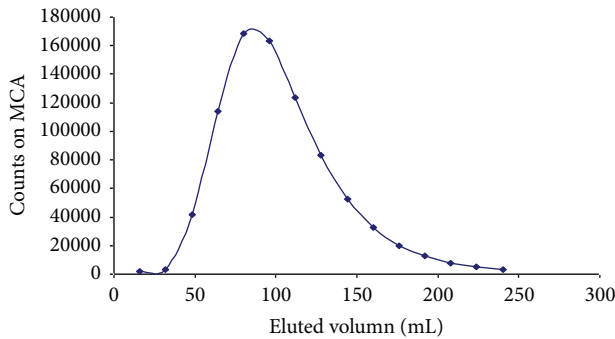
The dimensions of a suitable DOWEX-1 column and its operation parameters are determined in a similar way as demonstrated for the Al₂O₃ column. For a column of about 26 × 120 mm, a linear flow speed of 13 cm/min is the maximum. If the volume of the Mo solution is 2000 mL one would need theoretically 54.6 g of the ion exchange resin. DOWEX-1 in the dry form. Considering the density of 0.65 g/mL resin, this would give an 84 mL volume of the resin. For rinsing the column, 4 bed volumes are required which correspond to 340 mL. Table 3 summarizes the parameters for the DOWEX column process. The corresponding elution profile is shown in Figure 7.

3.8. Evaporation Step. The purification step at the DOWEX column delivers 200 mL of the ⁹⁹Mo molybdate in 1 M (NH₄)₂CO₃ solution. In the following step this eluted solution is evaporated to the dryness in a special evaporator, with condenser. During evaporation, the (NH₄)₂CO₃ is being decomposed; thus no additional salts are introduced into the final configured [⁹⁹Mo] molybdate solution.

The residue is redissolved in the desired volume of diluted NaOH solution forming the final product solution

TABLE 3: Optimal parameters for the DOWEX-1 column process.

DOWEX-1 column	About 26 mm × 120 mm, bottom G 3 frit
Loading process:	⁹⁹ Mo-solution in 1 M NH ₃ volume ~1.0 L, ~15 min
(1) Wash process	170 mL water, time about 3 min
(2) Wash process	170 mL water, time about 3 min
Liquid waste volume:	~1.4 L (depending on FEED and wash volume)
Elution	200 mL of 1 M (NH ₄) ₂ CO ₃ solution, time about 10 min
DOWEX column process:	Total time about 35–40 min

FIGURE 7: ⁹⁹Mo elution profile from the DOWEX-1 column with 1 M (NH₄)₂CO₃-solution using the parameters shown in Table 3.

[⁹⁹Mo]Na₂MoO₄. This final product solution is then transferred into a corresponding plastic vial and transferred into the hot cell 3 for further processing, precise measurement and distribution.

A sublimation step (at 1000°C) is foreseen as an additional reserve for improving purity, if required. In this case the residue after evaporation shall be redissolved in diluted HNO₃ or NH₄OH.

3.9. Radioactivity Balance during the Process. Careful studies have been performed to obtain a full picture on the behavior of the ⁹⁹Mo, of the most important impurities in ⁹⁹Mo preparations, for other fission products, and for the target element itself. On one hand, tracer activities of ⁹⁹Mo and ¹³¹I have been used, and after having optimized the separation conditions the same full protocol has been applied to study the separations technology with weak irradiated original target material (activity level ~4 GBq). Figure 8 summarizes gamma-spectroscopic measurements that illustrate how powerful the individual separation steps are. Segments of original measured gamma spectra are shown in one graph. Signals of the most critical radionuclides are clearly identified. In order to have a good overview, the original data of the different spectra have been expanded using a factor shown in the graph.

The upper spectrum has been taken from a small fraction of the filter cake (precipitate) followed by the spectrum from a sample from the filtrate. It is clearly seen that only few gamma lines are left in the filtrate, which correspond to ⁹⁹Mo,

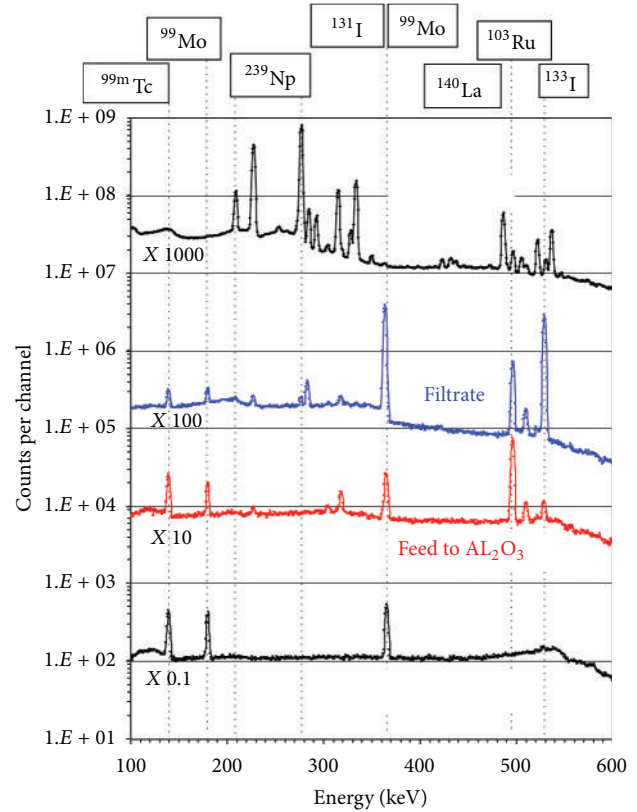


FIGURE 8: Gamma spectra of samples from the precipitate, filtrate, FEED solution (filtrate after iodine removal), from the final product illustrating the different separation and purification steps (for more details see text).

its daughter ^{99m}Tc, the radioiodine's, and some fractions of Ru. The strongest signals in the precipitate (²³⁹Np, and ¹⁴⁰La) are not seen in the filtrate solution. As said before the filtrate is passed through a silver-coated Al₂O₃ column prior to the acidification process. Thus comparing the spectra 2 and 3, one clearly sees that iodine is missing in the FEED solution (see also Figure 4). When interpreting spectrum 3, one needs to consider that the strongest gamma signal from ⁹⁹Mo is 739 keV with the branching of 12.13% (not shown in this graph). The two gamma lines here at 181 keV and 366 keV have a branching of only 5.99 and 1.19%, respectively. Finally the last spectrum below is taken from a sample of the final ⁹⁹Mo preparation. All measurements have been performed using a Pb absorber to suppress the strong gamma signal from ^{99m}Tc (and other low-energetic radiation).

3.10. Radioactivity Distribution between Precipitate and Filtrate. In total the precipitate collects more than 60% of the radioactivity formed in the nuclear process in the chemical form of hydroxides, oxides, or carbonates of the fission products. This corresponds to the fission products of Ba and Sr, the rear earth elements and actinides, Zr/Nb. Te and Sb are nearly quantitatively collected in the precipitate. The results of a corresponding tracer experiment, are summarized

TABLE 4: Radioactivity distribution between precipitate and filtrate after dissolving irradiated ^{nat}U -targets of original composition.

Nuclide	Precipitate (%)	Solution (%)
^{239}Np	100	$\ll 1$
^{132}Te	100	< 3
^{143}Ce	100	$\ll 1$
^{141}Ce	100	$\ll 1$
^{140}Ba	100	$\ll 1$
^{140}La	100	$\ll 1$
^{131}I	0.60	99.39
^{103}Ru	20–40	60–80
^{99}Mo	0.57	99.43

Note: Ru behaves in different experiments differently, thus these data provide just an estimate.

TABLE 5: Radioactivity distribution of ^{99}Mo and the most important impurities during the process.

	^{99}Mo	^{103}Ru	^{132}Te	^{131}I
Filter cake	$< 0.5\%$	19.20%	96.30%	n.d.
Filtrate	$> 99.5\%$	80.70%	3.70%	100%
Ag-column	n.d.	22.70%	1.00%	$> 98\%$
FEED	$> 99\%$	66.90%	1.60%	$< 2\%$
Al_2O_3 column	10.6%	0.10%	1.10%	n.d.
Al-waste	n.d.	75.40%	n.d.	n.d.
DOWEX column	0.003%	0.06%	n.d.	n.d.
Final	86.5%	$< 0.001\%$	$< 0.001\%$	$< 0.001\%$

The % values relates to the individual content of the specified nuclide and not to ^{99}Mo .
(n.d.: not detected).

in Table 4. In this experiments target plates of the original composition were used.

The most important impurities have been followed up quantitatively throughout the process as good as gamma-spectroscopy could do under practical conditions with limited measuring time. The results are summarized in Table 5. The FEED solution (filtrate after passing the silver column) contains already relatively clean ^{99}Mo , however in presence of high salt concentration (Al, Na including ^{24}Na and fission-Cs). Up to 80% of the Ru is found in the filtrate, at the silver column already about 22% are retained. The remaining Ru is passing the Alumina column during the loading procedure. Careful washing avoids the transfer of Ru to the next purification steps. Ru shows a nonstandard behavior, sometimes we observed significant higher Ru-retention in the filter cake.

The ^{132}Te is nearly quantitatively coprecipitated. The highest ^{132}Te -content in the filtrate was 3.7% of the original quantity. About half of this fraction is retained at the silver column, the other half fraction at the Alumina column. In the filtrate and wash solutions from the Alumina column the ^{132}Te could not be detected any more (with the applied spectrometric parameters).

The iodine is nearly quantitatively retained at the silver column. The small fraction that is passing the silver column

TABLE 6: Quality parameters of fission ^{99}Mo produced at PINSTECH meeting international standard.

Gamma	^{131}I	$\leq 5 \times 10^{-2} \text{ MBq/GBq } ^{99}\text{Mo}$
	^{103}Ru	$\leq 5 \times 10^{-2} \text{ MBq/GBq } ^{99}\text{Mo}$
Beta	^{89}Sr	$\leq 6 \times 10^{-4} \text{ MBq/GBq } ^{99}\text{Mo}$
	^{90}Sr	$\leq 6 \times 10^{-5} \text{ MBq/GBq } ^{99}\text{Mo}$
Alpha		$\leq 1 \times 10^{-6} \text{ MBq/GBq } ^{99}\text{Mo}$
Other gamma		$\leq 1 \times 10^{-1} \text{ MBq/GBq } ^{99}\text{Mo}$

is then distributed throughout the system, mainly in the waste solutions through the washing procedures of the columns. Summarizing, the separation and purification process is efficient and easy.

3.11. ^{99}Mo Production Facility at PINSTECH. The ^{99}Mo Production Facility (MPF) is installed at PINSTECH Phase-1 building near reactor hall of PARR-1. The technical realization of the ROMOL-99 process in a semiautomated separation facility has been carried out by ITD Dresden GmbH (former Hans Wälischmiller (HWM) GmbH, Branch office Dresden). The main working areas of this facility are the Hot Cell complex (3 Hot Cells), interim liquid storage tanks, charcoal filter beds for iodine retention, xenon delay tanks, and the operator and service areas interconnected with it. Additionally, there are the so-called lock rooms through which the activated targets, the final product, and solid and liquid wastes are moved. Still, there are areas for personnel, preparation of reagents, storage, dosimetry, measurement, and decontamination. Further equipment in other rooms or buildings, which participate in the ^{99}Mo production, is the existing equipment of the main exhaust system with filter chamber, Secomak blowers and the main exhaust blower. The spent target material (loaded filter plates enclosed in screw shut cans) is stored in Spent Fuel bay of PARR-1. The solid low-radioactive wastes (spent ion-exchange columns, tubes, interconnections, and other one-way materials) are stored, while decayed radioactive liquid waste is cementized in the radioactive waste management Group building.

More than 50 commercial batches of fission based ^{99}Mo using ROMOL-99 process have been successfully completed. After the evaporation step, the residue is dissolved in the desired volume of diluted NaOH solution forming the final product solution $[^{99}\text{Mo}]\text{Na}_2\text{MoO}_4$. This final product solution is then transferred to the PAKGEN $^{99\text{m}}\text{Tc}$ generator production site at PINSTECH. These generators are then distributed to the 35 nuclear medical centers in Pakistan. The performance of these generators is comparable to that of generators produced from imported fission ^{99}Mo . The quality of the ^{99}Mo preparations produced at PINSTECH corresponds to the required international standard (Table 6). Details about the preparation of PAKGEN $^{99\text{m}}\text{Tc}$ generators and their quality control have already been reported [12]. The next steps at PINSTECH related to the routine ^{99}Mo -production are upscaling the production capacity and transmutation to LEU (low enriched uranium) as target fuel.

4. Conclusion

The ROMOL-99 process allows dissolving UAlx/Al clad dispersion targets under reduced pressure conditions without generation of hydrogen at temperatures between 70 and 80°C. The technology implements the separation of NH₃ and radioiodine prior to the ⁹⁹Mo separation. Generated nitrite is safely destroyed during the acidification process by urea to N₂. The technical realization of the ROMOL-99 process in a semiautomated separation facility has been carried out by ITD Dresden GmbH (former Hans Wälischmiller (HWM) GmbH, Branch Office Dresden). More than 50 commercial batches of fission-based ⁹⁹Mo using the ROMOL-99 process have been successfully completed at PINSTECH. PAKGEN ^{99m}Tc generators were prepared by using this locally produced high purity fission ⁹⁹Mo and distributed to 35 nuclear medical centers in Pakistan. The performance of these generators is comparable to that of generators produced from imported fission ⁹⁹Mo.

Conflict of Interests

The authors declare that they have no conflict of interests.

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